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# A COLLEGE TEXT-BOOK

OF

# CHEMISTRY

BY

IRA REMSEN

*President of the John Hopkins University*

*SECOND EDITION, REVISED*

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## PREFACE TO THE SECOND EDITION.

This new edition is based upon a thorough revision In its preparation I have received valuable aid from Dr. Edward Renouf, Collegiate Professor of Chemistry in the Johns Hopkins University. In reading the proof and in preparing the index I have, further, been aided by my Assistant, Dr. Charles Rouillier. I take pleasure in returning to these gentlemen my sincere thanks.

IRA REMSEN.

BALTIMORE, March 4, 1908.

# PREFACE TO THE FIRST EDITION.

THIS book is intended to fill a place between "An Introduction to the Study of Chemistry" and the "Inorganic Chemistry" of this series. It is distinctly more advanced than the former and distinctly less advanced than the latter. The "Inorganic Chemistry" has been largely used in its preparation, but every part has been carefully revised. Especial attention has been given to the parts dealing with matters pertaining to physical chemistry, and it is hoped that the treatment will commend itself to those competent to judge.

In the opinion of the author the time has not yet come for the abandonment of the study of elements and their compounds in what some are pleased to call the old-fashioned way. Indeed it seems essential that such study must always form the basis of the higher or spiritual study of chemistry. All chemists are thankful for the new conceptions that have been given to them in the last few years, and students must be made familiar with them in a general way.

IRA REMSEN

BALTIMORE, September 11, 1901.

# CONTENTS.

## CHAPTER I.

CHEMICAL AND PHYSICAL CHANGE—EARLIEST CHEMICAL KNOWLEDGE—LAW OF THE INDESTRUCTIBILITY OF MATTER—LAW OF DEFINITE PROPORTIONS—LAW OF MULTIPLE PROPORTIONS—THE ELEMENTS.

PAGE

Matter and Energy—Chemical Change—Physical Change—Physics and Chemistry—Earliest Chemical Knowledge—Law of the Indestructibility of Matter—Conservation of Energy—Composition of Matter—Elements—Chemical Action—Chemical Affinity—Chemical Compounds and Mechanical Mixtures—Qualitative and Quantitative Study of Chemical Changes—Law of Definite Proportions—Law of Multiple Proportions—Combining Weights of the Elements—The Elements, their Symbols and Atomic Weights—Symbols of Compounds—Chemical Equations—The Scope of Chemistry—Chemical Action accompanied by other Kinds of Action.

EXPERIMENTS: Chemical Change Caused by Heat—Chemical Changes can be effected by an Electric Current—Mechanical Mixtures and Chemical Compounds—Other Examples of Chemical Action, . . . . . 1

## CHAPTER II.

A STUDY OF THE ELEMENT OXYGEN.

Historical—Occurrence—Preparation—Physical Properties—Chemical Properties—Burning in the Air and Burning in Oxygen—Combustion—Kindling Temperature—Slow Oxidation—Heat of Combustion—Heat of Decomposition—Chemical Energy and Chemical Work—Oxides—The Law of Gay-Lussac—Critical Points.

EXPERIMENTS: Preparation of Oxygen—Measurement of the Volume of Gases—Determination of the Amount of Oxygen liberated when a Known Weight of Potassium Chlorate is

PAGE

decomposed by Heat—Kipp's Apparatus—Physical Properties of Oxygen—Chemical Properties of Oxygen—Oxygen is Used up in Combustion—The Products of Combustion weigh more than the Substance burned, . . . . . 32

CHAPTER III.

A STUDY OF THE ELEMENT HYDROGEN.

Historical — Occurrence — Preparation — Physical Properties—Chemical Properties — Reversible Reactions — Reduction—Comparison of Oxygen and Hydrogen.

EXPERIMENTS: Preparation of Hydrogen—Something besides Hydrogen is formed—Determination of the Amount of Hydrogen evolved when a Known Weight of Zinc is dissolved in Sulphuric Acid—Hydrogen is Purified by passing through a Solution of Potassium Permanganate—Hydrogen passes readily through Porous Vessels—Diffusion—Chemical Properties of Hydrogen—Product formed when Hydrogen is burned—Reduction, . . . . . 54

CHAPTER IV.

STUDY OF THE ACTION OF HYDROGEN ON OXYGEN.

Burning of Hydrogen—Method of Dumas—Morley's Method—Eudiometric Method—Calculation of the Results Obtained in Exploding Mixtures of Hydrogen and Oxygen—Determination of the Volume of Water-vapor formed by Union of Definite Volumes of Hydrogen and Oxygen—Heat Evolved in the Union of Hydrogen and Oxygen—Combination of Oxygen and Hydrogen by Other Methods—Catalysis—Nature of Catalysers—Negative Catalysis—Application of the Heat formed by the Combination of Hydrogen and Oxygen—Oxyhydrogen Light—Summary.

EXPERIMENTS: Composition of Water—Eudiometric Experiments—Oxyhydrogen Blowpipe, . . . . . 72

CHAPTER V.

CONSTITUTION OF MATTER—ATOMIC THEORY—ATOMS AND MOLECULES—CONSTITUTION—VALENCE.

The Atomic Theory as proposed by Dalton—Use and Value of a Theory—Atomic Weights and Combining Weights—Mole-

PAGE

cules—Avogadro's Hypothesis—Distinction between Molecules and Atoms—Molecular Weights—Deduction of Atomic Weights from Molecular Weights—Exact Atomic Weights determined by the Aid of Analysis—Molecular Formulas—Constitution—Valence—Replacing Power of Elements.

EXPERIMENTS: Method of Dumas—Method of Victor Meyer, . 83

CHAPTER VI.

WATER.

Historical—Occurrence—Formation of Water and Proofs of its Composition—Kinetic Theory applied to Liquids—Vapor Pressure of Liquids—Vapor Pressure of Water—Properties of Water—Superheated Water—Heat of Vaporization of Water and Heat of Fusion of Ice—Chemical Properties of Water—Hydrates—Vapor Pressure of Hydrates—Hydroxides—Solution—Vapor Pressure of Solutions—Water as a Solvent—Solution as an Aid to Chemical Action—Natural Waters—What Constitutes a Bad Drinking Water—Purification of Water—Distilled Water.

EXPERIMENTS: Organic Substances Contain Water—Water of Crystallization — Efflorescent Salts — Deliquescent Salts — Purification of Water by Distillation, . . . . . 101

CHAPTER VII.

OZONE—ALLOTROPY—NASCENT STATE—HYDROGEN DIOXIDE.

Occurrence — Preparation — Properties — Detection of Ozone—Effect of Heat on Ozone—Relation between Oxygen and Ozone—Ozone in the Air—Allotropy—Varying Number of Atoms in the Molecules of one and the same Element—Nascent State—Hydrogen Dioxide or Hydrogen Peroxide—Properties—Occurrence in the Air—Characteristic Reactions—Uses.

EXPERIMENTS: Ozone—Hydrogen Dioxide, . . . . . 118

CHAPTER VIII.

CHLORINE—HYDROCHLORIC ACID.

Historical—Occurrence of Chlorine—Preparation—Deacon's Process—Laboratory Process—Electrolytic Process—Properties

PAGE

—Different Kinds of Action—Chlorine Hydrate and Liquid Chlorine—Application of Chlorine—Hydrochloric Acid—Historical—Study of the Action of Hydrogen upon Chlorine—Preparation—Occurrence—Properties—Chemical Action of Hydrochloric Acid.

EXPERIMENTS: Preparation of Chlorine—Chlorine Decomposes Water in the Sunlight—Chlorine Hydrate—Formation of Hydrochloric Acid—Preparation of Hydrochloric Acid.

ELECTROLYSIS.

Electric Current—Conductiors—Anions and Cations—Faraday's First Law—Electric Units—Faraday's Second Law—Primary and Secondary Products of Electrolysis—Commercial Methods for the Electrolysis of Sodium Chloride.

EXPERIMENTS: Electrolysis, . . . . . 129

CHAPTER IX.

COMPOUNDS OF CHLORINE WITH OXYGEN AND WITH HYDROGEN AND OXYGEN.

General—Principal Reactions for making Compounds of Chlorine with Hydrogen and Oxygen—Hypochlorous Acid—Perchloric Acid—General—Compounds of Chlorine with Oxygen.

EXPERIMENTS: Chloric Acid and Potassium Chlorate—Perchloric Acid, . . . . . 155

CHAPTER X.

ACIDS—BASES—NEUTRALIZATION—SALTS.

General—A Study of the Act of Neutralization—Gram-molecular Weights—Electrolytic Dissociation—Definitions of Acids and Bases in Terms of the Theory of Electrolytic Dissociation—Definitions—Distinction between Acids and Bases—Metals or Base-forming Elements—Constitution of Acids and Bases—Constitution of Salts—Basicity of Acids—Acidity of Bases—Salts—Application of the Theory of Electrolytic Dissociation to the Subjects above Presented—Basicity of Acids—Ionisation of Salts—Ionisation of Bases—Apparent Exceptions—Neutralization of Acids or Bases Insoluble in Water—Measurement of Ionisation—Activity of Acids and

PAGE

Bases—Strength of Acids—Acid Properties and Oxygen—Nomenclature of Acids—Nomenclature of Bases—Nomenclature of Salts.

EXPERIMENTS: Neutralization of Acids and Bases; Formation of Salts—Study of the Products formed, . . . . . 162

CHAPTER XI.

NATURAL CLASSIFICATION OF THE ELEMENTS—THE PERIODIC LAW.

Historical—Arrangements of the Elements—Position of Elements which show no Chemical Properties—Connection between the Position of the Elements in the Natural System and their Chemical Properties—Plan to be followed, . . . 187

CHAPTER XII.

THE ELEMENTS OF FAMILY VII, GROUP B: FLUORINE—CHLORINE—BROMINE—IODINE.

General — Bromine — Occurrence — Preparation — Properties — Chemical Conduct of Bromine—Uses of Bromine—Manufacture of Bromine—Hydrobromic Acid—Properties—Compounds of Bromine with Hydrogen and Oxygen—Iodine—Occurrence—Preparation—Commercial Production of Iodine—Properties—Hydriodic Acid—Properties—Electrical Energy Required to Electrolyze Different Electrolytes—Iodic Acid—Iodine Pentoxide or Iodic Anhydride—Anhydrides, or Acidic Oxides—Periodic Acid—Compounds of Iodine with Chlorine—Compound of Iodine with Bromine—Fluorine—Occurrence—Properties—Hydrofluoric Acid—Family VII, Group A—Manganese.

EXPERIMENTS: Preparation of Bromine—Hydrobromic Acid—Iodine—Iodine can be detected by Means of its Action upon Starch-paste—Action of Sulphuric Acid upon Potassium Iodide—Iodic Acid—Hydrofluoric Acid, . . . . . 200

CHAPTER XIII.

THE ELEMENTS OF FAMILY VI, GROUP B: SULPHUR—SELENIUM—TELLURIUM.

Introductory — Sulphur — Occurrence — Extraction of Sulphur from its Ores—World's Production of Sulphur—Properties—Uses of Sulphur—Compounds of Sulphur with Hydrogen—Hydrogen Sulphide, Sulphuretted Hydrogen—Properties

PAGE

—Action of Hydrogen Sulphide upon Solutions of Salts, Use in Chemical Analysis—Hydrosulphides—Hydrogen Persulphide—Compounds of Sulphur with Members of the Chlorine Group—Selenium—Occurrence—Properties—Tellurium—Occurrence—Properties.

EXPERIMENTS: Properties of Sulphur—Hydrogen Sulphide, . 220

CHAPTER XIV.

COMPOUNDS OF SULPHUR, SELENIUM, AND TELLURIUM WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

Introductory — Sulphuric Acid — Contact Process — Pure Sulphuric Acid — Tetrahydroxyl-Sulphuric Acid — Normal Sulphuric Acid—Disulphuric Acid, Pyrosulphuric Acid—Sulphurous Acid — Hyposulphurous Acid — Thiosulphuric Acid—Other Acids of Sulphur—Persulphuric Acid—Caro's Reagent—Compounds of Sulphur with Oxygen—Sulphur Dioxide—Sulphur Trioxide—Sulphur Hexoxide—Sulphuryl Chloride—Chlorsulphuric Acid, or Sulphurylhydroxyl Chloride—Compounds of Selenium and Tellurium with Oxygen and with Oxygen and Hydrogen—Selenous Acid—Selenic Acid—Selenium Dioxide—Tellurous Acid—Telluric Acid—Oxides of Tellurium—Family VI, Group A.

EXPERIMENTS: Manufacture of Sulphuric Acid—Sulphurous Acid and Sulphur Dioxide—Sulphurous Acid is a Reducing Agent—Sulphur Trioxide, . . . . . 237

CHAPTER XV.

NITROGEN—THE AIR—ARGON, ETC.

Nitrogen — General — Occurrence of Nitrogen — Preparation — Properties—The Air—Analysis of Air—Air and Life—Pure and Impure Air—Liquid Air—Argon—Other Gases in Air—Helium.

EXPERIMENTS: Preparation of Nitrogen—Analysis of Air, . . 262

CHAPTER XVI.

COMPOUNDS OF NITROGEN WITH HYDROGEN—WITH HYDROGEN AND OXYGEN—WITH OXYGEN, ETC.

General Conditions which give Rise to the Formation of the Simpler Compounds of Nitrogen—Relations between the Princi-

PAGE

pal Compounds of Nitrogen—Ammonia—Nitrides—Properties—Composition of Ammonia—Ammonium Amalgam—Hydrazine—Hydroxylamine—Triazoic Acid—Nitric Acid—Red Fuming Nitric Acid—Nitric Acid and Nitrates from Atmospheric Nitrogen—Nitrous Acid—Hyponitrous Acid—Nitrous Oxide—Nitric Oxide—Nitrogen Trioxide—Nitrogen Peroxide—Nitrogen Pentoxide—Compounds of Nitrogen with the Elements of the Chlorine Group.

EXPERIMENTS: Preparation and Properties of Ammonia—Ammonia burns in Oxygen — Ammonia forms Ammonium Salts with Acids—Composition of Ammonia—Preparation and Properties of Nitric Acid—Nitric Acid gives up Oxygen readily, and is hence a Good Oxidizing Agent—Metals dissolve in Nitric Acid, forming Nitrates—Nitrates are decomposed by Heat—Nitrates are Soluble in Water—Nitric Acid is reduced to Ammonia by Nascent Hydrogen—Nitrous Acid—Nitrous Oxide—Nitric Oxide—Nitrogen Trioxide—Nitrogen Peroxide, . . . . . 279

## CHAPTER XVII.

ELEMENTS OF FAMILY V, GROUP B: PHOSPHORUS—ARSENIC—ANTIMONY—BISMUTH—THE ELEMENTS AND THEIR COMPOUNDS WITH HYDROGEN AND OXYGEN.

General—Phosphorus—Occurrence—Preparation—Properties—Red Phosphorus—Applications of Phosphorus—Compounds of Phosphorus with Hydrogen—Phosphine, Gaseous Phosphuretted Hydrogen—Compounds of the Members of the Phosphorus Group with the Members of the Chlorine Group—Phosphorus Trichloride—Phosphorus Pentachloride—Phosphoric Acid, Orthophosphoric Acid—Properties—Pyrophosphoric Acid—Metaphosphoric Acid—Polyphosphoric Acids—Phosphorous Acid—Hypophosphoric Acid—Hypophosphorous Acid—Phosphorus Pentoxide, Phosphoric Anhydride—Phosphorus Trioxide, or Phosphorous Anhydride—Arsenic—Occurrence—Preparation—Properties—Arsine, Arseniuretted Hydrogen—Arsenic Acid—Arsenious Acid—Arsenic Trioxide—Properties—Arsenic Pentoxide—Sulphides—Arsenic Disulphide—Arsenic Trisulphide—Arsenic Pentasulphide—Arsenic Trichloride—Antimony—Occurrence—Properties—Applications of Antimony—Stibine

PAGE

—Methods of distinguishing between Arsenic and Antimony —Antimonic Acid—Antimony Trioxide—Salts of Antimony —Antimony Tetroxide—Antimony Pentoxide—Antimony Trisulphide—Antimony Pentasulphide—Compounds of Antimony and Chlorine—Oxychlorides of Antimony—Bismuth —Occurrence—Oxides of Bismuth—Salts of Bismuth—Bismuth Dioxide—Bismuth Peroxide—Bismuth Pentoxide—Bismuth Trisulphide—Bismuth and Chlorine—Family V, Group A—Vanadium—Vanadic Acid—Columbium—Tantalum—Didymium—Boron—General—Occurrence—Preparation—Properties—Boron Hydride—Boron Trichloride—Boric Acid—Salts of Boron—Nitrogen Boride.

EXPERIMENTS: Phosphorus—Phosphorus abstracts Oxygen from other Substances—Phosphine—Phosphoric Acid—Phosphorus Trichloride—Phosphorus Pentachloride—Arsenic—Arsine—Marsh's Test for Arsenic—Arsenic Acid—Reduction of Arsenic Trioxide—Sulphides of Arsenic—Antimony—Stibine—Sulphides of Antimony—Oxychlorides of Antimony—Bismuth—Basic Nitrates of Bismuth—Boron, . 309

## CHAPTER XVIII.

CARBON (C, AT. WT. 12) AND ITS SIMPLER COMPOUNDS WITH HYDROGEN AND CHLORINE.

Introductory—Occurrence of Carbon—Diamond—Graphite—Amorphous Carbon—Coal—Diamond, Graphite, and Charcoal are Different Forms of the Element Carbon—Chemical Conduct of Carbon—Compounds of Carbon with Hydrogen, or Hydrocarbons.

EXPERIMENTS: Carbon—Bone-black Filters—Charcoal absorbs Gases—Carbon combines with Oxygen to form Carbon Dioxide—Carbon reduces some Oxides when heated with them—Hydrocarbons, . . . . . 353

## CHAPTER XIX.

SIMPLER COMPOUNDS OF CARBON WITH OXYGEN, AND WITH OXYGEN AND HYDROGEN.

General—Carbon Dioxide—Preparation—Properties—Relations of Carbon Dioxide to Chemical Energy—Respiration—Carbon Dioxide and Life—Energy Stored up in Plants—Carbonic Acid and Carbonates—Carbon Monoxide—Thermochemistry

PAGE

of the Combustion of Carbon—Fuel Gases—Siemens Regenerative Apparatus—Methods of obtaining High Temperatures.

EXPERIMENTS: Carbon Dioxide is formed when a Carbonate is treated with an Acid—Preparation and Properties of Carbon Dioxide—Carbon Dioxide is given off from the Lungs—Formation of Carbonates—Preparation and Properties of Carbon Monoxide—Carbon Monoxide is a Good Reducing Agent, . 367

CHAPTER XX.

ILLUMINATION—FLAME—BLOWPIPE.
COMPOUNDS OF CARBON WITH NITROGEN AND SULPHUR.

Introduction — Illuminating Gas, Coal-gas — Flames — Kindling Temperature of Gases—Miner's Safety Lamp—Structure of Flames—Blowpipe—Causes of the Luminosity of Flames—Bunsen Burner—Illuminants—Compounds of Carbon with Nitrogen and with Sulphur—Cyanogen—Hydrocyanic Acid, Prussic Acid—Cyanic Acid—Carbon Bisulphide—Sulphocyanic Acid—Constitution of Cyanogen and its Simpler Compounds.

EXPERIMENTS: Coal-gas—Oxygen "Burns" in an Atmosphere of a Combustible Gas—Kindling Temperature of Gases—The Blowpipe and its Uses—Cyanogen, . . . . . 381

CHAPTER XXI.

ELEMENTS OF FAMILY IV, GROUP A:
SILICON—TITANIUM—ZIRCONIUM—CERIUM—THORIUM.

General — Silicon—Occurrence — Preparation—Silicon Hydride, Silico-methane—Titanium—Zirconium—Thorium — Cerium —Compounds of the Elements of the Silicon Group with those of the Chlorine Group—Silicon Tetrachloride—Silicon Hexachloride — Silicon Tetrafluoride — Compounds of the Members of the Silicon Group with Oxygen, and with Oxygen and Hydrogen—Silicon Dioxide—Properties—Uses—Quartz Glass — Silicic Acid — Polysilicic Acids — Disilicic Acid—Trisilicic Acids—Titanium Dioxide—Thorium Dioxide—Silicides—Family IV, Group B.

EXPERIMENTS: Silicon—Silicon Tetrafluoride and Fluosilicic Acid—Silicic Acid, . . . . . 396

PAGE

CHAPTER XXII.

CHEMICAL ACTION.

Retrospective—Classification of Reactions of the Elements and Compounds Studied—Kinds of Chemical Reactions—Direct Combination — Direct Decomposition — Metathesis — The Cause of Chemical Reactions—An Ideal Chemical Reaction —Influence of Mass—Reactions may be Complete if One of the Products formed is Insoluble or Volatile—Dissociation—Electrolytic Dissociation and Electrolysis—Raoult's Methods for the Determination of Molecular Weights—Determination of the Extent of Dissociation of a Dissolvèd Substance —Osmotic Pressure—Relations between Specific Heat and Atomic Weights—Exceptions to the Law of Specific Heats, . . . . . 410

CHAPTER XXIII.

BASE-FORMING ELEMENTS—GENERAL CONSIDERATIONS.

Introductory—Metallic Properties—Order in which the Base forming Elements will be Taken Up—Occurrence of the Metals—Extraction of the Metals from their Ores—The Properties of the Metals—Compounds of the Metals—Chlorides—Formation of Salts in General—General Properties of the Chlorides—The So-called Double Chlorides and Similar Compounds of Fluorine, Bromine, and Iodine—Different Chlorides of the same Metal—Oxides—Different Oxides of the Same Metal—Hydroxides—Decomposition of Salts by Bases—Sulphides—Hydrosulphides—Sulpho-salts —General Remarks regarding Binary Compounds—Nitrates —Chlorates — Sulphates — Carbonates — Phosphates — Silicates.

Experiments: Chlorides, Bromides, and Iodides—Hydroxides —Sulphates—Reduction of Sulphates to Sulphides—Carbonates, . . . . . 430

CHAPTER XXIV.

ELEMENTS OF FAMILY I, GROUP A:

THE ALKALI METALS:—LITHIUM—SODIUM—POTASSIUM—RUBIDIUM —CÆSIUM—AMMONIUM.

General — Potassium — Occurrence—Preparation—Properties— Potassium Hydride—Potassium Fluoride, Chloride, Bro-

PAGE

mide, Iodide—Properties—Applications—Potassium Hydroxide—Stassfurt Potash Industry—Properties of Potassium Hydroxide—Potassium Oxide—Potassium Hydrosulphide — Potassium Nitrate — Applications—Gunpowder—Potassium Nitrite—Potassium Chlorate—Potassium Perchlorate—Potassium Cyanide—Potassium Sulphocyanate—Potassium Sulphate—Primary, or Acid, Potassium Sulphate—Sulphites—Carbonates—Acid Potassium Carbonate—Phosphates—Potassium Silicate—Rubidium—Cæsium—Sodium — Occurrence — Preparation—Properties—Applications—Sodium Hydride—Sodium Chloride—Sodium Hydroxide—Oxides—Sodium Peroxide—Sodium Sulphantimonate — Sodium Nitrate — Sodium Sulphate — Sodium Thiosulphate — Sodium Carbonate—Properties—Applications—The LeBlanc Process for the Manufacture of Sodium Carbonate—Ammonia Process for the Manufacture of Soda—Mono-Sodium Carbonate, Primary Sodium Carbonate—Phosphates — Sodium Borate—Sodium Silicate — Sodium Cyanide—Lithium—Ammonium Salts—Ammonium Chloride—Ammonium Sulphide—Ammonium Sulphate—Ammonium Nitrate—Sodium-Ammonium Phosphate—Reactions of the Members of the Sodium Group which are of Value in Chemical Analysis—Flame Reactions and the Spectroscope.

EXPERIMENTS: Potassium Salts—Sodium Salts, . . . . . 460

## CHAPTER XXV.

### ELEMENTS OF FAMILY II, GROUP A : GLUCINUM—MAGNESIUM—CALCIUM—STRONTIUM—BARIUM [ERBIUM].

General—Calcium Sub-group—Calcium—Occurrence—Preparation—Properties—Calcium Chloride—Calcium Fluoride—Calcium Oxide — Calcium Hydroxide — Applications — Bleaching-powder — Applications — Calcium Carbonate — Applications — Calcium Sulphate—Applications—Calcium Phosphates—Production of Phosphate Rock for Fertilizers—Fertilizers—Action of Acid and Basic Fertilizers on Soils—Calcium Silicate—Glass—Theory of Glass—Mortar—Portland Cement—Concrete—Calcium Cyanamide—Calcium Sulphide—Calcium Nitride—Calcium Carbide—Strontium—Occurrence and Preparation—Properties—Compounds of Strontium—Barium—Occurrence and Preparation—Proper-

PAGE

ties—Barium Chloride—Barium Hydroxide—Barium Oxide —Barium Peroxide or Dioxide—Barium Sulphide—Barium Sulphate—Barium Carbonate—Phosphates of Barium—Reactions which are of Special Value in Analysis—Magnesium Sub-group — Glucinum (Beryllium) — Occurrence and Preparation—Magnesium—Occurrence—Preparation—Properties — Applications — Compounds of Magnesium — Magnesium Chloride — Magnesium Oxide — Magnesium Sulphate — Applications — Magnesium Carbonate — Phosphates — Borates—Silicates—Magnesium Silicide—Magnesium Nitride—Reactions of Magnesium Salts which are of Special Value in Chemical Analysis—Erbium.

EXPERIMENTS : Calcium Salts—Magnesium and its Salts . . 497

CHAPTER XXVI.

ELEMENTS OF FAMILY III, GROUP A :
ALUMINIUM—SCANDIUM—YTTRIUM—YTTERBIUM—SAMARIUM.

General — Aluminium—Occurrence—Preparation—Properties—Applications—Aluminium Chloride—Aluminium Hydroxide—Aluminates—Aluminium Oxide—Aluminium Sulphate —Alums—Potassium Alum, Potassium-Aluminium Sulphate — Applications — Ammonium Alum, Ammonium-Aluminium Sulphate—Sodium Alum — Aluminium Silicates—Alloys—Reactions of Aluminium Salts which are of Special Value in Chemical Analysis—Other Members of Family III, Group A—Scandium—Yttrium—Ytterbium—Samarium.

EXPERIMENTS : Aluminium Chloride, . . . . . 527

CHAPTER XXVII.

ELEMENTS OF FAMILY I, GROUP B :
COPPER—SILVER—GOLD.

General—Copper—General—Forms in which Copper Occurs in Nature—Metallurgy of Copper—Properties—Applications—Alloys—Cuprous Chloride—Cupric Chloride—Cuprous Hydroxide — Cuprous Oxide — Cupric Hydroxide — Cupric Oxide—Cupric Sulphate—Applications—Cupric Nitrate—Cupric Arsenite—Cupric Carbonates—Cuprous Sulphide—Cupric Sulphide—Copper Plating—Reactions which are of

PAGE

Special Value in Chemical Analysis—Silver—General—Forms in which Silver Occurs in Nature—Metallurgy of Silver—Zinc Method, or Parkes's Method—Amalgamation Process—Purification—Properties—Allotropic Forms of Silver—Silver Plating—Alloys of Silver—Argentous Chloride—Silver Chloride—Argentic Chloride—Silver Bromide and Silver Iodide—Application of the Chloride, Bromide, and Iodide of Silver in the Art of Photography—Silver Triazoate—Silver Oxide—Other Oxides of Silver—Sulphides of Silver—Silver Nitrate, Argentic Nitrate—Silver Cyanide—Reactions which are of Special Value in Chemical Analysis—Gold—General—Forms in which Gold occurs in Nature—Metallurgy of Gold—Production of Gold and Silver—Properties—Colloidal Gold—Alloys of Gold—Chlorides of Gold—Gold Sulphide—Gold and Silver Plating.

EXPERIMENTS: Copper and its Salts—Silver and its Salts . . 543

CHAPTER XXVIII

ELEMENTS OF FAMILY II, GROUP B:
ZINC—CADMIUM—MERCURY.

General—Zinc—General—Forms in which it occurs in Nature—Metallurgy—Properties—Applications—Primary Cells—Alloys—Zinc Chloride—Zinc Hydroxide—Zinc Oxide—Zinc Sulphide—Zinc Sulphate—Zinc Carbonate—Reactions which are of Special Value in Chemical Analysis—Cadmium—General—Preparation and Properties—Cadmium Sulphide—Analytical Reactions—Mercury—General—Forms in which Mercury occurs in Nature—Metallurgy of Mercury—Production—Properties—Applications—Amalgams—Mercurous Chloride—Mercuric Chloride, or Corrosive Sublimate—Mercurous Iodide—Mercuric Iodide—Mercuric Oxide—Mercuric Sulphide—Mercuric Cyanide—Mercurous Nitrate—Mercuric Nitrate—Compounds formed by Salts of Mercury with Ammonia—Reactions which are of Special Value in Chemical Analysis.

ELEMENTS OF FAMILY III, GROUP B:
GALLIUM—INDIUM—THALLIUM.

General—Gallium—Indium—Thallium.

EXPERIMENTS: Zinc and its Salts—Mercury and its Salts, . . 567

## CHAPTER XXIX.

ELEMENTS OF FAMILY IV, GROUP B:
GERMANIUM—TIN—LEAD.

PAGE

General—Germanium—Tin—General—Occurrence—Metallurgy—Production — Properties — Applications — Alloys—Stannous Chloride—Stannic Chloride—Stannic Hydroxide—Stannic Oxide—Stannous Sulphide—Stannic Sulphide—Reactions which are of Special Value in Chemical Analysis—Lead—General—Forms in which Lead occurs in Nature—Metallurgy — Production—Properties—Applications—Lead Chloride—Lead Tetrachloride—Lead Iodide—Oxides of Lead—Lead Suboxide—Lead Oxide—Lead Peroxide—Storage Battery—Red Lead, Minium—Lead Sulphide—Lead Nitrate—Lead Carbonate—Lead Sulphate—Reactions which are of Special Value in Chemical Analysis—Lanthanum, Cerium, Didymium — Lanthanum — Cerium—Didymium—Praseodymium and Neodymium.

EXPERIMENTS: Tin and its Compounds—Lead and its Compounds, . . . . . .

## CHAPTER XXX

ELEMENTS OF FAMILY VI, GROUP A:
CHROMIUM—MOLYBDENUM—TUNGSTEN—URANIUM.

General—Chromium—General—Forms in which Chromium occurs in Nature — Properties — Ferrochromium — Chromic Chloride—Chromic Hydroxide—Chromic Oxide—Chromic Sulphate—Chrome-Alums—Chromic Acid and the Chromates — Potassium Chromate — Potassium Bichromate — Chromium Trioxide—Relations between the Chromates and Bichromates—Sodium Chromate and Sodium Bichromate—Barium Chromate—Lead Chromate—Reactions which are of Special Value in Chemical Analysis—Molybdenum—General—Occurrence and Preparation—Molybdic Acid and the Molybdates—Lead Molybdate—Phospho-molybdic Acid—Tungsten—General—Occurrence and Preparation—Properties—Tungstic Acid and the Tungstates—Uranium—General—Occurrence and Preparation—Properties—Oxides—Uranous Salts—Uranyl Salts—Uranates—Radium.

EXPERIMENTS: Chromic Acid and the Chromates, . . . . . 602

## CHAPTER XXXI.

### ELEMENTS OF FAMILY VII, GROUP A: MANGANESE.

PAGE

General—Forms in which Manganese occurs in Nature—Preparation and Properties—Production—Manganous Chloride—General Remarks concerning the Oxides—Manganous Hydroxide—Manganous-manganic Oxide—Manganic Oxide—Manganese Dioxide—Weldon's Process for the Regeneration of Manganese Dioxide in the Preparation of Chlorine—Sulphides—Manganous Sulphate—Manganic Sulphate—Manganic Acid and the Manganates—Permanganic Acid and the Permanganates—Potassium Permanganate—Reactions which are of Special Value in Chemical Analysis.

EXPERIMENTS: Manganese and its Compounds, . . . . . 617

## CHAPTER XXXII.

### ELEMENTS OF FAMILY VIII, SUB-GROUP A: IRON—COBALT—NICKEL.

General—Iron—Introductory—Forms in which Iron occurs in Nature—Metallurgy—Varieties of Iron—Open-Hearth or Siemens-Martin Furnace—Properties of Iron—Ferrous Chloride—Ferric Chloride—Cyanides—Potassium Ferrocyanide—Ferrohydrocyanic Acid—Ferric Ferrocyanide, or Prussian Blue—Potassium Ferricyanide—Ferrihydrocyanic Acid—Ferrous Ferricyanide—Ferrous Hydroxide—Ferric Hydroxide—Ferrous-Ferric Oxide—Soluble or Colloidal Ferric Hydroxide—Ferric Oxide—Ferrous Sulphide—Ferrous Carbonate—Ferrous Sulphate—Ferric Sulphate—Ferrous Phosphate—Iron Disulphide—Reactions which are of Special Value in Chemical Analysis—Cobalt—General—Occurrence and Preparation—Properties—Cobaltous Chloride—Cobaltous Hydroxide—Cobaltic Hydroxide—Cobalt Sulphide—Cyanides—Nickel—General—Occurrence and Preparation—Properties—Alloys—Other Applications of Nickel—Nickelous Hydroxide—Nickelic Hydroxide—Cyanides—Nickel Carbonyl—Reactions of Cobalt and Nickel which are of Special Value in Chemical Analysis.

EXPERIMENTS: Iron and its compounds, . . . . . 628

## CHAPTER XXXIII.

ELEMENTS OF FAMILY VIII, SUB-GROUP B:
RUTHENIUM—RHODIUM—PALLADIUM.
ELEMENTS OF FAMILY VIII, SUB-GROUP C:
OSMIUM—IRIDIUM—PLATINUM.

PAGE

General—The Platinum Metals—Metallurgy—Ruthenium—Preparation — Properties — Osmium — Preparation—Properties — Rhodium — Iridium — Preparation — Properties — Palladium — Preparation — Properties — Palladium-Hydrogen—Platinum—Preparation—Properties—Applications of Platinum—Alloys of Platinum—Chlorides—Chlorplatinic Acid—Sulphides.

EXPERIMENTS: Platinum—Chemical Analysis, . . . . . 652

## CHAPTER XXXIV.

SOME FAMILIAR COMPOUNDS OF CARBON.

Organic Chemistry—Occurrence of the Compounds of Carbon—Formation of Hydrocarbons—Distillation of Coal—Distillation of Wood—Distillation of Bones—Fermentation—Classes of Compounds of Carbon—Hydrocarbons—Compounds of Carbon and Hydrogen—Petroleum—Refining of Petroleum—Hydrocarbons contained in Petroleum—Homology—The Ethylene Series of Hydrocarbons—The Acetylene Series—The Benzene Series—Marsh-gas, Methane, Fire-damp—Substitution-products of the Hydrocarbons—Chloroform—Iodoform—Ethylene, Olefiant Gas—Acetylene—Methyl Alcohol, Wood-spirit—Ethyl Alcohol, Spirits of Wine—What Change takes Place in Sugar?—What Causes the Change?—Germs in the Air—Different Kinds of Fermentation—Distillation of Fermented Liquids—Properties of Alcohol—Uses of Alcohol—Denatured Alcohol—Glycerin—Properties—Aldehydes—Formic Aldehyde, Formal—Acetic Aldehyde, Ordinary Aldehyde—Chloral—Acids—Formic Acid—Acetic Acid—Properties—Uses—Salts of Acetic Acid—Fatty Acids—Butyric Acid—Palmitic Acid—Stearic Acid—Soaps—Use of Soap—Action of Soap on Hard Waters—Relations of the Soap Industry to other Industries—Oxalic Acid—Lactic Acid—Malic Acid—Tartaric Acid—Citric Acid—Ethers—Ether—Ethereal Salts or Esters—Action of Acids upon Alcohols—Saponification—Fats—Ethereal Salts as Essences—

PAGE

Nitroglycerin—Relations between the Compounds Treated of—Comparison of the Formulas—Alcohols—More Complex Alcohols—Radicals or Residues—Acids.

EXPERIMENTS: Fermentation—Aldehyde—Soap—Hard Water, 659

## CHAPTER XXXV.

### OTHER COMPOUNDS OF CARBON.

The Carbohydrates—Grape-sugar, Glucose, Dextrose—Manufacture of Dextrose or Glucose—Properties—Levulose, Fruit-sugar — Cane-sugar—Sugar-refining—Molasses—Properties of Sugar—Sugar of Milk, Lactose—Souring of Milk—Cellulose—Properties—Gun-cotton, Pyroxylin, Nitrocellulose—Collodion — Celluloid — Paper—Starch—Manufacture of Starch — Properties — Flour—Breadmaking—A few Compounds from Coal-tar—Aromatic Compounds—Nitrobenzene—Aniline—Aniline Dyes—Phenol, Carbolic Acid—Trinitrophenol, Picric Acid—Explosives—Oil of Bitter Almonds, Benzoic Aldehyde—Benzoic Acid—Balsams and Odoriferous Resins—Gallic Acid—Tannic Acid, Tannin—Tanning — Indigo — Naphthalene — Anthracene — Alizarin — Glucosides — Myronic Acid — Alkaloids—Quinine—Cocaïne—Nicotine—Morphine, Codeine and Narcotine, . . 677

INDEX. . . . . 687

# A COLLEGE TEXT-BOOK OF

# CHEMISTRY.

## CHAPTER I.

CHEMICAL AND PHYSICAL CHANGE.—EARLIEST CHEMICAL KNOWLEDGE.—LAW OF THE INDESTRUCTIBILITY OF MATTER.—LAW OF DEFINITE PROPORTIONS.—LAW OF MULTIPLE PROPORTIONS.—THE ELEMENTS.

**Matter and Energy.**—The sensible universe is made up of matter and energy. It is difficult to give satisfactory definitions of either of these terms, but, in a general way, it may be said that matter is anything that occupies space, and energy is that which causes change in matter. It requires but little observation to show that there are many kinds of matter, and apparently many kinds of energy. As examples of the different kinds of matter, the many varieties of rocks and earth, as granite, limestone, quartz, clay, sand, etc.; the plants and their fruits; the substances which enter into the composition of animals; and innumerable manufactured products may be mentioned. Heat, light, motion, etc., are examples of the different forms of energy. Under the influence of the forms of energy the forms of matter are constantly undergoing change. Everywhere these changes are taking place. Changes in position and in temperature appeal most directly to our senses, and are most easily studied. But there are many other kinds of change that are

of the highest importance. Thus there are electrical changes, manifestations of which we see in thunder-storms; there are magnetic changes which may be studied to some extent by means of the magnetic needle; and there are, further, chemical changes that affect the composition of substances.

**Chemical Change.**—For the purpose of study it is convenient to distinguish between two classes of changes in matter, the difference between which can best be made clear by examples. Consider the changes involved in what we call fire. We see substances destroyed by fire, as we say. They disappear as far as we can determine by ordinary observation. When iron is exposed to the air a serious change takes place. It becomes covered with a reddish-brown substance called rust. If the piece of iron is comparatively thin, and it is allowed to lie in the air long enough, it is completely changed to the reddish-brown substance, and no iron as such is left. If the juices from fruits, as from apples, are allowed to stand in the air, they undergo change, becoming sour, and a somewhat similar change takes place in milk. If a spark is brought in contact with gunpowder there is a flash and the powder disappears, a dense cloud appearing in its place.

In the changes referred to the substances changed disappear as such. After the fire, the wood or the coal, or whatever may be burned, is no longer to be found. The rusted iron is no longer iron. The gunpowder after the flash is no longer gunpowder. Changes of this kind in which the substances disappear and something else is formed in their place are known as *chemical changes*.

**Physical Change.**—There are many changes taking place that do not affect the composition of substances. Iron, for example, may be changed in many ways and still remain iron. It may become hotter or colder. Its position may be changed, or, as we say, it may be moved. The iron may be struck in such a way as to cause it to give forth sound. It may be made so hot that it gives light. When, for example, it becomes red-hot, it can be

seen in a dark room. A piece of iron may be changed, further, by connecting it with what is known as a galvanic battery. A current of electricity then passes through it, and we can easily recognize the difference between a piece of iron through which a current of electricity is passing and one through which no current is passing. The former when brought into certain liquids will at once change their composition, while the latter will not cause such change. Finally, when a piece of iron is brought in contact with loadstone, it acquires new properties. It now has the power to attract and hold to itself other pieces of iron. In all these cases, the iron is changed, but it remains iron. After the moving iron comes to rest, it is the same thing that it was before it was moved. After the iron that is giving forth sound has ceased to give forth sound, it returns to its original condition. Let the heated iron alone, and it cools down, soon ceasing to give light, and presenting no evidence of being warm. Remove the iron from contact with the galvanic battery, and it loses those properties which are due to the current of electricity. In time, the iron that is magnetized by contact with the loadstone loses its magnetic properties. It then no longer has the power to attract other pieces of iron, and does not differ from ordinary iron.

While iron has been taken as an example, other substances undergo similar changes. These changes which do not affect the composition of the substances are called *physical changes*.

**Physics and Chemistry.**—According to what has been said, we have two classes of changes presented to us for study:

(1) Those which do not affect the composition of substances, or physical changes.

(2) Those which do affect the composition of substances, or chemical changes.

That branch of science which has to deal with physical changes is known as PHYSICS. And that which has to deal with chemical changes is known as CHEMISTRY.

Everything that has to do with motion, heat, light,

sound, electricity, and magnetism is studied under the head of Physics. Everything that has to do with the composition of substances is studied under the head of Chemistry. It is, however, impossible to study these two subjects entirely independently of each other. Whenever a chemical change takes place, it is accompanied by physical changes; and in order that the former may be clearly understood, a study of the latter is necessary.

**Earliest Chemical Knowledge.**—Those substances which are most abundant and most widely distributed in nature were, of course, the first known and studied; and the same is true of those chemical changes which occur most commonly and produce the most striking effects. Simply by observing those things which surround us and those changes in composition which take place naturally, a considerable amount of chemical knowledge might be gained, and indeed the earliest knowledge of chemistry was acquired in this way. It was not, however, until men came to experiment upon the substances which they found in nature, that knowledge of chemical changes made rapid progress. Since then an enormous amount of knowledge has been gained, and every year the stock is increased by new discoveries, until the field appears almost boundless.

**Law of the Indestructibility of Matter.**—One of the first facts of fundamental importance established by the study of chemical phenomena is that after a chemical change has taken place there is just as much matter as there was before the change. Whenever matter apparently disappears, it continues to exist in some other form. If it were possible to annihilate matter or to call it into being, it would be of little or no value to weigh things. The first fundamental law bearing upon the changes in composition which the different forms of matter undergo is the *law of the indestructibility of matter.* While, if we think of it, we can not conceive that this great law should not be true, we must not forget that the only way in which its truth could be established was by experiment The law may be stated thus:

*Whenever a change in the composition of substances takes place the amount of matter after the change is the same as before the change.*

According to this, and assuming that the law has always held good, it follows that the amount of matter in the universe is the same to-day as it has been from the beginning. Transformations are constantly taking place, but these involve no increase nor decrease in the total amount of matter.

**Conservation of Energy.**—Just as matter is neither created nor destroyed, so it has been made probable that the total amount of energy is unchangeable. One of the greatest discoveries ever made is that one form of energy can be transformed into others, and that in these transformations nothing is lost. We now know that for a certain amount of heat a certain amount of mechanical motion can be obtained, and that for a certain amount of mechanical motion a certain amount of heat can be obtained. It is known that a similar definite relation exists between heat and electrical energy, and between these and chemical energy. It is known, for example, that a definite amount of heat can be obtained by burning a definite amount of a given substance, and it is also known that with a definite amount of heat, a definite amount of chemical change can be produced. Modern investigation has shown that all the different forms of energy are convertible one into the other without loss. This important statement of fact is called the *law of the conservation of energy*. Transformations of energy are taking place constantly, as transformations of matter are, but the total amount in each case remains the same.

**Composition of Matter.**—The fact that first impresses one in studying the various forms of matter found in the earth is their great variety. An almost infinite number of kinds of matter are found, and the question suggests itself, of what are these things composed? This question has long been asked, and it will be long before an entirely satisfactory answer is reached. Still, much more is now known in regard to the subject than was known in past

ages, and progress is constantly being made towards a solution of the problem.

**Elements.**—As chemical experimenting upon things advanced, the fact impressed itself more and more strongly upon investigators, that, of the large number of substances known, some can be converted into simpler ones by chemical action and some cannot. In other words, some substances like water can be broken down by one method or another into two or more others of different properties, and these when brought together again under proper conditions form the original substance. Water can be decomposed into two gases, hydrogen and oxygen. Elaborate experiments have shown that the weight of water decomposed is exactly equal to the weight of the hydrogen plus that of the oxygen obtained, and that when the hydrogen and oxygen are brought together again under proper conditions exactly as much water is formed as was originally decomposed. It appears, therefore, that water consists of at least two simpler substances. A similar conclusion is reached by a study of by far the largest number of the substances with which we have to deal. On the other hand, no treatment to which hydrogen has been subjected has, as yet, effected its decomposition; and the same is true of oxygen. They can be made to combine with other substances, as, for example, with each other, and thus form more complex substances, but nothing simpler than hydrogen has ever been obtained from hydrogen, and nothing simpler than oxygen has ever been obtained from oxygen. Whether the decomposition of these substances will ever be effected is a question that cannot be answered. All that we know is that at present they cannot be decomposed. We therefore speak of them as elements, meaning by the term, that, with the means now at the disposal of chemists, it is impossible to get simpler substances from them. There are at present about eighty substances known which are called elements for the same reasons that hydrogen and oxygen are called elements. It is quite possible that the number may be increased in the future, and it is also quite possible that

the number may be decreased. New elements will in all probability be discovered, and probably some of the substances now included in the list of elements will eventually be shown to be capable of decomposition.

The view at present held in regard to the forms of matter which go to make up that part of the universe which comes under our observation is that they are all composed of the elementary substances. Many of them, like water, are composed of only two elements; others of three; and still others of four, five, six, and more; but most of them are comparatively simple, and rarely does any one contain more than four or five elements. Of the eighty elements known, only about twelve enter into the composition of those things with which we commonly have to deal. The others occur in relatively small quantity.

**Chemical Action.**—In the last paragraph it was stated that most substances can be decomposed, and that under proper conditions the elements combine. Let us now inquire more carefully into the meaning of these expressions. Among the elements are the well-known substances lead, iron, and sulphur. If some finely-divided iron is brought in contact with sulphur, apparently no action takes place. If the two are put in a mortar and mixed, no matter how thoroughly, there is no evidence of action. The mixture has, to be sure, a different appearance from that of either constituent, but still both substances are present, and can be recognized in various ways. If, for example, a little of the mixture is examined with the aid of a microscope, particles of iron and of sulphur will be recognized lying side by side. If, further, the mixture is treated with the liquid, carbon bisulphide, which has the power to dissolve the sulphur but not the iron, the sulphur will be dissolved while the iron will be left unchanged. Finally, if a dry magnet is introduced into the mixture, the iron will adhere to it, and by careful manipulation the two constituents can be separated. These facts furnish evidence that both iron and sulphur are present in the mixture in unchanged condition, just

as sugar and sand are present in a mixture of these two substances. If now the mixture of sulphur and iron is heated in a dry test-tube, marked changes will take place, and there will be formed a black substance entirely different from either of the elements used in the experiment. Carbon bisulphide can no longer extract sulphur from it. The magnet can no longer pick out the iron, and under the microscope one homogeneous substance is seen instead of the two elementary substances. If the experiment is performed with proper precautions, the amount of matter after the action will be found to be exactly the same as before the action. A serious change has taken place, but no change in the amount of matter. The act is one of chemical combination, and the substance formed is called a *chemical compound.*

A few other examples will aid in making the conception of chemical combination clear. When a bit of phosphorus is brought in contact with a little iodine, action takes place at once; the two elements combine, losing their own characteristic properties and forming a compound with properties quite different from those of the constituents. When the gases hydrogen and oxygen are brought together and a spark is passed through the mixture, an explosion occurs, and, in place of the gases, the liquid, water, is formed. When sulphur burns in the air the product formed is a pungent gas. It has been shown that the act consists in the combination of the sulphur with the gas, oxygen, which is contained in the air. All these cases are examples of chemical combination. But chemical action may be of the opposite kind, that is to say, instead of being *combination*, it may be *decomposition.* Thus, water which is formed by the chemical combination of hydrogen and oxygen may, by proper methods, be decomposed into the same elements. We may conveniently think of that which causes elements to combine as an attractive force exerted between the elements. Now, when some power which can overcome this attraction is brought to bear upon a compound, decomposition takes place, and the elements are, as we say, set free.

When, for example, the substance known as red oxide of mercury or mercuric oxide is heated to a sufficiently high temperature a colorless gas is given off from it, and globules of mercury are formed at the same time. The gas, as will be shown later, is oxygen, so that from the red oxide of mercury, which is a chemical compound of mercury and oxygen, the two elements are obtained in the free or uncombined state by heating. In this case, heat overcomes the chemical attraction which, in the compound, holds the elements together.

**Chemical Affinity.**—It is evident from what has already been said that there is some power that can hold elements together in a very intimate way, so intimate that we cannot recognize them by ordinary means. We do not know what causes the sulphur and iron to combine, but we do know that they combine. Similarly, we do not know what causes a stone thrown in the air to fall back again, but we know that it falls back. It is true we may say that the cause of the falling of the stone is the *attraction of gravitation*, but this does not help us for, if we ask what the attraction of gravitation is, we can only answer that it is that which causes all bodies to attract one another. We may also say, and do say, that the cause of chemical combination is *chemical affinity*. But in so doing we only give a name to something about which we know nothing except the effects it produces. All the chemical changes that are taking place around us may, then, be referred to the operation of chemical affinity. If this power should cease to operate, what would be the result? Nature would be infinitely less complex than it now is. All complex substances would be resolved into the elements of which they are composed, and, as far as we know, there would be only about eighty different kinds of substances. All living things would cease to exist, and in their place there would be three invisible gases, and something very much like charcoal. Mountains would crumble to pieces, and all water would disappear, giving two invisible gases. The processes of life in its many forms would be impossible, as, however

subtle that which we call life may be, we cannot imagine it to exist without the existence of certain complex forms of matter; and, as regards the life process of animals and plants, complex chemical changes are constantly taking place within them, and these changes are essential to the continuance of life.

**Chemical Compounds and Mechanical Mixtures.**—The substances formed by chemical combination of the elements are called chemical compounds. Most substances found in nature are made up of several others. Wood, for example, is very complex, containing a large number of distinct chemical compounds intimately mixed together. Some of these can be isolated, but it is impossible to isolate them all with the means at present at our command. Most of the rocks met with are also quite complex, and it is difficult to isolate the constituents. If we look at a piece of coarse-grained granite, we see plainly enough that it contains different things mixed together, and if it is broken up we can pick out pieces of different substances from the mass. If we now examine a piece of each of the different substances thus picked out of the granite, it appears to be homogeneous. If the piece is carefully selected and powdered finely in an agate mortar, the powder may be examined with a microscope without the presence of more than one substance being recognized. It is possible to isolate three substances from granite by simply breaking it up and picking out the pieces of different kinds. It might therefore be concluded that granite consists of three substances. This is true, but it is not the whole truth. For it is possible by proper means to get simpler substances from each of the three already separated. This is, however, a much more difficult process than the separation first accomplished. To effect the separation of each of the three constituents of granite into its elements requires more powerful means. Substances must be brought in contact with them which change their composition, that is to say, act chemically upon them, and high heat must be used to aid the action.

By skilful work it is, however, possible to separate the three components of granite into their elements.

From the above it is evident that substances may be united in different ways. They may be so united that it is a simple thing to separate them by mechanical processes. Or they may be so united that it is impossible to separate them by mechanical processes. By a mechanical process is meant any process that does not involve the use of heat, electricity, or chemical action. Thus, the mechanical process made use of in the case of granite consisted in picking out the pieces. The separation of the particles of different sizes by means of a sieve is a mechanical process. The separation of two liquids which do not mix with each other is a mechanical process. Complex substances which can be separated into their components by purely mechanical processes are called mechanical mixtures. Thus granite is a mechanical mixture of three chemical compounds. Similarly, most natural substances are more or less complex mechanical mixtures of chemical compounds, or, much more rarely, of elements. Air, for example, is a mechanical mixture consisting mainly of the two elements nitrogen and oxygen. It is not always an easy matter to distinguish between mechanical mixtures and chemical compounds, as there are mixtures which it is extremely difficult to resolve into their components, and there are, on the other hand, chemical compounds which are extremely unstable. Generally, however, the difference is recognized without much difficulty.

**Qualitative and Quantitative Study of Chemical Changes.**—In general there are two ways in which chemical changes may be studied. Substances may be brought together under a variety of conditions and, if action takes place, the properties of the product or products may then be studied and compared with those of the substances brought together. In the early periods of the history of chemistry the study was almost wholly of this kind. This is called *qualitative study*. But we may go farther than this, and take into consideration the weights or masses

of the substances we are dealing with. We should then be studying the changes *quantitatively*. By means of the quantitative method the law of the indestructibility of matter was established. By further use of this method other laws of the highest importance to the science of chemistry were soon brought to light.

**Law of Definite Proportions.**—The fact that sulphur and iron combine chemically when a mixture of the two is heated has been referred to. The question whether they combine in all proportions is one that can be answered only by a quantitative study of the process. If the process were to be studied for the first time the method of procedure would be this: We should mix the elements in different proportions and, after the action, we should determine whether any of either of the elements is left in the uncombined state; and, further, by decomposing the product, we should determine whether it always contains the elements in the same proportions. The problem, in this case, is by no means a simple one, but it has been repeatedly worked over with the greatest possible care, and, as the result of the work, the conclusion is justified, that the product always contains the elements in exactly the same proportions. Similar work has been done with most other chemical compounds known, and the general conclusion known as the *law of definite proportions* has been drawn. This law may be stated thus:

*A chemical compound always contains the same constituents in the same proportion by weight.*

The truth of this general statement or law has not always been acknowledged by chemists. At the beginning of the last century a discussion on the subject took place between Proust and Berthollet. The discussion led to a great deal of careful work which tended to confirm the law, and since that time it has not been seriously doubted.

About twenty years ago a Belgian chemist, Stas, by a long series of probably the most painstaking and accurate chemical experiments ever performed up to that time, showed that in the compounds which he worked with

there was no variation in composition that could be detected by the most refined methods of chemistry. In the present state of our knowledge it appears that the law of definite proportions is a law in the strictest sense.

**Law of Multiple Proportions.**—It does not require a very extensive study of chemical phenomena to show that from the same elements it is possible in many cases to get more than one product. Thus iron and sulphur form three distinct compounds with each other. Tin combines with oxygen in two proportions. The elements potassium, chlorine, and oxygen combine in four different ways, forming four distinct products. Nitrogen and oxygen form five products. In the early part of the last century the English chemist, Dalton, by a study of cases like those mentioned was led to the discovery of another great law of chemistry known as the *law of multiple proportions*. Many substances had been analyzed before his time, and the percentage of the constituents determined with a fair degree of accuracy. He examined, first, two gases, both of which consist of carbon and hydrogen. He determined the percentages of the constituents, and found them to be as follows:

Olefiant gas, 85.7 per cent carbon and 14.3 per cent hydrogen.

Marsh-gas, 75.0 per cent carbon and 25.0 per cent hydrogen.

On comparing these numbers, he found that the ratio of carbon to hydrogen in olefiant gas is as 6 to 1; whereas in marsh-gas it is as 3 to 1 or 6 to 2. The weight of hydrogen, combined with a given weight of carbon, is twice as great in the one case as in the other.

There are, further, two compounds of carbon and oxygen, and in analyzing these the following figures were obtained:

Carbon monoxide contains 42.86 per cent carbon and 57.14 per cent oxygen.

Carbon dioxide contains 27.27 per cent carbon and 72.73 per cent oxygen.

But 42.86 : 57.14 : : 6 : 8 and 27.27 : 72.73 : : 6 : 16.

The weight of oxygen combined with a given weight of carbon in carbon dioxide is twice as great as the weight of oxygen combined with the same weight of carbon in carbon monoxide. These facts and other similar ones led to the discovery of the law of multiple proportions, which may be stated thus:

*If two elements A and B form two or more compounds with each other, the different weights of B which combine with any fixed weight of A bear a simple ratio to one another.*

By way of further illustration we may take the three compounds which iron forms with sulphur. In one of these, approximately 7 parts by weight of iron are in combination with 4 parts of sulphur; in a second, 7 parts of iron are in combination with 6 parts of sulphur; and in the third, 7 of iron are in combination with 8 of sulphur. The figures 4, 6, and 8 bear a simple ratio to one another. The five compounds of nitrogen and oxygen contain 7 parts by weight of nitrogen combined with 8, 16, 24, 32, and 40 parts of oxygen respectively. The figures representing the parts by weight of oxygen combined with 7 parts by weight of nitrogen are to one another as 1 : 2 : 3 : 4 : 5. In the compounds formed by the elements chlorine, potassium, and oxygen the proportions by weight are represented in the following table:

| Chlorine. | Potassium | Oxygen. |
|---|---|---|
| 35.45 | 39.15 | 16 |
| 35.45 | 39.15 | 32 |
| 35.45 | 39.15 | 48 |
| 35.45 | 39.15 | 64 |

It will be observed that the ratio between the chlorine and potassium remains constant, but that the weight of oxygen varies regularly from 16 to 64; the weights bearing to one another the simple ratio 1 : 2 : 3 : 4.

The law of multiple proportions like the law of definite proportions is simply a statement in accordance with what has been found true by experiment. Although discovered by Dalton at the beginning of the last century

and put forward upon what now appears to be a slight basis of facts, all work since that time has confirmed it, and it forms to-day one of the corner-stones of the science of chemistry.

**Combining Weights of the Elements.**—A careful study of the figures representing the composition of chemical compounds reveals a remarkable fact regarding the relative weights of one and the same element that enter into combination with different elements. The proportions by weight in which some of the elements combine chemically with one another are stated in the following table:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | part | Hydrogen | combines | with | 35.45 | parts | Chlorine. |
| 1 | " | " | " | " | 79.96 | " | Bromine. |
| 1 | " | " | " | " | 126.97 | " | Iodine. |
| 35.45 | parts | Chlorine | combine | with | 39.15 | " | Potassium. |
| 79.96 | " | Bromine | " | " | 39.15 | " | " |
| 126.97 | " | Iodine | " | " | 39.15 | " | " |
| 16 | " | Oxygen | " | " | 65.4 | " | Zinc. |
| 16 | " | " | " | " | 24.36 | " | Magnesium. |
| 16 | " | " | " | " | 40.1 | " | Calcium. |
| 16 | " | " | " | " | 137.4 | " | Barium. |
| 65.4 | " | Zinc | " | " | 32.06 | " | Sulphur. |
| 24.36 | " | Magnesium | " | " | 32.06 | " | " |
| 40.1 | " | Calcium | " | " | 32.06 | " | " |
| 137.4 | " | Barium | " | " | 32.06 | " | " |

It will be seen that the figures that express the relative weights of chlorine, bromine, and iodine that combine with 1 part by weight of hydrogen also express the relative weights of these elements that combine with 39.15 parts by weight of potassium. So also the figures which express the relative weights of zinc, magnesium, calcium, and barium that combine with 16 parts by weight of oxygen also express the relative weights of these elements that combine with 32.06 parts by weight of sulphur. Hydrogen being the lightest element is taken as unity in stating the relative weights of the other elements which enter into combination. The weight of another element that combines with 1 * part by weight of hydrogen may

* See p. 20.

be called its *combining weight*. Thus, according to the above, the combining weights of chlorine, bromine, and iodine are respectively 35.45, 79.96, and 126.97. Similarly 39.15 is the combining weight of potassium, as it expresses the weight of potassium that combines with the above weights of chlorine, bromine, and iodine. Thus for every element a number can be selected that will express the proportions by weight in which the element enters into combination with others. These numbers are the *combining weights*.

In case two elements combine with each other in two or more proportions it may be difficult to decide which numbers are most convenient. For example, hydrogen and oxygen form two compounds with each other. In one of these 1 part by weight of hydrogen is combined with 8 parts by weight of oxygen, and in the other 1 part by weight of hydrogen is combined with 16 parts by weight of oxygen. We shall see a little later that, while the numbers primarily express the combining weights and nothing else, and are based solely upon a study of the composition of chemical compounds, they have come to have a deeper significance which will be explained in due time. Those adopted are called *atomic weights* because for strong reasons they are believed to express the relative weights of the minute particles or atoms of which the various kinds of matter are assumed to be made up. The atomic theory, as it is called, will be treated of farther on, and the relation between the theory and the figures called the atomic weights will be discussed at some length. For the present it will be best to use the figures as expressing the combining weights, and as being entirely independent of any speculations regarding the constitution of matter and the existence of atoms.

**The Elements, their Symbols and Atomic Weights.**— It has already been stated that there are about eighty elementary substances known, but that of these only a small number enter into the composition of common things to any great extent. It has been calculated that the nine most abundant elements occur in the solid crust

of the earth and the ocean approximately in the proportion represented in the subjoined table:

| | CRUST. | OCEAN. | AVERAGE INCLUDING AIR. |
|---|---|---|---|
| Oxygen | 47.29 | 85.79 | 49.98 |
| Silicon | 27 21 | .... | 29.30 |
| Aluminium | 7.81 | ... | 7.26 |
| Iron | 5 46 | .... | 5.08 |
| Calcium | 3 77 | 0.05 | 3.51 |
| Magnesium | 2.68 | 0 14 | 2.50 |
| Sodium | 2.36 | 1.14 | 2.28 |
| Potassium | 2.40 | 0.04 | 2.23 |
| Hydrogen | 0.20 | 10.67 | 0.94 |

While oxygen forms a large proportion of the solid crust of the earth, it forms a still larger proportion (eight-ninths) of water, and about one-fifth of the air. Carbon is the principal element that enters into the structure of living things, while hydrogen, oxygen, and nitrogen also are essential constituents of animals and plants. Nitrogen forms about four-fifths of the air.

In representing the results of chemical action, it is convenient to use abbreviations for the names of the elements and compounds. Thus, instead of oxygen we may write simply O; for hydrogen, H; for nitrogen, N; etc. These symbols are used in expressing what takes place when substances act upon one another. Very frequently the first letter of the name is used as the symbol. If the names of two or more elements begin with the same letter, this letter is used, and some other letter of the name is added. Thus, B is the symbol of boron, Ba of barium, Bi of bismuth; C is the symbol of carbon, Ca of calcium, Cd of cadmium, Ce of cerium, Cl of chlorine, Cr of chromium, Cs of cæsium, Cu of copper. In some cases the symbol is derived from the Latin name of the element. Thus, the symbol of iron is Fe, from the Latin *ferrum;* of copper Cu, from *cuprum;* of mercury Hg, from *hydrargyrum;* etc.

The names themselves are formed in a variety of ways.

Chlorine is derived from the Greek χλωρός, which means yellowish-green, as this is the color of chlorine. Bromine comes from βρῶμος, a stench, a prominent characteristic of bromine being its bad odor. Hydrogen comes from ὕδωρ, water, and γένειν, to produce, signifying that it is a constituent of water. Similarly nitrogen comes from νίτρον, nitre, and γένειν, to produce, nitrogen being one of the constituents of nitre. Potassium is an element found in potash, and sodium is found in soda. Some elements have been named after the country in which they were discovered. Thus gallium was discovered in France; scandium in Sweden; germanium in Germany. Tantalum was so called on account of the difficulties experienced in isolating it. Columbium received its name from the fact that it occurs in the mineral columbite, and this owes its name to the fact that it was first found in the United States of America.

On page 19 is given a table containing the names of all the elementary substances now known, together with their symbols and atomic weights. The names of those which are most widely distributed, and form by far the largest part of the earth, are printed in SMALL CAPITALS The names of those which are rare are printed in *italics.*

The symbols of the elements represent not only the names but relative quantities. Thus O stands for 16 parts by weight of oxygen; N for 14.01 parts by weight of nitrogen. Hydrogen enters into combination with other elements in the smallest relative quantity. It has the smallest combining weight, and it has been taken as the basis of the system. What the symbol O really means then is that the weight of matter represented by it is 16 times as great as the weight of matter represented by the symbol H, and the weight of matter represented by the symbol N is 14.01 times as great as that represented by the symbol H; and so on through the list. Accurate investigation has shown, however, that the ratio between the combining weights of hydrogen and oxygen is not as 1 : 16, but as 1 : 15.88. As many of the combining weights have been determined through the

aid of the oxygen compounds of the elements, and calculated on the assumption that the combining weight of oxygen is 16, it is plain that, if we accept 15.88 as the combining weight of oxygen, many of the other combining weights must be changed accordingly. A large number of chemists, however, favor keeping the combining weight of oxygen 16, and referring all the others to this as the basis of the system. This carries with it the

| Element | Symbol. | Atomic Weight. |
|---|---|---|
| ALUMINIUM | Al | 27.1 |
| Antimony | Sb | 120.2 |
| *Argon* | A | 39.9 |
| Arsenic | As | 75 |
| Barium | Ba | 137.4 |
| Bismuth | Bi | 208 |
| Boron | B | 11 |
| Bromine | Br | 79.96 |
| Cadmium | Cd | 112.4 |
| *Cæsium* | Cs | 132.9 |
| CALCIUM | Ca | 40.1 |
| CARBON | C | 12 |
| *Cerium* | Ce | 140.25 |
| CHLORINE | Cl | 35.45 |
| Chromium | Cr | 52.1 |
| Cobalt | Co | 59 |
| *Columbium* | Cb | 94 |
| Copper | Cu | 63.6 |
| *Erbium* | E | 166 |
| *Europium* | Eu | 152 |
| Fluorine | F | 19 |
| *Gadolinium* | Gd | 156 |
| *Gallium* | Ga | 70 |
| *Germanium* | Ge | 72.5 |
| *Glucinum* | Gl | 9.1 |
| Gold | Au | 197.2 |
| *Helium* | He | 4 |
| HYDROGEN | H | 1.008 |
| *Indium* | In | 115 |
| Iodine | I | 126.97 |
| Iridium | Ir | 193 |
| IRON | Fe | 55.9 |
| Krypton | Kr | 81.8 |
| *Lanthanum* | La | 138.9 |
| Lead | Pb | 206.9 |
| Lithium | Li | 7.03 |
| MAGNESIUM | Mg | 24.36 |
| Manganese | Mn | 55 |
| Mercury | Hg | 200 |
| Molybdenum | Mo | 96 |

| Element. | Symbol. | Atomic Weight. |
|---|---|---|
| *Neodymium* | Nd | 143.6 |
| *Neon* | Ne | 20 |
| Nickel | Ni | 58.7 |
| NITROGEN | N | 14.01 |
| *Osmium* | Os | 191 |
| OXYGEN | O | 16 |
| Palladium | Pd | 106.5 |
| Phosphorus | P | 31 |
| Platinum | Pt | 194.8 |
| POTASSIUM | K | 39.15 |
| *Praseodymium* | Pr | 140.5 |
| Radium | Ra | 225 |
| *Rhodium* | Rh | 103 |
| *Rubidium* | Rb | 85.5 |
| *Ruthenium* | Ru | 101.7 |
| *Samarium* | Sm | 150.3 |
| *Scandium* | Sc | 44.1 |
| *Selenium* | Se | 79.2 |
| SILICON | Si | 28.4 |
| Silver | Ag | 107.93 |
| SODIUM | Na | 23.05 |
| Strontium | Sr | 87.6 |
| Sulphur | S | 32.06 |
| *Tantalum* | Ta | 181 |
| *Tellurium* | Te | 127.6 |
| Terbium | Tb | 159.2 |
| *Thallium* | Tl | 204.1 |
| *Thorium* | Th | 232.5 |
| *Thulium* | Tu | 171 |
| Tin | Sn | 119 |
| Titanium | Ti | 48.1 |
| Tungsten | W | 184 |
| Uranium | U | 238 5 |
| Vanadium | V | 51.2 |
| *Xenon* | X | 128 |
| *Ytterbium* | Yb | 173 |
| *Yttrium* | Y | 89 |
| Zinc | Zn | 65.4 |
| Zirconium | Zr | 90.6 |

awkward necessity of changing the combining weight of hydrogen from 1 to 1.008. For all ordinary purposes we may continue to use 1 as the combining weight of hydrogen. The above table is the one recently (1907) recommended by an International Committee on Atomic Weights.

There are very serious difficulties encountered in determining the combining weights of the elements, and in regard to several given in the above table there is considerable doubt as to their accuracy. Those of the elements with which we most frequently have to deal have, however, been determined with great care. Work in this field is being constantly carried on, and every year our knowledge in regard to the combining weights becomes more accurate.

**Symbols of Compounds.**—As the elements enter into combination in the proportion of their respective combining weights or simple multiples of these weights, it is an easy matter to represent the composition of compounds by means of the symbols. Thus hydrogen and chlorine combine in the proportion of their combining weights to form the compound hydrochloric acid. The compound is represented by the symbol HCl, which signifies that the compound contains hydrogen and chlorine in the proportion of 35.45 parts by weight of chlorine to 1.008 parts of hydrogen. So the symbol ZnO means a chemical compound consisting of 65.4 parts by weight of zinc and 16 parts by weight of oxygen; HCN means a compound made up of 1.008 parts by weight of hydrogen, 12 parts by weight of carbon, and 14.01 parts by weight of nitrogen. Whenever the symbols of the elements are placed side by side with no sign between them, as in the above examples, the resulting symbol means that the elements are in chemical combination. But, as has been pointed out, elements may combine in more than one proportion. In one of the two compounds of carbon and oxygen the elements are combined in the proportion of their combining weights, and the compound is represented by the symbol CO; in the other compound the elements are

combined in the proportion of twice the combining weight of oxygen to the combining weight of carbon, and the compound is represented by the symbol $CO_2$. The three compounds of iron and sulphur to which reference has already been made are represented by the symbols FeS, $Fe_2S_3$, and $FeS_2$. The first represents a compound in which the elements are combined in the proportion of their combining weights, or 55.9 parts iron to 32.06 parts sulphur; the second represents a compound in which the elements are combined in the proportion of twice the combining weight of iron ($2 \times 55.9 = 111.8$ parts) to three times the combining weight of sulphur ($3 \times 32.06 = 96.18$ parts); and the third represents a compound in which the elements are combined in the proportion of the combining weight of iron (55.9 parts) to twice the combining weight of sulphur ($2 \times 32.06 = 64.12$ parts). The four compounds of potassium, chlorine, and oxygen above mentioned are represented by the symbols KClO, $KClO_2$, $KClO_3$, and $KClO_4$, the meaning of which will be clear from the explanation just given. By means of such symbols all chemical compounds can be represented, and they show not only what elements are contained in the compounds, but in what proportions by weight the elements are combined. They represent facts that have been determined by experiment. Knowing the actual weight of one constituent of any compound we can calculate by the aid of the symbol the actual weights of the other constituents and of the compound itself. Thus, if we know the actual weight of the chlorine contained in a quantity of potassium chlorate, $KClO_3$, we can calculate how much potassium and how much oxygen are contained in that same quantity, and also what the quantity of potassium chlorate is. Suppose, for example, we know that in a certain quantity of potassium chlorate there is contained 25 grams of chlorine, and it is desired to know how much potassium and how much oxygen there are in this quantity, and also what the quantity of potassium chlorate is. We know that the compound $KClO_3$ is made up of 39.15 parts by weight of potassium, 35.45 parts by weight

of chlorine, and 3 times 16, or 48 parts by weight of oxygen, the whole making 122.6 parts by weight. The solution of the following equations in proportion will give the quantities desired:

35.45 : 25 :: 39.15 : weight of potassium;
35.45 : 25 :: 48 : " " oxygen;
35.45 : 25 :: 122.6 : " " potassium chlorate.

**Chemical Equations.**—In dealing with cases of chemical action it is desirable to express by means of the symbols that represent the elements and compounds what takes place. In general, a chemical change is called a chemical reaction, and these reactions are of three kinds:

(1) Two or more elements or compounds may unite directly to form one product. This is called *combination*. The following examples will suffice. When mercury is kept boiling in the air for a time it becomes covered with a layer of a red substance which is a compound of mercury and oxygen represented by the symbol HgO. Magnesium burns in the air and forms the compound MgO. Hydrochloric acid, HCl, combines directly with ammonia, $NH_3$, and forms the compound known as ammonium chloride, $NH_4Cl$. Water, $H_2O$, combines directly with lime or calcium oxide, CaO, to form slaked lime or calcium hydroxide, $CaO_2H_2$. To represent these facts, the symbols of the elements or compounds that act upon each other are written with a plus sign between them, and the sign of equality is written before the symbol of the product. The chemical equations that represent the above-mentioned chemical reactions are:

Combination

$$\begin{aligned} Hg + O &= HgO; \\ Mg + O &= MgO; \\ HCl + NH_3 &= NH_4Cl; \\ H_2O + CaO &= CaO_2H_2. \end{aligned}$$

In reading the equations the plus sign is generally rendered by *and*, and the sign of equality by *give*. The first

equation should accordingly be read, "Mercury and oxygen give mercuric oxide;" but it also represents the exact relations by weight between the quantities of the elements and of the compound that take part in the reaction.

(2) The second kind of chemical reaction is *decomposition* or the opposite of combination. Examples are furnished by the decomposition of mercuric oxide into mercury and oxygen by heat; of potassium chlorate into potassium chloride and oxygen by heat; of water into hydrogen and oxygen by the electric current; and of calcium carbonate or limestone, $CaCO_3$, into lime or calcium oxide, CaO, and carbon dioxide, $CO_2$, by heat. These reactions are represented by the equations:

$$\begin{aligned} HgO &= Hg + O; \\ KClO_3 &= KCl + 3O; \\ H_2O &= 2H + O; \\ CaCO_3 &= CaO + CO_2. \end{aligned}$$

The expressions 3O and 2H mean respectively three times the combining weight of oxygen and twice the combining weight of hydrogen.

(3) The third kind of chemical reaction is that in which two or more compounds give rise to the formation of two or more others; or an element and a compound may act in such a way as to give another compound and another element. This is called *double decomposition* or *metathesis*. The following cases will serve as examples: Sulphuric acid, $H_2SO_4$, and potassium nitrate, $KNO_3$, or saltpetre, give potassium sulphate, $K_2SO_4$, and nitric acid, $HNO_3$; nitric acid, $HNO_3$, and sodium carbonate, $Na_2CO_3$, give sodium nitrate, $NaNO_3$, carbon dioxide, $CO_2$, and water, $H_2O$; hydrochloric acid, HCl, and zinc, Zn, give zinc chloride, $ZnCl_2$, and hydrogen. These facts are represented thus:

$$\begin{aligned} H_2SO_4 + 2KNO_3 &= K_2SO_4 + 2HNO_3; \\ 2HNO_3 + Na_2CO_3 &= 2NaNO_3 + CO_2 + H_2O; \\ 2HCl + Zn &= ZnCl_2 + 2H. \end{aligned}$$

In the expressions $2KNO_3$, $2HNO_3$, $2NaNO_3$, and $2HCl$, the large figures placed before the symbols of the compounds signify that the quantities of the compounds represented by the symbol are to be multiplied by the figure. Thus, HCl stands for 1.008 + 35.45 = 36.458 parts by weight of hydrochloric acid; but 2HCl stands for 2(1.008 + 35.45) = 72.916 parts.

(4) The fourth kind of chemical reaction is *substitution*. In this one element takes the place of another. The action of chlorine on marsh gas is a good example:

Substitution $CH_4 + 2Cl = CH_3Cl + HCl$.

This will be more fully explained later.

**The Scope of Chemistry.**—A complete study of chemistry would involve the study of the action of all the elements upon one another under all possible circumstances, and a study of the action of all compounds upon one another and upon the elements under all circumstances. This indicates that the field is almost boundless; and if the facts are not related in some way, if every time a reaction is studied we are to expect something entirely different from all other reactions, the task would be practically hopeless. Fortunately a great many general facts are known, and reactions which at first seem to have no connection are by careful study shown to be related. Thus the study is very much simplified and made interesting. It must be our purpose to study the facts in as systematic a way as possible, and to be constantly on the alert to detect relations. The habit of comparing a new reaction with others already studied should be cultivated. In this way light will come out of the darkness, and the subject will gradually become clear. While the simplest way to begin the study of chemistry is by a consideration of the elements, the subject is complicated by the fact that these elements generally cannot be obtained without the aid of substances that have not been studied, and of processes that are incomprehensible. There are, however, two elements that occur in nature in enormous

quantities, that can be obtained in the uncombined condition quite easily. As the kinds of action which they exhibit are of great importance and are well calculated to give an insight into the nature of chemical action in general, the study of chemical phenomena may profitably be begun by a study of these two elements. They are oxygen and hydrogen. In learning the main facts in regard to these two elements much will be learned that will be of importance for the study of other chemical phenomena.

**Chemical Action accompanied by other kinds of Action.**—Whenever a chemical change takes place it is accompanied by other changes and, in order to gain a complete knowledge of the phenomena, these other changes must be studied. Thus when sulphuric acid acts upon zinc the chemical change is represented both qualitatively and quantitatively by the equation

$$Zn + H_2SO_4 = ZnSO_4 + 2H.$$

In studying the reaction, the first thing to do is to learn the nature of the substances formed, and the relations between the substances that act upon each other and the products. This may be called the purely chemical study of the reaction. But much more can be learned in regard to it by careful observation. In the first place, the fact must be taken into account that a solid and liquid here react to form a solid and a gas; and the question suggests itself, does this change to the gaseous condition exert any influence on the reaction, or is this a fact of no special importance? Again, it will be observed that accompanying the chemical change there is a marked rise in temperature, and the inquiry naturally suggests itself whether the quantity of heat evolved is definite for definite quantities of the substances, and, if so, what relation exists between them. There are still other changes that must be taken into account in order to get a complete knowledge of a chemical reaction, but, as yet, the study of the other changes has not been taken up in a

general way, and our information in regard to them is comparatively limited. Within late years much progress has been made in the study of the heat changes that accompany chemical changes. It has been found that every chemical change gives rise either to an evolution or to an absorption of heat, and that for definite quantities of the same substances under the same circumstances the same amount of heat is evolved or absorbed. The special study of the heat changes connected with chemical changes is called *thermochemistry*. A consideration of the facts and laws of thermochemistry is of assistance in dealing with chemical reactions, and some attention will be paid to the subject in this book.

## EXPERIMENTS.

### Chemical Change Caused by Heat.

Experiment 1.—In a clean, *dry* test-tube put enough white sugar to make a layer ¼ to ½ an inch thick. Hold the tube in the flame of a spirit-lamp or a laboratory burner until no further change takes place. What evidence is furnished by this experiment that chemical change may be caused by heat? What is left in the tube? Is it soluble? Is it sweet? Is it sugar?

Experiment 2.—Half-fill the bulb of an arsenic-tube with red oxide of mercury, or, if such a tube is not available, proceed as follows: From a piece of hard-glass tubing of about 6 to 7 millimeters (¼ inch) internal diameter cut off a piece about 10 centimeters (4 inches) long by making a mark across it with a triangular file, and then seizing it with both hands, one on each side of the mark, pulling, and at the same time pressing slightly as if to break it. Clean and dry it, and hold one end in the flame of a blast lamp until it melts together. During the melting turn the tube constantly around its long axis so that the heat may act uniformly upon it. Put into the tube thus made enough red oxide of mercury (mercuric oxide) to form a layer about 12 millimeters (½ inch) thick. Heat the tube as in the last experiment. What change in color is noticed? What is deposited upon the glass in the upper part of the tube? What evidence is furnished by this experiment that chemical change can be effected by heat?

## Chemical Changes can be effected by an Electric Current.

Experiment 3.—To the ends of insulated copper wires connected with two cells of a Bunsen's or Grove's battery fasten platinum plates, say 25 mm. (1 inch) long by 12 mm. (½ inch) wide. Insert these platinum electrodes into water contained in a shallow glass vessel about 15 cm. (6 inches) wide and 7 to 8 cm. (3 inches) deep, taking care to keep them separated from each other. No action will take place, for the reason that water will not conduct the current, and hence when the platinum electrodes are kept apart there is no current. By adding to the water about one tenth its own volume of strong sulphuric acid, a current passes It will then be observed that bubbles rise from each of the platinum plates In order to collect them an apparatus like that shown in Fig. 1 may be used.

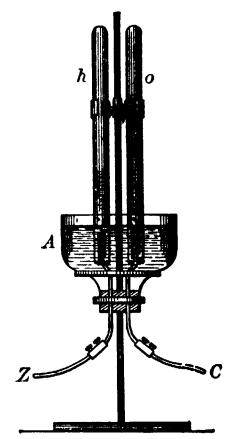


Fig. 1.

*h* and *o* represent glass tubes which may conveniently be about 30 cm. (1 foot) long and 25 mm. (1 inch) internal diameter. They are first filled with the water containing one tenth its volume of sulphuric acid, and then placed with the mouth under water in the vessel *A*. The platinum electrodes are now brought beneath the inverted tubes. The bubbles which rise from them will pass upward in the tubes, and the water will be pressed down. Gradually the water will be completely forced out of one of the tubes, while the other is still half full of water. The substances thus collected in the tubes are invisible gases. After the first tube is full of gas, place the thumb over its mouth and remove the tube. Turn it mouth upward and at once apply a lighted match to it. A flame will be noticed. The gas which was contained in the tube is therefore capable of burning. It cannot, therefore, have been air. In the meantime the second tube will have become filled with gas. Remove this tube in the same way and insert a thin piece of wood with a spark on it. The spark will at once burst into flame, and the burning of the wood will take place more actively than it does in ordinary air, as may be shown by withdrawing it and again inserting it into the tube. The gas in this tube, it will be noticed, does not take fire. Without going into further details, it is clear from the above experiment that when an electric current acts on acidulated water two invisible gases are produced. A chemical change is caused by an electric current.

## Mechanical Mixtures and Chemical Compounds.

Experiment 4.—Examine carefully a piece of coarse-grained granite ; break off some of it, and separate the constituents. How many are there? By what properties do you recognize them? Powder a small bit of one of the constituents, and examine the powder with the microscope. Do you recognize more than one kind of matter? Mix the powder of the three constituents, and see whether in the mixed powder there is any difficulty in detecting the three kinds of matter with the aid of the microscope.

Experiment 5.—Mix a gram or two of powdered roll sulphur and an equal weight of very fine iron filings in a small mortar. Examine a little of the mixture with a microscope. Not only can the particles of iron and of sulphur be recognized by means of the microscope, but the pieces of iron can be picked out by means of a magnet. The magnet attracts the iron but not the sulphur, so that by passing the magnet often enough through the mixture we can pick out all the iron and leave all the sulphur. This separation is really a mechanical separation. It is only a somewhat more refined method of picking out than that used in the case of granite.

Experiment 6.—Pass a small magnet through the mixture above prepared. Unless the substances used are thoroughly dry, particles of sulphur will adhere to the magnet, but even then it will be seen that most of that which is taken out of the mixture is iron.

The iron and sulphur can also be separated by treating the mixture with a liquid known as carbon bisulphide. Sulphur dissolves in this liquid, but iron does not. So that when the mixture is treated with it the iron is left behind, and can easily be recognized as such.

Experiment 7.—Pour a few cubic centimetres of carbon bisulphide on a little powdered *roll-sulphur* in a dry test-tube. What takes place? Treat iron filings in the same way. What takes place? Now treat a small quantity of the mixture with carbon bisulphide. After the sulphur is dissolved filter the solution upon a good-sized watch-glass and let it stand. Examine what remains undissolved in the test-tube, and satisfy yourself that it is iron. After the liquid has evaporated examine what is left in the watch-glass and satisfy yourself that it is sulphur. Why are you justified in concluding that the substance left in the test-tube is iron and that left on the watch-glass is sulphur?

Experiment 8.—Make a fresh mixture of three grams each of powdered roll-sulphur and fine iron filings. Grind them together intimately in a dry mortar and put them in a dry test-tube. Heat gradually until the mass begins to glow. At first the sulphur melts and becomes dark-colored. It may even take fire. But soon something else evidently takes place. The whole mass begins to glow, and if you at once take the tube out of the flame, the mass continues

to glow, becoming brighter. This soon stops ; the mass grows dark and gradually cools down. As soon as it reaches the ordinary temperature, the tube should be broken and the contents put in a mortar. A close examination will show that the mass does not look like the mixture of sulphur and iron with which we started. It has a bluish-black color, and is apparently homogeneous. An examination with the microscope, the magnet, and carbon bisulphide will prove that, while there may be a little iron left, and possibly a little sulphur, most of the bluish-black mass is neither iron nor sulphur, but a new substance with properties quite different from those of iron and from those of sulphur.

## Other Examples of Chemical Action.

Experiment 9.—Examine a piece of calc-spar or marble. You see that it is made up of pieces of definite shape. It is, as we say, crystallized. It is quite hard, though a knife will cut it. Heated in a hard-glass tube, as in Experiment 2, it does not melt, but remains essentially unchanged It does not dissolve in water. To prove this, put a piece the size of a pea in a test-tube with pure water. Thoroughly shake, and then, as heating usually aids solution, boil. Now pour off a few drops of the liquid on a piece of platinum-foil or an evaporating-dish, and by gently heating cause the water to evaporate. If there is anything in solution, there will be a solid residue on the platinum-foil or watch-glass If not, there will be no residue. Now treat a small piece of the substance with dilute hydrochloric acid and notice what takes place. Bubbles of gas are given off. After the action has continued for about a minute, insert a lighted match in the upper part of the tube. It is extinguished, and the gas does not burn. The gas formed in this case is therefore plainly not identical with either one of those obtained from water by the action of the electric current (see Experiment 3). It is what is commonly called carbonic-acid gas. As the action continues, the piece of calc-spar or marble grows smaller and smaller, and finally disappears, when there is a clear solution. The substance has dissolved in the hydrochloric acid. In order to determine whether anything else has taken place besides the dissolving, we shall have to get rid of the excess of hydrochloric acid. This we can easily do by boiling it, when it passes off in form of vapor, and then whatever is in solution will remain behind. For this purpose, put the solution in a small, clean porcelain evaporating-dish, and put this on a vessel containing boiling water, or a water-bath. The operation should be carried on in a place in which the draught is good, so that the vapors will not collect in the working-room. They are not poisonous, but they are annoying. The arrangement for evaporating is represented in Fig. 2.

After the liquid has evaporated and the substance in the evaporating dish is dry, examine it and carefully compare its properties

with those of the substance which was put into the test-tube. Its structure will be found not to present the regularities noticed in the original substance. It is much softer, dissolves in water, melts when heated in a hard-glass tube. It does not give off a gas when treated with hydrochloric acid. When exposed to the air it soon becomes moist, and after a time liquid. The experiment shows that when hydrochloric acid acts upon calc-spar or marble the latter at least loses its own properties. It might be shown that some of the hydrochloric acid also loses its properties. In place of the two we get a new substance with entirely different properties. The two substances have acted chemically upon each other and produced a chemical compound. In this case it was only necessary to bring the substances in contact in order to cause them to act chemically upon each other It was not necessary to heat them, as it was in the case of the iron and sulphur.

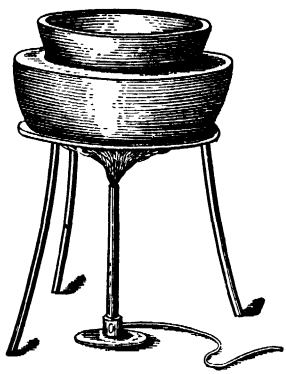


FIG. 2.

EXPERIMENT 10.—Bring together in a test-tube a few small pieces of copper and some moderately dilute nitric acid. In a short time action begins. The upper part of the tube becomes filled with a dark, reddish-brown gas which has a disagreeable smell. Do not inhale it, as when taken into the lungs it produces bad effects. The solution becomes colored dark blue, and the copper disappears. Examine this solution, as in Experiment 9, and see what has been formed. What are the properties of the substance found after evaporation of the liquid? Is it colored? Is it soluble in water? Does it change when heated in a tube? Is it hard or soft? Does it in any way suggest the copper with which you started?

EXPERIMENT 11.—Try the action of dilute sulphuric acid on a little zinc in a test-tube. A gas will be given off. Apply a lighted match to it. Does the result suggest anything noticed in an experiment already performed? After the zinc has disappeared, evaporate the solution as in Experiment 9. Carefully compare the properties of the substance left behind with those of zinc.

EXPERIMENT 12.—Hold the end of a piece of magnesium ribbon about 20 centimeters (8 inches) long in a flame until it takes fire; then hold the burning substance quietly over a piece of dark paper, so that the light, white product may be collected. Compare the properties of this white product with those of the magnesium. Here again a chemical act has taken place. The magnesium has combined with something which is found in the air, and heat was produced by the combination. The product is the white substance.

EXPERIMENT 13.—In a small, dry flask (400 to 500 ccm.) put a bit of granulated tin. Pour upon it 2 or 3 ccm. concentrated nitric acid. If no change takes place, heat gently, and presently there will be a copious evolution of a reddish-brown gas with a disagreeable smell (under what conditions has a gas like this already been obtained ?), the tin will disappear, and in its place will appear a white powder. Compare the properties of this white powder with those of tin. Why are you justified in concluding that they are not the same thing ?

## CHAPTER II.

### A STUDY OF THE ELEMENT OXYGEN.

**Historical.**—The older chemists considered air to be a simple substance, but the experiments of Priestley (1774) and of Scheele (1775) showed that the air contains two gases, only one of which has the power to support combustion; and they succeeded independently of each other in showing that oxygen is a distinct substance. The discovery of oxygen had a very important bearing on the work of Lavoisier on combustion, and it was he who gave the name oxygen (or *oxygène*) to the gas, for the reason that he supposed it to be the essential constituent of all those chemical substances which are known as acids, the word being derived from the Greek ὀξύς, acid, and γένειν, to produce. While this is generally true, it has since been found that the acid properties of substances are not dependent upon oxygen, and, therefore, the name is misleading.

**Occurrence.**—Oxygen is the most widely distributed and most abundant element of the earth. It forms, as has been stated, about 47 per cent of the solid crust of the earth; eight-ninths of water; and about one-fifth of the air. It occurs also in combination with carbon and hydrogen, or with carbon, hydrogen, and nitrogen in the substances which enter into the composition of living things, whether vegetable or animal. Besides this it forms a part of most manufactured chemical products.

**Preparation.**—Notwithstanding the abundant supply of oxygen in nature it is not a simple matter to get it in the free or uncombined state from most substances found in nature. As it forms eight-ninths of water, and water consists of only hydrogen and oxygen, the idea suggests itself at once that it may be made by the decomposition of water. This can be accomplished without serious difficulty by means of an electric current, and both hydro-

gen and oxygen can be obtained in this way; but the method is expensive and more complicated than others which are available. In the air the two gases nitrogen and oxygen are mixed together in the proportion of 1 volume of oxygen to 4 volumes of nitrogen. Here then, as in water, there is an enormous supply, but it is difficult to separate the oxygen from the nitrogen in such a way as to leave it uncombined. This can, however, be accomplished, and a method is now in practical use on the large scale for the purpose of preparing oxygen from the air. The method is based upon the fact that when barium oxide, BaO, is heated in a current of air it takes up oxygen and is converted into barium dioxide, $BaO_2$; and when the pressure upon the dioxide is sufficiently diminished at a high temperature, it is decomposed into the oxide, BaO, and oxygen, as represented in the equation

$$BaO_2 = BaO + O.$$

By this means oxygen can be extracted from the air and obtained in the free condition.

Air can be liquefied on the large scale. When the liquid is allowed to stand in an open vessel at ordinary temperatures, the nitrogen, having a lower boiling-point, passes off more rapidly than the oxygen and a part of the oxygen is left behind. Oxygen can thus be obtained from the air.

Among natural substances that can be used for the preparation of oxygen, manganese dioxide or pyrolusite, also called black oxide of manganese, $MnO_2$, is the most important. It gives off a part of its oxygen when heated to a comparatively high temperature. The decomposition is represented by this equation:

$$3MnO_2 = Mn_3O_4 + 2O.$$

As will be seen, only one-third of the oxygen contained in the dioxide is thus obtained in the free state. A similar method is that used by Priestley when he discovered oxygen. It consists in heating mercuric oxide, HgO, when it is decomposed as represented thus:

$$HgO = Hg + O.$$

The substance potassium chlorate, $KClO_3$, is manufactured on the large scale for a variety of purposes and is, therefore, easily obtained. It gives up its oxygen when heated. At first the decomposition represented by this equation takes place:

$$8KClO_3 = 5KClO_4 + 3KCl + 4O.$$

The products are potassium perchlorate, $KClO_4$, potassium chloride, KCl, and oxygen, one-sixth of the total oxygen being given off in the first stage. This part of the decomposition takes place readily, and at a comparatively low temperature. If, after it is complete, the temperature is raised considerably higher, more gas is given off and the change represented by the equation

$$KClO_4 = KCl + 4O$$

is accomplished. The final result is, therefore, the setting free of all the oxygen contained in the chlorate. This fact is represented thus:

$$KClO_3 = KCl + 3O.$$

The best laboratory method for the preparation of oxygen and regulating the supply at will depends on the interaction of potassium bichromate, hydrogen peroxide, and sulphuric acid.

The common laboratory method for the preparation of oxygen consists in heating a mixture of equal parts of coarsely-powdered manganese dioxide and potassium chlorate. This mixture gives up oxygen readily under the influence of heat. Potassium chlorate alone requires to be heated to a temperature of over 350° C. to effect its decomposition, but when mixed with manganese dioxide the decomposition takes place at about 200° C. The manganese dioxide does not lose any of its oxygen under these circumstances. Other substances, such as ferric oxide, copper oxide, etc., may be used with similar effect. A method that promises to displace all others has recently (1905) been devised. It consists in treating a product called "oxone" with water. The chief constituent of oxone is sodium peroxide, $Na_2O_2$.

**Physical Properties.**—Oxygen is a colorless, tasteless, inodorous gas. It is only slightly soluble in water, 100 volumes of water at 0° dissolving 4.1 volumes of oxygen. It is slightly heavier than air, its specific gravity is 1.1056, and 1 liter under 760 mm. pressure and at temperature 0° weighs 1.429 grams, while a liter of air weighs 1.2932 grams. In dealing with chemical elements and compounds that are gaseous, it is customary to use hydrogen instead of the air as the standard for specific gravity. While the specific gravity of oxygen in terms of air is 1.1056, in terms of hydrogen it is 15.89, or, in other words, a given volume of oxygen weighs 15.89 as much as the same volume of hydrogen under the same conditions. Under a pressure of 50 atmospheres and at a temperature — 119° it is condensed to a liquid of specific gravity 0.978. Liquid oxygen is a pale, steel-blue, transparent, and very mobile liquid which boils at — 182.8° at ordinary pressure. When the pressure is reduced or removed, evaporation takes place so rapidly that a part of the oxygen is often f ozen to a white solid. If the pressure is increased, the boiling point rises. Thus by applying a pressure of 50 atmospheres, the boiling point is raised to — 119°. If the temperature is above — 119° oxygen cannot be liquefied no matter how great the pressure. This is called the *critical temperature* of oxygen. The pressure required to liquefy oxygen at the critical temperature is called the *critical pressure.*

**Chemical Properties.**—At ordinary temperatures oxygen does not act readily upon most other things, as can be clearly shown by putting a variety of substances in the gas without heating them. If they are left for a considerable time some evidence of change may be observed, but generally the change is extremely slow unless the temperature is raised. At higher temperatures, different for different substances, it combines with all the elements except fluorine, helium, neon, argon, krypton, and xenon, and it acts readily upon a large number of compounds. Its action is generally accompanied by an evolution of heat and light, and the process under these circumstances

is called combustion. This action may be illustrated by first heating and then introducing into vessels containing oxygen, sulphur, charcoal, iron in the shape of a steel watch-spring, and a bit of phosphorus. The phenomena observed show that chemical action takes place, but they do not show what is formed. It is evident that in each case light and heat are evolved, and that the substances introduced into the oxygen are changed to other things. In the case of phosphorus the light given off is very intense, while in that of carbon and that of sulphur it is only slight. In the vessel in which the burning of the iron takes place a reddish-brown substance is deposited, while in that in which the phosphorus is burned dense white fumes are formed and at first the product is partly deposited upon the walls of the vessel in the form of a white powder that looks like snow. After standing for some time over water it disappears and the water evidently contains something in solution. A thorough study of the reactions above mentioned has shown that they consist in the chemical combination of oxygen with the substances burned. The light and heat are results of the chemical action. The reactions are represented by the following equations:

With sulphur, $S + 2O = SO_2$; With iron, $3Fe + 4O = Fe_3O_4$;
" carbon, $C + 2O = CO_2$; " phosphorus, $2P + 5O = P_2O_5$.

The products are sulphur dioxide, $SO_2$, a colorless, pungent gas; carbon dioxide, $CO_2$, a colorless gas; magnetic oxide of iron, $Fe_3O_4$, a reddish-brown substance; and phosphorus pentoxide, $P_2O_5$, a white solid that dissolves in water.

**Burning in the Air and Burning in Oxygen.**—One cannot help noticing a strong resemblance between the burning of substances in the air and in oxygen; and the question naturally suggests itself, Are these two acts the same in character, or is there a difference between them? To answer this question, it is necessary to burn the same substances in pure oxygen and in air, and to determine whether the same products are formed in the two cases, and whether anything else is formed. If this

comparison should be made in any case, it would be found that, whether a substance burns in the air or in pure oxygen, the same product is formed, and nothing else. It is therefore certain that the act of burning in the air is due to the presence of oxygen. But substances do not burn as readily in the air as in oxygen, and some which burn in oxygen do not burn in the air. This is due to the fact that only about one-fifth of the volume of the air is oxygen, while most of the remaining four-fifths consists of an extremely inactive element, nitrogen, which takes little part in the process of burning.

**Combustion.**—By the term combustion in its broadest sense is meant any chemical act that is accompanied by an evolution of light and heat. Ordinarily, however, it is restricted to the union of substances with oxygen, as this union takes place in the air, with evolution of light and heat. Substances that have the power to unite with oxygen are said to be *combustible*, and substances that have not this power are said to be *incombustible*. Most elements combine with oxygen, and are therefore combustible. Most compounds formed by the union of oxygen with combustible substances are incombustible. For example, the sulphur dioxide, carbon dioxide, magnetic oxide of iron, and phosphorus pentoxide, formed when sulphur, carbon, iron, and phosphorus are burned in oxygen, are incombustible. They contain oxygen and they cannot combine directly with more.

**Kindling Temperature.**—It has been seen that substances do not usually combine with oxygen at ordinary temperatures, but that in order to effect the union the temperature must be raised. If this were not the case, it is plain that every combustible substance in nature would burn up, for the air probably supplies a sufficient quantity of oxygen for this purpose. Some substances need to be heated to a high temperature before they will combine with oxygen; others require to be heated but little. When pieces of phosphorus, of sulphur, and of carbon are subjected to the same gradual rise in temperature, it is observed that the phosphorus takes fire very

easily, only a slight elevation of temperature being necessary; next in order comes the sulphur; and last the carbon. If these experiments should be repeated a number of times, it would be found that the phosphorus always takes fire at the same temperature, and a similar result would be reached in the case of sulphur and carbon. Every combustible substance has its *kindling temperature;* that is, the temperature at which it will readily combine with oxygen. If a piece of wood should be heated to its kindling temperature all at once, it would burn up as rapidly as it could secure the necessary oxygen; but the burning does not usually take place rapidly, for the reason that only a small part of it is at any one time heated to the kindling temperature. Watch a stick of wood burning, and see how, as we say, "the fire creeps" slowly along it. The reason of the slow advance is simply this: Only those parts of the stick which are nearest the burning part become heated to the kindling temperature. They take fire and heat the parts nearest them, and so on gradually throughout the length of the stick.

It would appear that most substances do not acquire the property of uniting with oxygen till a certain higher temperature is reached. This is not strictly true. Combustible substances are believed to unite with oxygen at all temperatures but with very different speed. While the union is rapid at a higher temperature, it becomes slower as the temperature falls, and gradually becomes so slow as to escape observation.

**Slow Oxidation.**—Substances may combine slowly with oxygen without evolution of light. Thus, if a piece of iron is allowed to lie in moist air, it becomes covered with rust. The rust is similar to the substance formed when iron is burned in oxygen. Both are formed by the union of iron and oxygen. Magnesium burns in the air and forms a white compound containing oxygen. It burns with increased brilliancy in oxygen, forming the same compound. If left in moist air for some days or weeks, it becomes covered with a layer of the same white substance. If this is scraped off, and the magnesium

again allowed to lie, it will again become covered with a layer of the compound with oxygen, and this may be continued until the magnesium has been completely converted into the same substance that is formed when it burns in oxygen or in the air. Many other cases of slow oxidation might be described, some of which, such as the decay of wood, are constantly taking place. The most important illustration of slow oxidation is that which takes place in our bodies, for the food of which we partake undergoes a great many changes, some of the substances uniting with oxygen, and thus keeping up the temperature. This, however, is done without evolution of light. We take large quantities of oxygen into our lungs in the act of breathing. This acts upon various substances presented to it, oxidizing them to other forms which can easily be got rid of. More will be said in regard to the breathing process of animals and plants when the subject of carbon and its compounds is taken up.

**Heat of Combustion.**—What is the chief difference between combustion, as we ordinarily understand it, and slow oxidation? As far as can be judged by a cursory examination, it is that in the former there is an evolution of light and much heat, while in the latter there is apparently but little heat evolved and no light. Remembering that the reason why a body gives light is that it is heated to a sufficiently high temperature, the problem resolves itself into a question of heat. What difference, if any, is there between the quantity of heat given off when a substance burns, and when it undergoes slow oxidation without evolution of light? Experiment has shown that *there is no difference.* In one case all the heat is given off in a short space of time, and therefore the temperature of the substance becomes high and it emits light. In the other the heat is given off slowly and continues for a much longer time, and therefore the temperature of the substance does not get high, as surrounding substances conduct off the heat nearly as rapidly as it is evolved. The *quantity* of the heat is, however, the same in both cases.

The heat given off or absorbed in a chemical reaction can be measured by allowing the reaction to take place in a vessel called a calorimeter, so constructed as to prevent loss of heat, and containing a known weight of water. The temperature of the water is noted at the beginning of the operation and at the end. A quantity of heat is generally stated by giving the number of grams of water which it will raise one degree (Centigrade) in temperature. The quantity of heat necessary to raise a gram of water from 0° to 1° Centigrade is the unit used in heat measurements. It is called the *calorie*. The statement that the quantity of heat evolved in any reaction is 250 calories (written generally 250 cal.) means a quantity of heat capable of raising the temperature of 250 grams of water one degree or of one gram of water 250 degrees in temperature. Sometimes it is convenient to use a larger unit. The quantity of heat required to raise the temperature of one kilogram of water one degree serves the purpose. This is the large Calorie. To distinguish it from the smaller one it is written with a capital. Thus, 250 Cal. means 250 large Calories. The large Calorie is obviously 1000 times greater than the small calorie.

To repeat, then: By the heat of combustion of a substance is meant the quantity of heat given off when a certain weight of the substance combines with oxygen. In order to avoid confusion it is necessary to have an agreement in regard to the weight of substance that shall be used as the standard. This may be a gram or any other weight, but for the purposes of chemistry it is most convenient to take weights in proportion to the combining or atomic weights. Thus, by the heat of combustion of carbon is meant the quantity of heat evolved in the combination of 12 grams of carbon with $2 \times 16 = 32$ grams of oxygen. By the heat of combustion of sulphur is meant the quantity of heat evolved in the combination of 32.06 grams of sulphur with $2 \times 16 = 32$ grams of oxygen, etc.

Not only is the heat of combustion the same whether the union with oxygen takes place slowly or rapidly, but the heat evolved in any given chemical reaction is always

the same, and chemical action is always accompanied by an evolution or absorption of heat.

**Heat of Decomposition.**—Just as it is true that a definite quantity of heat is evolved when two or more elements combine chemically, so also it is true that in order to overcome the force which holds these elements together the same quantity of heat is absorbed. Thus, the heat of formation of mercuric oxide, HgO, is 30,660 cal.; or, in other words, when 200.3 grams of metallic mercury and 16 grams of oxygen combine, 30,660 calories are evolved. Now, it has been seen that when heat is applied to the compound it is decomposed into its elements. When this decomposition is effected, just as much heat is absorbed as was evolved in the formation of the compound.

**Chemical Energy and Chemical Work.**—Any substance that has the power to unite with others can do *chemical work:* it possesses *chemical energy.* Thus, all combustible substances can do work. In uniting with oxygen heat is evolved, and this can be transformed into motion. In the case of the steam-engine, the source of the motion is the burning of the fuel, which is a chemical act. It is thus seen that the source of the power of the steam-engine is chemical energy. Substances, on the other hand, that have no power to combine with others have no power to do chemical work, or they have no chemical energy. So far as power to combine with oxygen is concerned, water is a substance of this kind, as is also carbon dioxide, the gas formed when carbon is burned in oxygen. In order that they may do work by combining with oxygen, they must first be decomposed, and their constituents put together in some form in which they have the power of combination. This decomposition of carbon dioxide and water is taking place constantly on the earth. All plant-life is dependent on it. The products of the action, such as the different kinds of wood, have chemical energy,—they can do chemical work. This power to do work has been acquired from the heat of the sun, which is the main force used in decomposing the carbon dioxide and water. We have thus a transfor-

mation of the sun's heat into chemical energy, which is stored up in the combustible woods. The quantity of heat which is given off in burning wood is believed to be exactly equal to the quantity of heat absorbed in its formation.

**Oxides.**—The compounds of oxygen with other elements are called *oxides*. To distinguish between different oxides, the name of the element with which the oxygen is in combination is prefixed. Thus, the compound of zinc and oxygen is called *zinc oxide;* that of calcium and oxygen, *calcium oxide;* that of silver and oxygen, *silver oxide;* etc. When an element forms more than one compound with oxygen, suffixes are used to distinguish between them. Thus in the case of copper there are two oxides which have the composition represented by the symbols $Cu_2O$ and CuO. The former is known as *cuprous oxide* and the latter as *cupric oxide*. That oxide which contains the smaller weight of oxygen in combination with a given weight of the other element is designated by the suffix *ous;* that which contains the larger proportion of oxygen is designated by the suffix *ic*. In other cases the number of combining weights of oxygen contained in the compound is indicated by the name. Thus, *manganese dioxide* is $MnO_2$; *sulphur trioxide* is $SO_3$; etc.

**The Kinetic Theory of Gases.**—This theory assumes that the constituent particles of the gas are perfectly elastic, that they are at such a distance apart as not to influence each other, that they occupy a space which is negligible when compared with that occupied by the gas as a whole, and that they are in continuous motion obeying the laws of dynamics.

Bernouilli, the originator of the theory (1738), says: "If the gas consists of a number of moving particles and the pressure exerted by it on the walls of the vessel arises from the impact of the particles against these walls, then if the gas is compressed and its volume diminished, the number of impacts of the now more closely packed particles against the walls of the vessel increases." He then proves mathematically that the number of impacts in a given time against a given part of the wall, is increased in a ratio which is the inverse of the ratio in which the volume of the gas is diminished.

**Boyle's law.**—the volume of a gas is inversely proportional to the pressure exerted upon it—is thus deduced from the kinetic theory.

The law of Gay-Lussac—that the volume of a gas increases regularly as the temperature increases—may also be deduced from the kinetic theory; as the rise in temperature steadily increases the velocity or kinetic energy of the particles increases.

In the kinetic theory it is assumed that the size of the molecules is negligibly small, and that the particles have no tendency to cohere. Neither of these assumptions is *exactly* true for any gas, and it can be shown that the deviations in behavior from that called for by the laws of Boyle and Gay-Lussac exhibited in varying degree by the individual gases at very high and very low temperatures can be accounted for in this way.

If the gas particles have some tendency to cohesion, increased pressure tends to make them cohere more closely and approach the liquid state, while lowered temperature diminishes their velocity or kinetic energy and thus aids cohesion.

Some gases, such as ammonia and carbon dioxide, can be liquefied by pressure alone at ordinary temperatures. The gases which obey the gas laws more closely, like oxygen and hydrogen, cannot be liquefied by pressure alone at ordinary temperature.

**Critical Points.**—There is a definite temperature for every gas, above which no amount of pressure liquefies it. This is called its *critical temperature*. The critical temperature of hydrogen is −234° of oxygen −118°, of carbon dioxide 31°.35, of ammonia 130°. The pressure required to liquefy a gas at its critical temperature is called its *critical pressure*. Data like these, the boiling points of liquids, melting points of solids, and the like, which are independent of the chemical behavior of the substance, are called *physical constants*.

## EXPERIMENTS.

### Preparation of Oxygen.

Experiment 14.—Make some oxygen by heating to redness 10 to 15 grams (about half an ounce) of manganese dioxide in an iron tube closed at one end and connected at the other end by means of a cork with a bent glass tube.

Experiment 15.—Make some oxygen by heating a few grams of mercuric oxide in a glass tube closed at one end and connected at the other end by means of a cork with a bent glass tube.

Experiment 16.—Arrange an apparatus as shown in Fig. 3. *A* represents a retort of about 100 ccm. capacity. Attach to the neck of the retort a piece of rubber tubing *B* provided with a bent glass tip *C*. Place this tip under the surface of the water in *D*. In *A* put 4 to 5 grams (about an eighth of an ounce) potassium chlorate, and gently heat by means of the lamp. Notice carefully what takes place. At first the potassium chlorate will melt, forming a clear liquid. If the heat is increased, the liquid will appear to boil, and it will soon be seen that a gas

is given off. Now bring the inverted cylinder *E* filled with water over the end of the tube, and let the bubbles of gas rise in the cylinder. After a considerable quantity of gas has been collected in this way the action stops, the mass in the flask becomes solid, and

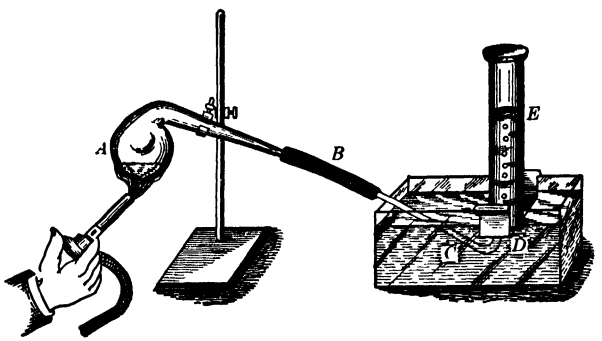



FIG. 3.

apparently the end of the process is reached. But if the temperature is raised higher, gas will again begin to come off, and in this second stage a larger quantity will be collected than in the first. Finally, however, the end is reached, and the substance left in the flask remains unchanged, no matter how high the temperature may be raised. An examination of the gas collected will show that a piece of wood will burn in it very readily. Explain the changes which have taken place in this experiment. Calculate how much oxygen can be obtained by heating 12 grams of potassium chlorate.

## MEASUREMENT OF THE VOLUME OF GASES.

In studying chemical changes it often becomes necessary to measure the volume of a gas, and it is important to know what precautions must be taken in such cases. For this purpose a tube is used which is graduated by marks etched on the outside. These marks may either indicate the number of cubic centimeters of gas contained in the tube, or the length of the column of gas. In the latter case it is of course necessary to determine what volume corresponds to a given length of the column, The chief difficulty encountered in measuring gas volumes is due to the fact that the volume varies with the temperature and pressure. When the temperature of a gas is raised one degree Centigrade its volume is increased $\frac{1}{273}$ part of its volume at 0°. If, therefore, the volume of a gas at 0° is $V$, at $t$° its volume $V'$ will be

$$V + \frac{t}{273} V, \text{ or } V' = \frac{V(273 + t)}{273}.$$

This expression may also be written thus :

$$V' = V + 0.00366t.\ V, \text{ or } V' = V(1 + 0.00366t).$$

From these we get the expressions

$$V = \frac{273\ V'}{273 + t} \text{ and } V = \frac{V'}{1 + 0.00366t}.$$

This is called the law of Dalton and Gay-Lussac and also the law of Charles.

On lowering the temperature of a gas below 0° the volume is diminished at the same rate, that is to say it loses $\frac{1}{273}$ part of its volume at 0° for each degree. If this diminution in volume should be regular, it is obvious that at a temperature of − 273° below 0° the volume of a gaseous substance would be reduced to nothing. This temperature is therefore called *absolute zero*. The nearest approach to this temperature thus far produced is 13° above the absolute 0° or − 260°. This was produced by Dewar by boiling liquid hydrogen in a vacuum.

It is customary to reduce the observed volume of a gas to the volume which it would have at 0°. The correction is easily made by the aid of the above formula. Thus, if the volume of a gas is found to be 250 cubic centimeters at 15°, and it is required to know what the volume would be if the temperature were reduced to 0°, the calculation is made thus: In this case the observed volume $V'$ is 250 cc.; $t$, the temperature, is 15°. Substituting those values in the equation

$$V = \frac{273\ V'}{273 + t}, \quad \text{or} \quad V = \frac{V'}{1 + 0.00366t},$$

we have

$$V = \frac{273 \times 250}{273 + 15}, \quad \text{or} \quad V = \frac{250}{1 + 0.00366 \times 15},$$

from which we get 236.99 as the value of $V$.

But the volume of a gas varies also according to the pressure. If the pressure is doubled, the volume is decreased one half; and if the pressure is decreased one half, the volume is doubled, and so on. In other words, the volume of a gas varies inversely according to the pressure. Increase the pressure two, three, or four times, and the volume becomes one half, one third, or one fourth, and *vice versa*. If the gas has the volume $V$ at the pressure $P$, and at pressure $P'$ the volume $V'$, these values are found to bear to one another the relations expressed in the equation

$$VP = V'P'.$$

This is called Boyle's law.

The pressure is usually stated in millimeters, and reference is to the height of a column of mercury which the pressure corresponds to. A gas contained in an open vessel, or in a vessel over mercury or water, in which the level of the liquid inside and outside the vessel is the same, is under the pressure of the atmosphere. What that is we learn from the barometer. As this pressure varies, it is necessary to read the barometer whenever a gas is measured, and then to reduce the observed volume to certain conditions which are accepted as standard. If the gas is measured in a tube over mercury or water, and the level of the liquid inside the tube is higher than that outside, the gas is under diminished pressure, the amount of diminution depending on the height of the column of mercury or water in the tube. Thus, if the arrangement is as represented in Fig. 4, the height of the mercury column above the level of the mercury in the trough being 100 millimeters, and the pressure of the atmosphere 760 millimeters of mercury, then the gas in the tube is plainly not under the full atmospheric pressure, for the atmosphere is supporting a column of mercury 100 millimeters high, and the pressure actually brought to bear on the gas corresponds to 760 — 100 = 660 mm. of mercury. Suppose that in this case the volume of gas actually measured is 75 cc. Call this $V'$. What would be the actual volume $V$ under the standard 760 mm.? We have seen that

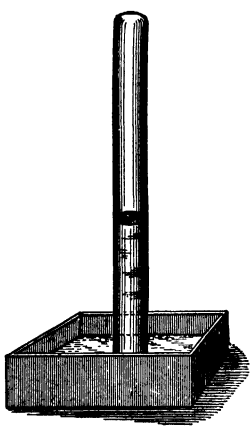


FIG. 4.

$$VP = V'P'.$$

Now, in this case $P = 760$, $V' = 75$, and $P' = 660$. Therefore, $760V = 75 \times 660$, or $V = \frac{75 \times 660}{760} = 65.13$.

In all cases it is necessary to make a correction similar to this in dealing with the volumes of gases. The correction for temperature and that for pressure may be made in one operation, the formula being

$$V = \frac{273\ V'P'}{760(273 + t)}, \quad \text{or} \quad V = \frac{V'P'}{760(1 + 0.00366t)},$$

in which $V$ = the volume of the gas at 0° and 760 mm. pressure; $V'$ = the observed volume; $t$ = the observed temperature; $P'$ = the pressure under which the gas is measured. Some of the most important ideas that have been introduced into chemistry with a

view to explaining the regularities observed in the quantities of substances which act upon one another chemically have their origin in observations on the conduct of gases. It is therefore of the highest importance that the student should familiarize himself with the meaning of the expression "the volume of a gas under standard conditions." The presence of water-vapor in a gas also influence its volume, see Exp. 62, p. 116, increasing it by the same amount as it would be increased if the pressure were diminished by a quantity equal to the pressure of the water-vapor for the given temperature. The formula for making all the corrections required in determining the volume of a gas is

$$V=\frac{273V'(P'-a)}{760(273+t)}, \text{ or } V=\frac{V'(P'-a)}{760(1+0.00366t)}$$

in which the letters $V$, $V'$, $P'$, and $t$ have the same significance as in the last formula given, while $a$ is the pressure of water-vapor at $t°$. The pressure of water-vapor was formerly called "aqueous tension," and this term is still often used. The amount of the pressure for various temperatures is to be found from tables.

A convenient apparatus for measuring gas volumes, which simplifies the process, is that represented in Fig. 5. It consists of two tubes connected at the base by means of a piece of rubber tubing, and containing water. The tube $A$ is graduated, the other is not. The gas the volume of which is to be measured is brought into the tube $A$, with the narrow opening at the top, and the other tube is then placed at the side of the one containing the gas, and its height adjusted so that the column of liquid in both tubes is at the same level. Under these circumstances, obviously, the gas is under the atmospheric pressure for which the necessary correction must of course be made. It is also necessary in this case

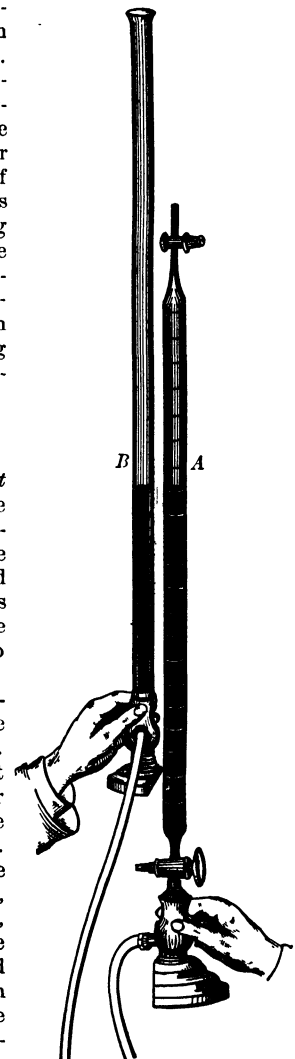



FIG. 5.

to make the corrections for temperature and the pressure of aqueous vapor. It is, further, sometimes convenient when the gas is measured over water to transfer the measuring-tube to a vessel containing enough water to permit the immersion of the tube to a point at which the level of the liquid inside and outside of the tube is the same. In this case the conditions are the same as in the apparatus described in the last paragraph. The arrangement is represented in Fig. 6.

### Determination of the Amount of Oxygen liberated when a Known Weight of Potassium Chlorate is decomposed by Heat.

Experiment 17.—To determine how much oxygen is given off when a known weight of potassium chlorate is decomposed by heat, proceed as follows: In a small, dry hard-glass tube about 10 cm. long and 5 to 7 mm. internal diameter, closed at one end, weigh out on a chemical balance about 0.25 gram dry potassium chlorate, first weighing the tube empty. Introduce just above the potassium chlorate a plug of asbestos which has been ignited; then, by means of a blast-lamp, soften the upper end of the tube, and draw it out so that it has the form shown in Fig. 7. Now weigh the tube again.

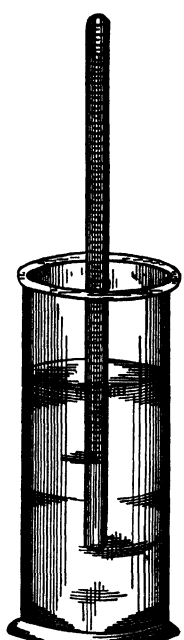


Fig. 6.

Let $a$ = weight of tube empty;

$b$ = weight of tube with potassium chlorate;

$c$ = weight of tube with potassium chlorate and plug.

Connect $A$ by means of a short piece of rubber tubing with the measuring-tube Fig. 5 so that the ends of the two tubes are almost in contact with each other, the measuring-tube having been

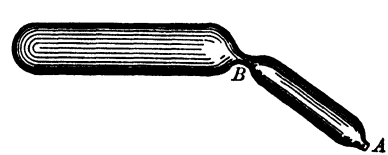



Fig. 7.

previously filled with water to the zero point, and the top closed by means of the stop-cock. Open the stop-cock, and now heat the potassium chlorate gently at first, and gradually higher until no more gas is given off. After the gas has stood for half an hour to cool it down to the temperature of the air, adjust the two tubes of the

measuring apparatus so that the level of the water in both is the same; read off the volume of gas. At the same time read the barometer and thermometer; and now make the corrections for pressure and temperature as above directed. The weight of a liter or 1000 cc. of oxygen at 0° and 760 mm. pressure is 1.429 grams. Knowing the volume of oxygen obtained, calculate the weight of this volume. Remove the tube containing the product left after the decomposition of the potassium chlorate and weigh it.

Let $d$ = weight of tube after decomposition of potassium chlorate.

Now $b - a$ = weight of potassium chlorate used;
$c - d$ = weight of oxygen given off.

This weight should, of course, be the same as that calculated from the measured volume of oxygen, and should further be in agreement with the results calculated by means of the equation

$$KClO_3 = KCl + 3O.$$

Make all the calculations, and see how nearly the results obtained agree with what is required by this equation. Should the results not be satisfactory the first time, repeat the work. The more carefully the work is done, the more nearly will the results agree with the equation.

EXPERIMENT 18.—Mix 25 to 30 grams (or about an ounce) of potassium chlorate with an equal weight of manganese dioxide in a mortar. The substances should be granulated, not powdered. Heat the mixture in a glass retort, and collect the gas by displacement of water in appropriate vessels — cylinders, bell glasses, bottles with wide mouths, etc. It will also be well to collect some in a gasometer, such as is commonly found in chemical laboratories, the essential features of which are represented in Fig. 8. It is made either of metal or of glass. The opening at $d$ can be closed by means of a screw cap. In order to fill it with water, open the stopcocks and pour the water into the upper part of the vessel after

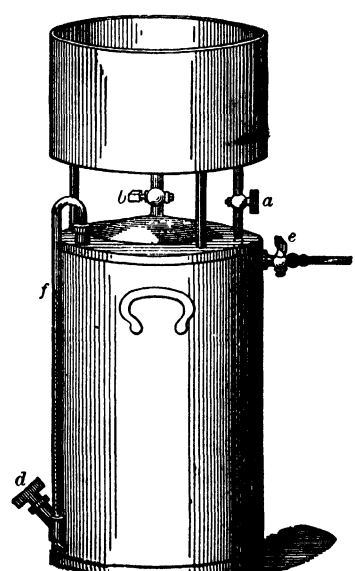


FIG. 8.

having screwed on the cap *d*. When it is full, water will flow out of the small tube *e*. Now close all the stop-cocks, and remove the cap *d*. The water will stay in the vessel for the same reason that it will stay in a cylinder inverted with its mouth below water. To fill the gasometer with gas, put it over a tub or sink, and introduce the tube from which gas is issuing into the opening at *d*. The gas will rise and displace the water, which will flow out at *d*. When full, put the cap on. To get the gas out of the gasometer, attach a rubber tube to *e*, pour water into the upper part of the gasometer, open the stop cock *a* and that at *e*, when the gas will flow out, and the current can be regulated by means of the stop-cock at *e*.

The arrangement of the retort is shown in Fig. 3, p. 44.

## Kipp's Apparatus.

For making oxygen as well as other gases Kipp's apparatus is often convenient. It is made up as shown in Fig. 9. The lower part consists of the vessel A B ; the upper part C is a funnel the tube of which reaches down nearly to the bottom of A. B and C are connected by a ground glass joint at D. The substance from which the gas is to be evolved is put in B. The acid that is to act upon B is poured into C, the stop-cocks in A and B having previously been closed. When the stop-cock of B is opened the acid runs down into A and rises until it comes in contact with the substance in B. Gas is evolved and, after driving the air out of B, escapes from the tube at E. If no more gas is needed the stop-cock of the tube in B is closed. The gas not being able to escape presses the acid out of B and soon the action ceases.

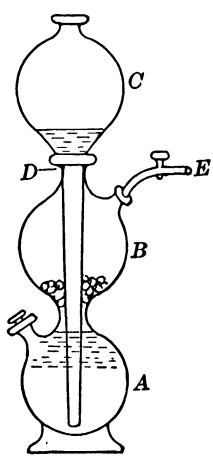


Fig. 9.

Experiment 19.—Large crystals of potassium bichromate are placed in bulb B of Kipp's apparatus, bits of glass or of granite having first been introduced to prevent the falling of pieces of the bichromate from B into A. In a separate vessel pour slowly 300 cc. concentrated sulphuric acid into 2 liters 3 per cent hydrogen peroxide. After this solution has cooled pour enough of it into the upper bulb C of Kipp's apparatus. When this solution comes in contact with the bichromate oxygen is at once given off. The current can be regulated at will.

## Physical Properties of Oxygen.

Experiment 20.—Inhale a little of the gas from one of the bottles. Has it any taste ? odor ? color ?

## Chemical Properties of Oxygen.

Experiment 21.—Turn three of the bottles containing oxygen with the mouth upward, leaving them covered with glass plates. Into one introduce some sulphur in a so-called deflagrating-spoon, which is a small cup of iron or brass attached to a stout wire which passes through a metal plate, usually of tin (see Fig. 10). In another put a little charcoal (carbon), and in a third a piece of phosphorus* about the size of a pea. Let them stand quietly and notice what changes, if any, take place. Sulphur, carbon, and phosphorus are elements, and oxygen is an element. It will be noticed that the sulphur and the carbon remain unchanged, while some change takes place in the vessel containing the phosphorus, as is shown by the appearance of white fumes. After some time the phosphorus will disappear entirely, the fumes will also disappear, and there will be nothing to show what has become of the phosphorus. If the temperature of the room is rather high, it may happen that the phosphorus takes fire. If it should it will burn with an intensely bright light. After the burning has stopped, the vessel will be filled with white fumes, but these will quickly disappear, and the vessel will apparently be empty. What do these experiments prove with reference to the action of oxygen on sulphur, carbon, and phosphorus at the ordinary temperature?

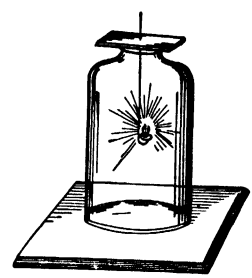


Fig. 10.

Experiment 22.—In a deflagrating-spoon set fire to a little sulphur and let it burn in the air. Notice whether it burns with ease or with difficulty. Notice the odor of the fumes which are given off. Now set fire to another small portion and introduce it in a spoon into one of the vessels containing oxygen. It will be seen that the sulphur burns much more readily in the oxygen than in the air. Notice the odor of the fumes given off. Is it the same as that noticed when the burning takes place in the air?

Experiment 23.—Perform similar experiments with charcoal.

Experiment 24.—Burn a piece of phosphorus *not larger than a pea* in the air and in oxygen. In the latter case the light emitted from the burning phosphorus is so intense that it is painful to some eyes. It is best to be cautious. The phenomenon is an extremely brilliant one. The walls of the vessel in which the burning takes

* Phosphorus should be handled with great care. It is always kept under water, usually in the form of sticks. If a small piece is wanted, take out a stick with a pair of forceps, and put it under water in an evaporating dish. *While it is under the water*, cut off a piece of the size wanted. Take this out by means of a pair of forceps, lay it for a moment on a piece of filter-paper, which will absorb most of the water, then quickly put it in the spoon.

place become covered with a white substance which afterwards gradually disappears.

What differences do you notice between the burning in the air and in oxygen? In the experiments is there any sulphur, or carbon, or phosphorus left behind? Do the experiments furnish any evidence that oxygen takes part in the action? or that oxygen is used up?

EXPERIMENT 25.—Straighten a steel watch-spring* and fasten it in a piece of metal, such as is used for fixing a deflagrating-spoon in an upright position; wind a little thread around the lower end, and dip it in melted sulphur. Set fire to this and insert it into a vessel containing oxygen. For a moment the sulphur will burn as in Experiment 22; but soon the steel begins to burn brilliantly, and the burning continues as long as there is oxygen left in the vessel. Notice that in this case *there is no flame*, but instead very hot particles are given off from the burning iron. The phenomenon is of great beauty, especially if observed in a dark room. The walls of the vessel become covered with a dark reddish-brown substance, some of which will also be found at the bottom in larger pieces.

## OXYGEN IS USED UP IN COMBUSTION.

EXPERIMENT 26.—Is the odor of the contents of the bottle in which the sulphur was burned the same as before the experiment? Introduce a stick with a small flame on it successively into the vessels used in burning sulphur, carbon, phosphorus, and iron. Is oxygen present or not? What evidence have you on this point?

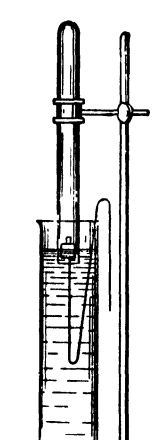


FIG. 11.

EXPERIMENT 27.—Fill a tube say 30 to 40 cm. (12 to 15 inches) long, and 2½ to 3 cm. (1 to 1¼ inches) wide, with oxygen, and arrange it in a vessel over water, as shown in Fig. 11. Now fasten a small stick of phosphorus to the end of a wire and push it into the tube so that about ¼ to ½ inch of the phosphorus is above the water and exposed to the oxygen. At first no action will take place, but after a time white fumes will be seen to rise from the phosphorus, and the phosphorus will begin to melt. This action will be accompanied by a diminution of the volume of oxygen, as will be shown by the rise of the water. When the water has risen so as to cover the phosphorus, shove the stick up so that it is again just above the surface of the water. Some of the oxygen will again be used up. By working carefully, and repeating this process as many times as may be necessary, the

* Old watch-springs can generally be had of any watchmaker or mender for the asking. A spring can be straightened by unrolling it, attaching a weight, and suspending the weight by the spring. The spring is then heated up and down to redness with the flame of a Bunsen burner.

oxygen can all be used up without the active burning of the phosphorus. Usually, however, before the action is completed, the temperature of the phosphorus becomes so high that it takes fire, when there is a flash of light in the tube and a sudden rise of the water, showing that the gas is suddenly used up.

EXPERIMENT 28.—Burn a steel watch-spring as directed in Experiment 25, with the difference that the spring is passed air-tight through a cork which is fitted tightly into the neck of the bell-jar (Fig. 12). As the spring burns, the water will rise from the vessel in which the bell-jar is standing, and it is necessary to pour water into this vessel. When the spring has burned near to the cork shove it through so that the burning may continue. If the experiment is properly performed the bell-jar will be nearly full of water at the end. What does this prove?

## THE PRODUCTS OF COMBUSTION WEIGH MORE THAN THE SUBSTANCE BURNED.

EXPERIMENT 29.—Weigh off about a gram of magnesium ribbon in a porcelain crucible. Heat over a Bunsen burner until the magnesium has turned to a white substance (magnesium oxide). After cooling, weigh again. Perform the same experiment with zinc, tin, and lead. What conclusion are you justified in drawing?

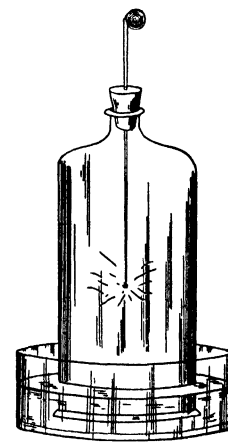


FIG. 12.

EXPERIMENT 30.—Over each pan of a large and rather sensitive balance suspend a glass tube filled with pieces of solid caustic soda. A balance that will answer the purpose very well can be made of wood with metal bearings. It may conveniently be about 2½ feet high, with a delicate beam about 3 feet long. The best tubes for the caustic soda are Argand lamp-chimneys, around the bottom of which is tied a piece of wire-gauze to prevent the caustic soda from falling out. On one pan of the balance place a candle directly under one of the caustic-soda tubes, so adjusted that the flame shall be not more than 2½ to 3 inches below the bottom of the tube. By means of weights placed on the other pan establish equilibrium. Now light the candle. Slowly, as it burns, the pan upon which it is placed will sink, showing that the products of combustion which are partly absorbed by the caustic soda are heavier than the candle was. While this is by no means an accurate experiment, it is a very striking one, and proves beyond question that in the process of combustion matter is taken up by the burning body.

## CHAPTER III.

### A STUDY OF THE ELEMENT HYDROGEN.

**Historical.**—Hydrogen was discovered as a distinct substance by Cavendish in 1766, although it had been observed as an inflammable gas before that time.

**Occurrence.**—It occurs to some extent in the free or uncombined condition, and issues from the earth in small quantity in some localities, as, for example, in the salt-mines at Stassfurt, Germany. It has also been shown to occur in enormous quantities in the atmosphere of the sun, stars, and nebulae. On the earth it occurs chiefly, however, in combination in water, of which it forms 11.19 per cent. It occurs further in most substances of animal and vegetable origin, such as the various kinds of wood and fruits, and the tissues of all animals. In these products of life it is contained in combination with carbon and oxygen, or with carbon, oxygen, and nitrogen.

**Preparation.**—The simplest way, theoretically, to prepare hydrogen is by the decomposition of water by the electric current. But this method is less convenient and more expensive than other methods, and it is therefore used only under special circumstances. It is particularly well adapted to the preparation of small quantities of pure hydrogen.

Some elements, as, for example, sodium and potassium, when brought in contact with water at the ordinary temperature decompose it and set hydrogen free. When a small piece (not larger than a pea) of potassium is thrown upon water, a flame is observed at once. When sodium is used, it is seen to form a small ball which moves about on the surface of the water with a hissing sound, but under ordinary circumstances no flame is observed. By applying a flame to the ball something takes fire and

burns. By filling a good-sized test-tube with water and inverting it in a larger vessel and bringing a *small* piece of sodium wrapped in a piece of filter-paper below the mouth of the tube, the sodium will rise to the top of the tube when released, and it will then be seen that a gas is evolved which gradually depresses the water in the tube.

A similar experiment with potassium gives a similar result. The gas given off in each case is hydrogen. By evaporating off the water left in the vessel there will be found in each case a white substance of marked chemical properties. That formed with the potassium is known as potassium hydroxide, or caustic potash, and has the composition represented by the symbol KOH; that formed with the sodium is known as sodium hydroxide, or caustic soda, and is represented by the symbol NaOH. The reaction between potassium and sodium and water are represented by the equations

$$K + H_2O = KOH + H; \text{ and}$$
$$Na + H_2O = NaOH + H.$$

Half the hydrogen of the water which is decomposed is replaced by the potassium or the sodium, as the case may be. These reactions are partly described by saying that the potassium or sodium is *substituted* for half the hydrogen in the water, and the act is called *substitution*. This is a very common kind of chemical action.

Some substances, such as iron, which decompose water slowly at the ordinary temperature do so readily at higher temperatures. At ordinary temperatures iron decomposes water, as is seen in the formation of a coating upon it when left in contact with water and the air. At higher temperatures when the iron is red-hot it decomposes water very readily, and hydrogen can be made in quantity by this means. In the laboratory the iron may be heated in a gun-barrel or in a porcelain tube. When steam is passed over it the decomposition represented in this equation takes place:

$$3Fe + 4H_2O = Fe_3O_4 + 8H.$$

The iron combines with the oxygen and liberates the hydrogen.

Carbon, in the form of charcoal or coal, may be used in a similar way to effect the decomposition of water and the liberation of hydrogen. At a high heat the reaction takes place mainly as represented thus:

$$C + H_2O = CO + 2H.$$

A mixture of two gases, carbon monoxide and hydrogen, is thus formed. This mixture is the essential part of the gas that has of late years come into such extensive use under the name "water-gas." This is formed by passing steam over highly-heated anthracite coal or coke.

By far the most convenient method for making hydrogen consists in treating a metal with an acid. Among the metals best adapted to the purpose are zinc and iron, and indeed zinc is almost exclusively used. As will be seen later, acids are substances that contain hydrogen, and are characterized by the property that they give up this hydrogen easily and take up other elements in the place of it. Among the common acids found in every laboratory are *hydrochloric acid*, *sulphuric acid*, and *nitric acid*. The chemistry of these compounds will be treated of in due time; but, as it will be necessary to use them before they are taken up systematically, a few words in regard to them are desirable in this place.

*Hydrochloric acid* is a compound of hydrogen and chlorine. It is a gas that dissolves easily in water. It is this solution that is used in the laboratory. It is manufactured in enormous quantities in connection with the manufacture of soda or sodium carbonate. Its chemical symbol is HCl. It was formerly called "muriatic acid."

*Sulphuric acid* is a compound of sulphur, oxygen, and hydrogen in the proportions represented by the formula $H_2SO_4$. It is a heavy liquid and was formerly called "oil of vitriol." It is manufactured in very large quantities, as it plays an important part in many of the most important chemical industries.

*Nitric acid* is a compound containing nitrogen, oxygen,

and hydrogen in the proportions represented by the formula $HNO_3$. It is a colorless liquid, though, as usually seen, it is slightly colored straw-yellow.

When a metal, such as zinc, is brought in contact with hydrochloric or sulphuric acid, an evolution of hydrogen takes place at once. The reactions are as represented in these equations:

$$Zn + 2HCl = \underset{\text{Zinc Chloride}}{ZnCl_2} + 2H;$$
$$Zn + H_2SO_4 = \underset{\text{Zinc Sulphate.}}{ZnSO_4} + 2H.$$

Each combining weight of zinc liberates and replaces two combining weights of hydrogen.

The action between iron and these two acids is of the same character:

$$Fe + 2HCl = \underset{\text{Ferrous Chloride.}}{FeCl_2} + 2H;$$
$$Fe + H_2SO_4 = \underset{\text{Ferrous Sulphate.}}{FeSO_4} + 2H.$$

The hydrogen obtained from acids by the action of metals is not pure, but it can be purified by treatment with appropriate substances. That obtained by the decomposition of water by the electric current is pure.

**Physical Properties.**—Hydrogen is a colorless, inodorous, tasteless gas. That made by the action of acids on zinc or iron has a somewhat disagreeable odor which is due to the presence of other gases in small quantity. It is not poisonous, and may therefore be inhaled with impunity. We could not, however, live in an atmosphere of hydrogen, as we need oxygen. It is the lightest known substance. Its specific gravity in terms of the air standard is 0.0696. A liter under 760 mm. pressure and at 0° weighs 0.08995 gram. Under Oxygen it was stated that in chemistry hydrogen is commonly taken as the standard of specific gravity, and that, hydrogen being unity, the specific gravity of oxygen is 15.89. The gas is only slightly soluble in water. 100 volumes of water

take up 1.93 volumes of hydrogen. The fact that hydrogen is lighter than the air is shown by opening a vessel which contains it and turning the mouth of the vessel upward. The gas escapes and in a very short time no evidence of its presence can be obtained. Light vessels, as, for example, soap-bubbles or collodion-balloons, filled with the gas rise in the air, and it is used for the purpose of filling large balloons.

At a very low temperature and high pressure, hydrogen can be converted into a liquid that boils at $-252.6°$. Its critical temperature is $-242°$. Liquid hydrogen is a colorless mobile liquid of very low specific gravity. A liter of liquid hydrogen weighs only 60 grams. By evaporating liquid hydrogen in a vacuum very low temperatures are reached and the hydrogen freezes forming white crystals which melt at $-258.9°$.

Hydrogen passes readily through porous substances, or it diffuses rapidly. This can easily be demonstrated in the case of porous earthenware and paper. It also passes readily through some metals, as iron and platinum when heated to redness. There is a direct relation between the specific gravity of gases and the rate at which they diffuse. The lower the specific gravity the more rapid the diffusion. The law governing these phenomena is:

*The rate of diffusion of gases is approximately inversely proportional to the square roots of their specific gravities.*

The specific gravity of hydrogen being 1 and that of oxygen nearly 16 (15.89), the rate of diffusion of oxygen is approximately $\frac{1}{4}$ that of hydrogen. If hydrogen is on one side of a porous wall, and oxygen on the other, the hydrogen will pass through the wall so much more rapidly than the oxygen that there will be an accumulation of hydrogen on one side of the wall, and if the vessel were closed there would be increased pressure on that side. The ready passage of gases through porous walls is a matter of great importance in connection with the ventilation of dwellings. Most of the materials used in building are porous and permit the passage of gases

through them in both directions, and to some extent change of air is secured in this way.

**Chemical Properties.**—Under ordinary circumstances hydrogen is not a particularly active element. It does not unite with oxygen gas at ordinary temperatures, but, like other combustible substances, it must be heated to the kindling temperature before it will burn. If a flame is applied to it, it takes fire at once. The flame is colorless or slightly blue. Generally the flame is somewhat colored in consequence of the presence of foreign substances; but that it is colorless when the gas is burned alone can be shown by burning it as it issues from a platinum tube which is itself not chemically changed by the heat. Although the flame is not luminous it is intensely hot, as can be seen by inserting into it a coil of platinum wire, which will at once become red-hot and emit light accordingly.

The burning of hydrogen in the air, like the burning of other combustible substances in the air, consists in a union of the gas with oxygen. This has been shown to be true by most elaborate experiments on the combustion of hydrogen in oxygen and in the air. On the other hand, substances that burn in the air are extinguished when put in a vessel containing hydrogen. The fact is expressed by saying that hydrogen does not support combustion. This can be shown by holding a vessel filled with hydrogen with the mouth downward, and inserting into it a lighted taper supported on a wire. The gas takes fire at the mouth of the vessel, but the taper is extinguished.

Ordinarily we say that hydrogen burns in oxygen, but, as the act consists in the union of the two gases, it would seem probable that oxygen will burn in an atmosphere of hydrogen. This can be shown to be true by a proper arrangement of apparatus. If we were surrounded by an atmosphere of hydrogen we should speak of oxygen as a combustible gas in the same way that we now speak of hydrogen as a combustible gas.

It can easily be shown that, when hydrogen is burned

either in oxygen or air, water is formed. The simplest way to show this is by holding a glass plate or some other incombustible object a short distance above a flame of hydrogen. It will be seen that, until it becomes heated, drops of water are condensed upon it.

Hydrogen combines with many other elements besides oxygen, and forms some of the most important and interesting compounds, such as hydrochloric acid, HCl; sulphuretted hydrogen or hydrogen sulphide, $H_2S$; ammonia, $NH_3$; marsh-gas, $CH_4$; and all the acids. On account of its power of combining with oxygen it is used very extensively in the laboratory for the purpose of extracting oxygen from compounds containing it. Thus, when hydrogen is passed over heated copper oxide, CuO, it combines with the oxygen to form water, and the copper is left in the free or uncombined state. The reaction is represented thus:

$$CuO + 2H = H_2O + Cu.$$

A similar reaction takes place when hydrogen is passed over highly-heated oxides of iron, $Fe_2O_3$ or $Fe_3O_4$:

$$Fe_2O_3 + 6H = 2Fe + 3H_2O;$$
$$Fe_3O_4 + 8H = 3Fe + 4H_2O.$$

**Reversible Reactions.**—On page 55 it was stated that hydrogen can be obtained by passing steam over heated iron:

$$3Fe + 4\,H_2O = Fe_3O_4 + 8H.$$

This equation is the same as the preceding one read backward. Such reactions are called reversible reactions and may be written with two arrows thus,

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 8H,$$

to indicate that the reaction may proceed in either direction. Which direction the reaction takes will depend

upon the temperature or upon other conditions which will be spoken of later. In the present case both reactions occur simultaneously at the same temperature. Hence if iron and water were heated in a closed vessel from which the products could not escape, a condition of equilibrium would occur in which the formation of hydrogen and iron oxide was balanced by the formation of steam and iron. In practice, if it is desired to obtain hydrogen, a current of steam is passed through a tube containing heated iron. Most of the hydrogen is thus carried off as soon as formed, and the amount of hydrogen which acts in the reverse sense is reduced to a minimum. If it were desired to obtain iron and water the iron oxide would be heated in a current of hydrogen. In this way most of the steam would be carried off as soon as formed, and a minimum of steam would act in the reverse sense.

**Reduction.**—The removal of oxygen from a compound is called *reduction*. Reduction is therefore plainly the opposite of oxidation. Any substance that has the power to abstract oxygen is spoken of as a *reducing agent*, just as any substance that has the power to add oxygen to a substance, or to decompose it by the action of oxygen, is called an *oxidizing agent*.

A number of metals have the power to absorb a large quantity of hydrogen when they are heated in a current of the gas. This phenomenon is shown most strikingly by palladium, which under the most favorable conditions takes up about 935 times its own volume of hydrogen. The gas is given up at an elevated temperature in a vacuum. When it absorbs hydrogen, palladium undergoes marked changes in properties. Its volume is increased, and its magnetic and electric properties are also changed. It was suggested by Graham that the hydrogen held in combination by the palladium is something quite different from ordinary hydrogen, and that it must have some properties like those of the so-called metals. He therefore called the combined hydrogen *hydrogenium*. Later studies, espe-

cially of liquid and solid hydrogen, have shown that there is little in common between hydrogen and the metals.

**Comparison of Oxygen and Hydrogen.**—Hydrogen and oxygen are different kinds of matter, just as heat and electricity are different kinds of energy. Heat can be converted into electrical energy, and electrical energy into heat, but one element cannot by any means known to us be converted into another.* They are apparently entirely independent of each other. The question will therefore suggest itself whether, in spite of their apparent independence, there is not some relation between the different elements that reveals itself by similarity in properties. It will be found that the elements can be separated into groups of families according to their properties. There are some elements, for example, which in their chemical conduct resemble oxygen markedly. These elements constitute the *oxygen family*. So far as hydrogen is concerned, however, it stands by itself. There is no other element that conducts itself like it. If it is compared with oxygen, little analogy between the two elements is observed. In their physical properties they are, to be sure, similar. Both are colorless, inodorous, tasteless gases. On the other hand, oxygen combines readily with a large number of substances with which hydrogen does not combine. Oxygen, as we have seen, combines easily with carbon, sulphur, phosphorus, and iron. It is a difficult matter to get any of these elements to combine directly with hydrogen. Further than this, substances which combine readily with hydrogen do not combine readily with oxygen. The two elements exhibit opposite chemical properties. What one can do the other cannot do. This oppositeness of properties is favorable to combination; for not only do

* This statement is not strictly true, in view of Ramsay's experiments on the formation of helium from radium emanation, on the apparent formation of a minute quantity of lithium from copper, and in view of the probable generation of radium through the disintegration of uranium.

hydrogen and oxygen combine with great ease under proper conditions, but, as we shall see later, it is a general rule that elements of like properties do not readily combine with one another, while elements of unlike properties do readily combine.

## EXPERIMENTS.

### Preparation of Hydrogen.

Experiment 31.—Repeat Experiment 3 and examine the gases.

Experiment 32.—Throw a small piece of sodium * on water. While it is floating on the surface apply a lighted match to it. A yellow flame will appear. This is burning hydrogen, the flame being colored yellow by the presence of the sodium, some of which also burns. Make the same experiment with potassium. The flame appears in this case without the aid of the match. It has a violet color, which is due to the burning of some of the potassium. The gas given off in these experiments is either burned at once or escapes into the air. In the case of the potassium it takes fire at once, because the action takes place rapidly and the heat evolved is sufficient to set fire to it; in the case of the sodium, however, the action takes place more slowly, and the temperature does not get high enough to set fire to the gas. In order to collect it unburned, it is only necessary to allow the decomposition to take place so that the gas will rise in an inverted vessel filled with water. For this purpose fill a good-sized test-tube with water and invert it in a vessel of water. Cut off a piece of sodium not larger than a pea, wrap it in a layer or two of filter-paper, and with the fingers or a pair of curved forceps bring it quickly below the mouth of the test-tube and let go of it. It will rise to the top, the decomposition of the water will take place quietly, and the gas formed, being unable to escape, will remain in the tube. By repeating this operation in the same tube a second portion of gas can be made, and so on until the vessel is full.

Examine the gas and see whether it acts like the hydrogen obtained from water by means of the electric current. What evidence have you that they are the same? Is this evidence sufficient to prove the identity of the two?

The metals sodium and potassium disappear in these experiments, and we get hydrogen. What becomes of the metals? and what is the source of the hydrogen? If after the action has stopped the

* The metals sodium and potassium are kept under oil. When a small piece is wanted, take out one of the larger pieces from the bottle, roughly wipe off the oil with filter-paper, and cut off a piece the size needed. It is not advisable to use a piece larger than a small pea.

water is examined, it will be found to contain something in solution. It now has a peculiar taste, which we call alkaline; it feels slightly soapy to the touch; it changes certain vegetable colors. If the water is evaporated off, a white substance remains behind, which is plainly neither sodium nor potassium. In solid form or in concentrated solution it acts strongly on animal and vegetable substances, disintegrating many of them. On account of this action it is known as *caustic* soda, or, in the case of potassium, as *caustic* potash.

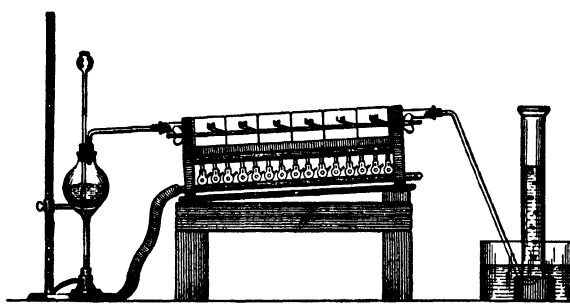


FIG. 13.

EXPERIMENT 33.—Certain metals that do not decompose water at ordinary temperatures, or decompose it slowly, decompose it easily at higher temperatures. This is true of iron. If steam is passed through a tube containing pieces of iron heated to redness, decomposition of the water takes place, and the oxygen is retained by the iron, which enters into combination with it, while the hydrogen is liberated. In this experiment an iron tube with an internal diameter of from 20 to 25 mm. (about an inch) and a gas-furnace are desirable, though a hard-glass tube and a charcoal-furnace will answer. The arrangement of the apparatus is shown in Fig. 13.

EXPERIMENT 34.—In a cylinder or test-tube put some small pieces of zinc, and pour upon it some ordinary hydrochloric acid. If the action is brisk, after it has continued for a minute or two apply a lighted match to the mouth of the vessel. The gas will take fire and burn. If sulphuric acid diluted with five or six times its volume of water * is used instead of hydrochloric acid, the same result will

* If it is desired to dilute ordinary concentrated sulphuric acid with water, the acid should be poured slowly into the water while the mixture is constantly stirred. If the water is poured into the acid, the heat evolved at the places where the two come in contact may be so great as to convert the water into steam and cause the acid to spatter.

be reached. The gas evolved is hydrogen. For the purpose of collecting the gas the operation is best performed in a wide-mouthed bottle, in which is fitted a cork with two holes (see Fig. 14), or in a bottle with two necks called a Woulff's flask (see Fig. 15) or a Kipp generator (see Fig. 9, p. 50). Through one of the holes a funnel-tube passes, and through the other a glass tube bent in a convenient form.

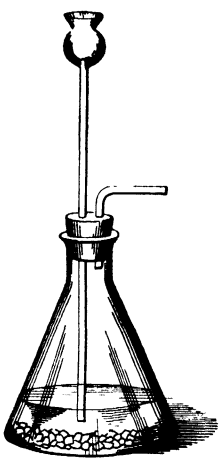


FIG. 14

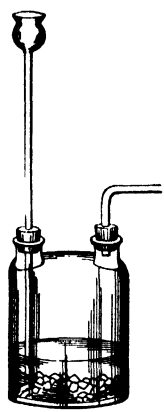


FIG 15

The zinc used is granulated. It is prepared by melting it in a ladle, and pouring the molten metal from an elevation of four or five feet into water. The advantage of this form is that it presents a large surface to the action of the acids. A handful of this zinc is introduced into the bottle, and enough of a *cooled* mixture of sulphuric acid and water (1 volume concentrated acid to 6 volumes water) poured upon it to cover it. Usually a brisk evolution of gas takes place at once. Wait for two or three minutes, and then collect some of the gas by displacement of water. When the action becomes slow, add more of the dilute acid. It will be well to fill several cylinders and bottles with the gas, and also a gasometer, from which it can be taken as it is needed for experiments.

### SOMETHING BESIDES HYDROGEN IS FORMED.

EXPERIMENT 85.—After the action is over pour the contents of the flask through a filter into an evaporating-dish, and boil off the

greater part of the water, so that, on cooling, the substance contained in solution will be deposited. If the operation is carried on properly, the substance will be deposited in regular forms called crystals. It is zinc sulphate, $ZnSO_4$, formed by the substitution of zinc for the hydrogen of the sulphuric acid.

PROBLEMS.—How much zinc would it take to give 200 liters of hydrogen? How much zinc sulphate would be formed? How much hydrogen would be formed by the action of 50 grams of zinc on sulphuric acid? How much sulphuric acid would be used up?

## DETERMINATION OF THE AMOUNT OF HYDROGEN EVOLVED WHEN A KNOWN WEIGHT OF ZINC IS DISSOLVED IN SULPHURIC ACID.

EXPERIMENT 36.—This determination can be made by means of an apparatus such as represented in Fig. 16. The bent tube leading

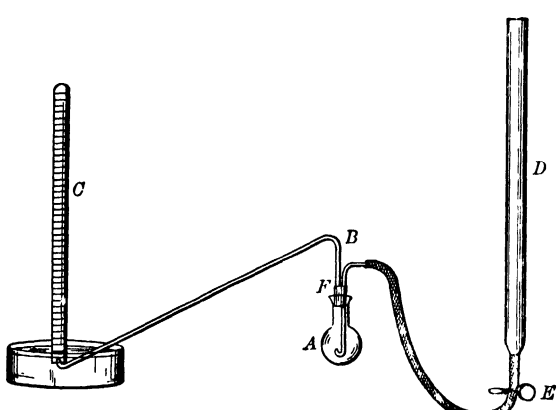



FIG. 16.

from the flask *A* is drawn out at *B*, and a plug of glass-wool introduced below the constriction. The other parts of the apparatus need no description. The flask should have a capacity of about 40 to 50 cc.; and the measuring tube *C* should have a capacity of about 100 cc., and be graduated to $\frac{1}{10}$ cc.

The experiment is conducted in the following manner: *D* is filled with distilled water; a piece of zinc weighing from 0.150 to 0.200 gram is placed in the flask; the pinch-cock *E* is then opened, and the whole apparatus thus filled with water. The apparatus is now examined in order to ascertain if gas-bubbles are lodged under the

stopper *F* or in the glass-wool. If so, they can usually be dislodged without difficulty. If they persist, a few moments' boiling of the water in the flask will effect their complete removal. . . . The eudiometer is now placed over the outlet of the delivery-tube, and the greater portion of the water remaining in *D* allowed to flow through the apparatus. Sulphuric acid of the concentration ordinarily employed in the laboratory (1 of $H_2SO_4$ to 4 of $H_2O$) is poured into the reservoir *D* until it is nearly full. The pinch-cock *E* is then opened, and the water which fills the apparatus is displaced by sulphuric acid. The action of the acid upon the metal may be facilitated by heat or by adding some platinum scraps When the action is over, the contents of the flask are swept through the delivery-tube by again opening the pinch-cock *E*. Finally, the measuring-tube is transferred to a cylinder of water, and the volume of the gas read and corrected in the usual manner If hydrochloric instead of sulphuric acid has been used, which would be the case when the metal employed is aluminium, a little caustic soda should be added to the water in the cylinder to which the eudiometer is transferred.

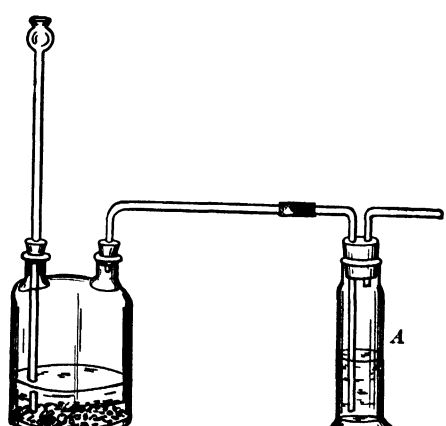



FIG. 17.

A liter of hydrogen at 0° and 760 mm. weighs 0.08995 gram. How much does the hydrogen obtained in the experiment weigh? How much ought to have been obtained? How many cubic centimeters of hydrogen ought to have been obtained?

Try the same experiment, using tin and hydrochloric acid. The action takes place as represented in the equation

$$Sn + 2HCl = SnCl_2 + H_2.$$

It would be well, further, to try the experiment also with iron and sulphuric acid, and with aluminium and hydrochloric acid, and to calculate from the results the relation between the weights of the four metals required to give equal volumes of hydrogen, and the volumes of hydrogen given by, say, a gram of each metal. The action between iron and sulphuric acid takes place according to the equation

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

That between aluminium and hydrochloric acid is represented by this equation

$$Al + 3HCl = AlCl_3 + 3H.$$

## Hydrogen is Purified by passing through a Solution of Potassium Permanganate.

Experiment 37.—Pass some of the gas, made by the action of zinc on sulphuric acid, through a wash-cylinder containing a solution of *potassium permanganate;* collect some of it, and notice whether it has an odor. The apparatus should be arranged as shown in Fig. 17. The solution of potassium permanganate is, of course, contained in the small cylinder *A*, and the tubes so arranged that the gas bubbles through it.

Has the gas any odor, taste or color?

Experiment 38.—Place a vessel containing hydrogen with the mouth upward and uncovered. In a short time examine the gas contained in the vessel, and see whether it is hydrogen. What does this experiment prove with reference to the weight of hydrogen as compared with that of the air?

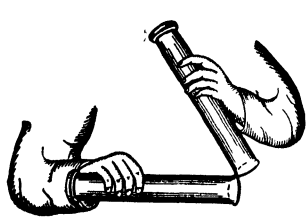


Fig. 18

Experiment 39.—Gradually bring a vessel containing hydrogen with its mouth upward below an inverted vessel containing air, in the way shown in Fig. 18. After the vessel which contained the hydrogen has been brought in the upright position beneath the other, examine the gas in each vessel. Which one contains the hydrogen?

Experiment 40.—Soap-bubbles filled with hydrogen rise in the air. This experiment is best performed by connecting an ordinary clay pipe by means of a piece of rubber tubing with the delivery-tube of a gasometer filled with hydrogen. Small balloons of collodion are also made for the purpose of showing the lightness of hydrogen.

## Hydrogen passes readily through Porous Vessels. Diffusion.

Experiment 41.—Arrange an apparatus as shown in Fig. 19*a*. It consists of a porous earthenware cup, such as is used in galvanic batteries, fitted with a perforated cork connected with a glass tube 2 to 3 feet long. The cork must fit air-tight into the mouth of the cup, as well as the tube into the cork This may be secured by shoving the cork into the cup until its outer surface is even with the edge of the cup, and then covering it carefully with sealing-wax. Put the lower end of the glass tube through a cork into one neck of a Woulff's bottle containing some water colored with litmus or indigo, so that the end of the tube is above the surface of the water. Through the other neck of the bottle pass a tube slightly bent outward and drawn out at the end to a fine opening. This tube must also be fitted to the bottle by an air-tight cork, and its lower end must be below the surface of the liquid. Now bring a bell-jar (Fig. 19*b*) containing dry hydrogen over the porous cup, when the liquid will be seen to rise in the short, bent tube that dips below the liquid, and be forced out of it, sometimes with considerable velocity. Withdraw the bell-jar, and bubbles will rise rapidly from the bottom of the tube which dips under the water, thus showing that air is entering the bottle. This is due to the diffusion of the hydrogen from the porous cup into the air. What are the observed phenomena due to?

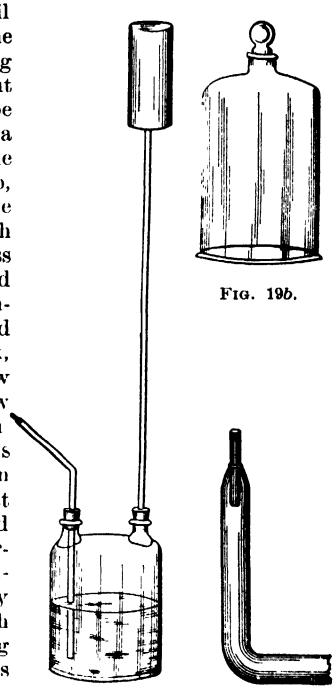


Fig. 19*b*.

Fig. 19*a*.

Fig. 20.

## Chemical Properties of Hydrogen.

Experiment 42.—If there is no small platinum tube available, roll up a small piece of platinum-foil and melt it into the end of a glass tube, as shown in Fig. 20. Connect the burner thus made with the gasometer containing hydrogen, and after the gas has been

allowed to issue from it for a moment, set fire to it. In a short time it will be seen that the flame is practically colorless, and gives no light. That it is hot can be readily shown by holding a piece of platinum wire or a piece of some other metal in it.

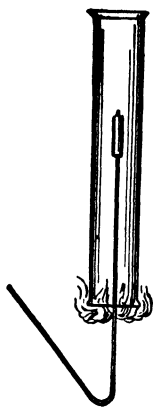


FIG. 21.

EXPERIMENT 43.—Into the flame of burning hydrogen introduce a small coil of platinum wire. What change is observed? Introduce also a piece of magnesium ribbon. Explain the difference between the two cases. What becomes of the magnesium? of the platinum?

EXPERIMENT 44.—Hold a cylinder filled with hydrogen with the mouth downward. Insert into it a lighted taper held on a bent wire, as shown in Fig. 21. The gas takes fire at the mouth of the vessel, but the taper is extinguished. On withdrawing the taper and holding the wick for a moment in the burning hydrogen, it will take fire, but on putting it back in the hydrogen it will again be extinguished. Other burning substances should be tried in a similar way. What conclusions are justified by the last two experiments?

## PRODUCT FORMED WHEN HYDROGEN IS BURNED.

EXPERIMENT 45.—Hold a clean, dry glass plate a few inches above a hydrogen flame. What do you observe? Remove what is deposited upon the plate, and hold the plate again over the flame. Repeat this a number of times. What does the substance deposited upon the plate suggest? Can you positively say what it is?

## REDUCTION.

EXPERIMENT 46.—Arrange an apparatus as shown in Fig. 22. The flask *A* contains zinc and dilute sulphuric acid; the cylinder *B* a solution of potassium permanganate; the tube *C* granulated calcium chloride; and the cylinder *D* concentrated sulphuric acid. The object of the potassium permanganate is to purify the hydrogen; the object of the concentrated sulphuric acid and calcium chloride is to remove moisture from the gas. In the tube *E* put a few pieces of the black oxide of copper, or cupric oxide, CuO. After hydrogen has been passing long enough to drive all the air out of the apparatus (about two or three minutes if there is a brisk evolution) heat the oxide of copper by means of a flame applied to the tube. What change in color takes place? Try the action of nitric acid on the substances before the action and after, and note whether there

is any difference. What appears in *G*? Explain what you have seen.

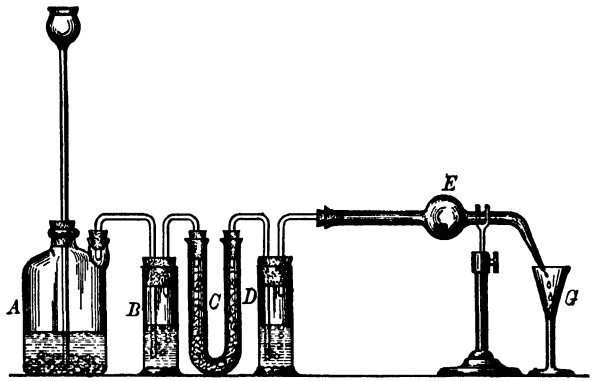



FIG 22.

EXPERIMENT 47.—Try the experiment just described, using ferric oxide, or oxide of iron, $Fe_2O_3$, instead of cupric oxide. What is the common feature in the two reactions?

## CHAPTER IV.

### STUDY OF THE ACTION OF HYDROGEN ON OXYGEN.

**Burning of Hydrogen.**—Attention has already been called to the fact that, when hydrogen burns, water is formed. One of the first questions to be answered is, What relation exists between the weight of the hydrogen burned, that of the oxygen used up in the burning process, and that of the water formed? But to weigh gases accurately and to collect small quantities of water and weigh it are by no means simple operations, and a great deal of work has been done upon the problem under consideration.

**Method of Dumas.**—The first accurate experiments on the combustion of hydrogen are those of Dumas. The method employed by this chemist was the following: He passed carefully purified hydrogen over heated copper oxide and collected the water formed. The reaction involved is that represented by the equation

$$CuO + 2H = H_2O + Cu.$$

The weight of the oxygen that entered into combination with hydrogen was obtained by weighing the vessel containing the copper oxide before and after the experiment. The loss in weight represented the weight of the oxygen abstracted. The water was collected by passing the vapor into an empty glass vessel in which most of it was condensed, and then through tubes containing potassium hydroxide and phosphorus pentoxide, substances which have a marked power to absorb water and hold it in combination. In nineteen experiments Dumas obtained a total of 945.439 grams water, and the total weight

of oxygen used in the formation of this amount of water was 840.161 grams. According to these results the ratio between hydrogen and oxygen in water expressed in percentages is:

| | |
|---|---|
| Oxygen | 88.864 |
| Hydrogen | 11.136 |
| | 100.000 |

**Morley's Method.**—Morley, who has done the most accurate work on this subject, proceeded thus: He weighed comparatively large volumes of oxygen in the form of gas; he then weighed hydrogen after it had been absorbed by palladium. The hydrogen being expelled from the palladium, it was brought together with the oxygen, with which it was caused to combine by means of electric sparks. The water thus formed was carefully collected in the same apparatus and weighed. Twelve experiments gave results that agreed closely with one another. The mean of these shows that hydrogen and oxygen combine in the ratio of 2 parts of hydrogen to 15.8792 parts of oxygen. Dumas' result expressed in the same way is 2: 15.961.

**Eudiometric Method.**—When hydrogen and oxygen are mixed at ordinary temperatures no perceptible chemical change takes place. If, however, a spark is brought in contact with the mixture, violent action takes place, accompanied by flame and explosion. The action consists in the sudden combination of the two gases to form water. It may be illustrated in a number of ways—most simply by filling soap-bubbles with the mixture of the two gases and applying a flame to them. The explosion which ensues is harmless. Plainly, to study the combination of hydrogen and oxygen by exploding a mixture of the gases will require special precautions. It can be carried out by the aid of the *eudiometer* (from εὐδία, good air, and μέτρον, a measure, an instrument for determining the purity of air). The eudiometer is simply a tube graduated in millimeters and having two small platinum wires passed through it at the closed end, nearly meeting inside and

ending in loops outside, as shown in Fig. 23. The eudiometer is filled with mercury, inverted in a mercury trough, and held in an upright position by means of proper clamps. For the purpose of the experiment a quantity of hydrogen is brought into the tube, and its volume ac-



FIG. 23.

curately measured. About half this volume of oxygen is then introduced and the volume again accurately determined, and after the mixture has been allowed to stand for a few minutes a spark is passed between the wires in the eudiometer by connecting the loops with the poles of a small induction coil. Under these circumstances the explosion takes place noiselessly and with little or no danger. After the explosion the interior of the tube will be seen to be moist, and a marked decrease in the volume of the gases is also observed. That water is the product of the action has been proved repeatedly by the most accurate experiments. As the liquid water which is formed occupies an inappreciable volume as compared with the volume of the gases which combine, the decrease in volume represents the total volume of the hydrogen and oxygen which have combined. Now, if the experiment is performed with the two gases in different proportions, it will be found that only when they are mixed in the proportion of 2 volumes of hydrogen to 1 volume of oxygen do they completely disappear in the explosion. If there is a larger proportion of hydrogen present, the excess is left over; and the same is true of the oxygen. It will thus be seen that when hydrogen and oxygen combine to form water, they do so in the proportion of 2 volumes of hydrogen to 1 volume of oxygen, or more accurately 2.0027 to 1.

**Calculation of the Results Obtained in Exploding Mixtures of Hydrogen and Oxygen.**—Having determined that

whenever hydrogen and oxygen combine, they do so in the proportion 1 volume oxygen to 2 volumes hydrogen, and that when they combine the volume of liquid water formed measures so little as to amount to nothing in the measurements, we know that whenever a mixture of hydrogen and oxygen is exploded, no matter in what proportions they may be present, the volume of gas which disappears as such consisted of 2 volumes of hydrogen and 1 volume of oxygen, or, in other words, one-third of the volume which disappears was oxygen and two-thirds hydrogen. Take this example: A quantity of hydrogen corresponding to 60 cc. under standard conditions is introduced into a eudiometer; 40 cc. of oxygen is added. What contraction will there be on exploding the mixture? Plainly the 60 cc. of hydrogen will combine with 30 cc. of oxygen. The 90 cc. of gas will disappear, and 10 cc. of oxygen will remain uncombined. From a total volume of 100 cc., therefore, there will be a contraction to 10 cc. One-third of the contraction represents the oxygen and two-thirds the hydrogen.

**Determination of the Volume of Water-vapor formed by Union of Definite Volumes of Hydrogen and Oxygen.**— The experiments which have been described enable us to draw the conclusion that hydrogen and oxygen combine in certain proportions by volume and by weight, and that a definite weight of water is formed; further, that the volume of liquid water formed when the two gases combine is inappreciable as compared with that of the gases. The question remains to be answered, What relation exists between the volumes of the combining gases and that of the water in the form of vapor? This can be determined by causing the gases to combine in a eudiometer at a temperature sufficiently high to keep the water in the form of vapor. The simplest arrangement for this purpose is that shown in Fig. 24. A long eudiometer, the upper half of which is divided into three equal parts marked on the outside, is filled with mercury and inverted in a bath of mercury. It is then surrounded by a large tube or jacket arranged as shown in Fig. 24. This is connected

through the cork at the lower end with a vessel from which a current of steam can be obtained. The steam is passed through the jacket until the temperature of the mercury has reached that of the steam. A mixture of hydrogen and oxygen in the proportions in which they combine, viz., 2 of hydrogen to 1 of oxygen, is then introduced into the eudiometer so that it is filled to the third mark. This must be somewhat above the level of the mercury in the bath, so that the gases in the eudiometer shall be under diminished pressure. On now passing the spark the gases unite and the water which is formed remains in the form of vapor, as the temperature inside the eudiometer is nearly that of boiling water, and the vapor is under diminished pressure. It is found that the volume of the water-vapor is less than that of the gases introduced into the eudiometer. In order to secure the same pressure as that under which the gases were measured, the eudiometer must be lowered until the height of the mercury column in it is the same as it was before the explosion. On now measuring the volume of water-vapor, it will be found to be two-thirds that occupied by the uncombined gases. Therefore 2 volumes of hydrogen combine with 1 volume of oxygen and form 2 volumes of water-vapor. It is an interesting fact that these simple relations exist between the volumes of the combining gases and the volume of the product. It will be shown that similar relations hold good in the case of other gases; and the following general statement is based upon a great deal of careful study:

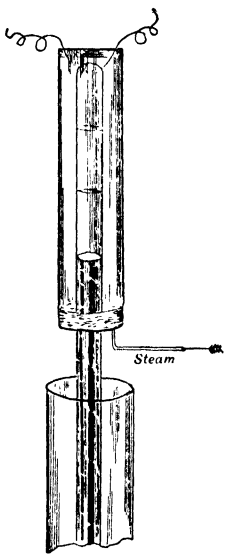


FIG. 24

*When two or more gaseous substances combine to form a gaseous compound, the volumes of the individual con-*

*stituents as well as their sum bear a simple relation to the volume of the compound.*

This is known as the law of combination by volume. As will be seen further on, it has a most important bearing upon some of the fundamental ideas held in regard to the constitution of matter.

**Heat Evolved in the Union of Hydrogen and Oxygen.**—To get as complete a knowledge as possible of the reaction which takes place between hydrogen and oxygen the amount of heat evolved in the reaction must be determined. The heat evolved in burning a gram of hydrogen can be determined, and from this the heat of formation of water can be calculated. This, according to the statement on page 40, is the amount of heat evolved by the combination of 2 grams of hydrogen with 15.88 grams of oxygen.

The determination is made by burning a known weight of hydrogen in a vessel surrounded by water and arranged in such a way that all the heat is absorbed by the water. Experiment has shown that when 1 gram of hydrogen is burned 34,180 calories are evolved. Or,

$$[H_2, O] = 68{,}360 \text{ cal.}$$

No other substance gives as much heat as this in proportion to the weight used.

**Combination of Oxygen and Hydrogen by Other Methods.**—Combination of oxygen and hydrogen is caused at ordinary temperatures by the mere presence of certain solid substances. Of such substances platinum is the most effective. If the platinum is in finely divided condition as in the so-called "spongy platinum," the speed of the action is increased. On introducing spongy platinum into a mixture of oxygen and hydrogen, the volume of the gas decreases, the platinum soon becomes hot and glows, and the hydrogen and oxygen unite with explosion. On examining the platinum it will be found unchanged. What is the cause of this action? Among the explanations suggested are these: that the hydrogen is made active by condensing on the surface of the platinum; that the hydrogen is made active by forming a compound with the metal; that the platinum combines with oxygen to form an oxide which is very sensitive to the action of hydrogen.

**Catalysis.**—Objections may be made to each of these explanations,

and the fact that the case under consideration is only one of many similar cases, has led to the classification of such phenomena. The action is called *contact action* or *catalytic action*. The substance whose presence causes the reaction is called the *catalyser*, the process is called *catalysis* (from κατα down, and λύειν, to loose). The function of a catalyser is to increase or decrease the speed of a reaction. A catalyser which increases the velocity of a reaction is called a *positive catalyser;* one which decreases the velocity of a given reaction a *negative catalyser*.

Many reactions take place so slowly that they escape observation. The coal in the cellar combines rapidly with the oxygen of the air in the furnace fire; it is, however, combining slowly with oxygen in the bin.

Measurements have shown that the average speed of chemical reactions is doubled by each increase of temperature of 10°. A reaction which at a given temperature requires 15 minutes to reach a given point, requires 7½ minutes at a temperature 10° higher, 30 minutes at a temperature 10° lower; if the temperature is lowered 100°, 1024 times 15 minutes or about 11 days is required; if the temperature is lowered 150°, a year is required for the reaction to reach the same point which it reaches in 15 minutes at the initial temperature.*

All catalytic reactions known could take place slowly and in all probability do take place slowly under the given conditions *without* the presence of the catalyser; add the catalyser and the speed of the reaction is increased enormously. Take the case of potassium chlorate and manganese dioxide, page 34. Potassium chlorate heated alone gives off a rapid current of oxygen at temperatures above 350°. It would require about 15 minutes roughly speaking to complete the reaction at this temperature. As shown above, at 200°—a temperature 150° lower—it would require about a year, and the reaction escapes observation. When the catalyser, manganese dioxide, is added, the speed of the reaction at 200° is approximately the same as with the chlorate alone at 350°.

**Nature of Catalysers.**—Limiting the discussion to one type, the chief catalysers for reactions yielding oxygen are platinum and certain metallic oxides. It has been found that platinum heated in air or oxygen takes up 2 per cent oxygen at 100° and 2½ per cent at 300°. This forms a coating of platinic oxide on the surface of the platinum. The oxide gives up all or part of its oxygen at higher temperature. It has been found that the metallic oxides used as catalysers give off part of their oxygen at red heat. While these properties are noteworthy and suggest that in the catalytic reactions these substances may act as oxygen carriers, the enormous speed of some catalytic reactions and the vast mass of material reacting in the presence of a very small mass of catalyser—notably in the con-

* Ostwald, Grundlinien, p. 109.

tact process for making sulphuric acid—are arguments against the acceptance of this or any other explanation thus far offered.

**Negative Catalysis.**—Small amounts of vapor of turpentine or of ethylene or of certain other gases added to air in a vessel containing ordinary phosphorus prevent the slow oxidation of the phosphorus, and no phosphorescence is perceptible. Such cases are very common in physiological chemical reactions.

**Application of the Heat formed by the Combination of Hydrogen and Oxygen.**—To burn hydrogen in oxygen requires a special apparatus to prevent the mixing of the gases before they reach the end of the tube where the combustion takes place. The *oxyhydrogen blowpipe* answers this purpose. This may be constructed in several ways, but the simplest is that represented in Fig. 25. It

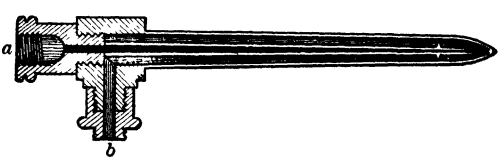



FIG. 25.

consists of a tube through which a smaller tube passes. The hydrogen is admitted through *a* and the oxygen through *b*. It will be seen that they come together only at the end of the tube. The hydrogen is first passed through and lighted; then the oxygen is passed through slowly, the pressure being increased until the flame appears thin and straight. It gives very little light but is intensely hot. Iron wire, steel, copper, zinc, and other metals burn in the flame with ease. Platinum vessels are made by melting the platinum by means of the oxyhydrogen flame.

**Oxyhydrogen Light.**—When the oxyhydrogen flame is allowed to play upon some substance which it cannot melt or burn, the substance becomes heated so high that it gives off an intense light. The substance commonly used for this purpose is lime. Hence the light is often called the lime-light. It is also known as the Drummond light.

The flame plays against the piece of lime, and from this

the light is given off when it has acquired a high temperature. Coal-gas may be and is generally used instead of hydrogen. Cylinders of compressed coal-gas and of oxygen can be bought, and the gases so prepared are used for the purpose of projecting pictures upon screens in illustrating lectures and for other similar purposes.

**Summary.**—The following facts have been established: (1) The relations between the weights of the hydrogen and oxygen which act upon each other; (2) the relations between the volumes of the combining gases; (3) the relations between the volumes of the combining gases and that of the water-vapor formed; and (4) the amount of heat evolved when a given weight of hydrogen combines with oxygen. It remains to study more carefully the product formed. This is water.

## EXPERIMENTS.

### Composition of Water.

Experiment 48.—Arrange the apparatus shown in Fig. 22 with a straight tube instead of the bent tube *E*, and connect this with a small bent tube containing calcium chloride, as shown in Fig. 26.

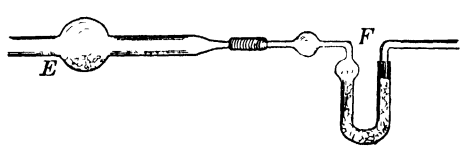



Fig 26.

Weigh tube *E* empty, and after the cupric oxide has been put into it. This gives the weight of the cupric oxide. Weigh the tube *F* before the experiment. Now proceed as in Experiment 46. In this case all the water formed by the action of the hydrogen on the cupric oxide will be absorbed by the calcium chloride in tube *F*. This tube will therefore gain in weight, and as oxygen is removed from the cupric oxide, tube *E* will lose in weight. After the reduction is complete weigh tube *E* and tube *F* again.

Let $x$ = weight of tube *E* + cupric oxide before the experiment;
$y$ = weight of tube *E* + copper after the experiment.
Then $x - y$ = weight of oxygen removed from the cupric oxide.
Let $a$ = weight of tube *F* before the experiment,
and $b$ = " " " after " "
Then $b - a$ = weight of water formed.

If the experiment is properly performed, it will be found that the ratio $\frac{x-y}{b-a}$ is very nearly $\frac{8}{9}$. Or the result may be stated thus: In nine parts by weight of water there are eight parts of oxygen.

EXPERIMENT 49.—The tubes in the apparatus used in Experiment 3, or some other similar apparatus, should be graduated. Let the gases formed by the action of the electric current, as in Experiment 3, rise in the tubes, and observe the volumes. It will be seen that when one tube is just full of gas, the other, if it is of the same size, will be only half full On examining the gases the larger volume will be found to be hydrogen, and the smaller volume oxygen. What are the relative weights of equal volumes of hydrogen and oxygen? In what proportion by weight are the two gases obtained from water in this experiment? How does this result agree with that obtained in the preceding experiment? Does this experiment prove that water consists only of hydrogen and oxygen?

EXPERIMENT 50.—Pass hydrogen from a generating flask or a gasometer through a tube containing some substance that will absorb moisture, as all gases made in the ordinary way and collected over water are charged with moisture. The calcium chloride should be in granulated form, not powdered After passing the hydrogen through the calcium chloride, pass it through a tube ending in a narrow opening, and set fire to it If now a *dry* vessel is held over the flame, drops of water will condense on its surface and run down. A convenient arrangement of the apparatus is shown in Fig. 27.

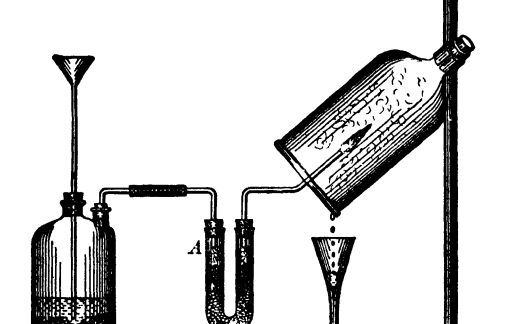



FIG. 27.

*A* is the calcium-chloride tube. Before lighting the jet hold a glass plate in the escaping gas, and see whether water is deposited

on it. Light the jet *before* putting it under the bell-jar, otherwise if hydrogen is allowed to escape into the vessel it will contain a mixture of air and hydrogen, and this mixture, as we shall soon see, is explosive.

EXPERIMENT 51.—Mix hydrogen and oxygen in the proportion of about 2 volumes of hydrogen and 1 volume of oxygen in a gasometer Fill soap-bubbles, as directed in Experiment 40, with this mixture and allow them to rise in the air. As they rise, bring a lighted taper in contact with them, when a sharp explosion will occur. Great care must be taken to keep all flames away from the vicinity of the gasometer while the mixture is in it. This experiment is conveniently performed by hanging up, about six to eight feet above the experiment-table, a good-sized tin funnel-shaped vessel with the mouth downward. Now place a gas jet or a small flame of any kind at the mouth of the vessel. If the soap-bubbles are allowed to rise below this apparatus they will come in contact with the flame and explode at once.*

What does this experiment show? Does it give any information in regard to the composition of water?

## EUDIOMETRIC EXPERIMENTS.

EXPERIMENT 52.—The general method of studying the combination of hydrogen and oxygen by means of the eudiometer was described in the text (see p. 73). To what was there said it need only be added that, in exploding the mixture in the eudiometer, the latter should be held down firmly, by means of a clamp, against a thick piece of rubber cloth placed on the bottom of the mercury-trough. In making the measurements of the volume of the gases and the height of the mercury column, care must be taken to have the eudiometer in a perpendicular position. This can be secured by means of plumb-lines suspended from the ceiling and reaching nearly to the table, by which the position of the eudiometer can be adjusted.

## OXYHYDROGEN BLOWPIPE.

EXPERIMENT 53—Hold in the flame of the oxyhydrogen blowpipe successively a piece of iron wire, a piece of a steel watch spring, a piece of copper wire, a piece of zinc, a piece of platinum wire.

EXPERIMENT 54.—Cut a piece of lime of convenient size and shape, say an inch long by three-quarters of an inch wide, and the same thickness. Fix it in position so that the flame of the oxyhydrogen blowpipe will play upon it. The light is very bright, but by no means as intense as the electric light.

* The same apparatus may be used in experimenting with soap-bubbles filled with hydrogen.

## CHAPTER V.

### CONSTITUTION OF MATTER.—ATOMIC THEORY.—ATOMS AND MOLECULES.—CONSTITUTION.—VALENCE.

**The Atomic Theory as proposed by Dalton.**—It has been pointed out that Dalton, at the beginning of the last century, discovered the law of multiple proportions. This law, as well as that of definite proportions, called for explanation.* The questions to be answered are: (1) Why do the elements combine in definite proportions? (2) Why, when elements combine with each other in more than one way, do the relative quantities that enter into combination in the different cases bear simple relations to one another? and (3) What is the significance of the figures representing the combining weights?

It is only necessary to assume that each element is made up of particles which are not divisible in chemical processes, and that these particles, or atoms, have definite weights. The atoms of any one element must be supposed to have the same weight, while the atoms of different elements have different weights. Now, when chemical combination takes place, Dalton supposed that the action is between the atoms. The simplest case is that in which combination takes place in such way that each atom of one element combines with one atom of another; but, besides this kind of combination, we may have that in which one atom of one element combines with two atoms of another, or two of one may combine with three of another, etc. Suppose two elements $A$ and $B$, the weights of whose atoms are to each other as 1 : 10, are brought to-

* Many laws are known for which no satisfactory explanation has been offered. See paragraph *Use and Value of a Theory*, p. 85.

gether, and they combine in the simplest way, i. e., one atom of one with one atom of the other, then it is plain that in the compound $AB$ the elements will be contained in the proportion of 1 part by weight of $A$ to 10 parts by weight of $B$, whether a small or a large quantity of the compound is formed, and no matter in what proportions the elements are brought together. If they should be brought together in the proportion of their atomic weights (1 : 10), then no part of either element will be left uncombined after the act of combination has taken place. If, however, a larger proportion of either element is taken than that stated, then the quantity of the one which is in excess of this proportion will be left uncombined. This is in accordance with what is known to take place, and it is a conclusion drawn from the theory. No matter how many atoms of $A$ may be taken, the same number of atoms of $B$ will be required to combine with them. But each atom of $B$ weighs 10 times as much as each atom of $A$, therefore the total mass of $B$ that enters into combination must be 10 times that of $A$ with which it combines. It may be, however, that these same elements can form other compounds with each other. If $A$ and $B$ represent the atoms of the elements and these atoms are assumed to be chemically indivisible, then the other compounds must be represented by such symbols as $AB_2$, $A_2B$, $AB_3$ $A_3B$, $A_2B_3$, etc., which represent compounds in which 1 atom of $A$ is combined with 2 atoms of $B$; 2 of $A$ with 1 of $B$; 1 of $A$ with 3 of $B$; 3 of $A$ with 1 of $B$; 2 of $A$ with 3 of $B$; etc.; or they also represent compounds in which 1 part by weight of $A$ is combined with 20 parts by weight of $B$; 2 of $A$ with 10 of $B$; 1 of $A$ with 30 of $B$; 3 of $A$ with 10 of $B$; 2 of $A$ with 30 of $B$; etc. It is therefore clear that, if the atomic theory as put forward by Dalton is true, the elements must combine according to the laws of definite and multiple proportions; and it appears that the figures which represent the combining weights of the elements must either bear to one another the same relation as the weights of the atoms, or the atomic weights or the rela-

tive weights of the atoms must be closely related to the combining weights, as will be pointed out more clearly presently.

**Use and Value of a Theory.**—The relation of a theory to facts is simple, but is frequently misunderstood. The relation may be conveniently illustrated by the case under consideration. By a careful investigation of a number of chemical compounds it was shown that in each of them the same elements always occur in the same proportion. This led to the belief that this is true of every chemical compound, and after further investigation which, as far as it went, showed the surmise to be correct, the law of definite proportions was proposed. This law is simply a statement of what has been found true in all cases examined. This statement involves no speculation. It is a statement of fact. It may be said that the statement or law must be open to some doubt for the reason that all possible cases have not been examined, and it may not hold true for some of these unexamined cases. The reply to this is that it has been found true in a very large number of cases and in all cases that have been investigated. It is true as far as we know and that is all we can demand of any law. Again, further investigation led to the discovery of the law of multiple proportions, which is also a statement of what has been found true in all cases investigated. It, like the law of definite proportions and in the same sense, is a statement of fact. But having gone thus far, it may now be asked what is the explanation of these laws? Given the facts—what is the explanation? By experiment it is difficult to go beyond these facts, but it is possible to imagine a cause and then proceed to see whether the imagined cause is sufficient to account for the facts. This is what Dalton did. He imagined that matter is made up of atoms of definite weights, and that chemical combination takes place in simple ways between these atoms. This imagined cause is the *atomic theory*. It is not a statement of anything found by investigation. It is not a statement of an established fact. It may or may not be liter-

ally true, but at all events it is the best guess that has ever been made as to the cause of the fundamental laws of chemical action, and it furnishes a very convenient means of interpreting the facts of chemistry. Since the atomic theory was first proposed it has been accepted by nearly all chemists. It has been of great value in suggesting methods of work, and has contributed largely to the advance of chemistry. Any theory which is in accordance with the facts and leads to the discovery of new facts is of value, whether it should eventually prove to be true or false. At the same time a false theory may do much harm, as it may lead men to misinterpret the facts which they observe, and thus retard progress.*

**Atomic Weights and Combining Weights.**—If the atomic theory is true, the atoms of each element must have definite weights, and the determination of these atomic weights must evidently be of great importance. By analysis of compounds it is only possible to determine the proportions by weight in which the elements combine with one another. Can the atomic weights be determined in this way? In the first place, it is clear that it is out of the question to think of determining the absolute weights of the atoms. All that is possible is to determine their relative weights. As of all the elements hydrogen enters into combination in smallest relative quantity, its atomic weight is taken as the unit of the system, and the problem before us is to determine how many times heavier the atoms of the other elements are than that of hydrogen. If every element combined with hydrogen in only one proportion the problem would be a comparatively simple one. Thus the three elements chlorine, bromine, and iodine combine with hydrogen, forming only one compound each. On analysis these are found to contain respectively

* The latest investigations make it appear highly probable that the chemical atoms are not indivisible, that they consist of very much smaller particles called *electrons*, and that some of these electrons may be split off from the atoms. To all intents and purposes, however, the atoms of the common elements may be regarded as indivisible, and the atomic theory is as helpful to-day as it ever was.

1 part of hydrogen to 35.18 parts of chlorine;
1 " " " 79.36 " " bromine; and
1 " " " 126.01 " " iodine.

There is no reason for believing that in these compounds the elements are combined in any but the simplest way, i. e., that each atom of hydrogen is combined with one atom of chlorine to form hydrochloric acid, etc. If this is true, then the atom of chlorine must weigh 35.18 times, that of bromine 79.36 times, and that of iodine 126.01 times as much as that of hydrogen, or, in other words, the atomic weights of chlorine, bromine and iodine are respectively 35.18, 79.36, and 126.01. It will, however, be observed that there is no evidence as to whether the elements in these compounds are combined in the simplest way or not. It is possible, as far as we know, that one atom of hydrogen may combine with two or three of chlorine, or that one of chlorine may combine with two or three of hydrogen. As there is, however, no evidence upon this point the simplest assumption is made.

In the case of oxygen the problem is more difficult. In water the elements are combined in the proportion of 7.94 parts by weight of oxygen to 1 of hydrogen, and from this we should naturally conclude that the atomic weight of oxygen is 7.94; but further study shows that this conclusion is not justified. Hydrogen and oxygen form a second compound known as hydrogen dioxide or hydrogen peroxide in which there are 15.88 parts by weight of oxygen to 1 of hydrogen. This may be explained in the terms of the atomic theory by assuming that water is represented by the formula HO, and hydrogen dioxide by $HO_2$. But it may be that the atomic weight of oxygen is 15.88, and then water must be represented by the formula $H_2O$, and hydrogen dioxide by HO. Simple analysis of the compounds is not sufficient to enable us to decide between these possibilities. It is, therefore, evident that in order to determine the atomic weights something besides the determination of the composition of compounds is necessary. The figures representing the combining weights found in this way will,

however, either be identical with the atomic weights or they will bear a simple numerical relation to them.

**Molecules.**— Investigation of certain phenomena of light, of electricity, of liquid films and the conduct of gases has led physicists to the conclusion that matter is not continuous, but made up of small particles, which are called *molecules.* A gaseous molecule is defined as "*that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas.*" It would be out of place here to present the physical facts upon which the molecular theory rests. Suffice it to say that it is the only theory that has been found adequate to account for the behavior of gases.

**Avogadro's Hypothesis.**—The fact that all gases conduct themselves in the same way under the influence of changes in temperature and pressure can only be explained by assuming that *equal volumes of all gases and vapors contain the same number of ultimate particles or molecules at the same temperature and pressure.*

This is a deduction from the well-tested molecular theory of gases. It was, however, originally put forward by the Italian chemist Avogadro as a result of his study of chemical as well as of physical facts, and a little later it was suggested as probable by the French physicist Ampère. It is therefore generally spoken of as Avogadro's hypothesis, and sometimes as Ampère's hypothesis. It is in thorough accordance with a large number of well-known facts, and it is undoubtedly true, if the molecular theory of matter is true. It may therefore be considered as furnishing a solid foundation for further conclusions bearing upon the problem of the determination of the atomic weights.

**Distinction between Molecules and Atoms.**—It is evident, that the smallest particle, or the molecule, of any chemical compound, as of water or hydrochloric acid, must be made up of still smaller particles. Thus, the smallest particle of water must contain smaller particles of hydrogen and oxygen, and the smallest particle of hydrochloric acid must

contain smaller particles of hydrogen and chlorine. These smallest particles of the molecules are the atoms. The molecules of the compounds are, according to this view, made up of the atoms of the elements. Similarly the elements themselves are, for good reasons which will be presented, believed to consist of molecules which are in turn made up of atoms of the same kind, though in a few cases the molecule of the element is identical with the atom. The difference between a compound and an element then is, in general, that the molecule of the compound consists of atoms of different kinds, while the molecule of an element consists of atoms of the same kind or, in a few cases, of one atom. Generally the atoms do not exist in the free or uncombined state, but, if they are set free by chemical action, they unite to form molecules. The following may serve as a definition of the conception of atoms at present held by chemists:

*Atoms are the indivisible* constituents of molecules. They are the smallest particles of the elements that take part in chemical reactions, and are mostly incapable of existence in the free state, being generally found in combination with other atoms, either of the same kind or of different kinds.*

It cannot be too strongly emphasized that the views held in regard to the relations between molecules and atoms are based upon an enormous amount of painstaking study of facts, and in order fully to comprehend their value a study of most of these facts would be necessary. These views have gradually become firmly established as knowledge of the facts has grown more and more profound.

**Molecular Weights.**—If equal volumes of gases contain the same number of molecules at the same temperature and pressure, it is only necessary to determine the weights of equal volumes of gases to learn the relative weights of their molecules. Thus, if a liter of each of three gases be weighed and it is found that the weights are to one

* See Foot-note, p. 86.

another as 1 to 2 to 3, then it follows that the relation between the weights of the molecules of these gases is expressed by these figures. The determination of the relative weights of the molecules of substances which either are gaseous or can be converted into gases resolves itself simply into a determination of the weights of equal volumes. In representing the molecular weights any figures that are most convenient may be used, provided only they bear to one another the relations determined by experiment. If, however, 16 be adopted as the atomic weight of oxygen, then the system of molecular weights must be based upon this standard. But on this basis 16 *is not the molecular weight* of oxygen. In other words, the atom and the molecule of oxygen are not identical. This conclusion is drawn from a large number of facts. One way in which it can be made clear is this: The weight of a given volume of oxygen gas as compared with the weight of the same volume of water in the form of gas under the same conditions of temperature and pressure is as 32 to 18.02. These equal volumes of gases contain the same number of molecules according to the hypothesis of Avogadro. Each molecule of water is made up of 1 atom of oxygen with the atomic weight 16 and 2 atoms of hydrogen with the atomic weight 1.008. If 16 is the atomic weight of oxygen, water cannot have a smaller molecular weight than 18.016. But, if the molecular weight of water is 18.016, that of oxygen must be 32, or it must be twice as great as the atomic weight. No matter what atomic weight may be adopted for oxygen this reasoning holds good. The standard molecule is therefore that of oxygen or, better, the basis of the system is a hypothetical gas having $\frac{1}{32}$ the weight of oxygen. This may be called the *normal gas.* Having adopted this standard, the molecular weight of a gas may be defined as its weight compared with that of the normal gas. Below are given the molecular weights of a few elements and compounds that have been determined by the method just described:

| Name. | Molecular Weight. | Molecular Formula. |
|---|---|---|
| Hydrogen | 2.016 | $H_2$ |
| Nitrogen | 28.02 | $N_2$ |
| Water | 18.016 | $H_2O$ |
| Hydrochloric acid | 36.458 | HCl |
| Ammonia | 17.034 | $NH_3$ |
| Marsh-gas | 16.032 | $CH_4$ |
| Carbon monoxide | 28 | CO |
| Carbon dioxide | 44 | $CO_2$ |

**Deduction of Atomic Weights from Molecular Weights.**—It is plain from what has been said that a knowledge of the molecular weight of an element does not convey a knowledge of its atomic weight. If, for example, it is known that the molecular weight of nitrogen is approximately 28, that furnishes no means of judging what the atomic weight is. It is plainly necessary to know of how many atoms each molecule of nitrogen is made up, and to learn this is not a simple matter. It is easier to determine the atomic weight of an element through a study of its compounds. Suppose it is desired to determine the atomic weight of oxygen. The molecular weights of a number of compounds that contain oxygen are first determined and these compounds are then analyzed. The smallest figure that is required to express the weight of the oxygen that enters into the composition of the molecules is then selected as the atomic weight. The molecular weights and the composition of several oxygen compounds are given in the following table. The figures in the third column are of course determined by analysis, an example of the methods used having been given in the chapter on water. Stated in ordinary language, the figures in the case of carbon monoxide mean that the molecule of this compound weighs 28 times as much as the normal gas, and the 28 parts by weight of matter are made up of 12 parts of carbon and 16 parts of oxygen. Considering now the composition of the compounds in the table, it will be seen that the small-

est weight of oxygen that enters into the composition of any of the molecules weighs 16 in terms of the nor-

| Compound. | Mod. Wt. Approx. | Composition. |
|---|---|---|
| Water | 18.016 | 2.016 parts hydrogen. |
| | | 16 " oxygen. |
| Carbon monoxide | 28 | 12 " carbon. |
| | | 16 " oxygen. |
| Carbon dioxide | 44 | 12 " carbon. |
| | | 32 " oxygen. |
| Nitric oxide | 30.01 | 14.01 " nitrogen. |
| | | 16 " oxygen. |
| Nitrous oxide | 44.02 | 28.02 " nitrogen. |
| | | 16 " oxygen. |
| Sulphur dioxide | 64.06 | 32.06 " sulphur. |
| | | 32 " oxygen. |
| Sulphur trioxide | 80.06 | 32.06 " sulphur. |
| | | 48 " oxygen. |

mal gas. Twice this weight is found, as in carbon dioxide and sulphur dioxide; and three times, as in sulphur trioxide, but no smaller weight. Now, an examination of all compounds of oxygen that are known in the form of gas or vapor shows the same thing; that is to say, the smallest weight of oxygen that enters into the composition of molecules is 16 times as great as that of the normal gas. The conclusion is therefore drawn that 16 is the atomic weight of oxygen. The possibility that the atomic weight of oxygen is less than this figure is not excluded. It may be that in the simplest oxygen compounds now known there are two or more atoms of this element in the molecules. But in the total absence of evidence on this point it is fair to accept the figure 16.

In this way the atomic weights of all elements that form gaseous compounds or compounds that can be converted into vapor have been determined; and the determinations made in this way are regarded as the most reliable.

**Exact Atomic Weights determined by the Aid of Analysis.**—By determining molecular weights it is possible to decide approximately what figure represents the atomic weight of an element, but the methods employed in making determinations of molecular weights are liable

to slight errors, and therefore the atomic weights obtained directly from the molecular weights deviate slightly from the true figures. In order to determine the atomic weights with the greatest possible accuracy, the most refined methods of chemical analysis are used, and the figures in the table on page 19 have been determined in this way by a combination of a study of the specific gravity of gases and by the most careful analyses, together with some other methods which will be taken up later.

**Molecular Formulas.**—The symbols of chemical compounds first used were intended to express simply the composition of the compounds, and this can be done as was explained in Chapter I, by adopting a system of combining weights of the elements. According to the theory above explained (p. 88), the smallest particle of every compound is a molecule, and each molecule is made up of atoms. It appears, therefore, desirable for the sake of uniformity that the symbols used to represent chemical compounds should represent molecules. Where the molecular weight of a compound, the atomic weights of the elements of which it is composed, and its composition are known, there is no difficulty in representing it by a molecular formula. Thus, the molecular weight of ammonia is found by experiment to be approximately 17, and the 17 parts by weight are made up of 14 parts by weight of nitrogen and 3 parts by weight of hydrogen. The atomic weight of nitrogen is found by the method which has just been described to be very nearly 14. Therefore the molecule of ammonia weighing 17 parts is composed of 1 atom of nitrogen weighing 14 parts and 3 atoms of hydrogen weighing 3 parts, and the composition of the molecule is represented by the formula $NH_3$. Similarly the composition of the molecule of water is represented by the formula $H_2O$; that of hydrochloric acid by HCl; that of marsh-gas by $CH_4$; etc., etc. Every formula now in use is intended to represent a molecule of the compound for which it stands. For the determination of the molecular weights of compounds that are not gaseous and not convertible into vapor, Avogadro's method cannot be used.

Methods have, however, been devised which are applicable to a number of these (see Chapter XXIII).

**Constitution.**—According to the theory, when hydrochloric acid is formed, each atom of hydrogen combines with one atom of chlorine, and each molecule of the resulting compound is made up of an atom of hydrogen and an atom of chlorine. What the act of combination consists in we do not know. We simply know that something very remarkable takes place, and that as a consequence the hydrogen and chlorine cease to exist in their original forms. It is idle at present even to speculate in regard to the character of the change. The fact of union is expressed by writing the symbols of the elements side by side without any sign between them, as HCl, or, sometimes, it is convenient to use a line to indicate chemical union thus H–Cl. According to the molecular theory the molecule of water consists of two atoms of hydrogen and one of oxygen, as represented by the formula $H_2O$, and the question now suggests itself whether all three atoms are in combination with one another or whether each of the hydrogen atoms is in combination with the oxygen atom but not with each other, as represented by the formula H–O–H. So, too, in the case of ammonia, the molecular formula of which is $NH_3$, the question suggests itself: Are the three atoms of hydrogen in combination with the atom of nitrogen, but not with one another, as represented in the formula $N\begin{smallmatrix}\diagup H\\ -H\\ \diagdown H\end{smallmatrix}$? It is extremely difficult to answer such questions, but, nevertheless, facts are known that lead to probable conclusions. Formulas that express the composition of molecules and at the same time express the relations, or the connections that exist, between the atoms are called *constitutional formulas*. These constitutional formulas are frequently used at present, but sometimes without a sufficient basis of facts to justify them. Whenever they are used in this book, the reasons for them will be stated as fully as may appear necessary.

**Valence.**—The formulas of the hydrogen compounds of

chlorine, oxygen, nitrogen, and carbon, all determined by the same method, are

$$ClH \quad OH_2 \quad NH_3 \quad CH_4.$$

A consideration of these formulas and of many similar ones has led to the conclusion that the atoms of different elements differ in their power of holding other atoms in combination. The simplest explanation of the composition of the compounds above represented is that the atoms of chlorine, oxygen, nitrogen, and carbon differ in their power of holding hydrogen atoms in combination. Hydrogen and chlorine combine in only one way, 1 atom of chlorine combining with 1 of hydrogen; 1 atom of oxygen combines with 2 of hydrogen; 1 atom of nitrogen with 3 of hydrogen; and 1 atom of carbon with 4 of hydrogen. The limit of the combining power of the atom of chlorine is reached when it has combined with one atom of hydrogen. And as one chlorine atom can hold but one atom of hydrogen in combination, so one atom of hydrogen can hold but one atom of chlorine. Either the hydrogen atom or the chlorine atom may be taken as an example of the simplest kind of atom. An element like hydrogen or chlorine is called a *univalent element;* an element like oxygen whose atom can hold two unit atoms in combination is called a *bivalent element;* an element like nitrogen whose atom can hold three unit atoms in combination is called a *trivalent element;* and an element like carbon whose atom can hold four unit atoms in combination is called a *quadrivalent element.* Most elements belong to one or the other of these four classes, though there are some which can hold five, six, and even seven unit atoms in combination. These are called *quinquivalent*, *sexivalent* and *septivalent* respectively.

*Valence* is defined as that property of an element by virtue of which its atom can hold a definite number of other atoms in combination. In the formation of compounds the valence of the elements determines how many atoms of any element can enter into combination with any

other. The atoms are sometimes spoken of as having bonds which are graphically represented by lines. Thus, a univalent element is said to have one bond, as represented by H–, Cl–, etc.; a bivalent element is said to have two bonds, –O–, –S–, etc.; a trivalent element three, $-\overset{|}{\underset{|}{N}}-$; and a quadrivalent element four, $-\overset{|}{\underset{|}{\overset{|}{\underset{|}{C}}}}-$. Of course, this is merely a symbolical representation of the idea that each atom has a definite power of combining with others.

It is further said that when the atoms unite these bonds become satisfied. Thus when one atom of hydrogen unites with one of chlorine, the bond of each is regarded as uniting with the bond of the other, and this is represented by the symbol H–Cl. So, too, when two atoms of hydrogen unite with one of oxygen, the compound is represented in this way: H–O–H or $O<^{H}_{H}$. In the union of atoms, further, to use the figurative language, two bonds may be satisfied by two univalent atoms or by one bivalent atom. Thus, in marsh-gas, $CH_4$, the four affinities or bonds of the quadrivalent carbon atom are regarded as being satisfied by the four univalent hydrogen atoms. In the compound $H-\overset{H}{\underset{|}{\overset{|}{C}}}=O$ however, two of the bonds are regarded as satisfied by two univalent hydrogen atoms, and the other two by one bivalent oxygen atom; and, again, in the compound O=C=O, the four bonds of the carbon atom are regarded as satisfied by two bivalent oxygen atoms.

**Replacing Power of Elements.**—As has been seen, when potassium acts upon water the action is represented by the equation

$$K + H_2O = KOH + H.$$

This reaction may be expressed as follows by means of formulas that take the valence of the elements into account:

$$K + H-O-H = K-O-H + H.$$

According to this, one atom of potassium is substituted for one atom of hydrogen in water, and in the compound formed, the atom of potassium is regarded as occupying the place of the hydrogen atom. The elements calcium and barium are bivalent like oxygen, as shown in the compounds $CaCl_2$ and $BaCl_2$, in which the atom of calcium as well as that of barium holds two univalent atoms of chlorine in combination. When these elements act upon water, hydrogen is liberated as in the case of potassium, but each atom replaces two atoms of hydrogen, as represented in the equations

$$Ca + 2HOH = CaH_2O_2 + 2H;$$
$$Ba + 2HOH = BaH_2O_2 + 2H.$$

These changes are expressed by valence formulas thus:

$$Ca + \begin{matrix} H-O-H \\ H-O-H \end{matrix} = Ca\begin{matrix} O-H \\ O-H \end{matrix} + H_2;$$

$$Ba + \begin{matrix} H-O-H \\ H-O-H \end{matrix} = Ba\begin{matrix} O-H \\ O-H \end{matrix} + H_2.$$

A trivalent element acting in the same way would give a compound of the general formula $M\begin{matrix} O-H \\ O-H \\ O-H \end{matrix}$, in which M represents any trivalent element.

So, too, in the action of various elements upon hydrochloric acid, HCl, a univalent element like sodium or potassium replaces one hydrogen atom in one molecule of the acid, and forms a compound of the general formula MCl, as, for example, KCl and NaCl. A bivalent element, like zinc, replaces two atoms of hydrogen in two molecules of the acid, forming the compound $ZnCl_2$:

$$Zn + \begin{matrix} HCl \\ HCl \end{matrix} = Zn\begin{matrix} Cl \\ Cl \end{matrix} + H_2.$$

A trivalent element forms a compound of the general formula $MCl_3$, as, for example, aluminium chloride:

$$Al\begin{matrix} Cl \\ -Cl \\ Cl \end{matrix}.$$

The above explanation of what is called valence will

suffice by way of introduction to the subject. The relation which it bears to the facts is simply this: On studying the composition of chemical compounds it is found that, in general, the elements combine with one another in comparatively few proportions. Thus, hydrogen and chlorine combine with each other in only one proportion; hydrogen and oxygen in two; nitrogen and oxygen in five; etc. There is something limiting the complexity of compounds. We might study the laws governing the complexity of compounds without any hypothesis as to the cause, but the conception of valence is a convenient explanation of these laws, and it has been of much service in furnishing chemists with a simple language for representing chemical changes. It will be pointed out farther on that there is a close relation between the phenomena of valence and certain electrical phenomena.

## EXPERIMENTS.

It would be well in this connection to determine the specific gravity of some substance in the form of vapor. The principal methods for this purpose are those of Dumas, Gay-Lussac, Hofmann, and Victor Meyer. That of Dumas, which consists in measuring the volume and determining the weight of the vapor under observation, is the most accurate. The method of Hofmann is a modification of that of Gay-Lussac. It consists in weighing a small quantity of the liquid the specific gravity of whose vapor is to be determined, and, after introducing the liquid in a minute glass vessel into a eudiometer over mercury, heating the eudiometer and its contents by passing steam through a jacket surrounding it and measuring the volume of vapor formed. The method of Victor Meyer is used when it is required to determine the specific gravity of the vapor of a substance which boils at a high temperature.

### Method of Dumas.

Experiment 55.—In this method the liquid to be vaporized is brought into a small balloon like that shown in Fig. 28. The dry balloon is first weighed, and a small quantity of liquid then introduced by gently heating the balloon and putting the point of its stem into the liquid, when, on cooling, the liquid rises and enough is easily brought into the balloon in this way. The balloon is now placed (in the position shown in Fig. 29) in a bath of water, oil, or paraffin, according to the boiling-point of the liquid. The bath is

heated 30–40° above the boiling-point of the liquid under examination. The air is thus driven out and the balloon is filled with the vapor. When vapor no longer escapes, the point of the stem is closed by melting it with a mouth blowpipe. The balloon is then

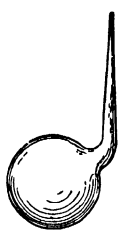


FIG 28.

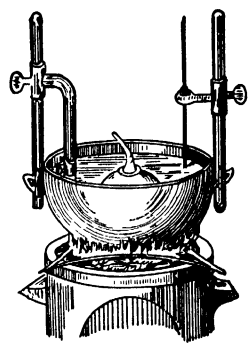


FIG 29.

cleaned, dried, and weighed. The temperature of the bath and the height of the barometer are observed at the time the balloon is closed. The point of the stem is broken off under mercury, when the mercury rises and fills the balloon. By pouring the mercury out into a graduated cylinder the capacity of the balloon is determined. The specific gravity of the vapor is calculated by the aid of the formula

$$D = \frac{(B_1 - B + p)\ (1 + 0.00366\ .\ t_1)\ .\ 760}{v\ .\ 0.001293\ .\ h_1}.$$

in which

$B$ = weight of balloon at $t°$ and $h$ mm.;
$B_1$ = " " " with vapor, at $t_1°$ and $h_1$ mm.;
$v$ = capacity of the balloon in cubic centimetres;
0.001293 = weight of 1 cc. air at 0° and 760 mm.;
$p$ = weight of air in balloon at $t°$ and $h$ mm.

## METHOD OF VICTOR MEYER.

EXPERIMENT 56.—In this method a known weight of substance is converted into vapor, and the volume of vapor formed is determined by measuring the volume of air which it displaces. The apparatus consists of an outer cylindrical vessel *A*, Fig. 30, and an inner vessel *B*, which is connected with a tube *C*. The vessel *B* has a capacity of about 100 cc., and is about 200 mm. long. The tube *C*, with its funnel-shaped end *E*, is about 600 mm. long. First, a small quantity of some substance with a boiling-point high enough to secure the complete conversion into vapor of the substance to be studied, is

put in the bottom of the vessel $A$, and a little ignited asbestos or dry mercury in the bottom of the vessel $B$. The substance in $A$ is now heated to boiling, and $E$ is closed with a rubber stopper. After a time the temperature of the air in $B$ is raised to that of the vapor in $A$, and no more escapes from the tube $D$. When this condition of equilibrium is reached, a small weighed quantity of the substance under examination is dropped into the vessel $B$, the stopper being removed from $E$ and quickly replaced. The substance is converted into vapor, and displaces an equivalent volume of air, and this displaced air is collected over water in the measuring-tube placed over the end of $D$. When no more air escapes, the volume is determined in the usual way The specific gravity of the substance is calculated by the aid of the following formula :

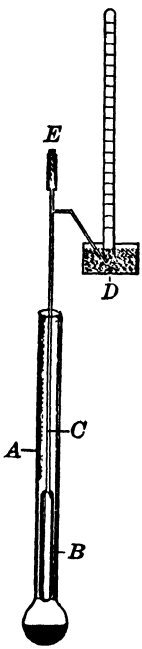


FIG. 30.

$$D = S \times \frac{(1 + 0.00366 \times t)\ 760}{(B - w)\ V \times 0.001293},$$

in which 0.001293 is the weight of 1 cc. air in grams at 760 mm. and 0° , and, further,

$S$ = weight of substance taken;
$t$ = temperature of the room, or of the water in the measuring apparatus;
$B$ = height of barometer;
$w$ = tension of aqueous vapor;
$V$ = observed volume of air;

or, the formula can be simplified by division, when it takes this form:

$$D = S \frac{(1 + 0.00366 \times t)587.780}{(B - w)\ V}.$$

The above is the simplest form of apparatus used. To avoid opening and shutting the vessel in order to introduce the substance, an arrangement has been devised for holding the substance below the stopper until the proper temperature is reached, and then releasing it without disturbing the stopper.

## CHAPTER VI.

### WATER.

**Historical.**—Water was long thought to be an elementary substance until, towards the end of the eighteenth century, the discovery of hydrogen and oxygen, and of the nature of combustion, led to the discovery of its composition.

**Occurrence.**—Besides the form in which water occurs in such enormous quantities in and on the earth, it also occurs in forms and conditions which prevent its immediate recognition. Thus all living things contain a large proportion of water, which can be driven off by heat. If a piece of wood or of meat is heated, liquids pass off, and by purification these can be shown to consist mainly of water. The proportion of water in animal and vegetable substances is very great. If the body of a man weighing 150 pounds were to be put in an oven and thoroughly dried, there would be only about 40 pounds of solid matter left, most of the rest being water.

Water also occurs in another form in which it does not directly reveal its presence. This is as *water of crystallization.* Many natural and manufactured chemical compounds give off water when heated. If, for example, the zinc sulphate formed in the preparation of hydrogen from zinc and sulphuric acid is dried by exposing it to the air or by pressing it between layers of filter-paper, it will be found that, when heated in a dry tube, it gives off water, and at the same time its appearance is markedly changed. The same is true of gypsum which is found in nature, and of copper sulphate or blue vitriol. In this last case the loss of water is accompanied by a change of color. After all the water is driven off, the powder left behind is white. This subject will be more fully discussed farther on. See p. 106.

**Formation of Water and Proofs of its Composition.**— When an electric current is passed through water, bubbles of gas rise from each pole of the battery. By placing each pole under the mouth of an inverted tube filled with water the gases may be easily collected. When one of the tubes has become full of gas the other one will only be half full. An examination will show that the gas in the tube which is full is hydrogen, whereas that in the one which is half full is oxygen. By decomposition of water by means of the electric current, then, two volumes of hydrogen are obtained for each volume of oxygen. The relative weights of equal volumes of the two gases are already known so that the relative weights of the gases obtained in the experiment can easily be calculated. The ratio of the weights of equal volumes of hydrogen and oxygen is 1 : 15.89. Therefore, if 2 volumes of hydrogen are combined with 1 volume of oxygen, the ratio between the weights is 2.0027 : 15.89 or 1 : 7.95. Although from the experiment referred to it is known that hydrogen and oxygen are obtained from water in certain proportions, it does not follow that this is the composition of water. For it may be that other elements besides hydrogen and oxygen are contained in it, and it may be also that all the hydrogen and oxygen are not set free by the action of the electric current. Whether either of these possibilities is true or not, could be determined by decomposing a weighed quantity of water, and weighing the hydrogen and oxygen obtained from it. If it should be found that the sum of the weights of hydrogen and oxygen is equal to the weight of the water decomposed, this fact would be evidence that only hydrogen and oxygen are contained in water, and that they are present in the proportions stated. The same thing can be satisfactorily proved by causing hydrogen and oxygen to combine, or by effecting the *synthesis* of water. It has been shown that by burning hydrogen in oxygen water is formed. This proves that water consists of hydrogen and oxygen, but it does not furnish any proof as to the relation between the weights of the gases that combine

It is a *qualitative synthesis.* Other methods have been described, the object of which was to show in what proportion by weight and by volume hydrogen and oxygen combine to form water. These methods are examples of *quantitative synthesis.* The results prove that to form water hydrogen and oxygen combine in the proportion of 1 volume of oxygen to 2 of hydrogen; and it therefore follows that the decomposition of water which is effected by the electric current is complete.

**Kinetic Theory applied to Liquids.**—In the conversion of gases into liquids or liquids into gases, as the critical point is reached the gaseous condition merges into the liquid condition and *vice versa* imperceptibly, hence the kinetic theory can be applied to liquids. As the molecules in the liquid are much more closely packed than in the gas, or in other words are in a greater state of concentration, there is a much larger number of molecules in a given volume of liquid than in the same volume of gas, and consequently they must collide more frequently. Some molecules moving with especial velocity toward the surface of the liquid pass into the space above the liquid in the form of vapor. Liquids give off vapor therefore at all temperatures, producing in a closed vessel a pressure upon the liquid called the vapor pressure or vapor tension.

**Vapor Pressure of Liquids.**—The vapor pressure of a liquid is definite for a given temperature, for some of the molecules of vapor moving in the space above the liquid will move toward it, come in contact with it, and liquefy again. The liquid molecules passing into vapor and the vapor molecules passing into liquid will reach a condition of equilibrium. Equilibrium is not to be understood as cessation of motion. It means as here used that, in a given time, as many molecules of vapor are condensed as molecules of liquid are vaporized. The escape of molecules is due to the velocity of their motion. By heating the liquid the velocity of its molecules is increased and the vapor pressure increases. The vapor pressure of liquids is measured by the pressure exerted on a barometric column of mercury and is expressed in mm. of mercury. See Exp. 64.

**Vapor Pressure of Water.**—The vapor pressure of water is a subject important to chemists because it has to be taken into account in many chemical phenomena. At 0° the vapor pressure of water is 4.6 mm., at 50°, 92 mm., at 100°, 760 mm.; i. e. water boils when its vapor pressure equals the atmospheric pressure. At 200° the vapor pressure of water is over 15 atmospheres. The atmospheric pressure at Mt. Blanc averages 423.7 mm.: water boils there at 84.4°, the vapor pressure of water at 84.4° being 423.7 mm. If the pressure of the steam in a steam boiler is 5 atmospheres, the water in the boiler boils at 152°.

**Properties of Water.**—Pure water is tasteless and inodorous, and in small quantities colorless. Thick layers are, however, blue. This is seen by filling a long tube with carefully purified water, and examining it by transmitted light, when it appears blue. Some mountain lakes also have a marked blue color. When cooled, water contracts until it reaches the temperature of 4°. At this point it has its maximum density. If cooled below this it expands, and the specific gravity of ice is somewhat less than that of water. Hence ice floats on water. If this were not so, in cold climates the water in the streams would freeze solid. As it is, the lower layers of water are protected by the ice and the cold water just below it, which are poor conductors of heat. This expansion of water on freezing is the cause of the constant disintegration or "weathering" of rock through water freezing in the crevices. On the weathering of rock depends largely the fertility of soil. Water can be cooled down below its freezing temperature, or 0°, if it is kept perfectly quiet, protected from the air, or cooled in capillary tubes. Water thus cooled down will suddenly solidify when a crystal of ice is dropped into it and then its temperature rises to 0°. If carefully kept from contact with ice it will not solidify.

This phenomenon has to do with vapor pressure. At 0° the vapor pressure of ice is the same as that of water at 0°, 4.6 mm., but *supercooled* water, i. e. water at a temperature below 0°, has a greater vapor pressure than ice at the same temperature; hence the water gives off vapor constantly which is taken up by the ice and this process continues till all the water is changed into ice.

**Superheated Water.**—This expression signifies water heated above the boiling-point. Under ordinary atmospheric pressure water boils at 100°, so that water heated above this temperature under ordinary atmospheric pressure is said to be superheated. As the boiling point changes with the pressure the point above which the water must be heated to be superheated varies with the pressure. The phenomenon is most easily shown thus: A flask is carefully cleaned first with sodium hydroxide and then with dilute acid. Afterwards pure water is brought into it, and the water kept boil-

ing for some time. The phenomenon of "bumping" will then be observed. The boiling will be irregular; it will stop for a time, and then take place violently for a short time, again stopping, etc. This is due to superheating in the quiet intervals and sudden excessive conversion into vapor. Regular boiling is facilitated by the escape of gas bubbles from the liquid and from the surface of the vessel. The careful cleaning of the vessel removes the adherent gas, and prevents the escape of bubbles. "Bumping" can be prevented by putting some porous substance into the liquid. Air escapes from the substance and prevents the superheating. Superheating is one of the causes of boiler explosions.

**Heat of Vaporization of Water and Heat of Fusion of Ice.**—These names are given to the heat required to change water into steam and ice into water respectively.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| To heat | 1 | gram | ice | at | 0° | to form | 1 | gram | water at | 0° | requires 80 cal. |
| " | 1 | " | water | at | 0° | " | 1 | " | " | " 100° | " 100 " |
| " | 1 | " | " | | 100° | " | 1 | " | steam at 100° | | " 540.4 " |
| | | | | | | | | | | | From ice to steam, 720.4 " |

The importance of these facts is evident when we consider what it would mean if great bodies of ice melted suddenly, or if a liter of water at 100° passed suddenly into steam, thereby increasing its volume to nearly 1700 liters. The enormous waste of energy in burning coal to heat water to form steam for steam power is also shown by these figures, as is conversely the efficiency of a steam jet for heating, as one gram steam at 100° in condensing to 1 gram water at 100° gives off 540.4 cal. This figure is the *heat of condensation of steam.*

**Chemical Properties of Water.**—Water is a very stable chemical compound. An indication of the great energy of the act of combination of hydrogen and oxygen is given in the great evolution of heat accompanying it. In order to decompose water by heat, as much heat must be used as is evolved when it is formed. At high temperatures it is decomposed into its elements. The decomposition begins at 1000° and is half complete at 2500°. On cooling the mixed gases they recombine. The amount of decomposition is constant for a given temperature. This kind of gradual decomposition of a compound by heat, followed by a recombination on reversing the conditions, is called *dissociation.* It is a common phenomenon in chemistry, and farther on it will be discussed more fully. Water is decomposed by an electric current, when something is added to it to make it a conductor of electricity,

and partly by contact with sodium and potassium at ordinary temperatures, and by iron and carbon at higher temperatures. It combines directly with a large number of substances to form *hydrates*.

**Hydrates.**—Some of these hydrates lose the combined water through a simple rise in temperature; others are more stable. Some hydrates are crystalline solids. Other are liquids. As examples, the gaseous element chlorine forms a crystalline hydrate with a definite amount of water, $Cl_2 + 10H_2O$. Sulphur trioxide is crystalline and melts at 15°. It forms the following hydrates with water, $SO_4H_2$, $SO_5H_4$, $SO_6H_6$, $S_2O_7H_2$ and $S_2O_9H_6$. Each of these can be obtained as a crystalline substance, differing from the others in crystalline form and in melting point.

On adding water to those anhydrous salts, or oxides which form hydrates, the hydrate is formed with evolution of heat. Copper sulphate, $CuSO_4$, a white substance, forms three hydrates $CuSO_4 + H_2O$, $CuSO_4 + 5H_2O$, and $CuSO_4 + 7H_2O$, each of which differs in crystalline form and melting point from the others, all being blue. While there are well-grounded theories in regard to the constitution, or arrangement of atoms of some of these hydrates—those of sulphur trioxide, $SO_3$, for example,—little or nothing is known in regard to the constitution of such hydrates as $CuSO_4 + 5H_2O$, $CuSO_4 + 7H_2O$. In such cases the water is generally called "water of crystallization." This is, however, not an attempt at an explanation, and no one assumes that the hydrate consists of the anhydrous substance and water in some new kind of combination. Blue vitriol considered as a hydrate is a definite compound of unknown constitution. It is decomposed by heat and then its physical properties are changed as a matter of course.

Further, each hydrate has its own vapor pressure and by watching the changes in vapor pressure during evaporation the formation of new hydrates can be determined.

**Vapor Pressure of Hydrates.**—Every hydrate has a definite vapor pressure at a definite temperature. Air

always contains water vapor, the pressure of which interferes with the decomposition of hydrates. The average vapor pressure of the water vapor in the air is less than that of Glauber's salt. All hydrates which like Glauber's salt and sodium carbonate have a greater vapor pressure than ordinary air will decompose and lose water or *effloresce* when exposed to the air. Hydrates with a lower vapor pressure than ordinary air like gypsum and blue vitriol do not decompose. They are not *efflorescent* under like conditions. Very soluble substances like magnesium chloride and calcium chloride *deliquesce* when exposed to the air because the moisture of the air dissolves the surface and forms a concentrated solution of the salt, the vapor pressure of which is lower than that of the water in the air. The condensation of the water from the air will continue, thus diluting the solution of the substance, until the vapor pressure of the solution is equal to that of the air.

**Hydroxides.**—The oxides of potassium, $K_2O$, and of sodium, $Na_2O$, combine with water with evolution of much heat to form the compounds potassium hydroxide, KOH, and sodium hydroxide, NaOH, which, it will be remembered, are also formed by the action of the elements potassium and sodium on water. The reactions between the oxides and water are represented thus:

$$K_2O + H_2O = 2KOH;$$
$$Na_2O + H_2O = 2NaOH.$$

Similarly, lime or calcium oxide, CaO, acts upon water with evolution of heat, as is observed in the process of slaking. The change is like that which takes place with potassium and sodium oxides, and is represented thus:

$$CaO + H_2O = CaO_2H_2 \text{ [or } Ca(OH)_2\text{]}.$$

The product represented by the symbol $Ca(OH)_2$ is known as calcium hydroxide or slaked lime. In the same way barium oxide, BaO, forms barium hydroxide:

$$BaO + H_2O = BaO_2H_2 \text{ [or } Ba(OH)_2\text{]}.$$

The hydroxides form two of the most important classes of compounds, known as *acids* and *bases*. The hydroxides

of potassium, sodium, calcium, and barium are, for example, bases; while certain hydroxides containing sulphur, nitrogen, and carbon are acids,—such as sulphuric acid, $SO_2(OH)_2$, nitric acid, $NO_2(OH)$, and carbonic acid, $CO(OH)_2$. Water as such is, of course, not contained in these hydroxides. Nevertheless, when heated many of them give off water. Thus, when heated to a red heat, calcium hydroxide is decomposed into the oxide and water according to the equation

$$Ca(OH)_2 = CaO + H_2O.$$

Many substances that contain hydrogen and oxygen act in the same way. This is due to the great stability of water even at elevated temperatures. As the temperature becomes higher and higher the constituents of the compound are held together less and less firmly. When a point is reached at which the attraction of the hydrogen for the oxygen is greater than that required to hold the constituents of the heated compound together, a rearrangement takes place, and compounds which are stable at the higher temperature are formed. Among these is water.

**Solution.**—When a little fine clay is put in a flask containing water, the flask shaken, and then allowed to rest, some of the clay will settle at once while the remainder will be evenly distributed throughout the liquid. This part is said to be in *suspension*. It may remain suspended for days or weeks, but finally it will settle. The suspended clay and water form a mixture, not homogeneous. When sugar is brought into water and the whole shaken, the sugar *dissolves*, forming an *aqueous solution*. A solution is homogeneous throughout and may be infinitely diluted. Here water is the *solvent*, and sugar the *solute*.

| | |
|---|---|
| Gases dissolve in liquids. | Example, oxygen in water. |
| Liquids dissolve in liquids. | Example, alcohol in water. |
| Solids dissolve in liquids. | Example, sulphur in carbon bisulphide. |
| Gases dissolve in solids. | Example, hydrogen in palladium. |
| Solids dissolve in solids. | Example, metallic oxide in glass. |

The *concentration* of a solution refers to the amount of solute dissolved in a given amount of solvent; a dilute solution contains a small amount of solute; a 10 per cent solution contains 10 per cent of the solute to 90 per cent of the solvent; a *concentrated* solution contains a large amount of solute; a *saturated* solution contains as much solute as the given volume of solvent can dissolve at the given temperature; *concentrating* the solution is removing a portion of the solvent (generally by evaporation); *evaporating to dryness* is removing all of the solvent by evaporation.

There is a limit to the amount of substance that can be dissolved in a solvent.* This varies with the substance, the solvent, and the temperature, and, in the case of gases, with the pressure.

Examples: Copper sulphate is insoluble in alcohol; is very soluble in hot water, much less soluble in cold water, the solubility of solids in liquids generally increasing with the temperature. At 0° and 760 mm. pressure 1 liter water dissolves 1.8 liter carbon dioxide gas; at 15° and 760 mm. pressure only 1 liter. Under greater pressure more dissolves. In accordance with the kinetic theory, the weight of gas dissolved is proportional to the pressure at a given temperature,—but, as shown, under a given pressure the solubility of the gas *decreases* with *increase* of temperatures.

**Vapor Pressure of Solutions.**—When into the barometric vacuum (see Exp. 64) two solutions of a given solid in a given liquid of different concentrations are introduced and the vapor pressures measured, they will be found to be less than the vapor pressure of the pure solvent. The pressure of the more concentrated solution will be found less than that of the other. The lowering of the pressure of solutions is proportional to their concentration. Hence the boiling point of a solution is higher than the boiling point of the solvent, and rises as concentration increases. In other words, the rise in the boiling point of a solution, compared with the boiling point of the pure solvent, is proportional to the concentration of the solution.

* In the case of liquids dissolving in liquids, there are some couples, alcohol and water for example, in which there is no limit.

**Water as a Solvent.**—Water dissolves a great many substances. In a solution the particles of the substance dissolved are in some way held in combination by the particles of the liquid. If a very small quantity of substance is dissolved in a large quantity of water and the solution thoroughly stirred, the dissolved substance is uniformly distributed throughout the liquid, as can be shown by refined chemical methods. That the dissolved substance is everywhere present in the solution can be shown further by the aid of certain dye-stuffs, as, for example, magenta. A drop of a concentrated solution of this substance brought into many gallons of water imparts a distinct color to all parts of the liquid.*

Some substances are easily soluble, others are difficultly soluble. When the solutions are boiled the water passes off and leaves the dissolved substance behind, if it is a non-volatile solid. If, however, the substance in solution is a liquid, a partial separation will take place, the extent of the separation depending largely upon the difference between the boiling-points of the water and the other liquid. A complete separation of two liquids by boiling is difficult and in many cases impossible. If, finally, the substance in solution is a gas, it generally passes off when the solution is heated, though in some cases water is given off leaving the gas, or more probably a hydrate formed by the combination of the gaseous substance with water, in solution, which of course then becomes more concentrated. When a certain concentration is reached the hydrate passes over. Solutions in general seem to differ from true chemical compounds in some important particulars, and also from mechanical mixtures. Definiteness of composition appears to be characteristic of chemical compounds, or, at least, it is characteristic of a large number of compounds that we

* An experiment of this kind gives some idea of the extent to which the division of matter can be carried. For it is evident that in each drop of the dilute solution there must be present some of the coloring matter, though the quantity must be what we should ordinarily speak of as infinitesimal.

call chemical compounds. But solutions have no definite composition. We can dissolve any quantity of a substance from the minutest particle to a certain fixed quantity, and the solutions formed are uniform and appear to be just as truly solutions as that which contains the largest quantity which can be held in combination. On the other hand, in a mechanical mixture the constituents may be present in all proportions, while this is not true of solutions. The subject of solution is under investigation, and it has been made highly probable that some substances, when dissolved, are partly or wholly broken down into smaller parts charged with positive and negative electricity respectively. These smaller parts are called *ions*.

**Solution as an Aid to Chemical Action.**—When it is desired to secure the chemical action of one solid substance upon another, it is generally necessary to bring them together in solution. One reason why they do not act readily when mixed in the solid condition is to be found in the fact that, under these circumstances, the particles of the two substances remain separated from each other by sensible distances, no matter how finely the mixture may be powdered. If, however, the substances are dissolved, and the solutions poured together, the particles of the liquid move so freely among one another that they come in intimate contact, thus facilitating chemical action. Many substances which do not act upon one another at all when brought together in dry condition act readily when brought together in solution. It is believed that this is due principally to the splitting of the compounds into *ions* by the action of the water. These ions are free to act upon other ions which may be brought into the same solution. This idea will be developed farther on in other connections. Although it is highly probable, then, that when a reaction takes place in a water solution the water itself plays a very important part, the reaction is generally represented by an equation in which the water does not appear. Of course, such an equation is imperfect, but it answers certain

purposes quite satisfactorily, and may be used without danger of confusion. Thus, when hydrochloric acid acts upon zinc, hydrogen is liberated and zinc chloride is formed. What we call hydrochloric acid in the laboratory is the liquid which is formed by the absorption of hydrochloric acid gas, HCl, by water. When this liquid is used, however, the chemical act which makes itself known to us is that which gives hydrogen gas and zinc chloride in solution. Apparently this reaction is independent of the water, and it may be represented thus:

$$Zn + 2HCl = ZnCl_2 + 2H.$$

Sometimes such reactions are written as follows in order to express the fact that water is present, though, as will be observed, no attempt is made to tell what part the water plays:

$$Zn + 2HCl + Aq = ZnCl_2 + 2H + Aq; \text{ or}$$
$$Zn + 2HCl + H_2O = ZnCl_2 + 2H + H_2O.$$

There is no objection to this, certainly, but it is questionable whether, considering the purposes for which chemical equations are generally used, this increases their value.

**Natural Waters.**—All water found in nature is more or less impure or, in other words, contains something in solution. In the first place, waters which are exposed to the air dissolve some of the gases of which the air is composed, as oxygen, nitrogen, and carbon dioxide. Again, natural waters are necessarily in contact with the earth; they always dissolve some of the earthy substances; and, finally, many waters come in contact with animal and vegetable substances and dissolve something from these. The water which is carried up as vapor from the surface of natural bodies of water is approximately pure. When this is precipitated as rain it dissolves certain substances from the air, and the first rain that falls during a storm is always more or less contaminated. In a short time, however, the air becomes washed and the rain which falls thereafter is approximately pure water. If it remains

in contact with insoluble rocks, as for example, quartzite or sandstone, it remains pure, and mountain-streams which flow over sandstone beds are, in general, the purest. Water which flows over limestone dissolves some of this and becomes "hard." A similar change is brought about in water by contact with gypsum and magnesium sulphate. The condition of hardness will be taken up more fully under calcium and magnesium compounds. The many varieties of mineral springs have their origin in the presence in the earth of certain substances which are soluble in water. Among those most frequently met with in solution in natural waters are carbonic acid, sodium carbonate, sodium sulphate or Glauber's salt, sodium chloride or common salt, magnesium sulphate, iron carbonate, and hydrogen sulphide.

*Effervescent* waters are those which contain a large quantity of carbonic acid in solution and give off carbon dioxide gas when exposed to the air.

*Chalybeate* waters are those which contain some compound of iron in solution.

*Sulphur* waters contain the gas, hydrogen sulphide.

Common salt occurs in large quantities in different parts of the earth. As it is easily soluble in water, many streams contain it; and as most streams find their way to the ocean, it will readily be seen why the water of the ocean should be salt.

As streams approach the habitation of man they are subjected to a serious cause of contamination. The drainage from the neighborhood of human dwellings is apt to find its way into a near stream. The substances thus carried into the stream undergo decomposition and give rise to the formation of larger or smaller quantities of new products, some of which have the power to produce disturbances when taken into the system, and others to produce disease. This condition of things is most strikingly illustrated by the case of a large town situated on the banks of a river. It frequently happens that the water of the river is used for drinking purposes, and it also frequently happens that the water is contami-

nated by sewage. River water when once contaminated by sewage tends to become pure again by contact with the air, the change consisting largely in the slow oxidation of the substances which are of animal or vegetable origin, and their conversion into harmless products. If water is to be used for drinking purposes, however, it is not well to rely upon this process of purification. So much has of late years been said about drinking-water that excessive alarm has been created, and water is no doubt frequently held responsible for sickness with which it has nothing to do. In some places the war against the water-supply has been carried so far that those who can afford it drink only artificially purified and distilled water. It is undoubtedly well to be cautious, but it is possible to be over-cautious.

**What Constitutes a Bad Drinking-water.**—A good drinking-water should be free from odor and taste and should not contain anything that can act injuriously upon the system. It is, however, difficult to decide by chemical means whether the water contains anything injurious or not, as there may be a very minute quantity of an extremely injurious substance, for example disease germs, present, and chemical analysis would be powerless to detect it. On the other hand, water which is very considerably contaminated by sewage may be harmless, and yet the latter might be pronounced "bad" and the former "good." The rule generally adopted by chemists in dealing with water is to pronounce any water dangerous that is contaminated by sewage. Such contamination can generally be detected by analysis or by analysis and inspection of the sources. Microscopic examination by a bacteriologist to detect the presence of disease germs is also advisable.

**Purification of Water.**—Impure water may become purer by natural methods as has been stated, and it may be rendered fit for drinking purposes by filtering through such substances as charcoal, sand, spongy iron, etc. A filter, no matter of what it may be made, will not, however, remain efficient for any length of time, as the sub-

stances contained in the impure water are retained by it and, after a time, it becomes a source of pollution instead of a purifier. The water furnished to many cities is filtered through large sand filters. More and more it is becoming customary to treat the sewage of towns in some way to make it harmless. Filtering through sand is one of the most commonly used and most efficient methods of purification of sewage.

**Distilled Water.**—For refined work in chemistry pure water is prepared by distilling natural waters. The process of distillation consists in boiling the water and then passing the steam through a tube or system of tubes surrounded by cold water. Thus the steam is condensed, and the distilled water is approximately pure. Of course, it is necessary that the tubes in which the condensation takes place should be of such material that water does not act upon it to any extent. The materials used are glass, block tin, and platinum. Chemically pure water is a very rare substance even in the best chemical laboratories. The slight impurities present in ordinary distilled water are not, however, of special importance under ordinary circumstances.

## EXPERIMENTS.

### Organic Substances Contain Water.

Experiment 57.—In dry test-tubes heat gently various organic substances as a piece of wood, fresh meat, fruits, vegetables, etc.

### Water of Crystallization.

Experiment 58.—Take some of the crystals of zinc sulphate obtained in Experiment 35. Spread them out on a layer of filter-paper, and finally press two or three of them between folds of the paper. Examine them carefully. They appear to be quite dry, and in the ordinary sense they are dry. Put them in a dry tube and heat them gently, when it will be observed that water condenses in the upper part of the tube, while the crystals lose their lustre, becoming white and opaque, and at last crumbling to powder.

Experiment 59.—Perform a similar experiment with some gypsum, which is the natural substance from which "plaster of Paris" is made.

EXPERIMENT 60.—Heat a few small crystals of copper sulphate, or blue vitriol. In this case the loss of water is accompanied by a loss of color. After all the water is driven off, the powder left behind is white. On dissolving it in water, however, the solution will be seen to be blue ; and if the solution is evaporated until the substance is deposited, it will appear in the form of blue crystals.

### EFFLORESCENT SALTS.

EXPERIMENT 61.—Select a few crystals of sodium sulphate which have not lost their lustre. Put them on a watch-glass, and let them lie exposed to the air for an hour or two. They soon lose their lustre, and undergo the changes noticed in heating zinc sulphate.

### DELIQUESCENT SALTS.

EXPERIMENT 62.—Expose a few pieces of calcium chloride to the air. Its surface will soon give evidence of the presence of moisture, and after a time the substance will dissolve in the water which is absorbed.

### PURIFICATION OF WATER BY DISTILLATION.

EXPERIMENT 63.—In an apparatus like that shown in Fig. 31 distil a dilute solution of copper sulphate or some other colored substance. A slow current of cold water must be kept running through the con-

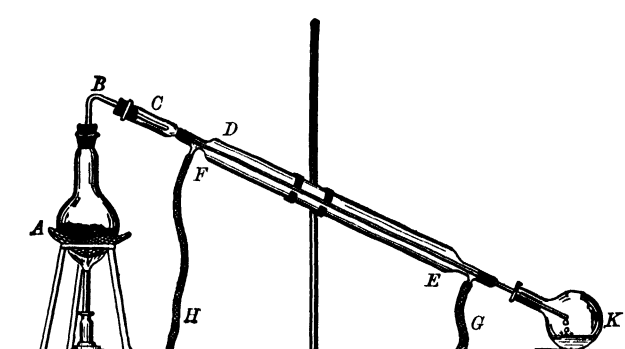



FIG. 31.

denser by connecting the lower rubber tube with a water-cock. When the water is boiled in the large flask, the steam passes into the inner tube of the condenser. As this is surrounded by cold water, the steam condenses and the distilled water collects in the receiver.

EXPERIMENT 64.—Fill a tube 36 inches long, closed at one end, with mercury ; close the open end with the thumb and invert the tube with the open end below the surface of mercury in a dish ; remove the thumb ; the mercury sinks in the tube, leaving a column of mercury the height of which depends upon the pressure of the atmosphere, but at sea level it will be not far from 760 mm. above the surface of the mercury in the dish. This is a barometer. The space above the mercury is the *barometer vacuum*. Prepare another tube in the same way and bring it into the dish beside the first ; the height of the mercury column will be the same in both. Introduce a few drops of water into one tube, *a*, the mercury sinks because the pressure of the water vapor is pushing the mercury down. Ascertain the temperature of the room. Measure the difference in height of the mercury columns. This difference (expressed in mm.) is the measure of the vapor pressure of water for that temperature. Carry the apparatus to a hot room ; the mercury column in the tube *a* will fall, indicating greater vapor pressure. In a cold room it will rise, indicating a lower vapor pressure.

## CHAPTER VII.

### OZONE.—ALLOTROPY.—NASCENT STATE.—HYDROGEN DIOXIDE.

**Occurrence.**—Ozone has long been thought to be present in the air in small quantity, but careful research has made this occurrence appear doubtful, so far as the lower layers of the air are concerned. As it is formed wherever electric discharges of high tension, or rays of ultra-violet light pass through the air, it must be formed in the upper part of the earth's atmosphere, where the ultra-violet rays from the sun act on the air at low temperatures.

**Preparation.**—It was observed in the eighteenth century that, when a powerful electric machine is worked in a room, something is formed which has a strong odor, and the same odor was noticed during thunder-showers. Afterwards the same thing was noticed when water is decomposed by an electric current, and when phosphorus is exposed to moist air. The substance was at first supposed to be a compound of water and oxygen, but long-continued investigation showed that it could be made from pure dry oxygen, and that by heat and other means it is converted into oxygen.

It is prepared mixed with oxygen by passing electric

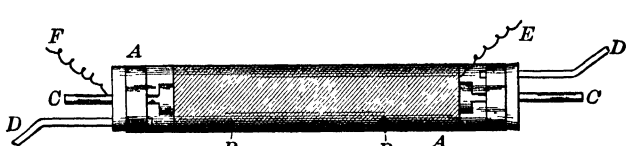



Fig. 32.

sparks through ordinary oxygen in an apparatus constructed on the principle of that represented in Fig. 32.

*AA* is a glass tube about an inch in diameter closed at the ends with brass caps or with corks, covered with shellac on the inner side. A metallic cylinder *BB* covered with tin-foil is placed inside this tube. The cylinder is connected with the tubes *CC*, and through these and the cylinder a current of cold water is kept flowing. The oxygen passes through the glass tube by means of the tubes *DD*, and necessarily passes through the narrow space between the glass tube and the metallic cylinder. Around the outside of the glass tube is wound a strip of tin-foil. By means of the wires *F* and *E* connection is established with the poles of an induction-coil, or a Holtz electrical machine.

Ozone is also made by placing a few pieces of phosphorus in the bottom of a good-sized bottle and partly covering them with water; and, finally, it is made by treating barium dioxide, $BaO_2$, and some other compounds rich in oxygen with sulphuric acid.

Ozone has recently been made by simply heating oxygen or air, and rapidly cooling the ozone formed. The reaction is purely thermal; it makes no difference whether the heat is produced by the electric arc, by burning hydrogen, or by other means. The temperature required is about 1700°. As ozone breaks down readily into oxygen at lower temperatures very rapid cooling was necessary. This was ingeniously secured by obtaining the required high heat in a very small area in liquid oxygen or air which was in a tube surrounded by a bulb filled with liquid air. While this explains the formation of ozone in thunder-storms as a simple heat reaction, it is not as convenient or cheap a method of obtaining ozone as the method described above.

**Properties.**—Ozone is a gas of blue color. At low temperatures it condenses to a dark blue liquid, which boils at about −120°. Liquid ozone can be separated from liquid air or oxygen by distillation. Ozone has a characteristic disagreeable odor, and is irritating to the membranes of the throat. Its chemical conduct is entirely different from that of oxygen. While the latter at ordi-

nary temperature is not an active substance, ozone is. It acts slowly on water forming hydrogen peroxide (which see) and therefore water left in contact with ozone shows oxidizing properties, which has led to the common but false belief that ozone is readily soluble in water, and that an "ozone-water" or "liquid-oxygen" of medicinal and antiseptic properties can be made. Ozone is soluble in turpentine and in oil of cinnamon. Ozone oxidizes many organic compounds energetically; hence it is now prepared commercially, for disinfection, bleaching, purification of water, and manufacture of dextrin. Ozone changes oxidizable substances into their highest oxides. Silver is changed to silver peroxide, phosphorus to phosphorus pentoxide, ammonia to ammonium nitrate, etc.

**Detection of Ozone.**—Among the characteristic changes which may be made use of for the purpose of detecting ozone are the following: (1) It liberates iodine when brought in contact with potassium iodide; the action being represented thus:

$$2KI + H_2O + O = 2KOH + 2I.$$

Now, iodine has the power to turn starch blue. Therefore, if ozone is brought into a solution containing starch and potassium iodide, a blue color is produced. As hydrogen peroxide and oxides of nitrogen, both of which occur in the air, act in the same way on potassium iodide, the reaction is inconclusive. (2) Ozone combines with metallic silver to form silver peroxide, which is brown. In order to detect ozone, therefore, a strip of polished silver may be exposed to the gas, and if it turns brown ozone is present. Ozone is the only oxidizing gas that shows this reaction, hence it is reliable as is the following very sensitive reaction: A test paper called "tetra base" paper, which can be bought, is colored violet by ozone. Oxides of nitrogen color this paper pale yellow. Hydrogen peroxide does not change its color. The *odor* is the most delicate test for ozone.

**Effect of Heat on Ozone.**—When heated to 300° ozone loses its characteristic odor and is converted into ordinary

oxygen. It thus appears that we can start with ordinary oxygen, and by means of an electric current convert it into a substance with much more active chemical properties and differing from it so markedly that one would not suspect the close relation between the two; and then, further, by simply passing the active substance, or ozone, through a tube heated to 300°, it is converted into oxygen without loss of weight.

**Relation between Oxygen and Ozone.**—When experiment had shown that oxygen and ozone are convertible one into the other without change of weight, the suggestion was made that the difference between them might be due to a difference in the number of atoms of oxygen contained in the molecule of each. It might be, for example, that in the molecule of oxygen there are two atoms and in that of ozone three or more. If this view is correct there should be a difference between the specific gravities of the two gases, and by a study of this difference it should be possible to draw a conclusion as to the constitution of the molecule of ozone. That there is a change of volume when oxygen is changed to ozone was shown by enclosing the former in a tube constructed as shown in Fig. 33. The wide part of the tube is furnished with two platinum wires which pass through the glass. By means of these wires a silent discharge of electricity is kept up through the oxygen which is thus partly converted into ozone. In the smaller bent part of the tube there is a small column of concentrated sulphuric acid which serves as a stopper. Any change in the volume of the gas in the tube will cause this sulphuric acid to change its position. Now, during the conversion of the oxygen into ozone it was noticed that the volume of the gas decreased, and that, on heating the tube and thus converting the ozone into oxygen again, the original volume of the latter was restored.



FIG. 33.

The most satisfactory determination of the relation between the weights of equal volumes of oxygen and of ozone has been made as follows: A mixture of ozone and oxygen containing about 8 to 9 per cent of ozone was liquefied by placing the vessel in which it was contained in liquid air. After the vessel was filled with the mixture it was raised above the liquid air so that its temperature became somewhat higher. Under these circumstances the oxygen boiled off, leaving a little ozone. More of the mixture was then liquefied in the same vessel, and the oxygen again allowed to boil off. In this way a small amount of a blackish-blue, opaque liquid was obtained, which was probably the purest specimen of ozone that has ever been made. This liquid was then converted into gas, and the weight, as compared with that of the same volume of oxygen, determined. The ratio was found to be 1.3698 : 1. But this gas still contained oxygen, and an analysis showed that only 86.16 per cent of the mixture was ozone. Making allowance for this, it appears that the weight of a given volume of oxygen to that of the same volume of ozone is 1 : 1.5. Interpreting this fact in terms of the molecular theory, it is clear that, if the molecular weight of oxygen is 32, that of ozone is 48. Or, further, if there are two atoms in the molecule of oxygen, there are three in that of ozone. These conclusions are represented by the symbol $O_2$ for oxygen and $O_3$ for ozone.

**Ozone in the Air.**—Ozone is doubtless present in small quantity in the upper regions of the atmosphere above the clouds, being formed by the action of the unclouded ultra-violet rays of the sun's light. It is present at the earth's surface during thunder-storms dissolved in the rain water in minute quantities. Under ordinary conditions atmospheric ozone could scarcely reach the lower layer of the air. On account of its great chemical activity, the dust particles of the air would change it to ordinary oxygen at some distance above the earth. As a matter of fact no atmospheric ozone has ever been detected at the earth's surface, except during thunder-storms; hence the popular

belief that ozone is present in the air, in pine woods, after showers, etc., is incorrect. The effects usually ascribed to ozone are perhaps due to the inhalation of clean dust-free air.

**Allotropy.**—The occurrence of an element in two or more different modifications is called *allotropy*. Thus, ozone is called an allotropic form of oxygen. There are, however, a number of other cases of a similar kind. Phosphorus, for example, presents itself in three or four different varieties which, in some respects, differ markedly from one another. Carbon also appears in three different forms. Whether in all cases the differences between the allotropic forms of an element are due to differences in the molecular constitution, as in the case of oxygen, it is impossible to say, for the reason that the molecular weights of the substances cannot always be determined. The facts learned in regard to the relations between oxygen and ozone make it appear probable that the explanation which holds good for this case will probably hold good for others.

**Varying Number of Atoms in the Molecules of one and the same Element.**—It has been pointed out that the molecules of hydrogen, oxygen, and some other elements consist of two atoms each. It has just been shown that the molecule of ozone consists of three atoms. There are some elements which contain a different number of atoms in their molecules, according to the temperature. Thus, sulphur is a solid substance that boils at 440° C. The specific gravity of its vapor between 450° and 500° leads to the molecular weight about 192. But the atomic weight of sulphur is very nearly 32, therefore the molecule of sulphur just above its boiling-point appears to contain six atoms. As the temperature is raised, the specific gravity becomes less, and above 800° it corresponds to the molecular weight 64, showing that at this high temperature the molecule apparently consists of two atoms. Above that point the specific gravity does not change materially. According to the latest investigations on this subject, it appears probable that at low tempera-

tures the molecular weight of sulphur in the form of vapor is 256, or, in other words, that there are eight atoms in the molecule. Facts somewhat similar to those just mentioned have been brought to light in the case of iodine, only here the vapor at the lower temperature has a specific gravity showing that the molecule consists of two atoms, but at very high temperatures the specific gravity shows that the molecule contains only one atom. The atomic weight of mercury is the same as its molecular weight, or, in other words, the molecule and atom are in this case identical.

**Nascent State.**—One of the most curious and interesting phenomena connected with chemical action is that of the nascent state. Some elements, which under ordinary circumstances are inactive, show themselves possessed of marked activity if they are allowed to act the instant they are set free from their compounds. Thus, if carbon monoxide, CO, and ordinary oxygen are brought together at the ordinary temperature, no action takes place. If, however, carbon monoxide is brought in contact with something that easily gives off oxygen, it is converted into carbon dioxide. At ordinary temperatures, for example, chromium trioxide gives up oxygen to carbon monoxide as represented thus:

$$3CO + 2CrO_3 = 3CO_2 + Cr_2O_3.$$

So, too, hydrogen at ordinary temperatures is an inactive element, but, if brought in contact with substances the instant it is set free from a compound, it produces marked changes. Many substances which would be left unchanged, if hydrogen were passed over them at ordinary temperatures, are changed if put in the liquid from which the hydrogen is being evolved. The most plausible explanation of facts like these is to be found in the molecular theory. Free oxygen and free hydrogen consist of molecules made up of atoms which are in combination with each other. Before these molecules can act chemically they must be broken up into atoms. When car-

bon monoxide is brought together with oxygen in the molecular state, the condition is represented thus:

$$CO + O_2.$$

Before combination can take place the molecule, $O_2$, must be decomposed as represented thus:

$$O_2 = O + O;$$

and the atoms of oxygen then combine with the carbon monoxide. Now there are some substances which at ordinary temperatures yield oxygen atoms more readily than free oxygen does. This is true of chromium trioxide, $CrO_3$. In contact with substances that have the power to combine with oxygen it breaks up thus:

$$2CrO_3 = Cr_2O_3 + O + O + O.$$

When hydrogen is liberated from a compound by chemical action the uncombined atoms are believed to be given off first; if there is nothing present with which the hydrogen can combine, these atoms combine with each other in pairs to form the molecules of ordinary hydrogen.

The examples furnished by allotropy and the phenomena of the nascent state show how chemical facts which otherwise appear entirely incomprehensible may be explained by the aid of the molecular theory.

**Hydrogen Dioxide or Hydrogen Peroxide,** $H_2O_2$.—When barium dioxide or sodium peroxide is treated with ice-cold, dilute acids the reactions represented by the following equations take place:

$$2NaO_2 + 2HCl = 2NaCl + H_2O_2;$$
$$BaO_2 + 2HCl = BaCl_2 + H_2O_2;$$
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

In the latter case the compound $BaSO_4$, or barium sulphate, is insoluble, and the liquid can easily be separated from it by filtration. If the liquid is boiled, the hydrogen dioxide is decomposed, oxygen being liberated and

water left behind. The decomposition is represented thus:

$$2H_2O_2 = 2H_2O + O_2; \text{ or } H_2O_2 = H_2O + O.$$

The dioxide can be obtained in the form of a colorless liquid by allowing the solution to stand in a vacuum over sulphuric acid, or by distilling its solution in a vacuum. It boils at 84°–85° under a pressure of 68 mm. In a freezing mixture it solidifies, forming colorless crystals, which melt at −2°.

**Properties.**—Hydrogen dioxide is a clear, syrupy liquid. It is characterized by marked instability. It breaks down slowly even at ordinary temperatures if simply allowed to stand. The decomposition takes place easily under the influence of heat, and if heated rapidly to 100° explosion is apt to take place. The products are water and oxygen, as indicated above. In consequence of the ease with which hydrogen dioxide gives off oxygen it is a good oxidizing agent, and it is now manufactured on the large scale for use in bleaching and in medicine, and comes into the market in solutions of different strengths. The solution has a bitter taste; in concentrated form it affects the skin, causing a pricking sensation, and making white spots, which, however, disappear in a few hours.

**Occurrence in the Air.**—That hydrogen dioxide occurs in the air has already been stated. It is also found in rain and snow. The quantity in the air is extremely small, and it varies at different times of the day, the action of sunlight being evidently favorable to its formation.

**Characteristic Reactions.**—Like ozone, hydrogen dioxide decomposes potassium iodide, setting iodine free:

$$H_2O_2 + 2KI = 2KOH + I_2.$$

This fact may be utilized for the purpose of detecting the compound. The separation of the iodine does not take place readily as in the case of ozone, but the action is hastened by the addition of a very small quantity of a dilute solution of ferrous sulphate, $FeSO_4$.—An acid solu-

tion of potassium permanganate is decolorized by hydrogen dioxide.—If in a glass cylinder a layer of ether is poured upon a solution of hydrogen dioxide and a drop of a solution of potassium bichromate is then added, and the cylinder thoroughly shaken, the ether will take up a blue compound, and will itself become blue.

When hydrogen dioxide is brought together with substances that give up oxygen readily, action generally takes place involving decomposition of the hydrogen dioxide as well as of the other substance. Thus when it is brought together with silver oxide, $Ag_2O$, this reaction takes place:

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$

So, also, it undergoes decomposition with ozone as represented thus:

$$O_3 + H_2O_2 = H_2O + 2O_2.$$

**Uses.**—Hydrogen peroxide is used for bleaching delicate silk tissues, ostrich feathers, and ivory; for changing the color of furs by oxidation (Ursol); for the same action on living hair (Aureoline), because it injures these animal tissues less than any other oxidizer.

## EXPERIMENTS.

### Ozone.

Experiment 65.—Put a few sticks of ordinary phosphorus on the bottom of a good-sized bottle with a wide mouth, and partly cover the phosphorus with water. In a short time the odor of ozone will be perceptible, and the gas can also be detected by means of strips of paper which have been moistened with a dilute solution of potassium iodide and starch paste. See whether such papers are changed in the air? What is the cause of the change? If convenient, examine the air in the neighborhood of a frictional electrical machine, and see whether it causes the papers to change color.

### Hydrogen Dioxide.

Experiment 66.—Powder some barium dioxide, and add some of the powder to dilute sulphuric acid. Filter from the precipitated barium sulphate, and with the solution try the following reactions:

Heat some in a test-tube. What takes place? Add to another small portion a little of a dilute solution of potassium permanganate. To another portion add a little finely powdered manganese dioxide What is given off? To a dilute solution contained in a small stoppered cylinder add a few drops of a dilute solution of potassium bichromate, and quickly add ether, and shake the cylinder thoroughly.

## CHAPTER VIII.

### CHLORINE.—HYDROCHLORIC ACID.

**Historical.**—Sodium chloride or common salt, which is the principal compound of chlorine found in nature, has been known from the earliest times. In 1774 Scheele first called attention to chlorine in his treatise on the black oxide of manganese or manganese dioxide. In accordance with the ideas then prevailing, he called it "dephlogisticated muriatic acid." Berthollet suggested in 1785 that it is oxidized hydrochloric acid, and it was then regarded as consisting of the hypothetical element, *murium*, in combination with oxygen. In 1810 Davy pointed out that the idea, previously expressed by Gay-Lussac and Thénard, that the substance is an element is in the highest degree probable, and he gave it the name chlorine (from χλωρός greenish-yellow). Since that time everything learned in regard to chlorine has gone to show that it is an element.

**Occurrence of Chlorine.**—Though widely distributed in nature, chlorine never occurs in the uncombined state, for the reason that it combines with other substances with great ease, and, if it were set free, it would at once enter into combination. It does not occur in large quantity as compared with oxygen and hydrogen. It is found chiefly in combination with the element sodium as common salt, or sodium chloride, NaCl. It is also found in combination with other elements, as potassium, magnesium, etc., as in the celebrated mines at Stassfurt, Germany. In comparatively small quantity it occurs in combination with silver, forming one of the most valuable silver ores. All the chlorine we have to deal with is made from common salt.

**Preparation.**—Chlorine can be obtained directly from salt only by electrolysis. In all other methods, the

problem to be solved in the preparation of chlorine from common salt is the separation of the two elements sodium and chlorine. This cannot be accomplished directly as the separation of mercury and oxygen in the decomposition of mercuric oxide, HgO, and there is no easily obtained compound that gives off chlorine when heated. The method adopted consists in making hydrochloric acid, HCl, from sodium chloride, and then treating this acid with some substance which readily gives off oxygen. The change of sodium chloride to hydrochloric acid is readily accomplished by treating salt with ordinary sulphuric acid—a reaction carried on on the large scale in the manufacture of sodium carbonate or "soda." When the two are brought together a change takes place which will be studied more in detail farther on. The reaction is represented by the equation

$$(1) \qquad \underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Hydrochloric acid}}{2HCl}.$$

As will be seen, the sodium of the sodium chloride and the hydrogen of the sulphuric acid exchange places.

The decomposition of the hydrochloric acid and liberation of chlorine under the influence of oxygen takes place as represented in this equation:

$$(2) \qquad 2HCl + O = H_2O + Cl_2.$$

As there is an unlimited supply of oxygen in the air, it would be advantageous if the decomposition of the hydrochloric acid could be effected by means of the element in the free state. But free oxygen alone will not accomplish the change.

**Deacon's Process.**—A process has been invented for the manufacture of chlorine on the large scale which depends upon the decomposition of hydrochloric acid by the oxygen of the air. This is Deacon's process. It consists in passing hydrochloric acid and air together through a heated tube containing clay balls saturated with a solution of copper sulphate, and then dried. If the temperature of the tube is not raised too high the copper sulphate re-

mains unchanged. This is another example of catalysis, the copper sulphate being the catalyser. Deacon's process is used quite extensively on the continent of Europe, while in England and Scotland another method, apparently more complicated, known as Weldon's process (which see), is chiefly used.

**Laboratory Process.**—In the laboratory chlorine is generally made by treating hydrochloric acid with manganese dioxide. The reaction is represented thus:

(1) $$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The first change should perhaps be represented thus:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

But the compound $MnCl_4$ gives up half its chlorine when heated:

$$MnCl_4 = MnCl_2 + Cl_2;$$

so that the action of hydrochloric acid on manganese dioxide is represented by equation (1).

Another technical method consists in heating magnesium chloride with air at high temperatures.

$$2\,MgCl_2 + O_2 = 2\,MgO + 2\,Cl_2.$$

**Electrolytic Process.**—Various processes have been devised for the preparation of chlorine by the action of an electric current on a solution of sodium chloride or of hydrochloric acid. Such electrolytic processes are now in use, and by means of them the price of chlorine has been much lowered.

The principles involved in electrolytic processes and the more important processes will be discussed later. The subject is of great scientific and practical interest.

The best method of obtaining chlorine for laboratory use is to treat bleaching powder with commercial hydrochloric acid in a Kipp's apparatus (see Fig. 9, p. 50); chlorine is instantly generated under pressure enough to force it through drying apparatus if desired, and the current can be regulated at will.

**Properties.**—Chlorine is a greenish-yellow gas. It has

a disagreeable odor, and acts upon the membranes lining the throat and nose, causing irritation and inflammation, suggesting a "cold in the head." Inhaled in concentrated form it would cause death. Its specific gravity at 20° is 2.49 (air = 1), and as compared with oxygen (16) it is 35.45. A liter of chlorine gas, under standard conditions, weighs 3.22 grams. It is soluble in water and acts upon mercury, and therefore cannot be collected by displacement of either of these liquids. The most convenient way to collect it is by displacement of air. It can also be collected over warm water, in which it is less soluble than in cold water, or over a saturated solution of sodium chloride, in which it is but slightly soluble. It is easily compressed to an orange-yellow liquid and is now sold in this form in cast-iron cylinders. Liquid chlorine boils at 33.6°. and solidifies at −102°. Its critical temperature is 146°.

It is a remarkably active substance, combining with or acting in some way upon most other substances even at ordinary temperature. This activity may be illustrated by introducing into vessels containing chlorine a little finely-powdered antimony, a few pieces of thin copper-foil, a piece of paper with ink-marks on it, some flowers, and pieces of cotton-prints. The antimony will take fire and a white substance will be formed. The reaction is represented by the following equation:

$$Sb + 3Cl = SbCl_3.$$

The copper-foil also takes fire, and is converted into a chloride as represented thus:

$$Cu + Cl = CuCl.$$

Many other substances unite directly with chlorine with evolution of heat and light, and form compounds which are called *chlorides*. This kind of action is of the same character as that which takes place in oxygen. There is, however, this difference between reactions in oxygen and in chlorine: the latter frequently take place at ordinary temperatures, whereas those in oxygen

generally require an elevation of temperature to start them. In both cases the gases combine with the other substances directly, and disappear as such, and the light and heat are caused by the act of combination.

Dry liquid chlorine, at its boiling temperature ($-33.6°$) does not act on potassium, sodium, or aluminium.

The action of chlorine upon ink, flowers, and cotton-prints illustrates its power to *bleach*. It is important to notice that if the colored objects are introduced dry into dry chlorine the action does not take place. Moisture is essential to bleaching by chlorine. Chlorine acts directly upon some dye-stuffs, converting them into colorless substances. In other cases it has been shown that the destruction of the color is due to the action of oxygen, which is set free from water by chlorine. In direct sunlight chlorine decomposes water partly according to the equation

$$H_2O + Cl_2 = 2HCl + O;$$

and partly according to the equation

$$Cl_2 + H_2O = \underset{\text{Hypochlorous Acid.}}{HOCl} + HCl.$$

This decomposition can be illustrated by filling a long tube with a solution of chlorine in water, and inverting it in a shallow vessel containing some of the same solution. If this is placed in the direct sunlight, bubbles of gas will be seen to rise in the tube and these will collect at the top, while the color of the solution, which was at first greenish-yellow like that of chlorine, will disappear. The gas that collects in the upper part of the tube is oxygen.

The disintegrating action of chlorine upon substances of animal and vegetable origin may be illustrated by moistening a piece of filter-paper with some oil of turpentine, and introducing it into a vessel of chlorine. A flash of light is seen, and a dense black cloud is formed. The black substance is mainly carbon. Oil of turpentine is a compound of carbon and hydrogen. Chlorine abstracts

the hydrogen from the carbon, leaving the latter mainly in the uncombined state. If the chlorine is allowed to act slowly upon the oil of turpentine and similar organic substances, the chlorine is substituted atom for atom for the hydrogen, and a series of so-called substitution-products is obtained.

Chlorine dissolves readily in water (at 8° 1 vol. water dissolves 3 vol. chlorine) and forms a solution known as chlorine water. It has the odor and color of the gas, and it is sometimes used in the laboratory instead of the gas. From what has been said it is evident that it must be kept protected from the sunlight, or decomposition will take place, resulting in the formation of hydrochloric acid and oxygen.

**Different Kinds of Action.**—The different kinds of action exhibited by chlorine may be classified under three heads:

(1) First it acts by direct combination with elements as in the experiments with antimony and copper, and, as will be shown, with hydrogen and many other elements. Just as the compounds of oxygen with other elements are called oxides, so the compounds of chlorine with other elements are called *chlorides*. Thus the compound of antimony and chlorine, $SbCl_3$, is called antimony chloride; that of zinc and chlorine, $ZnCl_2$, is called zinc chloride; etc. In case an element forms more than one compound with chlorine, the names used to distinguish between them are similar to those used for oxides. Mercury forms two chlorides which have the composition represented by the formulas HgCl and $HgCl_2$. The one with the smaller proportion of chlorine is called *mercurous chloride*, and the one with the larger proportion of chlorine is called *mercuric chloride*. So, too, there are two chlorides of iron which correspond to the formulas $FeCl_2$ and $FeCl_3$. The former is called *ferrous chloride*, and the latter *ferric chloride*.

(2) The second kind of action of chlorine is that which is called substitution. The general character of this kind of action may be illustrated by the following example. There is an important compound of carbon and hydrogen

called benzene, which has the formula $C_6H_6$. When chlorine is passed through this compound, which is a liquid, hydrochloric acid gas is given off. This action continues until there is no hydrogen left in combination with the carbon, but in place of the benzene there is now a compound of the formula $C_6Cl_6$. This has been shown to be the final product of a series of reactions represented by these equations:

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl;$$
$$C_6H_5Cl + Cl_2 = C_6H_4Cl_2 + HCl;$$
$$C_6H_4Cl_2 + Cl_2 = C_6H_3Cl_3 + HCl;$$
$$C_6H_3Cl_3 + Cl_2 = C_6H_2Cl_4 + HCl;$$
$$C_6H_2Cl_4 + Cl_2 = C_6HCl_5 + HCl;$$
$$C_6HCl_5 + Cl_2 = C_6Cl_6 + HCl.$$

In each stage one atom of chlorine is substituted for an atom of hydrogen, but the hydrogen does not escape as such. It combines with chlorine and passes off in the form of hydrochloric acid.

(3) The third kind of action is that noticed in bleaching, which depends upon the decomposition of water and the escape of oxygen as already explained. This action does not take place in the dark, but does take place readily in the direct sunlight. When, however, oxygen acts upon hydrochloric acid under proper conditions, water is formed and chlorine set free. It appears, therefore, that, under some circumstances, this reaction is possible:

$$2HCl + O = H_2O + Cl_2;$$

and, under other circumstances, this one:

$$H_2O + Cl_2 = 2HCl + O.$$

These facts appear to be contradictory. What part the sunlight plays is not known, though it is well known that it is capable of producing a great variety of chemical changes. It will soon be shown that it is only necessary to allow it to act for an instant upon a mixture of hydrogen and chlorine to cause them to combine with violence. Then, too, the various processes known under the general

name of photography depend upon chemical changes brought about by the sunlight. Leaving out of consideration this kind of action, the decomposition of hydrochloric acid by oxygen and that of water by chlorine can be explained by a consideration of the heat relations. The heat evolved in the formation of 1 molecule of water in the gaseous form is 58,069 cal., while that absorbed in the decomposition of 2 molecules of hydrochloric acid is 44,002 cal. Therefore, the reaction,

$$2HCl + O = H_2O + Cl_2,$$

is accompanied by an evolution of heat. It is exothermic, and can take place without the addition of energy from without. If water is formed as a liquid, the heat evolved for 1 molecule is 68,360 cal., while that evolved by the formation of 2 molecules of hydrochloric acid in solution is 78,630 cal. Therefore, the heat evolved in the formation of hydrochloric acid in solution is greater than that required to decompose water, and this reaction takes place. This does not, however, explain what part the sunlight plays in the process.

**Chlorine Hydrate and Liquid Chlorine.**—When chlorine gas is passed into water cooled down almost to the freezing-point, crystals appear in the vessel. These consist of chlorine and water as represented by the formula $Cl + 5H_2O$; or, assuming that it is formed by the combination of the molecules of chlorine with water, the formula should be written $Cl_2 + 10H_2O$. It gives off chlorine at the ordinary temperature and, if allowed to stand, undergoes complete decomposition into chlorine and water. (See Hydrates, p. 106). If gently heated the chlorine is given off rapidly. This fact was taken advantage of by Faraday for the purpose of subjecting the gas to high pressure and low temperature. For this purpose he placed some of the hydrate in a strong glass tube of the form represented in Fig. 34. The compound was put in the part of the tube marked *AB*, and the other end *C*, then sealed. The arm *AB* was warmed by dipping it in warm water, while the other arm was placed

in a freezing mixture. Under these circumstances the chlorine was given off from the hydrate, but being unable to escape from the tube the pressure was increased to such an extent that at the low temperature the gas assumed the liquid form.

**Applications of Chlorine.**—Chlorine is used extensively in the arts, especially for the purpose of bleaching. It is also used in the manufacture of a large number of compounds that contain chlorine, the principal ones being bleaching powder or calcium hypochlorite, and potassium chlorate. If used in sufficient quantity chlorine is an excellent disinfectant and deodorizer. By far the largest quantity of the chlorine manufactured is converted into bleaching powder or calcium hypochlorite, as this can be conveniently transported, and the chlorine can be obtained from it when desired. It is only necessary to expose it to the air to effect a partial decomposition, accompanied by a liberation of chlorine; and the addition of hydrochloric or sulphuric acid causes it to give it up completely, as will be shown farther on. This bleaching powder is now used almost exclusively instead of chlorine gas for bleaching.

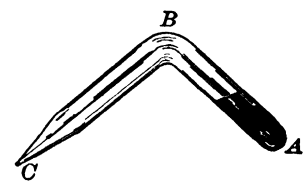


FIG. 34.

## HYDROCHLORIC ACID.

**Historical.**—Hydrochloric acid was first prepared in large quantity by Glauber in the seventeenth century, and his description of it is not unlike those which one frequently reads nowadays referring to some patent medicine. The method of preparation used by him was the same as that used at present, *viz.*, the action of sulphuric acid upon common salt.

**Study of the Action of Hydrogen upon Chlorine.**—When hydrogen and chlorine are brought together in the dark no action takes place. If, however, the mixture is put in diffused sunlight, gradual combination takes place; and

if the direct light of the sun is allowed to fall for an instant on the mixture, explosion occurs, and this is the sign of the combination of the two gases. The same sudden combination is effected by applying a flame or spark to the mixture, or by illuminating it for an instant with the light from burning magnesium or with an electric light. On comparing these facts with those learned in studying the action of hydrogen on oxygen a marked difference is evident. Hydrogen and oxygen do not combine either in the dark or the direct sunlight, but only when a spark is brought in contact with the mixture.

Another way in which hydrogen can be made to combine with chlorine is by introducing a jet of burning hydrogen into a vessel containing chlorine. The hydrogen will continue to burn, but the character of the flame will change completely, and above the vessel white fumes will appear. This burning of hydrogen in chlorine is entirely analogous to the burning of hydrogen in oxygen. It is simply an act of combination of the two gases, in each case accompanied by an evolution of light and heat. And just as oxygen can be burned in hydrogen by a proper arrangement of apparatus, so chlorine can also be burned in hydrogen.

To determine the relation between the volumes of hydrogen and chlorine that combine with each other and the volume of the product formed is more difficult than in the case of hydrogen and oxygen, mainly for the reason that chlorine acts upon mercury and is dissolved by water. It is necessary to proceed indirectly.

Instead of causing hydrogen and chlorine to combine, hydrochloric acid is decomposed and the volumes of the hydrogen and chlorine obtained are determined. One method of doing this consists in decomposing hydrochloric acid by an electric current in an apparatus like that referred to in connection with decomposition of water. As chlorine is, however, soluble in water, the apparatus is filled with a saturated solution of common salt to which a strong solution of hydrochloric acid in water is added. On passing a fairly strong current, the

hydrochloric acid is decomposed, hydrogen being given off at one pole and chlorine at the other. For a given volume of hydrogen the same volume of chlorine is liberated, which makes it appear probable that hydrogen and chlorine are combined in hydrochloric acid in the proportion of volume to volume.

For the purpose of further studying the volume relations, the following experiment is of value: A tube is filled with hydrochloric acid gas. A small piece of potassium is then introduced, when decomposition takes place as represented in the equation

$$K + HCl = KCl + H.$$

The gas left in the vessel is hydrogen, as can easily be shown. On measuring its volume it is found to be just half that of the hydrochloric acid gas decomposed. Taking this fact into consideration with the fact that whenever hydrochloric acid is decomposed by an electric current equal volumes of hydrogen and chlorine are obtained, it appears that in the formation of hydrochloric acid gas 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid, a fact which was mentioned in the chapter on the Atomic Theory. The weight of the hydrogen is found to bear to the weight of the hydrochloric acid the proportion 1.008 : 36.458. In other words, in 36.458 parts by weight of hydrochloric acid there are 35.45 parts of chlorine and 1.008 parts of hydrogen.

**Preparation.**—For the preparation of hydrochloric acid in the laboratory as well as on the large scale, common salt is treated with ordinary sulphuric acid. Two reactions may take place between these substances, depending largely upon the amount of sulphuric acid used. If the two substances are brought together in the proportion of their molecular weights, the principal reaction is the one represented in the following equation:

$$NaCl + H_2SO_4 = \underset{\text{Acid Sodium Sulphate.}}{NaHSO_4} + HCl.$$

In this case the atom of sodium of the molecule of sodium chloride is substituted for one atom of hydrogen in the molecule of sulphuric acid, while the hydrogen and chlorine unite to form hydrochloric acid. If, on the other hand, the substances are brought together in the proportion of 2 molecules of sodium chloride to 1 molecule of sulphuric acid the principal reaction is the following:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The most convenient way to make hydrochloric acid in the laboratory is to use a Kipp's apparatus (see Fig. 9, p. 50) filled with lumps of *fused* ammonium chloride* and cold concentrated sulphuric acid. This yields a current of pure *dry* hydrochloric acid gas. The filled apparatus can stand for months without decomposition of the contents.

Commercially, hydrochloric acid is also now made by heating crystallized magnesium chloride:

$$MgCl_2 + H_2O = MgO + 2HCl.$$

**Occurrence.**—Gaseous hydrochloric acid is contained in the gases escaping from volcanoes. Aqueous hydrochloric acid is an animal product; it occurs in stomach juices and is an important factor in digestion; the juices of the human stomach in normal condition contain 0.33 per cent of free hydrochloric acid.

**Properties.**—Hydrochloric acid is a colorless transparent gas, and has a sharp penetrating taste and smell. Inhaled it produces suffocation. It is easily liquefied. Liquid hydrochloric acid boils at $-83.7°$ and becomes solid at $-111.1°$. The critical temperature is 52°; the critical pressure, 86 atmospheres. It is extremely easily soluble in water, 1 volume of water at ordinary temperatures dissolving 450 times its own volume of the gas, and at 0°, 500 times. The solution of the gas in water is what is generally called hydrochloric acid. So great is the attraction of the gas for water that it condenses moisture

* Ammonium chloride can only be fused under pressure. It can be obtained from the dealers in fused form.

from the air; hence, although the gas itself is quite colorless and transparent, when it comes in contact with the air dense white clouds are formed, which are not formed if it is kept from contact with the air, as can easily be shown by filling glass vessels with the gas. Hydrochloric acid does not burn and does not support combustion. This is equivalent to saying that it does not combine with oxygen under ordinary circumstances, and that substances which combine with the oxygen of the air do not combine with hydrochloric acid. On the other hand, we have seen that under some circumstances oxygen does act upon hydrochloric acid and cause an evolution of chlorine.

When a concentrated solution of hydrochloric acid in water is heated, gas is given off, but if a dilute solution is heated water is given off. In either case, when the composition of the liquid is that represented by the formula $HCl + 8H_2O$, it boils under the ordinary pressure of the atmosphere unchanged. If the pressure is lowered the composition of the liquid which passes over in the process of distillation changes, so that it contains a larger percentage of hydrochloric acid the lower the pressure becomes. This fact seems to show that the liquid of the composition $HCl + 8H_2O$, which boils unchanged at the temperature 110° under the ordinary pressure of the atmosphere, is not a chemical compound. On the other hand, it does not conduct itself like most ordinary solution of gases.

There is a definite compound of hydrochloric acid with water called *hydrochloric acid hydrate*, which has the composition $HCl + 2H_2O$. This is formed by passing hydrochloric acid gas into the concentrated aqueous solution cooled down to — 22°. Under these circumstances the hydrate separates in the form of crystals.

*Commercial hydrochloric acid* is a colorless liquid, though sometimes it is colored yellow on account of the presence of impurities, such as iron and organic substances. The solution is obtained in the factories in which "soda" or sodium carbonate is made. This is an

extremely important substance in the arts. It does not occur in nature, but is manufactured from common salt. In the process most commonly used salt is first converted into sodium sulphate, $Na_2SO_4$, by treating it with sulphuric acid. Hydrochloric acid is necessarily given off. When the factories were first established in England, the gas was allowed to escape as a waste product, but the effects produced by it upon the vegetation of the surrounding country were so injurious that a law was passed prohibiting the manufacturers from allowing the gas to escape. It is now collected by causing it to pass through towers so constructed as to expose a large surface of bricks or sandstone plates over which a current of cold water is constantly kept flowing. This water dissolves the hydrochloric acid, and the solution collected below is commercial hydrochloric acid. In this way enormous quantities of the acid are produced.

*Pure hydrochloric acid* is a solution of the pure gas in pure water. It is colorless, and in concentrated form it gives off fumes when exposed to the air. The solution when heated gives off a large part of the gas contained in it, and by boiling it can all be evaporated.

**Chemical Action of Hydrochloric Acid.**—If the action of hydrochloric acid towards the elements should be studied systematically it would be found that many of them act by simply taking the place of hydrogen, as has already been illustrated in the preparation of hydrogen by treating hydrochloric acid with zinc, when this reaction takes place:

$$Zn + 2HCl = ZnCl_2 + H_2.$$

With iron the reaction is

$$Fe + 2HCl = FeCl_2 + H_2;$$

with tin:

$$Sn + 2HCl = SnCl_2 + H_2;$$

with potassium:

$$K + HCl = KCl + H, \text{ or}$$

$$K_2 + 2HCl = 2KCl + H_2;$$

with sodium:

$$Na_2 + 2HCl = 2NaCl + H_2;$$

with calcium:

$$Ca + 2HCl = CaCl_2 + H_2; \text{ etc., etc.}$$

On the other hand, there are many elements that do not act in this way towards hydrochloric acid. Sulphur, nitrogen, phosphorus, carbon, and boron may be taken as examples. These elements do not act upon hydrochloric acid at all. We might, therefore, divide the elements into two classes: (1) those which act upon hydrochloric acid setting hydrogen free and forming chlorides; and (2) those which do not act upon hydrochloric acid.

Again, when hydrochloric acid acts upon the oxides of those elements which have the power to liberate hydrogen from it, it forms the same chlorides as are formed when the element alone acts, but instead of hydrogen being liberated water is formed. Thus when the acid acts upon zinc oxide, ZnO, the reaction takes place thus:

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$

With lime or calcium oxide, CaO, it is:

$$CaO + 2HCl = CaCl_2 + H_2O.$$

With potassium oxide:

$$K_2O + 2HCl = 2KCl + H_2O; \text{ etc., etc.}$$

When the so-called hydroxides of those elements which act upon hydrochloric acid are brought in contact with the acid, action takes place even more readily than with the oxides, and the products are the same. Thus potassium hydroxide and hydrochloric acid give potassium chloride and water:

$$KOH + HCl = KCl + H_2O.$$

Calcium hydroxide and hydrochloric acid give calcium chloride and water, thus:

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O.$$

Aluminium hydroxide and hydrochloric acid give aluminium chloride and water, thus:

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O; \text{ etc., etc.}$$

There are therefore elements which act upon hydrochloric acid liberating hydrogen and forming chlorides; and the oxides and hydroxides of these elements act upon hydrochloric acid forming chlorides and water. The elements which act in this way are commonly called *metals* or, for reasons which will be discussed farther on, *base-forming elements.*

If those elements which do not set hydrogen free from hydrochloric acid are treated directly with chlorine, they generally combine with it to form chlorides. But these chlorides differ markedly from the chlorides of the metals, especially in their conduct towards water. Two examples will suffice for the present. Phosphorus forms a chloride of the formula $PCl_3$, known as phosphorus trichloride. In contact with water it undergoes decomposition according to this equation:

$$PCl_3 + 3H_2O = PO_3H_3 + 3HCl;$$

so, too, the chloride of boron, $BCl_3$, undergoes the same kind of change:

$$BCl_3 + 3H_2O = BO_3H_3 + 3HCl.$$

Similarly, the other chlorides of the elements of this class tend to pass into the oxides or hydroxides when brought in contact with water. Those elements which do not act upon hydrochloric acid setting hydrogen free and forming chlorides are generally called *non-metals* or, for reasons which will appear later, *acid-forming elements.* The chlorides of the acid-forming elements are generally decomposed by water and the corresponding oxides or acids are formed. In general terms, the oxide of a base-forming element or of a metal is acted upon by hydrochloric acid, a chloride and water being formed; and the chloride of an acid-forming element or of a non-metal is

acted upon by water, an acid, or oxide, and hydrochloric acid being formed. Many illustrations of the opposite chemical character of these two classes of elements will be given and it will be seen that many of the most important and characteristic chemical reactions are associated with these differences.

## EXPERIMENTS.

EXPERIMENT 67.—Pour 2 to 3 cc. concentrated sulphuric acid on a gram or two of common salt in a test tube. A gas will be given off which forms dense white fumes in the air and has a sharp penetrating taste and smell. This is hydrochloric acid.

EXPERIMENT 68.—The best way to make chlorine is the following: Mix 5 parts (say 50 grams) coarsely-granulated manganese dioxide and 5 parts coarsely granulated common salt. Make a mixture of 12 parts concentrated sulphuric acid and 6 parts water. Let this mixture cool down to the temperature of the room, and then pour it upon the mixture of salt and manganese dioxide. Gently heat on a sand-bath, and a regular current of chlorine will be given off. The gas is collected by displacement of air in a *dry* glass vessel. The apparatus for the purpose is arranged as shown in Fig. 35. The delivery-tube should reach to the bottom of the collecting vessel, and the mouth of the vessel should be covered with a piece of paper to prevent currents of air from carrying away the chlorine. As the gas collects in the vessel the experimenter can judge of the quantity present by the color.

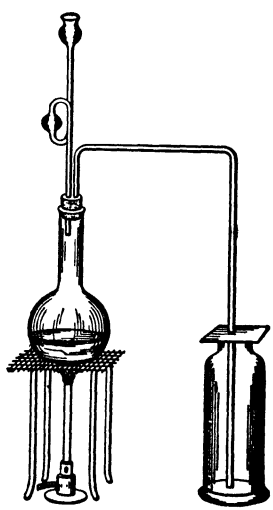


FIG. 35.

EXPERIMENT 69.—Collect six or eight dry cylinders or bottles full of chlorine. Make the gas from about 30 grams of manganese dioxide, using the other substances in the proportion already stated.

(1) Introduce into one of the vessels containing chlorine a little finely-powdered antimony.

(2) Into a second vessel put a few pieces of heated thin copper-foil.

(3) Into a third vessel put a piece of paper with some writing on it, some flowers, and pieces of cotton print. The substances used must be moist.

(4) Into the fourth vessel put a dry piece of the same cotton print as that used in the previous experiment.

What conclusions do the results of the above experiments justify as to the conduct of chlorine?

EXPERIMENT 70.—Cut a piece of filter-paper about an inch wide and six to eight inches long. Pour on this some ordinary oil of turpentine previously warmed slightly. Introduce this into one of the vessels of chlorine. A flash of flame is noticed, and a dense black cloud is formed The action in this case is due to the great affinity of chlorine for hydrogen. Oil of turpentine consists of carbon and hydrogen. The main action of the chlorine consists in extracting the hydrogen and leaving the carbon. The experiment is interesting chiefly in so far as it illustrates the general tendency of chlorine to act upon vegetable substances.

## CHLORINE DECOMPOSES WATER IN THE SUNLIGHT.

EXPERIMENT 71.—Seal the end of a glass tube about a meter (or about a yard) long and about 12 mm. ($\frac{1}{2}$ inch) internal diameter. Fill this with a strong solution of chlorine in water. Invert it as shown in Fig. 36, in a shallow vessel containing some of the same solution of chlorine in water. Place the tube in direct sunlight. Gradually bubbles of gas will be seen to rise and collect in the upper end, and the color of the solution, which is at first greenish-yellow, like that of chlorine, disappears. The gas can be shown to be oxygen.



FIG. 36.

## CHLORINE HYDRATE.

EXPERIMENT 72.—Conduct chlorine into a flask containing water cooled down to about 2° or 3° C. If crystals are formed remove some by filtering out-of-doors if the weather is cold. Expose some of the crystals on filter-paper under a hood in the laboratory. What changes have taken place?

## FORMATION OF HYDROCHLORIC ACID.

EXPERIMENT 73.—Light a jet of hydrogen in the air and carefully introduce it into a vessel containing chlorine. It will continue to burn, but the flame will not appear the same. A gas will be given off which forms clouds in the air. This gas has a sharp, penetrating taste and smell.

EXPERIMENT 74.—Half fill a small, wide-mouthed cylinder over salt water with chlorine gas. Then fill it with hydrogen. The

direct sunlight must not shine upon the cylinder while it contains the mixture. Turn it mouth upward and apply a flame.

## Preparation of Hydrochloric Acid.

**Experiment 75.**—Arrange an apparatus as shown in Fig. 37.

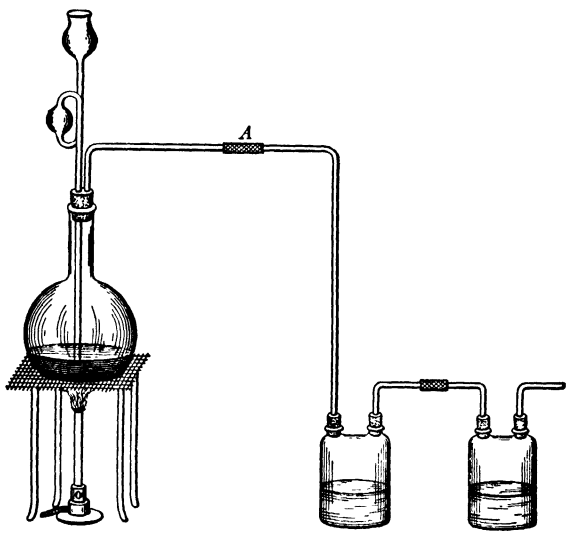



Fig. 37.

Weigh out 5 parts common salt, 5 parts concentrated sulphuric acid, and 1 part water. Mix the acid and water, taking the usual precautions; let the mixture cool down to the ordinary temperature, and then pour it on the salt in the flask. For the purposes of the experiment take about 20 grams of salt. Now heat the flask gently, and the gas will be regularly evolved. Conduct it at first over water contained in the two Woulff's bottles. When the air has been displaced, the gas is all absorbed as soon as it comes in contact with the water.—After the gas has passed for ten or fifteen minutes, disconnect at *A*. Notice the fumes. These become denser by blowing the breath on them. Why?—Apply a lighted match to the end of the tube. Does the gas burn?—Collect some of the gas in a dry cylinder by displacement of air, as in the case of chlorine. The specific gravity of the gas being 1.26, the vessel must of course be placed with the mouth upward. That the gas is colorless and transparent is shown by the appearance of the generating-flask, which is filled with the gas. Insert a burning stick or candle in the cylinder filled with the gas.—Reconnect the generating-flask with

the series of bottles containing water, and let the process continue until no more gas comes over. The reaction represented in the equation

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

is now complete. Disconnect the flask, and after it has cooled down pour water on the contents; when the substance is dissolved filter it and evaporate to such a concentration that, on cooling, the sodium sulphate is deposited. Pour off the liquid and dry the solid substance by means of filter-paper. Compare the substance with the common salt which you put in the flask before the experiment. What proofs have you that the two substances are not the same?—Heat a small piece of each in a dry tube closed at one end. What differences do you notice? Treat a small piece of each in a test-tube with sulphuric acid. What difference do you notice?—If in the experiment we should recover all the sodium sulphate formed, how much should we have?—Put about 50 cc. of the liquid from the first Woulff's bottle in a porcelain evaporating-dish. Heat over a small flame just to boiling. Is hydrochloric acid given off? Can all the liquid be driven off by boiling?—Try the action of the solution on some iron filings. What is given off?—Add some to a little granulated zinc in a test-tube. What is given off?—Add a little to some manganese dioxide in a test-tube. What is given off?—Add a few drops of the acid to 2 to 3 cc. water in a test-tube. Taste the dilute solution. It has what is called a *sour* or *acid taste*, the two terms being practically synonymous.—Add a drop or two of a solution of *blue* litmus, or put into it a piece of paper colored *blue* with litmus. What change takes place? Litmus is a vegetable color prepared for use as a dye. Other vegetable colors are changed by hydrochloric acid.—The color will be restored by adding a few drops of a solution of caustic soda.—In what experiment has caustic soda been obtained? What relation does it bear to water?—To the dilute solution of hydrochloric acid add drop by drop a dilute solution of caustic soda. Is the acid taste destroyed?

## Electrolysis.

**Electric Current.**—By galvanic batteries, by dynamos, and by other methods a condition may be produced in conductors of electricity which is called an *electric current.* This current can perform mechanical work, cause chemical change, develop heat, etc.; it is therefore a form of energy.

**Conductors.**—Some substances conduct the electric current, others do not. Metals are conductors. Non-metallic elements generally are not. There are two classes of con-

ductors. The metals are in the first class. Such conductors are heated but not otherwise changed by the passage of the current. Conductors of the second class are chemically changed by the passage of the current, their components being chemically separated at the points where they are in contact with the electrodes or metallic conductors of the current from the battery. Aqueous solutions of acids, bases and salts are conductors of the second class at ordinary temperature. These substances, in the absence of water, do not conduct the current or are very poor conductors. If they are solids, however, they become conductors when fused.

**Electrolysis.**—The phenomenon of decomposition by the electric current is called *electrolysis.* The conductors of the second class are called *electrolytes.* The metallic ends of the electric circuit which come in contact with the electrolyte are called *electrodes.*

Water does not conduct electricity.* That this is so, and that solutions of acids, bases and salts in water are conductors may be proved by a simple experiment (see Exp. 76).

The molecule is the unit of matter. In the decomposition of electrolytes their molecules are broken down into smaller units which may contain one or more than one atom. These units are called *ions.* The dissociation of molecules into ions is called *ionisation.*

**Anions and Cations.**—A study of electrolysis shows that the hydrogen of acids always collects at the *negative* electrode, that is the electrode at which the positive electric current leaves the electrolyte to pass into the metallic circuit. The metal of salts and the metal of bases appears at the same electrode. The ions which move to the negative electrode are called *cations* and the electrode is called the cathode. Hydrogen is the cation of acids, the cations of bases and salts are the metals.

* This is not absolutely true; but a column of water 1 centimeter in diameter and one centimeter high does not conduct as well as would a column of mercury of the same diameter and one million kilometers high.

In the electrolysis of hydrochloric acid or of a metallic chloride, the chlorine is found at the positive electrode. Ions which collect at the positive electrode are called *anions*, and the electrode is called the anode.

**Faraday's First Law.**—Faraday (1833) experimentally proved the facts which are expressed in the law: *The amount of matter which is discharged at the electrodes in a given time is strictly proportional to the strength of the electric current passing through the electrolyte.* Hence it is believed that passage of the electricity through the electrolytes depends on the simultaneous movement of the ions, so that there can be no passage of the electric current unless the ions carry it.

Ions are conceived as matter charged with electricity while the same matter in its ordinary state is not charged with electricity; hence the ion of a substance differs from the non-ionised substance by the electric energy of its charge.

**Electric Units.**—According to Faraday's law a definite amount of copper is deposited from the solution of a copper salt by a definite amount of electricity. It is evident that by weighing the amount of copper deposited in a given time from a solution of a copper salt by electric currents from different sources, the relative amounts of electricity can be measured.

The unit of the amount of electricity is called a *coulomb*. To set free 1.008 grams hydrogen from the solution of an acid 96540 coulombs must pass through the electrolyte.

A current which carries one coulomb per second through an electrolyte is called an *ampere*.

The number of amperes alone does not determine the properties of the current, for according to the arrangement of the conductor a current of a given ampere strength can perform different amounts of work. This may be compared with a current of water, the energy of which is measured by the product of the amount of water and its pressure. Thus electrical energy is the product of the *amount* of electricity or current strength per second, and its electromotive force or *difference in*

*potential;* this last factor corresponds to the pressure of the water; its unit is the *volt.* This need not be further considered at present

**Faraday's Second Law.**—It has been shown that in the electrolysis of hydrochloric acid the hydrochloric acid molecule, HCl, dissociates into hydrogen cation and chlorine anion which are written thus $\overset{+}{H}$, $\overset{-}{Cl}$, the plus sign denoting cations, the minus sign, anions. As the hydrogen ion carries a definite charge of positive electricity, the chlorine ion must carry *an equal charge* of negative electricity. As the atomic weight of hydrogen is 1.008 and that of chlorine 35.45 and as the molecule of hydrochloric acid, HCl, is made up of one atom of hydrogen and one of chlorine, it follows that if 1.008 grams hydrogen carries a positive charge of 96540 coulombs, 35.45 grams chlorine carry a negative charge of 96540 coulombs. This is expressed by Faraday as follows. *The amounts of the different elements which are separated by electricity bear the same relation to one another as the equivalents of their elements.*

Hence if 1.008 grams of hydrogen when ionised and 35.45 grams chlorine each carries 96540 coulombs, 23.05 grams of sodium ionised carries the same.

If we assume as unit the amount or *charge* of electricity carried by *one hydrogen ion,* it follows that the chlorine ion carries one charge and the sodium ion also one charge. Calcium chloride has the composition $CaCl_2$; when the molecule $CaCl_2$ is ionised it gives the ions $\overset{++}{Ca}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$. Each chlorine ion carries one charge of negative electricity, hence the calcium ion must carry two charges of positive electricity, or as the atomic weight of calcium is 40.1, 40.1 grams of calcium carry $2 \times 96540$ coulombs.

Hence in the ionisation of salts the ion of a univalent metal carries one charge, the ion of a bivalent metal two charges, the ion of a trivalent metal three charges. This shows the relation referred to (see Valence, p. 94) between valence and electrical energy.

**Primary and Secondary Products of Electrolysis.**—When

very dilute hydrochloric acid is ionised hydrogen is given off at the cathode, but no chlorine at the anode; in its place an equivalent amount of oxygen is given off. This is due to the fact that the water is decomposed by the chlorine: $2H_2O + 4Cl = 4HCl + O_2$. The hydrogen and chlorine are *primary products*, oxygen a *secondary product* of electrolysis.

Such secondary products are often formed when the substance first given off is not stable under existing conditions.

In the electrolysis of copper or silver salts, copper or silver is obtained at the cathode; they are primary products; but if sodium chloride is electrolyzed hydrogen is given off at the cathode. This is due to the fact that the primary product, sodium, acts on the water forming sodium hydroxide, which dissolves in the water, and hydrogen, which escapes (see Exp. 77).

When a solution of sodium hydroxide, NaOH, is electrolyzed, hydrogen is given off at the cathode for the above reason, and oxygen at the anode. The ions of sodium hydroxide are $\overset{+}{Na}$ and $\overset{-}{OH}$, the primary anode product is hydroxyl, OH; this cannot be isolated on account of its instability, and the reaction $4OH = 2H_2O + O_2$ occurs, the secondary product, oxygen, being actually given off.

If in the electrolysis of sodium chloride or of sodium hydroxide, the platinum cathode is replaced by a mercury cathode, no hydrogen escapes as the sodium dissolves in the mercury. If the solution of sodium in mercury is put into pure water, hydrogen escapes and the water becomes alkaline: $2Na + 2H_2O = 2NaOH + H_2$ (see Exp. 78).

**Commercial Methods for the Electrolysis of Sodium Chloride.**—The products of the commercial electrolysis are chlorine, sodium hydroxide, and hydrogen generally, though, by a modification of the process, *both* of the primary products, sodium and chlorine, are obtained (see SODIUM). The principle of the electrolysis of sodium chloride is explained above and shown in Experiment 78. (See also SODIUM HYDROXIDE.)

The percentage of chlorine made electrolytically and by the chemical process in different countries in 1905 is shown in the following table:

| | Electrolytic. | Chemical. |
|---|---|---|
| United States | 100 | — |
| Germany | 65 | 35 |
| Great Britain | 18 | 82 |
| France | 19 | 81 |
| Austria | 66 | 34 |
| Spain and Italy | 100 | — |
| Russia | 55 | 45 |
| Belgium | 54 | 46 |

Cheap electric-power is the chief factor in the introduction of electrolytic processes. Regions where there is plentiful water-power are becoming the seats of such industries.

## EXPERIMENTS.

EXPERIMENT 76.—Bring an electric bell into the circuit from a battery. The wire leading from the bell ends in a platinum electrode; this electrode and another fastened to the end of the second wire from the battery dip into a beaker glass as shown in Fig. 38.

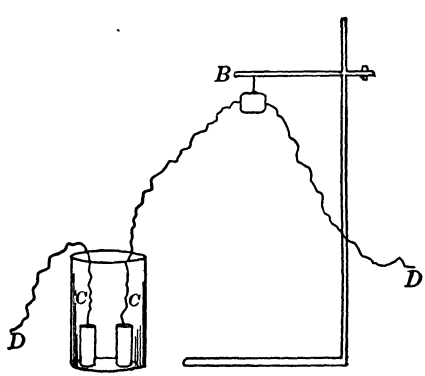



FIG. 38.

Turn on the current and bring the electrodes together; this completes the circuit, and the bell rings. Separate the electrodes; the bell stops ringing. Pour pure water into the beaker so that the electrodes dip into it; the bell does not ring.

Pour hydrochloric acid into the water; the bell rings and bubbles of gas escape from the electrodes.

Wash out the beaker and repeat the experiment with the solution of sodium chloride in the beaker. Repeat again with a solution of sodium hydroxide in the beaker.

Repeat the experiment with a solution of copper sulphate in the beaker. Note the deposit of metallic copper on the *cathode.*

Repeat the experiment with a solution of silver nitrate in the beaker. Note the deposit of silver on the cathode

EXPERIMENT 77.—Instead of the beaker use the apparatus shown in diagram Fig. 39. It consists of two glass tubes about ¾ inch diameter and 5 inches long, connected 2 inches from the bottom by a short piece of tube about ⅛ inch inside diameter. Let thin platinum wires ending in narrow strips of platinum foil as electrodes dip into the tubes as shown. Connect with the wires from the battery. Make a concentrated solution of sodium chloride in water ; add enough red litmus solution to give it a pink tinge. Pour the solution into the apparatus until it reaches just above the cross-piece. Turn on the current. The liquid over the cathode will turn blue, indicating the presence of a dissolved base (sodium hydroxide); hydrogen escapes. The liquid over the anode will become colorless owing to the bleaching action of the chlorine. The odor of chlorine is also noticeable.

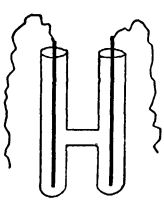


FIG 39

EXPERIMENT 78.—Instead of the beaker of Exp. 76, take a piece of glass tubing ¾ inch inside diameter and 4 or 5 inches long Close one end with a cork, through which the sharpened end of the *cathode* wire has been pushed so that it projects ¼ inch into the tube. Fasten the tube by a clamp in vertical position with cork at bottom. Pour mercury into tube to the depth of ¾ inch. Introduce the anode into the upper part of the tube. Pour in some of the same concentrated solution of sodium chloride colored with red litmus as that used in the last experiment. Turn on current. Chlorine is given off, bleaching the litmus at the anode, but no hydrogen escapes, and no sodium hydroxide is formed. After a few moments shut off the current ; pour off as much of the liquid in the tube as you can without losing mercury. Pour the mercury into the dish, remove the remainder of the solution of salt by absorbing with filter paper, add pure water. Hydrogen escapes slowly as the sodium amalgam * decomposes. Add a drop of red litmus. The solution turns blue.

* The alloys of mercury with other metals, i. e , the solutions of other metals in mercury, are called (

## CHAPTER IX.

### COMPOUNDS OF CHLORINE WITH OXYGEN AND WITH HYDROGEN AND OXYGEN.

**General.**—As has been seen, chlorine combines very readily with hydrogen, and hydrogen with oxygen, and the products are stable compounds. On the other hand, chlorine cannot be made to combine directly with oxygen. By indirect processes they can be combined, but the compounds undergo decomposition easily, giving back the chlorine and oxygen contained in them. Before taking up the compounds of chlorine and oxygen, however, it will be best to discuss, as far as may be necessary, the compounds of chlorine, hydrogen, and oxygen. These are more easily made, and from them the oxides are made.

**Principal Reactions for making Compounds of Chlorine with Hydrogen and Oxygen.**—When chlorine acts upon water in direct sunlight one of the reactions that takes place is represented by the equation

$$Cl_2 + H_2O = HOCl + HCl.$$

The compound represented by the formula HOCl is called *hypochlorous acid.* So, also, when chlorine acts upon a dilute solution of potassium hydroxide, KOH, a similar reaction takes place. It is represented thus:

$$Cl_2 + KOH = KOCl + HCl.$$

The hydrochloric acid formed acts upon some of the potassium hydroxide thus:

$$KOH + HCl = KCl + H_2O.$$

Or, combining the two equations we have:

$$Cl_2 + 2KOH = KOCl + KCl + H_2O.$$

The product represented by the formula KOCl is known as *potassium hypochlorite*, and that represented by the formula KCl is known as *potassium chloride.*

When the temperature of a solution of potassium hypochlorite is raised, the substance undergoes a change as represented thus:

$$3KOCl = KClO_3 + 2KCl.$$

The compound represented by the formula $KClO_3$ is known as *potassium chlorate.* This compound has already been employed in the preparation of oxygen.

When, further, chlorine is passed into a warm concentrated solution of potassium hydroxide all the above reactions take place, and they may be represented in one equation:

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

*Potassium chlorate,* $KClO_3$, and *potassium hypochlorite,* KClO, bear the same relation to two compounds, $HClO_3$ and HClO, that potassium chloride, KCl, and sodium chloride, NaCl, bear to hydrochloric acid, HCl. But it has been seen that hydrochloric acid can easily be obtained from sodium chloride by treating it with sulphuric acid. Potassium chloride undergoes the same change when treated with sulphuric acid. Indeed, it will be shown that nearly all compounds containing sodium or potassium give up these metals when treated with sulphuric acid, and take up hydrogen in their place.

When potassium chloride is treated with sulphuric acid this reaction takes place:

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl.$$

Similarly, when potassium chlorate is treated with sulphuric acid, this reaction takes place:

$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3.$$

The compound $HClO_3$ is called *chloric acid.* Further, when potassium hypochlorite is decomposed by sulphuric acid under proper circumstances, it undergoes the same kind of decomposition:

$$2KClO + H_2SO_4 = K_2SO_4 + 2HClO.$$

The compound HClO is called *hypochlorous acid.*

**Hypochlorous Acid,** $HClO$.—The formation of this compound by the action of chlorine on water and that of potassium hypochlorite, $KClO$, by the action of chlorine on caustic potash have been mentioned. A similar reaction is employed on the large scale in the manufacture of bleaching powder or "chloride of lime." This consists in treating slaked lime or calcium hydroxide with chlorine. The action is represented thus:

$$2Ca(OH)_2 + 2Cl_2 = Ca(ClO)_2 + CaCl_2 + 2H_2O.$$

The compound $Ca(ClO)_2$, known as calcium hypochlorite, is derived from hypochlorous acid by substituting one atom of the bivalent metal calcium for two atoms of hydrogen in two molecules of the acid:

$$\begin{matrix} HClO \\ HClO \end{matrix} \text{ gives } Ca\begin{pmatrix} ClO \\ ClO \end{pmatrix} \text{ or } Ca\ (ClO)_2.$$

The concentrated solution of hypochlorous acid has a peculiar odor suggesting that of chlorine. It is the odor which is familiar as that of bleaching powder or "chloride of lime." The acid undergoes decomposition very readily, forming chlorine and a compound of chlorine and oxygen. A solution of the acid bleaches about as well as chlorine, and when bleaching powder is used for bleaching it is largely the hypochlorous acid set free from the hypochlorite that effects the desired changes.

Like chloric acid, hypochlorous acid is an excellent oxidizing agent, and is used in the laboratory in this capacity.

**Perchloric Acid,** $HClO_4$.—When the preparation of oxygen by heating potassium chlorate was studied, it was pointed out that in the first stage of the decomposition a reaction of this kind takes place:

$$2KClO_3 = KCl + KClO_4 + O_2.$$

The compound $KClO_4$, or *potassium perchlorate*, can be separated from the chloride by treating the mixture with cold water in which the chloride is easily soluble, while the perchlorate is difficultly soluble. When the per-

chlorate is treated with sulphuric acid, perchloric acid can be obtained from the mixture by distillation.

Pure perchloric acid, $HClO_4$, can be obtained in the form of a colorless fuming liquid. It is a *dangerous substance to deal with*, as it produces bad wounds and in contact with combustible substances in general causes explosion in consequence of the ease with which it gives up oxygen and converts the combustible substances into gaseous products.

**General.**—From the above it will be seen that the compounds of chlorine with hydrogen and oxygen form a series, the members of which bear a simple relation to one another. Beginning with hydrochloric acid the series is as follows:

| | |
|---|---|
| Hydrochloric acid. . . . . | $HCl$ |
| Hypochlorous acid. . . . . | $HClO$ |
| Chlorous acid. . . . . | $HClO_2$ |
| Chloric acid. . . . . | $HClO_3$ |
| Perchloric acid. . . . . | $HClO_4$ |

The successive members differ from each other by one atom of oxygen, the ratio between the hydrogen and the chlorine remaining the same throughout the series. While the compounds differ markedly from one another in many ways, they have some common features. Upon metals, and their oxides and hydroxides, all the members of the series act in general in the same way that hydrochloric acid does, the result being the formation of products which do not contain hydrogen, but do contain a metal in the place of the hydrogen. Examples of these compounds are potassium chlorate, $KClO_3$, calcium hypochlorite, $Ca(ClO)_2$, potassium chlorite, $KClO_2$, and potassium perchlorate, $KClO_4$. All these compounds belong to the class called *salts*, which will presently be taken up. On the other hand, while there is a class of elements upon which hydrochloric acid does not act, the oxygen compounds of the above series will in many cases act upon these elements and convert them into oxides. Thus sulphur and phosphorus, which are not acted on

by hydrochloric acid, are converted into oxides by the oxygen compounds of chlorine.

Finally, the addition of oxygen to hydrogen and chlorine decreases the stability of the compound. Hydrochloric acid, for example, is characterized by great stability, while hypochlorous acid, HClO, and the other members of the series are characterized by instability. The larger the proportion of oxygen, however, the greater the stability of the compound. The most stable member of the series of oxygen compounds is perchloric acid. Another fact that is worthy of special notice is that the metal derivatives or salts of these acids are more stable than the acids themselves. Many of them can be heated to a comparatively high temperature without undergoing decomposition. This is most marked in the case of the perchlorates. It will be remembered that in decomposing potassium chlorate for the purpose of making oxygen the change takes place in two stages. In the first stage, potassium perchlorate is formed. In order to decompose this, however, the temperature must be raised considerably higher than that required to effect the decomposition of the chlorate.

**Compounds of Chlorine with Oxygen.**—The compounds of chlorine with oxygen are:

*Chlorine monoxide* $Cl_2O$, *chlorine dioxide*, $ClO_2$, and *chlorine heptoxide*, $Cl_2O_7$. These are unstable substances that easily break down into chlorine and oxygen.

## EXPERIMENTS.

### Chloric Acid and Potassium Chlorate.

Experiment 79.—Dissolve 40 grams (or about 1¼ ounces) caustic potash in 100 cc. water in a beaker, warm the solution, and, under a hood, pass into it chlorine generated as in Experiment 68, from a generator containing about 75 grams of salt and the other constituents in proportion. Arrange an inverted funnel on the end of the delivery-tube to prevent the choking of the delivery-tube by the formation of chlorate crystals in it.

Shake or stir the solution by moving the funnel up and down in the solution; when a strip of pink litmus-paper dipped in the solu-

tion no longer turns blue, but is bleached instead, the reaction is complete. Next, to remove the excess of chlorine, boil the solution which now contains a mixture of potassium chlorate and chloride and set aside to crystallize. The chlorate, being much less soluble in cold water than the chloride, is deposited when the liquid cools, but the crystals are not pure. In order to separate the chloride completely, filter the solution, dissolve the chlorate in boiling-hot water, using as little as possible, filter while boiling-hot. The substance which separates out is pure chlorate. Filter off the crystals and dry them. Evaporate the solution from which the potassium chlorate was originally obtained to half its volume and, after cooling, filter off any substance that may be deposited. Evaporate the filtrate to dryness. This substance is potassium chloride.

*Chlorate.*—Heat some of the salt in an arsenic-tube. Is oxygen given off? Treat a *very little* in a test-tube with a *few drops* of concentrated sulphuric acid, holding the mouth of the test-tube away from the face. What happens? Perform the same experiments with potassium chlorate from the laboratory bottle. Are the two identical?

*Chloride.*—Heat some in an arsenic-tube. Is oxygen given off? Treat some with concentrated sulphuric acid. What gas is given off? Do you get the same gas as from sodium chloride? Is it fair then to assume that any chloride will give this gas when treated in this way?

Perform the same experiments with potassium chloride from the laboratory bottle. Are they identical?

What is left in the test-tube after the chlorate or the chloride has been treated with concentrated sulphuric acid?

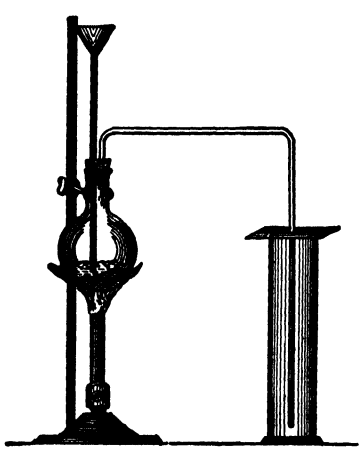


FIG. 40.

EXPERIMENT 80.—Place the slaked lime, made by slaking 20 to 30 grams of quicklime with enough hot water to make a dry powder, in a 250-cc. flask with a two-hole stopper. Introduce a glass tube through one of the holes and pass chlorine in slowly, while constantly shaking the flask, for about ten minutes. Introduce a funnel and delivery-tube as shown in Fig. 40. Pour a mixture of equal parts of sulphuric acid and water slowly through the funnel-tube. Collect by displacement of air the gas given off. What evidence have you that the gas is chlorine?

## Perchloric Acid.

Experiment 81.—(This experiment is somewhat dangerous and should not be performed by a beginner.) Make potassium perchlorate as follows: Gently heat 50 to 100 grams potassium chlorate until after having been liquid it becomes thick and pasty, and gas is not given off without raising the temperature. After cooling, break up the mass and treat it with cold water. This dissolves the potassium chloride and leaves the perchlorate, which can then be crystallized from hot water. After the crystallized salt is dried it is decomposed by sulphuric acid. To effect this decomposition, the finely-powdered salt (10 parts) is treated in a retort with 20 parts of pure sulphuric acid which is free from nitric acid and diluted with $\frac{1}{10}$ its volume of water. The retort is connected with a receiver which can be well cooled. The mixture is heated, and when the perchloric acid begins to come over, the heat is so regulated that the temperature does not rise above 140°. When the mixture has become colorless the operation is ended.

## CHAPTER X.

### ACIDS.—BASES.—NEUTRALIZATION.—SALTS.

**General.**—In dealing with ordinary chemical phenomena constant reference is made to acids, and in what has preceded a number of substances belonging to this class have been met with. It is now time to inquire what features these substances have in common that lead chemists to call them all acids. What is there in common between the heavy liquid, sulphuric acid, the colorless gas, hydrochloric acid, and the unstable compounds, chloric and hydrochlorous acids? To understand the common features requires some knowledge of a class of substances to which attention has already been called. These are substances like caustic potash and caustic soda, or potassium and sodium hydroxides, called *alkalies*, which are the most marked representatives of the class of substances known as *bases*. These two classes, *acids* and *bases*, have the power to destroy the characteristic properties of each other. When an acid is brought in contact with a base in proper proportions, the characteristic properties of both the acid and the base are destroyed. They are said to *neutralize* each other. They form new products that are said to be neutral, which means that they have not the properties of an acid nor those of a base. This act of neutralization is an extremely important one constantly met with in chemical operations.

**A Study of the Act of Neutralization.**—The fact having been learned that acids and bases neutralize one another, the next thing to do is to study the act of neutralization as carefully as possible, and learn what chemical changes are involved in it. For this purpose let us take sulphuric, hydrochloric, and nitric acids; and potassium, sodium,

and calcium hydroxides. The composition of these substances is shown below:

| | |
|---|---|
| Hydrochloric acid | $HCl$ |
| Nitric acid | $HNO_3$ |
| Sulphuric acid | $H_2SO_4$ |
| Potassium hydroxide | $KOH$ |
| Sodium hydroxide | $NaOH$ |
| Calcium hydroxide | $Ca(OH)_2$ |

The first question to be answered is whether, in order to effect neutralization, definite quantities of the substances are necessary. To decide this, solutions of the acids and of the bases should be prepared and allowed to act upon one another in different proportions. But how shall we determine whether the solutions we are working with are acid, basic, or neutral? It has been found that all acids have the power to change the color of certain substances. For example, the dye litmus is blue. If a solution which is colored blue with litmus is treated with a drop or two of an acid, the color is changed to red. If now the red solution is treated with a few drops of a solution of a strong base, the blue color is restored. There are many other substances which change markedly in color by the addition of acids or bases. These facts furnish a means of recognizing whether a solution is acid or basic. Now, suppose that to a carefully-measured quantity of one of the acid solutions a few drops of blue litmus are added. It will at once turn red. On adding slowly a solution of one of the bases the color will remain red as long as the solution is acid, but the instant it is basic it will turn blue. By noticing when the change in color takes place, it is possible to determine exactly how much of a certain basic solution is required to neutralize the quantity of the acid solution taken. If it is found in the case studied that to neutralize 20 cc. of the acid solution 30 cc. of the basic solution are required, then, using the same solutions, it will be found in every experiment that the same quantities are required to effect neutralization, or that the change of color takes place when-

ever these proportions are reached. And no matter how the quantity of one of the liquids is varied, the quantity of the other required for neutralization varies in the same proportion. A great many experiments of this kind have been performed with many different acids, and what is true in one case has been found to be true in all. It appears, therefore, that *the act of neutralization is a definite one, which takes place between definite quantities of acid and base; that for a certain quantity of base a certain quantity of acid is required to effect neutralization, and vice versa.*

The next question to be answered is, What is formed when the acid and base are neutralized? To determine this, larger quantities of acids should be neutralized with bases, and the substance or substances formed should then be studied. When hydrochloric acid is neutralized with sodium hydroxide a solid product, sodium chloride, is formed. The action takes place according to the following equation:

$$HCl + NaOH = NaCl + H_2O.$$

Hydrochloric acid and potassium hydroxide act thus:

$$HCl + KOH = KCl + H_2O.$$

Nitric acid acts upon the two bases mentioned above as represented in these equations:

$$HNO_3 + KOH = KNO_3 + H_2O;$$
$$HNO_3 + NaOH = NaNO_3 + H_2O;$$

**Gram-molecular Weights.**—By this term is designated the molecular weight of a compound expressed in grams. Thus hydrochloric acid has the molecular weight 36.458, and 36.458 grams of hydrochloric acid gas is one *gram-molecular weight*, abbreviated to gr. mol. wt.

From the above equations it follows that if we prepare aqueous solutions of hydrochloric acid, nitric acid, potassium hydroxide, and sodium hydroxide in which one liter of solution contains one gr. mol. wt. of the respective substances, equal volumes of the solutions of either one of the acids must exactly neutralize the same volumes of the solutions of either of the bases.

Mol. wt. HCl, 36.45; $HNO_3$, 63.018; KOH, 56.158; NaOH, 40.058.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| The solution of | | | | H | | | |
| HCl contains in the liter | | | 1.008 gr. | H | | | |
| $HNO_3$ | " | " | 1.008 | OH | 62.01 | " | $NO_3$ |
| KOH | " | " | 17.008 | " | 39.15 | " | K |
| NaOH | " | " | 17.008 | " | 23.05 | " | Na |

Sulphuric acid acts upon these same base thus:

$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O;$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$$

From these equations it is evident that it would require 2 liters of the above-mentioned solutions of either of the bases to neutralize 1 liter of an aqueous solution of sulphuric acid, containing one gr. mol. wt. $H_2SO_4$ (mol. wt. $H_2SO_4$, 98.076. One gr. mol. wt. sulphuric acid contains 2.016 gr. H). It is also evident that $\frac{98.076}{2}$ grams sulphuric acid diluted with water to one liter would contain 1.008 gram hydrogen, and that a given volume of this solution must exactly neutralize the same volume of either of the above mentioned solutions of bases.

The neutralization of calcium hydroxide by acids is represented thus:

$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O;$$
$$2HNO_3 + Ca(OH)_2 = Ca(NO_3)_2 + 2H_2O;$$
$$H_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O.$$

Mol. wt. $Ca(OH)_2 = 74.116$. One gr. mol. wt. contains 34.016 grams of OH. By reasoning similar to that in the preceding paragraph, it is evident that if we made an aqueous solution of calcium hydroxide containing $\frac{74.116}{2}$ grams of calcium hydroxide, $Ca(OH)_2$, in one liter, any volume of this solution would exactly neutralize an equal volume of the solutions of nitric acid or hydrochloric acid or of the solution of sulphuric acid containing $\frac{98.076}{2}$ grams sulphuric acid, $H_2SO_4$, in the liter.

What have these equations in common? In each case 1.008 gram hydrogen has combined with 17.008 grams hydroxyl, OH, to form water.

.—It has been shown that a very
ıg m
upon a solution of an electro-
e the *ions* to appear at the poles.
able if it is assumed that the current is
decomposition of the electrolyte. This, and
facts which will be referred to farther on, make
probable that electrolytes are at least to some extent decomposed into their constituent *ions* when they are dissolved in water; that these ions charged with electricity transfer their charges in the solution and thus conduct the current; and that when an ion charged with negative electricity reaches the positive pole its electricity is discharged, and the ion then ceases to be an ion and becomes an element in the free state or some compound which appears either as such or in the form of other products. According to this conception, *the act of solution of an electrolyte, in water at least, involves partial breaking down or dissociation of the compound into its ions.* The extent of this breaking down is determined primarily by the concentration of the solution—the greater the dilution the greater the dissociation. At infinite dilution there is complete dissociation. A water solution of hydrochloric acid containing 36.18 grams of the acid in 1000 liters has been shown to be completely dissociated, or it is to be regarded as containing only hydrogen ions and chlorine ions. These and all other ions are carefully to be distinguished from the atoms or definite compounds. An ion always carries with it a certain charge of electricity. When this is discharged the ion becomes either an element or a compound in the free state. When a solution of one electrolyte acts upon a solution of another the reaction observed is probably due to the interaction of the ions, and it is further probable that, so far as the compounds are present in the undissociated condition, they do not act upon each other. When, for example, an acid acts upon a base in solution it appears that, so far as they react, they are in dissociated condition. Thus hydrochloric acid and sodium hydroxide

are to be regarded as acting as represented in the following equation:

$$\overset{+}{H} + \overset{-}{Cl} + \overset{+}{Na} + \overset{-}{OH} = \overset{+}{Na} + \overset{-}{Cl} + H_2O.$$

The act consists in the union of the hydroxyl ion of the base with the hydrogen ion of the acid to form water, the sodium and chlorine ions remaining as ions. In the case of nitric acid and potassium hydroxide the following equation represents the reaction at infinite dilution:

$$\overset{+}{H} + \overset{-}{NO_3} + \overset{+}{K} + \overset{-}{OH} = \overset{+}{K} + \overset{-}{NO_3} + H_2O.$$

And so also whenever the act of neutralization takes place there is simply a union of hydrogen ions with hydroxyl ions to form water.

This conception finds strong confirmation in the fact that the heat evolved in neutralizing equivalent quantities of all acids at infinite dilution is always the same—a fact difficult to explain if it is assumed that in the act of neutralization a salt is formed in the solution.

In the following table the heats of neutralization of a few acids and bases are given:

| Acid and Base. | Heat of Neutral. |
|---|---|
| Hydrochloric acid and sodium hydroxide . . . . | 13,700 |
| " " " lithium " . . . . | 13,700 |
| " " " potassium " . . . . | 13,700 |
| " " " barium " . . . . | 13,800 |
| " " " calcium " . . . . | 13,900 |
| Hydrobromic " " sodium " . . . . | 13,700 |
| Nitric " " " " . . . . | 13,700 |
| Iodic " " " " . . . . | 13,700 |

As will be seen, the heat of neutralization is the same no matter what the base or what the acid may be, and this fact is easily understood, if the act of neutralization consists in the union of a hydroxyl ion with a hydrogen ion to form water.

Thus it appears that the formation of water is not only the action common to every act of neutralization of an

acid by a base, but it is the only action occurring at great dilutions. If the neutralized solution is evaporated and the water driven off the number of ions decreases as molecules of the salt are formed in the concentrated solution. When all the water is evaporated practically no ions are present, as dry salts do not conduct electricity at ordinary temperatures.

**Definition of Acids and Bases in Terms of the Theory of Electrolytic Dissociation.**—According to what has just been said it appears that when any acid is dissolved in water it is dissociated into *hydrogen ions* and something else. This power to yield hydrogen ions is characteristic of acids. On the other hand, the most marked examples of bases, such as sodium and potassium hydroxides, when dissolved in water give *hydroxyl ions*, and this conduct is characteristic of bases.

**Definitions.**—It has already been seen that hydrochloric acid and sulphuric acid act upon certain metals, as iron and zinc, and that the action consists in giving up hydrogen and taking up metal in its place. The products of this action are the same in character as those formed by the action of acids on bases.

An *acid* is a substance containing hydrogen, which it easily exchanges for a metal, when treated with a metal itself, or with a compound of a metal, called a base.

A *base* is a substance containing a metal combined with hydrogen and oxygen (hydroxyl). It easily exchanges its metal for hydrogen when treated with an acid.

The products of the action of an acid on a base are, first, *water*, and, second, a neutral substance called a *salt*.

In the examples above cited the products $KNO_3$, potassium nitrate; $NaNO_3$, sodium nitrate; $Ca(NO_3)_2$, calcium nitrate; $K_2SO_4$, potassium sulphate; $Na_2SO_4$, sodium sulphate; $CaSO_4$, calcium sulphate, are salts. The relations between them and the acids from which they are derived will be easily recognized on comparing their formulas with those of the acids.

**Distinction between Acids and Bases.**—Although there is no difficulty in distinguishing between most acids and

most bases, there are some compounds that act sometimes in one way and sometimes in the other. Sulphuric acid, nitric acid, and hydrochloric acid always act as acids, and sodium and potassium hydroxides always act as bases, but some substances, that are generally basic, under some circumstances act as acids, and some that act as acids occasionally act as bases. What is the standard? How shall we tell whether a substance is an acid or a base? We may take a pronounced acid, such as hydrochloric acid, and say that any hydroxide which has the power to neutralize this acid and form with it a salt shall be called a base; and in the same way we may take a pronounced base, like potassium hydroxide, and say that any substance which has the power to neutralize this shall be called an acid. Having made the division in this way, it would be found that a few substances would be included in both lists, or, in other words, some substances which are basic toward hydrochloric acid are acid toward potassium hydroxide. Aluminium hydroxide, $Al(OH)_3$, is a case in point. This neutralizes hydrochloric acid and forms aluminium chloride according to the equation

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O.$$

And it also neutralizes potassium hydroxide according to the equation

$$Al(OH)_3 + 3KOH = Al(OK)_3 + 3H_2O.$$

It may be said in regard to this case, as in regard to most others of the kind, that the hydroxide in question is basic toward nearly all substances toward which potassium hydroxide is basic; whereas it is acid toward only three or four of the most energetic bases. Bearing in mind, then, the fact that there are some exceptional cases, it may be said that the distinction between acids and bases is easily made.

**Metals or Base-forming Elements.**—The question may fairly be asked, What is a metal? Unfortunately it is by no means an easy matter to give a satisfactory answer

to the question. Examples of metals can be given, such as iron, zinc, silver, calcium, magnesium, etc.; but it is not easy to state the distinguishing features of these substances. In general, it may be said that to the chemist any element is a metal which with hydrogen and oxygen forms a base or a product which has the power to neutralize acids. In general, any element which has the power to enter into an acid in the place of the hydrogen is called a metal, or is said to have metallic properties. This is the sense in which the word metal is used in this book. A better, though a longer, name for metals, is *base-forming elements.*

**Constitution of Acids and Bases.**—As has been pointed out, the bases are hydroxides, and these hydroxides are regarded as derived from water by the substitution of metals for the hydrogen. Examples of the hydroxides of univalent, bivalent, and trivalent metals were given in a previous chapter (see pp. 107, 143). Similarly, those acids which contain oxygen are regarded as hydroxides,* or as derived from water. This view is illustrated by the following formulas of some of the more common acids:

| | |
|---|---|
| Nitric acid | $(HO)NO_2$ |
| Sulphuric acid | $(HO)_2SO_2$ |
| Phosphoric acid | $(HO)_3PO$ |
| Carbonic acid | $(HO)_2CO$ |
| Metaphosphoric acid | $(HO)PO_2$ |
| Nitrous acid | $(HO)NO$ |
| Arsenious acid | $(HO)_3As$ |
| Hypochlorous acid | $(HO)Cl$ |
| Perchloric acid | $(HO)ClO_3$ |

There are three classes of acids represented in this list: (1) those with one, (2) those with two, and (3) those with three atoms of hydrogen in the molecule. Or, regarding the compounds as hydroxides, these classes are: (1) those derived from one molecule, (2) those derived

* This refers to the acids in concentrated form. When dissolved in water they are dissociated, yielding hydrogen ions.

from two molecules, and (3) those derived from three molecules of water by substitution of something else for half the hydrogen. It is interesting to observe, also, that this something which is substituted for the hydrogen is in most cases an element in combination with oxygen or, if it is not in combination with oxygen, it has the power to take up more oxygen. Thus hypochlorous and arsenious acids are regarded as derived from water by the substitution of chlorine and arsenic for hydrogen in water as shown

thus: H–O–Cl and  As. But, in each case, the

element which is in combination with hydroxyl has the power to combine with oxygen. Hypochlorous acid forms the products $(HO)ClO$, $(HO)ClO_2$, and $(HO)ClO_3$, while arsenious acid forms arsenic acid $(HO)_3AsO$.

Water may be regarded as the connecting link between the oxygen acids and bases. If A stands for any acid-forming element, and B for any base-forming element, then the general formula of a base is B(OH), and that of an oxygen acid A(OH) or $O_xA(OH)$, in which $O_x$ stands for some number of oxygen atoms from one to three or four. These relations then hold good:

| | Bases. | Water. | Acids. |
|---|---|---|---|
| I. | $B'(OH)$ | HOH | $(O_xA)'(OH)$ |
| II. | $B''(OH)_2$ | HOH<br>HOH | $(O_xA)''(OH)_2$ |
| III. | $B'''(OH)_3$ | HOH<br>HOH<br>HOH | $(O_xA)'''(OH)_3$ |

In these general formulas B″ means any bivalent metal, and B‴ any trivalent metal; and $(O_xA)''$ means any group of atoms which has the power to hold two hydroxyl groups in combination, and is therefore bivalent like $(O_2S)$, and $(O_xA)'''$ means a trivalent group like (OAs).

**Constitution of Salts.**—The view held in regard to the

constitution of salts is based directly upon those held in regard to the constitution of acids and bases. It is believed that when an oxygen acid acts upon a base the action takes place as represented in the following equation:

$$O_2N\text{-}O\text{-}|\overline{H + H\text{-}O}|\text{-}K = O_2N\text{-}O\text{-}K + H\text{-}O\text{-}H.$$

**Basicity of Acids.**—In working with acids and bases it is noticed that some acids have the power to form but one salt with a base like potassium hydroxide, while others have the power to form two or more salts with such a base. Thus, for example, hydrochloric acid, HCl, and nitric acid, $HNO_3$, can form but one salt with potassium hydroxide, and the reactions are represented by the following equations:

$$KOH + HCl = KCl + H_2O;$$
$$KOH + HNO_3 = KNO_3 + H_2O.$$

If only half the quantity of base that is required to neutralize the acid is added, half the acid remains unchanged, and on evaporating the solution the excess of acid will pass off. So, also, if only half the quantity of acid that is required to neutralize the base is added, half the base will remain unchanged. On the other hand, in the case of an acid like sulphuric acid, it is found that this has the power to form two salts with potassium hydroxide, in one of which there is twice as much of the metal as in the other. The reactions are represented thus:

$$KOH + H_2SO_4 = KHSO_4 + H_2O;$$
$$2KOH + H_2SO_4 = K_2SO_4 + H_2O.$$

If to a given quantity of sulphuric acid only half the quantity of potassium hydroxide that is required to neutralize it is added, the first reaction takes place; but if twice as much potassium hydroxide is used the second reaction takes place. An acid of this kind can, further, form one salt with two bases, in which one metal is substituted for one of the hydrogen atoms of the acid and a second metal for the other.

The different properties of the two kinds of acids referred to are ascribed to differences in constitution. In the molecule of hydrochloric acid, as in that of nitric acid, there is but one atom of hydrogen according to the views at present held. If, therefore, the act of neutralization takes place in each molecule it is complete, and the salt is said to be a *neutral* or *normal salt.* In sulphuric acid, however, there are two atoms of hydrogen in each molecule, and either one or both of these may be replaced. If only one is replaced a salt of the general formula $MHSO_4$ is obtained. This is still an acid, while also partly a salt. It is in fact an *acid salt* or a *salt acid.*

Acids like hydrochloric and nitric acids have not the power to form acid salts. They are called *monobasic acids.* While acids like sulphuric acid, which can form two salts with one base, one of which is acid, are called *dibasic acids.*

Monobasic acids are those which contain but one replaceable hydrogen atom in the molecule. Dibasic acids are those which contain two replaceable hydrogen atoms in the molecule.

Similarly, there are *tribasic acids*, like phosphoric acid, $H_3PO_4$, arsenic acid, $H_3AsO_4$, etc.; *tetrabasic acids*, like pyrophosphoric acid, $H_4P_2O_7$; *pentabasic acids*, like periodic acid, $H_5IO_6$; etc., etc. The higher the basicity of the acid the greater the variety of salts it can yield.

**Acidity of Bases.**—Just as we speak of monobasic, dibasic, tribasic acids, etc., so we distinguish between bases of different acidity. Thus there are the *monacia bases*, like potassium and sodium hydroxides, KOH and NaOH; *diacid bases*, like calcium and barium hydroxides, $Ca(OH)_2$ and $Ba(OH)_2$; *triacid bases*, like aluminium and ferric hydroxides, $Al(OH)_3$ and $Fe(OH)_3$; etc., etc.

If a monobasic acid acts upon a monacid base, one molecule of one forms a salt with one molecule of the other, and, in general, no other reaction between the two is possible. If a monobasic acid acts upon a diacid base two reactions are possible, just as when a monacid base acts upon a dibasic acid. Thus, when, for example,

hydrochloric acid acts upon zinc hydroxide, $Zn(OH)_2$, two reactions are possible:

$$Zn(OH)_2 + HCl = Zn<\begin{matrix}Cl\\OH\end{matrix} + H_2O;$$
$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O.$$

The compound ZnCl(OH) is still basic, and it is called a *basic salt.* Similarly, a triacid base can form three salts with a monobasic acid as, for example, in the case of bismuth hydroxide and nitric acid, in which three reactions are possible:

$$Bi\begin{Bmatrix}OH\\OH\\OH\end{Bmatrix} + HNO_3 = Bi\begin{Bmatrix}NO_3\\OH\\OH\end{Bmatrix} + H_2O;$$
$$Bi\begin{Bmatrix}OH\\OH\\OH\end{Bmatrix} + 2HNO_3 = Bi\begin{Bmatrix}NO_3\\NO_3\\OH\end{Bmatrix} + 2H_2O;$$
$$Bi\begin{Bmatrix}OH\\OH\\OH\end{Bmatrix} + 3HNO_3 = Bi\begin{Bmatrix}NO_3\\NO_3\\NO_3\end{Bmatrix} + 3H_2O.$$

The salts $Bi\begin{Bmatrix}NO_3\\(OH)_2\end{Bmatrix}$ and $Bi\begin{Bmatrix}(NO_3)_2\\OH\end{Bmatrix}$ are basic salts or basic nitrates of bismuth, while the salt $Bi(NO_3)_3$ is the neutral or normal salt.

**Salts.**—From the above it appears that there are three classes of salts: (1) *Normal salts*, which are derived from the acids by the substitution of metal atoms for all the acid hydrogen atoms; (2) *Acid salts*, which are derived from the acids by the substitution of metal atoms for part of the hydrogen; and (3) *Basic salts*, which are derived from the bases by neutralization of part of the basic hydroxyl by acids. Normal salts are generally neutral; or, if by a neutral substance is meant one which has not the power to form salts with acids nor with bases, then the expression normal salt is synonymous with neutral salt. But some normal salts have an acid reaction, and others have an alkaline or basic reaction. Thus a normal salt of a weak acid with a strong base as sodium carbonate, $Na_2CO_3$, has an al-

kaline reaction. So, also, a normal salt of a strong acid with a weak base may have an acid reaction, as in the case of aluminium sulphate, $Al_2(SO_4)_3$. As generally used, the expression neutral salt means a salt that has neither an acid nor an alkaline reaction towards certain colored substances such as litmus or methyl orange. But a sharp distinction cannot be made by this method, as the colored substances used as indicators do not all act in the same way. The alkaline reaction of normal salts of weak acids, and the acid reaction of normal salts of weak bases is due to the action of the water upon these salts. Thus, in solution, sodium carbonate, $Na_2CO_3$, is decomposed to a slight extent by the water, and the strong base sodium hydroxide gives the solution an alkaline reaction. So also, aluminium sulphate, $Al_2(SO_4)_3$, is slightly decomposed by the water, and the strong acid, sulphuric acid, gives the solution an acid reaction. A clearer and more satisfactory explanation of these phenomena, called *hydrolysis*, will be given later.

In naming acid salts various methods are adopted. In the case of a dibasic acid, the only distinction necessary is between the acid and the normal salts. The expressions *acid potassium sulphate* and *normal potassium sulphate* mean, of course, the salts which have the formulas $KHSO_4$ and $K_2SO_4$, and there is no danger of confusion. We may, however, use the names *mono-potassium sulphate* and *di-potassium sulphate*, or *primary* and *secondary potassium sulphates*. The last names are convenient and readily convey to the mind the nature of the salts spoken of. Just as dibasic acids yield primary and secondary salts, so tribasic acids yield primary, secondary and tertiary salts. For example, phosphoric acid yields three classes of salts: *primary phosphates*, of the general formula $MH_2PO_4$; *secondary phosphates*, of the general formula $M_2HPO_4$; and *tertiary phosphates*, of the general formula $M_3PO_4$. The phosphates of the first two classes are called, in general, *acid phosphates*. The tertiary phosphate is identical with the normal phosphate. In naming basic salts there is no difficulty in the simplest cases. Thus, taking the

three bismuth nitrates the formulas of which are given above, the one of the formula $Bi\begin{cases} NO_3 \\ (OH)_2 \end{cases}$ is called the *mono-nitrate;* that of the formula $Bi\begin{cases} (NO_3)_2 \\ OH \end{cases}$, the *di-nitrate;* and that of the formula $Bi(NO_3)_3$, the *tri-nitrate*, or *normal nitrate.*

APPLICATION OF THE THEORY OF ELECTROLYTIC DISSOCIATION TO THE SUBJECTS ABOVE PRESENTED.

**Basicity of Acids.**—An acid whose molecule in aqueous solution yields one hydrogen ion is monobasic. Examples: $\overset{+}{H},\overset{-}{Cl}$ and $\overset{+}{H},\overset{-}{NO_3}$. An acid whose molecule in *dilute* aqueous solution yields two or three hydrogen ions is dibasic or tribasic respectively. Examples: $\overset{+}{H},\overset{+}{H},\overset{=}{SO_4}$ and $\overset{+}{H},\overset{+}{H},\overset{+}{H},\overset{\equiv}{PO_4}$.

$SO_4$ ion, $\overset{=}{SO_4}$, carries two charges or electrical units, i. e. is bivalent. $PO_4$ ion, $\overset{\equiv}{PO_4}$, carries three charges, i. e. is trivalent. *Concentrated* aqueous solutions of dibasic acids dissociate chiefly into one hydrogen cation, and an anion. The second hydrogen atom of the acid molecule is in the anion. Thus sulphuric acid in concentrated aqueous solution is expressed by the symbol $\overset{+}{H},H\overset{=}{SO_4}$. Similarly, a tribasic acid in concentrated solution may yield one or two hydrogen ions according to the concentration. Examples: $\overset{+}{H},\overset{+}{H},H\overset{\equiv}{PO_4}$, $\overset{+}{H},H_2\overset{\equiv}{PO_4}$.

In the acids thus far mentioned all of the hydrogen atoms in the molecule are ionisable. This is not always the case. Phosphorous acid, $H_3PO_3$, is dibasic; only two of its three hydrogen atoms are replaceable by metals. It could therefore according to the concentration of its aqueous solution yield the ions $\overset{+}{H},\overset{+}{H},\overset{=}{HPO_2}$ or the ions $\overset{+}{H},H_2\overset{-}{PO_3}$, but *not* $\overset{+}{H},\overset{+}{H},\overset{+}{H},\overset{\equiv}{PO_3}$. Hypophosphorous acid, $H_3PO_2$ is monobasic; only one of its three hydrogen atoms is replaceable by metal, and its ionisation in solution is

into $\overset{+}{H}$ and $H_2\overline{PO_3}$. Similar conditions are presented by most organic acids. Acetic acid, for example, is monobasic; its composition is represented by the formula $C_2H_4O_2$; it is ionised into $\overset{+}{H}$ and $C_2\overline{H_3O_2}$.

**Ionisation of Salts.**—Soluble salts of monobasic acids ionise in only one way. For example $\overset{+}{Na},\overline{NO_3}$, $\overset{++}{Ca},\overline{Cl},\overline{Cl}$. (Calcium ion $\overset{++}{Ca}$ carries two charges of electricity, i.e. it is bivalent.)

Soluble normal salts of the di- and tribasic acids (an ionise in only one way. Example $\overset{+}{Na},\overset{+}{Na},\overline{SO_4}$.

Primary salts of dibasic acids and primary and secondary salts of tribasic acids may ionise, like the acids, in more than one way according to the concentration of the solution. Example: primary sodium sulphate $NaHSO_4$ may yield the ions $\overset{+}{Na},\overset{+}{H},\overline{\overline{SO_4}}$ on the ions $\overset{+}{Na},\overline{HSO_4}$.

*Basic salts* are all insoluble in water, and hence are not ionised.

**Ionisation of Bases.**—Few bases are soluble in water; all of these ionise in the same way, yielding metal cation, and hydroxyl anion or anions. Examples: $\overset{+}{Na},\overline{OH}$ and $\overset{++}{Ca},\overline{OH},\overline{OH}$.

**Apparent Exceptions.**—As mentioned on pp. 174, 175, aqueous solutions of salts formed by the action of weak bases on strong acids or strong bases on weak acids are partially hydrolysed by the water. In the case of sodium carbonate, $Na_2CO_3$, the reaction is $Na_2CO_3 + H_2O = \overset{+}{Na} + \overline{OH} + \overset{+}{Na} + \overline{HCO_3}$. Here hydroxyl ion is present which turns red litmus blue. In the case of aluminium sulphate, $Al_2(SO_4)_3$, the reaction is too complex to be expressed by an equation at this stage. As stated on page 175 the hydrolysis forms free sulphuric acid which ionises into $\overset{+}{H},\overset{+}{H},\overline{\overline{SO_4}}$, or $\overset{+}{H},\overline{HSO_4}$. Hydrogen ions are present which color blue litmus red.

**Neutralization of Acids or Bases insoluble in Water.**—

Most bases and some acids are insoluble in water. These are not ionised, and a mixture of such a base with water does not act on litmus. Yet when treated with acids they form salts, many of which are soluble in water. Copper hydroxide, for example, dissolves in dilute sulphuric acid forming copper sulphate and water: $Cu(OH)_2 + H_2SO_4 = CuSO_4 + 2H_2O$. The explanation offered for the formation of such salts is that no acid or base is *absolutely* insoluble in water. The copper hydroxide is believed to dissolve enough in water to yield a few ions, $\overset{++}{Cu}$ and $\overset{-}{OH},\overset{-}{OH}$. As these hydroxyl ions combine with the hydrogen ions of the acid to form water, more base dissolves yielding more hydroxyl ions, and this action continues until all the base has dissolved, when the action is complete, and it is only necessary to evaporate the water to obtain the salt. Analogous reactions occur in the action of a soluble base on an insoluble acid.

If both acid and base are insoluble, they must be mixed in the calculated proportions and the mixture fused to form a salt.

**Normal Solutions.**—Aqueous solutions of acids containing 1.008 gram hydrogen in the liter are called *normal solutions*, or N-solutions. Aqueous solutions of bases containing 17.008 grams hydroxyl in the liter are called *normal solutions* of bases (see p. 165). One-tenth normal solutions of acids (N/10) contain 0.1008 grams ionisable hydrogen in the liter; N/10-solutions of bases contain 17.008 grams hydroxyl in the liter.

**Measurement of Ionisation.**—It follows from Faraday's first law that by measuring the amount of current passing through a solution of an electrolyte of known dilution, at a given temperature, and comparing it with the amount of current passing through the same electrolyte at the same temperature and at infinite dilution, the degree of ionisation of the electrolyte can be measured. The property of electrolytes to conduct electricity is called their *conductivity*. Conductivity measurements may be made by several methods.

**Activity of Acids and Bases.**—Since the act of neutralization consists in the formation of water, the relative activity of an acid depends upon the number of hydrogen ions present in its solution and the relative activity of a base on the number of hydroxyl ions present in its solution, in other words, upon the degree of electrolytic dissociation of a given acid or base in a solution of given concentration at a given temperature.

The great differences in the ionisation of some of the common electrolytes is shown in the following table which gives the proportions of the molecules ionised.

*Fractions of a Molecule Ionised.*

*Temperature 18°. N-solutions unless otherwise stated.*

| *Acids.* | | *Bases.* | |
|---|---|---|---|
| Nitric acid | 0.820 | Potassium hydroxide | 0.77 |
| Nitric acid (conc. 62 per cent) | 0.096 | Sodium hydroxide | 0.73 |
| Hydrochloric acid | 0.784 | Ammonium hydroxide | 0.004 |
| Sulphuric acid, $\overset{+}{H}, \overset{+}{H}, \overline{\overline{SO_4}}$ | 0.510 | | |
| Phosphoric acid, $\overset{+}{H}, \overline{HPO_4}$, N/10 25° | 0.170 | | |
| Acetic acid | 0 004 | | |
| Carbonic acid N/10 $\overset{+}{H}, \overline{HCO_3}$ | 0.0017 | *Salts.* | |
| Hydrogen Sulphide N/10 $\overset{+}{H}, \overline{S}$ | 0.0007 | Sodium chloride | 0.676 |
| | | Copper Sulphate | 0.22 |

From this table it will be seen that nitric, hydrochloric, and sulphuric acids are relatively active, being all ionised over 50 per cent, that acetic acid is much less active, while carbonic acid and hydrogen sulphide are very inactive or weak acids.

It should be clearly understood that the activity of an acid has nothing to do with the *amount* of acid required to neutralize a given weight of base, or to dissolve a given weight of metal, but expresses the *reaction velocity* of the acid. The *amount* of an acid required depends on its molecular weight, for it requires 1 gr. mol. wt. each of

hydrochloric or acetic acids to neutralize 1 gr. mol. wt. of sodium hydroxide. The relative *velocity* of these reactions is shown in the table. The great reaction velocity of these acids with solutions of bases prevents ocular demonstration, but by comparing their action on a metal where only surface action is possible, the difference in their reaction velocity is noticeable. (See Experiment 86.)

**Strength of Acids.**— The term strength applied to acids is misleading because it is too general, and is applied to different properties of acids. It was formerly largely based on the property of certain concentrated acids to expel other acids from their salts, and concentrated sulphuric acid was called the "strongest." This action, however, depends on the relative boiling points of the two acids, as sulphuric acid boils at 338°, and hydrochloric acid is a gas at ordinary temperature. Hence in the reversible reaction $H_2SO_4 + NaCl \rightleftarrows HNaSO_4 + HCl$, if the sulphuric acid is concentrated and the sodium chloride dry so that no water is present to dissolve the hydrochloric acid gas, the reaction moves practically in the direction of the upper arrow and hydrochloric acid escapes as gas as fast as formed. If, however, a concentrated solution of hydrochloric acid gas in water acts upon primary sodium sulphate, the reaction is reversed and moves in the direction of the lower arrow, because sodium chloride being insoluble in concentrated hydrochloric acid is precipitated as fast as formed and is thus removed from the field of action.

Phosphoric acid is properly considered a weak acid because it is very inactive, but it is not readily vaporized and, if sodium sulphate and phosphoric acid are heated together at temperatures above the boiling point of sulphuric acid (338°), sodium metaphosphate is formed, and the reaction is completed, as shown in the equation, because sulphuric acid as gas escapes from the field of action:

$$2PO_4H_3 + Na_2SO_4 = 2PO_3Na + H_2SO_4 + 2H_2O.$$

At the present time there is a tendency to retain the word "strength" and make it synonymous with *activity*. This too is misleading. Concentrated sulphuric acid, for example, destroys organic tissues, chars wood, and has many characteristic and violent properties which dilute sulphuric acid does not have. We properly consider it, like concentrated nitric and hydrochloric acids, very "strong" in many respects. But as ionisation, i. e. activity, of acids increases with dilution, if "strength" and activity are synonymous, a sulphuric acid so dilute that it could be swallowed with impunity is stronger than oil of vitriol.

**Acid Properties and Oxygen.**—Almost all those substances which are called acids contain oxygen, as, for example, nitric acid, $HNO_3$; sulphuric acid, $H_2SO_4$; phosphoric acid, $H_3PO_4$; silicic acid, $H_2SiO_3$; carbonic acid, $H_2CO_3$; boric acid, $H_3BO_3$; etc. The presence of oxygen in acids was recognized by Lavoisier. As he showed its presence in acids to be general, and as he found that several elements and some compounds are converted into acids by combination with oxygen, he concluded that this element is an essential constituent of all acids, and therefore called it oxygen, a name which, as already stated (see p. 32), means the acid-former. According to Lavoisier, hydrochloric acid, like other acids, contained oxygen, and this view prevailed for many years. As has been pointed out under the head of Chlorine, many investigations were undertaken with the object of determining whether this element does or does not contain oxygen, the result being to show that in chlorine, and consequently in hydrochloric acid, there is no oxygen. Several acids are now known which are like hydrochloric acid in this respect, but the latter is the best known example. Similar compounds are hydrobromic acid, HBr; hydriodic acid, HI; and hydrocyanic acid, HCN. The number of these acids is, however, quite small, and it is undoubtedly true that, of the compounds commonly called acids, by far the larger number contain oxygen as an essential constituent. Further, some compounds which are basic can

be converted into acids by causing them to combine with oxygen.

**Nomenclature of Acids.**—The names of the acids of chlorine illustrate some of the principles of nomenclature in use in chemistry. The acid of the series which is best known is called chloric acid. In naming acids the suffix *ic* is always used to designate the principal member of a group of acids containing the same elements. This is seen in the names hydrochloric, sulphuric, nitric, phosphoric, silicic, carbonic, acetic, etc. If there are two acids containing the same elements, that one of the two which contains the smaller proportion of oxygen is given a name ending in *ous*. Thus there are the two series:

| | | | |
|---|---|---|---|
| Chloric acid..... | $HClO_3$ | Chlorous acid..... | $HClO_2$ |
| Sulphuric acid.... | $H_2SO_4$ | Sulphurous acid..... | $H_2SO_3$ |
| Nitric acid..... | $HNO_3$ | Nitrous acid..... | $HNO_2$ |
| Phosphoric acid.. | $H_3PO_4$ | Phosphorous acid.... | $H_3PO_3$ |

For most cases this method will suffice, but in others the number of acids known is larger than two, as, for example, in the series of chlorine acids. In such cases recourse is had to prefixes. If there is an acid known containing a smaller proportion of oxygen than the one whose name ends in *ous*, it is generally designated by means of the prefix *hypo*, from the Greek ὑπό, under. Examples: Hypochlorous acid, HClO; hyposulphurous acid, $H_2SO_2$; and hypophosphorous acid, $H_3PO_2$. It will be seen on comparing the formulas of these acids with those above given that they differ from them in a simple way.

In the series of chlorine acids there is one that contains a larger proportion of oxygen than chloric acid. This is called perchloric acid, the Latin prefix *per* signifying here very or fully. Similarly there is a perbromic acid and a permanganic acid. Other cases arise, but they are of a more or less special character, and the compounds are given special names according to circumstances.

**Nomenclature of Bases.**—As pointed out above, a base is a compound of a metal with hydroxyl, OH. The bases are commonly known as hydroxides; and in order to distinguish between the hydroxides of the different metals, the names of the metals are placed before the name hydroxide, as in naming the oxides and chlorides. Thus, caustic soda, NaOH, is called sodium hydroxide, etc. It is necessary in some cases to distinguish between two hydroxides of the same metal. This is done by using the suffixes *ous* and *ic* in the same sense as they are used in naming oxides and chlorides. Thus ferric hydroxide has the composition $Fe(OH)_3$, and ferrous hydroxide the composition $Fe(OH)_2$; cuprous hydroxide is CuOH, and cupric hydroxide $Cu(OH)_2$, etc. These compounds are sometimes called *hydrates*. On the other hand, there are compounds which apparently contain hydrogen and oxygen in a different condition from that in which these elements are contained in the hydroxides. These have already been discussed under the head of Hydrates (which see). As examples of hydrates we have salts with their "water of crystallization," chlorine hydrate, $Cl_2 + 10H_2O$; hydrochloric acid hydrate, $HCl + 2H_2O$; etc. While some of the compounds which are commonly regarded as hydrates should probably be classed with the hydroxides, there seem to be two classes, and it is therefore desirable to have two names.

**Nomenclature of Salts.**—Theoretically every metal can yield a salt with every acid. The salts derived from a given acid receive a general name, and this general name is qualified in each case by the name of the metal contained in the salt. Thus, all the salts derived from nitric acid are called *nitrates;* all the salts derived from chloric acid are called *chlorates;* the salts of sulphuric acid are called *sulphates;* * the salts of phosphoric acid are called *phosphates;* * etc. So, too, the salts of chlorous acid are called *chlorites;* those of nitrous acid, *nitrites;*

* Strictly speaking, the salts of sulphuric acid should be called *sulphurates*, and those of phosphoric acid *phosphorates*, but for the sake of euphony these names are shortened to the above forms.

those of sulphurous acid, *sulphites;* etc., etc. It will be noticed that the final syllable of the name of the salt differs according to the name of the acid. If the name of the acid ends in *ic*, the name of the salt derived from it ends in *ate.* If the name of the acid ends in *ous*, the name of the salt ends in *ite.* To distinguish between the different salts of the same acid, the name of the metal contained in it is prefixed. Thus, the potassium salt of nitric acid is called potassium nitrate, the sodium salt is called sodium nitrate; the calcium salt of sulphuric acid is called calcium sulphate; the magnesium salt of nitrous acid is magnesium nitrite; the calcium salt of hypochlorous acid is calcium hypochlorite; etc., etc. If a metal forms two salts with the same acid in one of which the valence of the metal is lower than in the other, the one in which the valence of the metal is lower is designated by means of the suffix *ous*, while the one in which the valence of the metal is higher is designated by means of the suffix *ic.* Thus there are two series of salts of iron which correspond to the two chlorides $FeCl_2$ and $FeCl_3$. In one series the iron appears to be bivalent, in the other trivalent. Examples are, $Fe(NO_3)_2$ and $Fe(NO_3)_3$; $FeSO_4$ and $Fe_2(SO_4)_3$; etc. Those salts in which the iron is bivalent are called ferrous salts, as ferrous nitrate, ferrous sulphate, etc.; and those in which it is trivalent are called ferric salts, as ferric nitrate, ferric sulphate, etc. Similarly there are two series of copper salts known as cuprous and cupric salts; and two series of mercury salts known as mercurous and mercuric salts.

If the salts of hydrochloric acid were named in accordance with the principle just explained, they would be called *hydrochlorates*, and this name is sometimes used for complex salts, but in the case of the salts of the metals it will be observed that these are identical with the products formed by direct combination of the metals with chlorine. Thus, hydrochloric acid and zinc act as represented in the equation

$$Zn + 2HCl = ZnCl_2 + H_2;$$

while zinc and chlorine act thus:

$$Zn + Cl_2 = ZnCl_2.$$

In each case the same product, $ZnCl_2$, is formed. But these compounds of metals with chlorine are called *chlorides*. Hence for these the name *hydrochlorate* is unnecessary.

## EXPERIMENTS.

### Neutralization of Acids and Bases; Formation of Salts.

Experiment 82.—Prepare a dilute solution of sodium hydroxide by dissolving 1 gram of the substance in 200 cc. of water. Prepare a solution of 4 cc. dilute hydrochloric acid in 200 cc. water. Shake well and partly fill each burette (see Fig. 41) with one of the solutions. After reading the height of the liquid in the tubes, draw off into a beaker about 5 cc. of the alkali solution, add two or three drops of methyl orange solution, and add the acid drop by drop until the color just changes to pink. If too much acid should be added the solution can be made alkaline again and the neutralization repeated until the exact turning point is reached. The difference between the final reading and the first reading of the height of the liquid in the tubes will give the total amount of each used. From these the ratio of the acid and base can be calculated. This experiment should be repeated until a series of concordant results are obtained. Secure from the instructor standard solutions of acids and bases, the strength of one of which is given, and determine by comparison with the known solution the absolute strength of the others. The amount of the substance in 1 cc. of the unknown solution can be determined by calculating the amount that should be in a solution of equal strength and determining the relative strength of the two solutions and correcting for this ratio. For example, suppose a solution of hydrochloric acid containing 0.020 gram of HCl in each cc. was given.

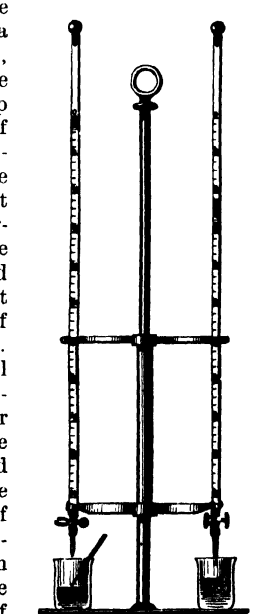


Fig. 41.

The amount of the sodium hydroxide equivalent to this can be calculated from the equation $HCl + NaOH = NaCl + H_2O$:

HCl NaOH

(1 + 35.45) : (23.05 + 16 + 1.008) :: wt. of HCl : wt. of NaOH

36.45 : 40 058 :. 0.020 : x

x = 0.022 gram of NaOH

Now suppose 1 cc. of HCl will neutralize 2 cc. of NaOH, then the amount of sodium hydroxide in each cc. will be $\frac{0.022}{2}$ or 0.011 gram, as the value of x represents the amount of NaOH equivalent to 1 cc. HCl and this is contained in 2 cc. of the sodium hydroxide solution.

## Study of the Products formed.

Experiment 83.—Dissolve about 10 grams caustic soda in 100 cc. water. Add hydrochloric acid slowly, examining the solution from time to time by means of a piece of paper colored blue with litmus As long as the solution is alkaline it will cause no change in the color of the paper. The instant the point of neutralization is passed, the solution changes the color of the paper to red; when exactly neutral, it will neither change the blue to red, nor, if the color is changed to red by means of another acid, will it change it back again. When this point is reached, evaporate to complete dryness on the water-bath, and see what is left Taste the substance. Has it an acid taste? Does it suggest any familiar substance? If it is sodium chloride, how ought it to conduct itself when treated with sulphuric acid? Does it conduct itself in this way? Satisfactory evidence can be given that the substance is sodium chloride. It is not an acid nor an alkali. It is neutral.

Experiment 84.—Perform a similar experiment, using dilute nitric acid and caustic soda. What evidence have you that the product in this case is different from caustic soda?

Experiment 85.—Perform similar experiments with dilute sulphuric acid and caustic soda; with sulphuric acid and caustic potash; with nitric acid and caustic potash; with hydrochloric acid and caustic potash. Dry and examine the product carefully in each case; and keep for future study what is not used in these experiments.

Experiment 86.—The dilute acids of the laboratory should be about 2N (twice normal). Take three pieces of zinc of about the same size, and put a piece into each of three test-tubes. Pour into the first tube about 5 cc. dilute hydrochloric acid, into the second the same volume of dilute sulphuric acid, and into the third the same volume of dilute acetic acid. Note the differences in the velocity of the escape of hydrogen and compare with the table on p. 179.

## CHAPTER XI.

### NATURAL CLASSIFICATION OF THE ELEMENTS.—THE PERIODIC LAW.*

**Historical.**—It has long been known that simple relations exist between the atomic weights of some elements which resemble one another closely. Thus chlorine, bromine, and iodine are very similar elements. Their atomic weights are 35.45, 79.96, and 126.97 respectively. It will be seen that the atomic weight of bromine, 79.96, is approximately the mean of those of chlorine and iodine. We have

$$\frac{35.45 + 126.97}{2} = 81.21.$$

A similar group is that of sulphur, selenium, and tellurium, which resemble one another as closely as chlorine, bromine, and iodine do. The atomic weights are S = 32.06, Se = 79.2, and Te = 127.6. We have here

$$\frac{32.06 + 127.6}{2} = 79.83.$$

Other groups are those of phosphorus, 31, vanadium, 51.2, and arsenic, 75:

$$\frac{31 + 75}{2} = 53;$$

lithium 7.03, sodium, 23.05, and potassium, 39.15:

$$\frac{7.03 + 39.15}{2} = 23.09.$$

**Arrangements of the Elements.**—Mendeléeff (1869) and Lothar Meyer (1870) have proposed several arrangements for the purpose of making clear the connection between

* A large table of the Natural System of the elements should be hung up in a conspicuous place in the laboratory.

## MENDELÉEFF'S TABLE I.

| Series. | Group 0. R. | Group I. RH. $R_2O$. | Group II. $RH_2$ RO. | Group III. $RH_3$(?). $R_2O_3$. | Group IV. $RH_4$. $RO_2$. | Group V. $RH_3$. $R_2O_5$. | Group VI. $RH_2$. $RO_3$. | Group VII. RH. $R_2O_7$. | Group VIII. — $RO_4$. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | H=1 | | | | | | | |
| 2 | He=4 | Li=7 | Gl=9.1 | B=11 | C=12 | N=14 | O=16 | F=19 | |
| 3 | Ne=20 | Na=23 | Mg=24.4 | Al=27 | Si=28 | P=31 | S=32 | Cl=35.5 | |
| 4 | A=39.9 | K=39.1 | Ca=40 | Sc=44 | Ti=48.1 | V=51.2 | Cr=52.3 | Mn=55 | Fe=56, Ni=58.5, Co=59.1, Cu=63.3. |
| 5 | — | (Cu)=63.3 | Zn=65.4 | Ga=69.9 | Ge=72 | As=75 | Se=79 | Br=80 | |
| 6 | Kr=81.8 | Rb=85.4 | Sr=87.5 | Y=89 | Zr=90.7 | Cb=94.2 | Mo=95.9 | —=100 | Rh=103, Ru=103.8, Pd=108, Ag=107.9. |
| 7 | — | (Ag)=107.9 | Cd=112 | In=113.7 | Sn=118 | Sb=120.3 | Te=125.2 | I=126.9 | |
| 8 | Xe=128 | Cs=132.9 | Ba=137 | La=138.5 | Ce=141.5 | — | — | — | — — — |
| 9 | — | (—) | — | — | — | — | — | — | |
| 10 | — | — | — | Yb=173.2 | — | Ta=182.8 | W=184 | — | Ir=193.1, Pt=194.8, Os=200, Au=196.7, |
| 11 | — | (Au)=196.7 | Hg=200.4 | Tl=204.1 | Pb=206.9 | Bi=208 | — | — | |
| 12 | — | — | Ra=225 | — | Th=233.4 | — | U=239 | — | — — — |

MENDELÉEFF'S TABLE II.

| | | | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|---|---|
| $R_2O$ | I. | | Li — 7 | K 39 | Rb 85 | Cs 133 | — — | — — |
| RO | II. | | Gl — 9 | Ca 40 | Sr 87 | Ba 137 | — — | — — |
| $R_2O_3$ | III. | | B —11 | Sc 44 | Y 89 | La 138 | Yb 173 | — — |
| $RO_2$ | IV. | ($H_4C$) | C —12 | Ti 48 | Zr 90 | Ce 142 | — — | Th 231 |
| $R_2O_5$ | V. | ($H_3N$) | N —14 | V 51 | Cb 94 | Di 146 | Ta 182 | — — |
| $RO_3$ | VI. | ($H_2O$) | O —16 | Cr 52 | Mo 96 | — — | W 184 | U 240 |
| $R_2O_7$ | VII. | (HF) | F —19 | Mn 55 | — — | — — | — — | — — |
| $RO_4$ | | | | Fe 56 | Ru 103 | — — | Os 192? | — — |
| | VIII. | | | Co 58 | Rh 104 | — — | Ir 193 | — — |
| | | | | Ni 59 | Pd 106 | — — | Pt 195 | — — |
| $R_2O$ | I. | H —1 | Na —23 | Cu 63 | Ag 108 | — — | Au 196 | — — |
| RO | II. | | Mg 24 | Zn 65 | Cd 112 | — — | Hg 200 | — — |
| $R_2O_3$ | III. | | Al 27 | Ga 69 | In 113 | — — | Tl 204 | — — |
| $RO_2$ | IV. | ($H_4R$) | Si 28 | Ge 72 | Sn 118 | — — | Pb 206 | — — |
| $R_2O_5$ | V. | ($H_3R$) | P 31 | As 75 | Sb 120 | — — | Bi 209 | — — |
| $RO_3$ | VI. | ($H_2R$) | S 32 | Se 79 | Te 125? | — — | — — | — — |
| $R_2O_7$ | VII. | (HR) | Cl 35.5 | Br 80 | I 127 | — — | — — | — — |

the properties and atomic weights of the elements. Those which have proved most useful will first be given, and then the connection between the atomic weights and properties will be discussed briefly. The different arrangements are to be regarded only as different ways of expressing the same law, and no one of them is perfect. The investigation of the relations between the atomic weights and the properties of the elements has not yet been pushed far enough to justify a final opinion as to the character of the relations, but it has nevertheless reached a stage in which the statement is justified that these relations are general and deep-seated.

In the above tables the approximate atomic weights are used instead of those which have been determined and calculated with the greatest care. For most purposes in the laboratory the approximate figures answer well enough, and they are commonly used. In the following table of Lothar Meyer the refined atomic weights are used. The difference between the two sets of figures is in most cases slight.

In Mendeléeff's Table I the elements are arranged in horizontal lines, beginning with lithium.

At the left of the table are five elements which fall into the vertical column marked group 0. These elements are not included in the numerical relations spoken of in the following pages. Their significance is treated of on p. 196.

When the eighth element, sodium, in the order of the increasing atomic weights is reached it is found that it is very much like lithium. If this is placed below lithium, and the next six elements in the same horizontal line, when the fifteenth element is reached, it is found like the eighth to be similar to lithium. Up to and including manganese there are twenty-one * elements excluding hydrogen. These fall then naturally into three series of seven members each, and placing these horizontally, those elements which fall in the same perpendicular lines have the same general character. This is seen most strikingly in Group I, in which lithium, sodium, and potassium fall, and in Group V, in which nitrogen, phosphorus, and vanadium fall; but there is no difficulty in recognizing the similarity in the other groups. The three elements following manganese, *viz.*, iron, nickel, and cobalt, are very much alike, and they certainly do not belong in Groups I, II, and III, while the next element, copper, has some properties which ally it to the members of Group I. The next six elements fall in Groups II to VII, and are evidently in

* Since this table was prepared by Mendeléeff three additional elements have been discovered that have atomic weights lower than that of manganese. These are helium (at. wt. 4), neon (at. wt. 20), and argon (at. wt. 40).

## NATURAL SYSTEM OF THE ELEMENTS. (LOTHAR MEYER.)

HYDROGEN, H=1.01.

| A I. B | A II. B | A III. B | A IV. B | A V. B | A VI. B | A VII. B | VIII. |
|---|---|---|---|---|---|---|---|
| Li, 7.03 | Gl, 9.1 | B, 11 | C, 12 | N, 14 01 | O, 16 | F, 19 | |
| Na, 23.05 | Mg, 24.36 | Al, 27.1 | Si, 28.4 | P, 31 | S, 32.06 | Cl, 35.45 | |
| K, 39.15 | Ca, 40.1 | Sc, 44.1 | Ti, 48.1 | V, 51.2 | Cr, 52.1 | Mn, 55 | Fe, 55.9, Co, 59, Ni, 58.7 |
| Cu, 63.6 | Zn, 65.4 | Ga, 70 | Ge, 72.5 | As, 75 | Se, 79.2 | Br, 79.96 | |
| Rb, 85.5 | Sr, 87.6 | Y, 89 | Zr, 90.6 | Cb, 94 | Mo, 96 | | Ru, 101.7, Rh, 103, Pd, 106.5 |
| Ag, 107.93 | Cd, 112.4 | In, 115 | Sn, 119 | Sb, 120 2 | Te, 127.6 | I. 126.97 | |
| Cs, 132.9 | Ba, 137.4 | La, 138.9 | Ce, 140.25 | | | | |
| | | | | | | | |
| | E, 166 | Yb, 173 | | Ta, 181 | W, 184 | | Os, 191, Ir, 193, Pt, 194.8 |
| Au, 197.2 | Hg, 200 | Tl, 204.1 | Pb, 206.9 | Bi, 208 | | | |
| | | | Th, 232.5 | | U, 238 5 | | |
| 1 [2, 3] | 2 [1] | 3 [1] | 4 [2] | 5 [3] | 6 [2] | 7 [1] | 8 [2, 3, 4] |

place, and the six following fall in Groups I to VI, and are also in their proper places. After molybdenum in the sixth series comes a blank which means that there is no element to fill that place, and suggests that there is one undiscovered which has the atomic weight approximately 100, and has properties similar to those of manganese. Then follow three elements which resemble one another as closely as iron, nickel, and cobalt do. These do not belong in Groups I, II, and III, but form a small independent group. These two groups of three elements occur at the end of the fourth and sixth series respectively. We should therefore expect to find a similar group at the end of the eighth series. No such group is known, however, though at the end of the tenth series, where we should look for the next similar small group, there are the three elements iridium, platinum, and osmium. The elements of series 2 beginning with lithium and ending with fluorine differ in some respects quite markedly from all the other elements, as will be seen when they are taken up. Beginning with sodium, it will be seen that there are two series of seven elements and a short series of three; then again two series of seven and a series of three; and, although the following series are imperfect, it is not difficult to recognize that the same general arrangement of the elements holds good to the end. A series of seven elements is called a *short period;* while two short periods with the accompanying three similar elements constitute what is called a *long period.*

In Mendeléeff's Table II the long periods are arranged in perpendicular lines, each long period beginning and ending with a short period and having a side group of three elements in the middle. Thus in the column beginning with potassium there is, first, the short period potassium to manganese, then the side group iron, cobalt, nickel, and then the short period copper to bromine. In this table similar elements occur in the same horizontal lines. Thus in one line there are lithium, potassium, rubidium, and cæsium; in another sulphur, selenium, and tellurium; and in another chlorine, bromine, and iodine.

The symbols at tbe top of each column in Table I have reference to the general formulas of the compounds which the elements in each group form with oxygen and with hydrogen. Beginning with Group I, the general formula of the oxygen compounds of the members of this group is $R_2O$, in which R represents any element of that group; the general formula of the oxygen compounds of the members of Group II is RO; and so on. It will be observed that the oxygen compounds grow more and more complex from Group I to Group VII. Writing RO, $RO_2$ and $RO_3$ with double formulas, thus: $R_2O_2$, $R_2O_4$, and $R_2O_6$, the series of oxygen compounds is represented as below:

$$R_2O, \quad R_2O_2, \quad R_2O_3, \quad R_2O_4, \quad R_2O_5, \quad R_2O_6, \quad R_2O_7.$$

As regards the composition of the oxygen compounds of the members of Group VIII, it must be said that it does not in general correspond to the composition $RO_4$. Osmium and ruthenium do, however, form the oxides $OsO_4$ and $RuO_4$.

There is also regularity in the composition of the hydrogen compounds. Beginning with Group VII, those members which combine with hydrogen form compounds of the general formula RH, as, for example, ClH, hydrochloric acid; FH, hydrofluoric acid; etc. Those members of Group VI which combine with hydrogen form compounds of the general formula $RH_2$, as, for example, water, $H_2O$, and hydrogen sulphide, $H_2S$. The maximum power of combining with hydrogen is met with in Group IV, in which occur the elements carbon and silicon. These form the hydrogen compounds $CH_4$ and $SiH_4$. The members of Groups I, II, and III do not readily form compounds with hydrogen. A few are known, but they are quite unstable.

The hydroxides vary in composition from the simple form R(OH) to $R(OH)_7$. While in the first four groups well-marked examples of the hydroxides R(OH), $R(OH)_2$, $R(OH)_3$ and $R(OH)_4$ are found, in the fifth group the hydroxides have not the general formula $R(OH)_5$, though

several of them have the formula $OR(OH)_3$, as phosphoric, arsenic, and antimonic acids, which are respectively $OP(OH)_3$, $OAs(OH)_3$, and $OSb(OH)_3$. These may be regarded as derived from the hydroxides of the general formula $R(OH)_5$ by loss of water:

$$R(OH)_5 = OR(OH)_3 + H_2O.$$

Hydroxyl derivatives of the members of Group VI corresponding to the general formula $R(OH)_6$ are known, as, for example, the so-called hydrate of sulphuric acid, $S(OH)_6$. The maximum hydroxides of Group VII should have the general formula $R(OH)_7$, but those known do not correspond to this. The nearest approach to it is found in crystallized periodic acid, $H_5IO_6$, which may be regarded as derived from the hydroxide $I(OH)_7$ by loss of one molecule of water, thus:

$$I(OH)_7 = OI(OH)_5 + H_2O.$$

The arrangement of Lothar Meyer is a continuous one. The elements are arranged on a spiral beginning with lithium and ending with uranium. The divisions are such that when the two ends of the table are brought together on a cylinder, the line ending with fluorine will join that beginning with sodium; that ending with nickel will join that beginning with copper; and so on. In other respects the arrangement is much like that in Mendeléeff's Table I. What Mendeléeff calls a Group, Lothar Meyer calls a *Natural Family*, while those elements which fall in the same horizontal line are said to form a series. Now, each natural family falls into two groups indicated by the letters A and B placed above. Thus the first natural family falls into Group A, consisting of lithium, sodium, potassium, rubidium, and cæsium, and Group B, consisting of copper, silver, and gold. Family II falls into Group A, consisting of glucinum, magnesium, calcium, strontium, barium, and perhaps erbium, and Group B, consisting of zinc, cadmium, and mercury; etc. The members of each group in a family

resemble one another much more closely than they resemble the members of the other group.

The figures at the bottom of the table of Lothar Meyer refer to the valence of the elements in each group. Judging by the composition of the oxides and hydroxides, the valence increases from 1 to 8 from Families I to VIII. But the valence of the elements in each family varies according to conditions. Thus the valence of the elements of Family IV is generally 4, as shown in the compounds $CH_4$, $CCl_4$, $CO_2$, $SiH_4$, $SiCl_4$, $SiO_2$, etc.; but they may also appear as bivalent elements as seen in the compound CO. So, too, while the elements of Family V are quinquivalent, as in $PCl_5$, $NH_4Cl$, etc., they may also be trivalent, as in $PCl_3$, $NH_3$, etc.

What we call valence does not then appear to be an unchangeable property of the elements, but a property which may change according to conditions. It appears further that a given element may have one valence towards one element and another valence towards another element. This is most strikingly seen on comparing the formulas of the hydrogen compounds of the elements of Families V, VI, and VII with those of their oxygen compounds. The members of Family VII combine with hydrogen in only one proportion, and that is the simplest possible. Towards hydrogen these elements are univalent, and their valence towards hydrogen is constant. On the other hand, they combine with oxygen and with hydroxyl in several proportions, and judging by the composition of these compounds, the valence towards oxygen varies from 1 to 7. The members of Family VI are bivalent towards hydrogen, and their hydrogen valence is constant; but they combine with oxygen and hydroxyl in several proportions, and the composition of the compounds indicates that their valence towards oxygen varies from 2 to 6. The hydrogen valence of the members of Family V is 3, while the oxygen valence varies from 1 to 5. Finally, the hydrogen valence of the members of Family IV is 4, while the oxygen valence varies from 2 to 4. As regards the hydrogen valence of the members

of Families I to III, but little is known. These elements do not generally combine with hydrogen, though some of them do. Towards oxygen their valence is fairly constant, though some variations are observed as in the case of copper and mercury.

Judging then by the composition of the compounds, we are justified in making a distinction between the *hydrogen-valence* of some elements and their *oxygen-valence.* While the former is constant, the latter is subject to variations. In those cases in which there is a marked difference between the *hydrogen-valence* of an element and its maximum *oxygen-valence*, the maximum valence towards chlorine is greater than the hydrogen-valence and less than the maximum oxygen-valence. This is shown in the case of sulphur; the formulas of its hydrogen compound and of its highest compounds with chlorine and oxygen being respectively

$$SH_2, \qquad SCl_4, \qquad SO_3.$$

From this it appears that the maximum valence of sulphur towards hydrogen is 2, towards chlorine 4, and towards oxygen 6. On the other hand the valence of sulphur towards fluorine is 6 as is shown by the stable compound sulphur hexafluoride, $SF_6$.

**Position of Elements which show no Chemical Properties.**—The Elements of Group 0 given in Mendeléeff's Table I show no chemical properties. Efforts to cause any of them to combine with other elements have thus far proved fruitless. Our knowledge of them is confined to their physical properties. They are all mon-atomic, i. e. contain but one atom in the molecule.

Their atomic weights place them as links between the extremely active non-metallic elements of Group VII and the extremely active metallic elements of Group I, a very suggestive position, showing in the series chlorine-argon-potassium for example, a complete extinction of chemical activity, an inert mon-atomic element midway between the active non-metal chlorine and the active metal potassium.

**Connection between the Position of the Elements in the Natural System and their Chemical Properties.**—The changes in composition of the oxygen and hydrogen compounds and of the hydroxides from Family I to VII have been referred to. Another fact of great importance is that the elements of Group I are the most strongly marked base-forming elements, while those of Group VII are the most strongly marked acid-forming elements. Passing in either direction, the character of the elements becomes less pronounced, until in the middle (Group IV), elements which form neither strongly-marked acids nor strongly-marked bases are found. Thus, beginning with sodium, this element forms a strong base, magnesium forms a weaker base, and the hydroxide of aluminium is a still weaker base. Beginning, on the other hand, with chlorine at the other end of the same series, its hydrogen compound is a strongly-marked acid; that of sulphur is an acid, but less marked in character than hydrochloric acid; that of phosphorus has no acid properties, nor has that of silicon. The hydroxides of these four elements have acid properties. Each one, however, forms several acids, and it is difficult to compare them, as some of those of chlorine are strongly marked and others are not, as we have seen.

Some very interesting variations in properties are also noticed in passing from one end of a group of a natural family to the other. Thus in Group B, Family VII, the activity of the elements grows less from fluorine to iodine, or, as we commonly say, fluorine is the most active element in the group, and then follow, in order, chlorine, bromine, and iodine.

The remarkable relations above referred to are summed up in the periodic law:

*The properties of an element are periodic functions of the atomic weight.*

It appears that if an element has a certain atomic weight it must have certain properties, and that if the atomic weight is known the properties can be stated, just as, if the properties are known, the atomic weight can be

approximately stated. When the law was first stated, Mendeléeff predicted the discovery of certain elements to fill some of the vacant places in the table. At that time the elements gallium, Ga, scandium, Sc, and germanium, Ge, were not known. Not only was their discovery predicted, but their properties were clearly stated years before they were brought to light. Not long afterward these three elements were discovered, and there is a remarkable agreement between their properties as determined by observation and as foretold by Mendeléeff by the aid of the periodic law.

The relations between the atomic weights and properties will appear more and more clearly as our knowledge of the elements advances. The natural arrangement of the elements suggested by the periodic law is adopted in this book. The elements hydrogen, oxygen, and chlorine were studied at the outset in order to illustrate the methods of studying chemical problems, and as examples of chemical elements in general. It is, however, now time to take up the elements systematically, and to learn what may be necessary in regard to them in order to get as clear a notion as possible of the facts and principles of the science of chemistry.

**Plan to be followed.**—The most systematic method of procedure in studying the elements would be to begin with Family I, Group A (see Lothar Meyer's Table, p. 191), then to take up Group B of the same family; and so on in order, ending with Family VIII. It seems better, however, to begin with Family VII; to follow with Families VI, V, and IV; and then to take up in order Families I, II, III, and VIII. The main reason for this is that it is impossible to study most of the members of Families I, II, III, and VIII without a knowledge of several of the elements of Families VII, VI, V, and IV, while these last families can be studied with only slight reference to the others. It is proposed then to begin with Group B, Family VII, the members of which are very much like chlorine. The only member of Group A of this family is manganese. While manganese resembles the members of

the chlorine group in some respects, it has other properties which ally it to the so-called base-forming elements. So also the members of Group A, Family VI, are like the members of the oxygen or sulphur group, but they are also allied to the base-forming elements. A similar difference is observed between the members of Groups A and B, Family V.

While the plan above sketched takes into consideration the greater number of analogies of the elements, there are other analogies that are not brought out. Thus, as will be seen in due time, the elements aluminium, chromium, manganese, and iron are analogous in some respects, but by following the plan sketched, they will be taken up in different groups. This appears to be justified, however, when we take into account the whole conduct of these elements, and do not confine ourselves to a study of a few reactions which, being useful for analytical purposes, have been studied more carefully than others which from a scientific point of view are just as important.

But, making all concessions, it must be acknowledged that the periodic law gives only an imperfect view of the relations between the elements. That there is a close connection between the properties of an element and its atomic weight is clear, and until we have some better guide to the classification of the elements than the periodic law, it seems wise to follow this.

## CHAPTER XII.

### THE ELEMENTS OF FAMILY VII, GROUP B: FLUORINE.—CHLORINE.—BROMINE.—IODINE.

**General.**—The elements of this group are commonly called the *halogens*. The best known member of the group is chlorine. Although fluorine is in general like the other members of the group, it differs from them in some respects. While chlorine, bromine, and iodine accompany one another in nature, fluorine compounds are not generally found in company with compounds of the other elements of the family. In those cases in which chlorine, bromine, and iodine are found together, chlorine is generally present in largest quantity, and iodine in smallest quantity. Fluorine and chlorine are gases under ordinary conditions, while bromine is a liquid and iodine is a solid. Fluorine, bromine, and iodine form with hydrogen the compounds hydrofluoric acid, HF, hydrobromic acid, HBr, and hydriodic acid, HI, which are analogous to hydrochloric acid. All these compounds are gases which have marked acid properties. With oxygen, fluorine does not combine, whereas chlorine, bromine, and iodine combine with it in a number of proportions, as has already been seen in the case of chlorine. Among themselves these elements also form some compounds. Thus bromine and chlorine form the compound BrCl; iodine forms the compounds ICl, $ICl_3$, IBr, and $IF_5$. It appears from this that the valence of iodine towards bromine is 1, towards chlorine 3, and towards fluorine 5.

Towards base-forming members the elements of this group are univalent, as shown in such compounds as NaCl, KBr, $CaCl_2$, KI, etc.

## Bromine, Br (At. Wt. 79.96).

**Occurrence.**—Bromine occurs in nature in company with chlorine. Chlorine, as has been stated, occurs mostly in combination with sodium, as sodium chloride, or common salt. In several of the great salt-beds bromine occurs in the form of sodium bromide, NaBr, and in some places it occurs as magnesium bromide, $MgBr_2$, especially in the great beds at Stassfurt. The chief source of bromine in the United States is the mother-liquors from the salt-works, especially in Michigan, Southern Ohio and West Virginia. When a solution containing a large quantity of sodium chloride and a small quantity of the bromide is evaporated, the chloride is first deposited, and from the mother-liquors the bromide mixed with chloride is deposited.

**Preparation.**—Bromine can be prepared from the bromides in the same way that chlorine is made from the chlorides. The reaction is represented by the equation

$$2NaBr + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Br_2.$$

Another method for the preparation of bromine depends upon the fact that chlorine has the power to set bromine free from its compounds. If, therefore, a solution containing a bromide is treated with manganese dioxide and hydrochloric acid, the chlorine set free from the hydrochloric acid will act upon the bromide, and bromine will be given off.

**Properties.**—Bromine is a heavy, dark-red liquid at ordinary temperatures. If exposed to the air it is converted into a vapor of a brownish-red color. It boils at 58–58.6°, and at − 7.3° it solidifies. It has an extremely disagreeable odor, to which fact it owes its name (from βρῶμος, a stench). From carbon bisulphide at − 90° it crystallizes in fine dark-red needles.

Its properties are similar to those of chlorine. It acts violently upon organic substances, attacking the skin, and the membranes lining the passages of the throat and lungs. Wounds caused by the liquid coming in contact

with the skin are painful and serious, and it must therefore be handled with great care.

Like chlorine, bromine is dissolved by water, one part dissolving in 33.3 parts at 15°. The solution, which has a reddish color and the odor of bromine, is called *bromine water*. At a low temperature bromine forms with water a compound in every way analogous to chlorine hydrate, *viz.*, bromine hydrate, $Br_2 + 10H_2O$. This decomposes when left in contact with the air at ordinary temperatures.

**Chemical Conduct of Bromine.**—Bromine acts chemically like chlorine. It was pointed out that chlorine acts in three ways: (1) By direct addition; (2) by substitution; and (3) by liberating oxygen from water, as in bleaching and other oxidizing processes. Bromine is also capable of acting in all three ways.

**Uses of Bromine.**—Bromine and its compounds are used in photography, in medicine, and to some extent in the manufacture of coal-tar colors.

**Manufacture of Bromine.**—Bromine is made in Germany from the Stassfurt deposits, and in the United States. In 1905 Germany produced 700 tons and the United States 596 tons. In Germany bromine is obtained from the mother-liquors of carnallite ($MgCl_3K$, magnesium potassium chloride containing magnesium bromide) in the manufacture of potassium hydroxide. In this process the potassium chloride is separated from magnesium chloride and bromide by crystallization and is then electrolyzed, forming potassium hydroxide and chlorine. This chlorine either as gas or liquefied is used to set free the bromine, which is then driven out of the solution by a current of steam. This process is also used in the United States. In both countries bromine is, further, obtained by electrolysis of the bromides. Whether the chemical or electrolytic process is best depends upon the local market value of chlorine.

**Hydrobromic Acid,** HBr.—The only compound that bromine forms with hydrogen alone is hydrobromic acid. This is in all respects very much like hydrochloric acid.

It is set free from bromides by the action of sulphuric acid, but owing to its instability it acts upon the sulphuric acid causing decomposition. Hydrochloric acid does not act upon sulphuric acid at all. Hydrobromic acid acts according to the following equation:

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$

The action consists in the decomposition of the hydrobromic acid into bromine and hydrogen and the subsequent action of the nascent hydrogen upon the sulphuric acid thus:

$$2HBr = 2H + Br_2; \text{ and}$$
$$H_2SO_4 + 2H = 2H_2O + SO_2.$$

The hydrobromic acid acts here as a reducing agent, and the sulphuric acid as an oxidizing agent. It is plain that hydrobromic acid cannot be made in pure condition by the action of sulphuric acid upon a bromide. Some of the hydrobromic acid, to be sure, escapes the action of the sulphuric acid, but at best it is always mixed with sulphur dioxide, $SO_2$, which is a gas, and with bromine.

The method commonly adopted in the laboratory for the preparation of hydrobromic acid consists in treating phosphorus with bromine and water. The bromine acts first upon the phosphorus, forming the product $PBr_3$ or $PBr_5$ according to the proportions of the substances used. Both these substances are decomposed by water, the first forming phosphorous acid and hydrobromic acid, according to this equation:

$$PBr_3 + 3H_2O = PO_3H_3 + 3HBr;$$

the second forming phosphoric acid and hydrobromic acid:

$$PBr_5 + 4H_2O = PO_4H_3 + 5HBr.$$

The gas thus formed can be freed from bromine by passing it through a tube containing phosphorus.

**Properties.**—Hydrobromic acid is a colorless gas that forms fumes in contact with the air in consequence of its power of combining with water. It solidifies at — 87.9°.

Its boiling point is — 64.9°. It dissolves in water in large proportion. The solution conducts itself much like hydrochloric acid.

Bromides, especially potassium bromide, are used in medicine. The physiological action consists in a lessening of nerve and brain activity inducing sleep.

**Compounds of Bromine with Hydrogen and Oxygen.**— With hydrogen and oxygen bromine forms compounds that closely resemble those which chlorine forms with the same elements. They are: Hypobromous acid, HBrO; bromic acid, $HBrO_3$; and perhaps perbromic acid, $HBrO_4$.

## Iodine, I (At. Wt. 126.97).

**Occurrence.**—Iodine occurs associated with chlorine and bromine in nature, but in smaller quantity than these. The relative quantity in sea-water is extremely small. The sea-plants, however, assimilate it, and the ashes of these plants contain a considerable quantity of compounds of iodine. It also occurs in the great beds of soda saltpetre, or sodium nitrate, which are found in Chili, South America. It occurs in small quantity in combination with silver, and also in combination with lead and with mercury; and in the thyroid glands of human beings and other animals.

**Preparation.**—The method of obtaining iodine from iodides is like that used in making chlorine and bromine from the chlorides and bromides. It consists in treating the iodides either with sulphuric acid and manganese dioxide, or with chlorine:

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$
$$2KI + Cl_2 = 2KCl + I_2.$$

The iodine, although solid at the ordinary temperature, is easily volatilized, and if the mixtures mentioned are heated, iodine vapor passes over and may be condensed in appropriately arranged vessels.

On the large scale iodine is obtained either from seaweed or from the mother liquors of Chili saltpetre. On

the coasts of Scotland, Ireland, and France the seaweed thrown up by storms is gathered, dried, and burned. In this method much iodine was wasted, partly by exposure, partly by volatilization in burning. The incombustible residue is called *kelp*. It contains a small percentage of potassium iodide, from 0.5 to 2 per cent according to the seaweed used.

The iodine occurring in Chili saltpetre, $NaNO_3$, is in the form of sodium iodate, $NaIO_3$, and iodide, NaI, and to some extent as magnesium iodide, $MgI_2$. The competition of iodine made from this material has led to a careful study of the process for obtaining iodine from kelp. Seaweed is now collected from certain parts of the ocean where it grows in large quantity, vessels being sent out for the purpose.

**Commercial Production of Iodine.**—In 1905, 300 tons of iodine were made from Chili saltpetre, and 294 tons from kelp, Scotland producing 130 tons, Japan 90, France 50, and Norway 24. There are different processes for treating the seaweed; the most scientific are those in which the fresh weed is allowed to ferment in tanks till it begins to rot and is then burned. In the fermentation alkaline sulphides and hydrogen sulphide are formed from organic sulphur compounds in the weed; the hydrogen sulphide reduces the organic iodine compounds to hydriodic acid which acts on the alkaline sulphides to form iodides. Iodides are not volatilized by burning the weed. The yield of iodine is tripled by this process.

The mother-liquor of Chili saltpetre contains 22 per cent sodium iodate. Iodine is obtained from it by reduction with sodium sulphite and sodium bisulphite:

$$2NaIO_3 + 3Na_2SO_3 + 2NaHSO_3 = 5Na_2SO_4 + H_2O + 2I.$$

The iodine is precipitated and is then purified by sublimation.

**Properties.**—Iodine is a grayish-black crystallized solid. At ordinary temperatures it is volatile. It melts at 116°, and boils at 183°. The vapor has a violet color when mixed with air. When pure the vapor is intensely blue.

At temperatures considerably above the boiling-point the specific gravity of iodine vapor is such as to show that its molecular weight is approximately 254, or twice the atomic weight. As the temperature is raised, however, the specific gravity is lowered, until, finally, at a very high temperature, it becomes about half what it is at lower temperatures. This is accounted for by assuming that at the lower temperatures the molecules of iodine consist of two atoms each, while as the temperature is raised these molecules are gradually broken down, so that at the temperature at which the lowest specific gravity is reached the iodine vapor consists of free atoms, or the atoms and molecules are then identical, and the specific gravity is therefore only half what it is when the molecules consist of two atoms.

Iodine has a characteristic strong taste. It acts upon the mucous membranes, but much less energetically than chlorine or bromine. It colors the skin yellowish-brown.

Tincture of iodine acts as a counter-irritant on bruises and sprains. Goitrous swellings of the throat are caused by a lack of the normal iodine compound which is present in the thyroid glands of persons in health. The thyroid gland of the sheep is particularly rich in this compound which is called *thyroiodine*, and contains 9.3 per cent of iodine. It is now extracted from the sheep glands and used as a remedy for goitre.

Iodine dissolves slightly in water, easily in alcohol, and easily in a water solution of potassium iodide. The solution in alcohol is known as tincture of iodine. It dissolves also in carbon bisulphide, $CS_2$, and in chloroform, forming solutions which have a beautiful deep-violet color.

In general, iodine conducts itself chemically like bromine and chlorine, only it acts in almost all reactions less energetically than the other two elements. It combines directly with a number of elements, as with hydrogen, sulphur, phosphorus, iron, mercury, etc. In presence of water it acts as an oxidizer just as chlorine and bromine

do, but less energetically. Thus it oxidizes sulphurous acid, $H_2SO_3$, to sulphuric acid, $H_2SO_4$:

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

As a substituting agent it does not act as readily as chlorine and bromine, though iodine substitution-products are made in large quantities, particularly in connection with the manufacture of dye-stuffs.

Iodine is used extensively in the dye-stuff industry, in photography, and in medicine.

**Hydriodic Acid,** HI.—Pure hydriodic acid cannot be made by treating an iodide with sulphuric acid. The hydrogen of the hydriodic acid acts upon the sulphuric acid very readily, and according to the conditions the following reactions may take place:

$$H_2SO_4 + 8HI = 4H_2O + SH_2 + 4I_2;$$
$$H_2SO_4 + 6HI = 4H_2O + S + 3I_2;$$
$$H_2SO_4 + 2HI = 2H_2O + SO_2 + I_2.$$

On treating potassium iodide with sulphuric acid, therefore, there may be formed, in addition to hydriodic acid and free iodine, sulphur dioxide, sulphur and hydrogen sulphide.

The method adopted for the preparation of hydriodic acid is like that used for the preparation of hydrobromic acid.

**Properties.**—Hydriodic acid is a colorless transparent gas like hydrochloric and hydrobromic acid. It solidifies at — 50.8°, and boils at — 34.1°. It also like these dissolves in water in large quantity, and when brought in contact with the air it forms dense white fumes. When boiled the water solution conducts itself like those of hydrochloric and hydrobromic acids.

When heated, the gas begins to decompose at 180°, and at higher temperatures the decomposition takes place rapidly. The products are simply hydrogen and iodine. In consequence of the ease with which hydriodic acid breaks down, yielding free hydrogen, it is an excellent

reducing agent, and it is frequently used in the laboratory for the purpose of extracting oxygen from substances. Its action upon sulphuric acid has already been spoken of. The reason why it acts so well as a reducing agent is that the hydrogen is separated from the iodine with little expenditure of energy, and the hydrogen thus separated is in the nascent state.

It has been seen that hydrochloric acid is a stable substance, and that hydriodic acid is unstable, and that it requires less chemical energy to decompose hydriodic acid than hydrochloric. It also requires less heat energy. When one gr. mol. wt. hydrochloric acid in aqueous solution is decomposed, 39,300 calories heat are absorbed, while for one gr. mol. wt. hydriodic acid 13,100 calories are absorbed.

**Electrical Energy Required to Electrolyze different Electrolytes.**—If different amounts of chemical energy and heat energy are required to decompose these acids it may be inferred that different amounts of electrical energy would be required. This is the case.

On page 150 it is stated that electrical energy is the product of two factors, the amount of electricity and the electro-motive force or difference in potential, the unit of the latter being the volt. The *amount* of electricity was compared with the volume of water in a stream passing a given point, the difference in potential with the fall or pressure of the water at that point.

If the fall of water on a water-wheel in a saw-mill gives just pressure enough to saw a log one foot in diameter, an attempt to saw a log two feet in diameter stops the wheel.

A current of an electro-motive force of 0.53 volts suffices to electrolyze hydriodic acid. An attempt to electrolyze hydrochloric acid with this current would stop the flow of electricity, a current of 1.41 volts electro-motive force being required to electrolyze hydrochloric acid.

While according to Faraday's first law, the *amount* of electricity required to electrolyze one equivalent of every electrolyte is the same, the *electro-motive force* required

and hence the *electric energy* required is greater or less according to the stability of the electroiyte.

**Iodic Acid,** $HIO_3$.—This compound is strictly analogous to chloric and bromic acids, but differs from them in being much more stable.

When iodine is dissolved in an alkali the reaction that takes place is the same as that which takes place with chlorine and bromine under like circumstances. A mixture of the iodide and iodate is formed:

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

Iodic acid is a crystallized solid. When heated to 170° it loses water and is converted into iodine pentoxide, $I_2O_5$:

$$2HIO_3 = I_2O_5 + H_2O.$$

Its salts have the general formula $MIO_3$, though it also forms salts $MH(IO_3)_2$ and $MH_2(IO_3)_3$. It gives up its oxygen readily and is therefore a good oxidizing agent just as hydriodic acid is a good reducing agent.

**Iodine Pentoxide or Iodic Anhydride,** $I_2O_5$.—This compound is formed, as was stated in the last paragraph, by heating iodic acid to 170°. It is a white solid, easily soluble in water, and forming iodic acid with it. It is decomposed when heated to 300°. It will be observed, therefore, that this compound of iodine and oxygen is much more stable than any of the compounds of chlorine or bromine and oxygen; and it is interesting to note that as the stability of the oxygen compounds of these elements increases, that of the hydrogen compounds decreases.

**Anhydrides, or Acidic Oxides.**—An oxide which, like iodine pentoxide, forms an acid when dissolved in water, or which forms salts by treatment with basic hydroxides, is called an *anhydride* or *acidic oxide*. The oxides of the base-forming elements form bases when dissolved in water, and they are, therefore, called *basic oxides*. As examples of acidic oxides or anhydrides, there may be mentioned, besides iodic anhydride, sulphuric anhydride, $SO_3$; sul-

phurous anhydride, $SO_2$; phosphoric anhydride, $P_2O_5$; carbonic anhydride, $CO_2$. When dissolved in water these oxides are converted into acids as represented in these equations:

$$SO_3 + H_2O = H_2SO_4;$$
$$SO_2 + H_2O = H_2SO_3;$$
$$P_2O_5 + H_2O = 2HPO_3;$$
$$CO_2 + H_2O = H_2CO_3.$$

Silicic anhydride, $SiO_2$, is an example of an acidic oxide that does not dissolve in water,* but it does form salts when treated with basic hydroxides:

$$SiO_2 + 2KOH = K_2SiO_3 + H_2O.$$

As examples of basic oxides or oxides which when treated with water yield bases, the following may be taken: Calcium oxide, CaO; potassium oxide, $K_2O$; barium oxide, BaO. As has already been shown, when treated with water these are respectively converted into calcium hydroxide, $Ca(OH)_2$; potassium hydroxide, KOH; and barium hydroxide, $Ba(OH)_2$. There are, however, many basic oxides which do not dissolve in water,* but which, nevertheless, have the power to neutralize acids and form salts. (See p. 178.)

**Periodic Acid,** $H_5IO_6$.—This acid is analogous to perchloric acid. Its salts are formed by oxidation of iodates or by heating iodates, just as perchlorates are formed by heating chlorates. The simplest way to make a periodate is to pass chlorine into a solution containing sodium hydroxide and sodium iodate, when a reaction takes place which is at least partly represented by the following equation:

$$NaIO_3 + 3NaOH + Cl_2 = Na_2H_3IO_6 + 2NaCl.$$

The salt $Na_2H_3IO_6$ is difficultly soluble in water, and therefore separates from the solution. From the sodium

*The expression "does not dissolve in water" is not strictly correct. It generally is equivalent to "very slightly soluble."

salt the corresponding silver salt, $Ag_2H_3IO_6$, can be obtained, and when this silver salt is treated with nitric acid it is converted into the simpler salt, $AgIO_4$, which is evidently derived from the simpler acid, $HIO_4$:

$$2Ag_2H_3IO_6 + 2HNO_3 = 2AgNO_3 + 4H_2O + 2AgIO_4.$$

The acid when separated from its solutions is a crystallized solid of the composition $H_5IO_6$. When heated it undergoes decomposition, losing water and oxygen, and yielding iodic acid. It cannot, however, be converted into a compound of the composition $HIO_4$, for the loss of water is always accompanied by a loss of oxygen. Like iodic acid, periodic acid is a good oxidizing agent because it gives up its oxygen easily.

**Compounds of Iodine with Chlorine.**—When chlorine is passed over dry crystallized iodine it is absorbed, and a compound of the formula ICl is formed. This is a thick reddish-brown, very volatile liquid. Under proper conditions it solidifies in crystals, of which two kinds with different melting-points, 14° and 27°, have been described. Iodine chloride is decomposed by water, the products being iodic acid, hydrochloric acid, and free iodine.

If the passage of chlorine over iodine is continued beyond the point required for the formation of the simple compound ICl, the trichloride $ICl_3$ is formed. This is a crystallized compound of a yellow color. When heated it breaks down into chlorine and iodine monochloride. When treated with water it is partly dissolved without decomposition, but it is partly decomposed, yielding iodic acid, iodine monochloride, and hydrochloric acid.

**Compound of Iodine with Bromine.**—There is only one compound of iodine and bromine known, and this has the formula IBr. It is a crystallized compound formed by direct combination of the two elements. It is decomposed by heat and by water.

## Fluorine, F (At. Wt. 19).

**Occurrence.**—This element occurs in large quantity in nature, and is widely distributed, but it is always in com-

bination with other elements. It is found chiefly in combination with calcium, as *fluor-spar* or *calcium fluoride*, $CaF_2$, and in combination with sodium and aluminium, as *cryolite*, a mineral of the composition $Na_3AlF_6$ or $AlF_3.3NaF$ occurring abundantly in Greenland. It is called fluorine from the fact that it occurs in fluor-spar, which in turn receives its name for the reason that it melts when heated and is therefore used as a flux in heating chemical substances together (from *fluo*, I flow). On account of the remarkable power of combination of fluorine with other elements, all attempts to prepare it in the free condition failed until 1886, when its isolation was effected by Moissan by passing an electric current through a solution of acid potassium fluoride, $KHF_2$, in dry hydrofluoric acid contained in a platinum vessel. It has since been shown that a copper vessel may be used.

**Properties.**—Fluorine is a light greenish-yellow gas of penetrating odor. It solidifies at $-$ 233° and boils at $-$ 187°. It is the most active of all the elements. Thus, it decomposes water, yielding ozone and hydrofluoric acid; it combines directly with hydrogen at the ordinary temperature, and even at $-$ 253° *solid* fluorine combines explosively with liquid hydrogen. Lead, iron, the alkali metals, calcium, barium and strontium combine with fluorine gas at ordinary temperature burning with great violence. Copper is instantly covered with a dense coating of copper fluoride protecting the metal from further action. Magnesium, aluminium, nickel, and silver also burn in fluorine, but they must first be warmed. Gold and platinum are not acted upon by fluorine at ordinary temperature, but combine with it at between 300° and 400°. Nitrogen, oxygen, and chlorine, however, do not combine with fluorine.

**Hydrofluoric Acid,** HF.—Hydrofluoric acid is made by treating a fluoride with sulphuric acid. Thus, when calcium fluoride or fluor-spar is used, this reaction takes place:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The reaction must be performed in vessels of platinum or lead, as glass is disintegrated by the acid. In perfectly pure anhydrous condition it can be obtained by heating the pure dry salt $KHF_2$, known as acid potassium fluoride. It is a liquid that boils at — 19.4° and solidifies at — 92.3°. The pure dry acid in the liquid form does not act upon glass. It does not dissolve the acid-forming elements but does dissolve most of the base-forming elements, with evolution of hydrogen and formation of fluorides. The gas acts upon the skin, causing swellings and violent pains. Inhaled it is poisonous. To preserve it, vessels of platinum, caoutchouc, or paraffin must be used. In the moist condition it attacks glass, converting the silicon into the fluoride, $SiF_4$, and the metals into their fluorides. A silicate of the formula $CaSiO_3$ would undergo the changes represented in the following equation:

$$CaSiO_3 + 6HF = CaF_2 + SiF_4 + 3H_2O.$$

Silicon fluoride is a gas, and calcium fluoride is soluble in acids. Thus calcium silicate, which is insoluble in water, is so changed by hydrofluoric acid as to be rendered soluble. In a similar way glass, which is a compound resembling calcium silicate, is rendered soluble, or is, as we commonly say, dissolved, by hydrofluoric acid.

When an aqueous solution of hydrofluoric acid is boiled it passes over at 120°, and the distillate contains 36 to 38 per cent of the acid.

Hydrofluoric acid is used for the purpose of etching glass, particularly for marking scales on thermometers and other graduated glass instruments. The glass is covered with a thin layer of wax or paraffin and, at the places where the etching is required, marks are made through the paraffin, so that the glass is exposed. Those parts of the glass which are covered are not acted upon by the hydrofluoric acid, while those parts which are not covered are corroded and, when the paraffin is removed, permanent marks are found corresponding to those made through the paraffin. A solution of hydrofluoric acid in

water is manufactured and sold in rubber or paraffin bottles.

The specific gravity of hydrofluoric acid gas at about 100° leads to the molecular weight corresponding to the formula HF, fluorine having the atomic weight 19. At about 30° the specific gravity corresponds to the formula $H_2F_2$. At lower temperatures the molecular weight appears to be still greater.

### Family VII, Group A—Manganese.

Manganese belongs to the same family as the halogens, and resembles them in some respects, but at the same time it differs from them markedly in other respects. It acts in fact in two ways, and is one of those elements, already referred to, that are both acid-forming and base-forming. Some of its compounds with hydrogen and oxygen are distinctly acid, others are distinctly basic. So far as it acts like the members of the chlorine family a brief reference to it here is desirable. On the other hand, it will be dealt with chiefly in connection with those base-forming elements which it most resembles, as, for example, iron.

Manganese occurs in nature principally in the form of *pyrolusite* or manganese dioxide, $MnO_2$, also known as the black oxide of manganese. It forms with oxygen compounds of the following formulas: MnO, $Mn_2O_3$, $Mn_3O_4$, $MnO_2$, and $Mn_2O_7$. When a compound of manganese is subjected to the influence of powerful oxidizing agents in the presence of an alkali it is converted into a salt of *manganic acid*, $H_2MnO_4$, which in its composition resembles sulphuric acid. If the salt of manganic acid thus obtained is dissolved in water it undergoes partial decomposition, which is complete if the solution is boiled, or if carbon dioxide is passed through it. The change consists in the transformation of manganic acid into *permanganic acid*, $HMnO_4$:

$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O;$$ or
$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

*Permanganic acid*, $HMnO_4$, is a compound which in many respects resembles perchloric acid. It can be obtained in water solution by decomposition of certain of its salts, but like perchloric acid it is easily decomposed. In consequence of the ease with which it gives up oxygen it is a good oxidizing agent, and is extensively used in the laboratory in this capacity. It is employed in the form of the potassium salt, *potassium permanganate*, $KMnO_4$, which will receive special attention under the head of Manganese Compounds. In order, however, to make clear the difference in conduct between perchloric and permanganic acids a few characteristic facts will be mentioned here. The conduct of permanganic acid and of potassium permanganate will be understood, if it is borne in mind that in the presence of substances of strongly acid character manganese tends to act as a base-forming element, and in this capacity to form salts with the acids. Thus in presence of sulphuric acid potassium permanganate forms potassium sulphate, manganous sulphate, and oxygen, if there is anything present which has the power to take up oxygen. In the salts in which it plays the part of a metal manganese is generally bivalent. With hydrochloric acid, as we have already seen in studying the action of hydrochloric acid upon manganese dioxide, it forms the chloride $MnCl_2$. When now potassium permanganate is treated with hydrochloric acid it is decomposed according to the following equation:

$$2KMnO_4 + 6HCl = 2KCl + 2MnCl_2 + 3H_2O + 5O.$$

The nascent oxygen, further, acts on more hydrochloric acid to form chlorine:

$$5O + 10\ HCl = 5Cl_2 + 5H_2O.$$

Similarly, with sulphuric acid manganous sulphate is formed, thus:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Such reactions do not take place with perchloric acid, as

chlorine is entirely lacking in the power to enter into acids in the place of the hydrogen and form salts.

Manganese forms some other acids besides permanganic acid, but they exhibit little or no analogy with compounds of chlorine, and their study will therefore be postponed until manganese itself is taken up. The point of chief interest to be noted here is that this element is unmistakably like chlorine in its highest oxygen compounds, but entirely different from it in most of its compounds. The compound *manganese heptoxide*, $Mn_2O_7$, stands in the relation of an anhydride to permanganic acid. In water solution it forms the acid:

$$Mn_2O_7 + H_2O = 2HMnO_4.$$

It is formed by treating potassium permanganate with the most concentrated sulphuric acid:

$$2KMnO_4 + H_2SO_4 = K_2SO_4 + Mn_2O_7 + H_2O.$$

It is extremely unstable, giving up oxygen readily. In contact with organic substances or other substances which have the power to take up oxygen it decomposes so rapidly as frequently to lead to explosions. It is plainly analogous to the oxide of chlorine of the formula $Cl_2O_7$.

## EXPERIMENTS.

### Preparation of Bromine.

Experiment 87.—Mix 3.5 grams potassium bromide and 7 grams manganese dioxide Put the mixture into a 500 cc. flask; connect with a condenser (see Fig. 31) Mix 15 cc. concentrated sulphuric acid and 90 cc. water. After cooling pour the liquid on the mixture in the flask. Gently heat, when bromine will be given off in the form of vapor. A part of this will condense and collect in the receiver. Perform this experiment under a hood with a good draught.

### Hydrobromic Acid.

Experiment 88.—In a small porcelain evaporating-dish put a few crystals of potassium bromide. Pour on them a few drops of concentrated sulphuric acid. The white fumes of hydrobromic acid and the reddish-brown vapor of bromine are noticed. Treat a few

crystals of potassium or sodium chloride in the same way. What difference is there between the two cases?

The preparation of hydrobromic acid may be shown in the lecture-room as follows:

EXPERIMENT 89.—Arrange an apparatus as shown in Fig 42. In the flask put 1 part red phosphorus and 2 parts water. Let 10 parts

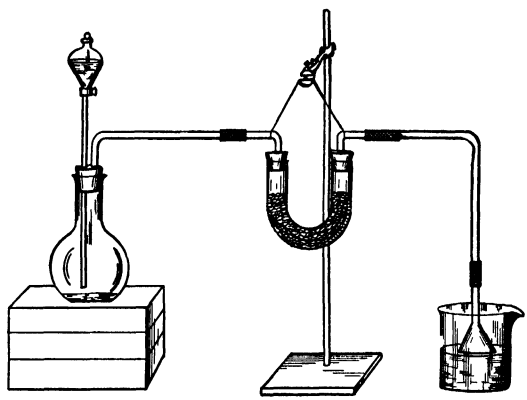


FIG. 42

bromine gradually drop into the flask from the glass-stoppered funnel. Pass the gas through a U-tube loosely packed with asbestos containing moistened red phosphorus in order to free the hydrobromic acid from bromine, which to some extent passes over with it. Collect some of the gas in water, and examine the solution. How does the gas act when allowed to escape in the air? Fill a cylinder with the gas in the same way as was done with hydrochloric acid, and fill another with chlorine. While covered with glass plates bring their mouths together. Then withdraw the plates. What change is observed? What is this due to?

EXPERIMENT 90.—To a dilute solution of sodium hydroxide add bromine water made by shaking up a little liquid bromine in a bottle with water. What change takes place? Add sulphuric acid until the liquid shows an acid reaction. What takes place? The changes here referred to are perfectly analogous to those which would take place if chlorine were used instead of bromine. Shake a solution containing a little free bromine with ether; with chloroform; with carbon bisulphide. What changes do you observe?

## IODINE.

EXPERIMENT 91.—Mix about 2 grams of sodium or potassium iodide and 4 grams manganese dioxide. Treat with a little con-

centrated sulphuric acid in a one- to two-liter flask. Heat gently on a sand-bath. Gradually the vessel will be filled with the beautiful colored vapor of iodine. In the upper parts of the flask some of the iodine will be deposited in the form of crystals of a grayish-black color.

EXPERIMENT 92.—Make solutions of iodine in water, in alcohol, and in a water solution of potassium iodide. Use small quantities in test-tubes.

EXPERIMENT 93.—Dissolve a piece of potassium iodide the size of a small pea in about 100 cc. water in a stoppered cylinder. Add enough carbon bisulphide to make a layer about an inch thick at the bottom of the cylinder. Shake the two liquids together. Does the carbon bisulphide become colored? Add a drop of chlorine water and shake again What difference do you observe in the two cases? Explain this. Try the same experiment, using chloroform instead of carbon bisulphide.

### IODINE CAN BE DETECTED BY MEANS OF ITS ACTION UPON STARCH-PASTE.

EXPERIMENT 94.—Make some starch-paste by covering a few grains of starch in a porcelain evaporating dish with cold water, grinding this to a paste, pouring 200–300 cc. boiling hot water on it, and stirring. After cooling add a little of this paste to a dilute water solution of iodine in a solution of potassium iodide in water. The solution will turn blue. Now add a little of the paste to a dilute water solution of potassium iodide alone. Is there any change? Add a drop or two of chlorine water. Why the difference? Will not chlorine water alone act this way toward starch-paste?

### ACTION OF SULPHURIC ACID UPON POTASSIUM IODIDE.

EXPERIMENT 95.—Bring a piece of potassium iodide the size of a pea in a dry test-tube; add *one* drop of water and three or four drops of concentrated sulphuric acid; the salt becomes brown; heat gently; violet-colored vapor escapes, and with it a gas with an odor like that of rotten eggs. At the same time a yellow coating appears on the inside of the tube above the acid. Add five or six drops more of the acid and continue to heat gently. The bad odor first noticed disappears gradually, and another, quite different odor, irritating to the throat, is now perceptible. This is sulphur dioxide, $SO_2$.

### IODIC ACID.

EXPERIMENT 96.—Pass chlorine into a test-tube containing iodine in suspension in water; or add chlorine water. What becomes of the iodine?

EXPERIMENT 97.—Add chlorine water to a dilute solution of potassium iodide, and note the successive changes.

EXPERIMENT 98.—Dissolve iodine in caustic soda. Add an acid to the solution. Explain the changes.

## HYDROFLUORIC ACID.

EXPERIMENT 99.—In a lead or platinum vessel put a few grams (5–6) of powdered fluor-spar and pour on it enough concentrated sulphuric acid to make a thick paste. Cover the surface of a piece of glass with a thin layer of wax or paraffin, and through this scratch some letters or figures, so as to leave the glass exposed where the scratches are made. Put the glass over the vessel containing the fluor spar, and let it stand for some hours, Take off the glass, scrape off the coating, and the figures which were marked through the wax or paraffin will be found *etched* on the glass.

## CHAPTER XIII.

### THE ELEMENTS OF FAMILY VI, GROUP B : SULPHUR.—SELENIUM.—TELLURIUM.

**Introductory.**—The elements of this group bear to oxygen relations somewhat similar to those which the elements of group B, Family VII, bear to fluorine. The three members sulphur, selenium, and tellurium resemble one another fully as strikingly as chlorine, bromine, and iodine do. Their compounds bear a general resemblance to those of oxygen, and yet they form characteristic compounds with oxygen, while oxygen forms no analogous compounds with any of them. Just as iodine forms a compound with fluorine of the formula $IF_5$, but fluorine does not form with iodine a compound $FI_5$, so sulphur, selenium, and tellurium form with oxygen the compounds $SO_3$, $SeO_3$, and $TeO_3$, while oxygen does not form analogous compounds with these other elements. The valence of the elements of this group towards hydrogen is 2, as shown in the compounds $H_2O$, $H_2S$, $H_2Se$, and $H_2Te$. Of oxygen and sulphur there are other hydrogen compounds, as hydrogen dioxide, $H_2O_2$, and an analogous compound of sulphur, but there is much uncertainty in regard to the constitution of the latter compound, and practically nothing is known in regard to the valence of sulphur in it. In general the hydrogen valence is constant. Towards the members of the chlorine group the valence varies from 2 to 6. Oxygen never exhibits a higher valence than 2 towards chlorine and its analogues. The compound $OCl_2$, illustrates the bivalence of oxygen towards chlorine. Sulphur forms with chlorine the compounds $S_2Cl_2$ and $SCl_2$ in both of which the sulphur is probably bivalent. It also forms the compound $SCl_4$, in which it is quadrivalent. With iodine it is said to form

the unstable compounds $S_2I_2$, and $SI_6$. With fluorine it forms the stable fluoride, $SF_6$. Selenium and tellurium form similar compounds, and the stability of the compounds of the members of the sulphur group with the members of the chlorine group increases in the order sulphur, selenium, tellurium.

Towards oxygen the three elements of the sulphur group are quadrivalent and sexivalent, as seen in the compounds $SO_2$, $SeO_2$, $TeO_2$, and $SO_3$, $SeO_3$, and $TeO_3$.

Of the three elements of this group sulphur occurs in greatest abundance in nature, selenium next in order, and finally tellurium. Just as bromine frequently accompanies chlorine, so selenium frequently accompanies sulphur, but it is always present in much smaller quantity than sulphur. Tellurium occurs in very small quantity relatively, and not uncommonly in combination with valuable metals like gold and silver. Large quantities of sulphur are found in the *native* or uncombined condition. Only extremely small quantities of selenium and tellurium are found native.

### Sulphur, S (At. Wt. 32.06).

**Occurrence.**—The principal deposits of native sulphur are found in Sicily, Italy, and Spain. In California and in Louisiana there are considerable deposits. Sulphur is found near dying or extinct volcanoes as a product of volcanic action, and in sedimentary rocks, largely as a product of bacterial and plant action. Some of the fresh water algæ store up so much sulphur that it forms 10–25 per cent of their living weight. Volcanic sulphur is formed by the action of sulphur dioxide on hydrogen sulphide:

$$2H_2S + SO_2 = 3S + 2H_2O.$$

Sedimentary sulphur is formed by the oxidation of hydrogen sulphide by oxygen from the air with or without the intervention of lower forms of life:

$$H_2S + O = H_2O + S.$$

The hydrogen sulphide is formed by the fermentation of cellulose in contact with gypsum. Both of these methods of making sulphur are in use in technical processes.

Sulphur occurs in nature, further, in the form of the hydrogen compound, hydrogen sulphide, $H_2S$, issuing from the earth in volcanic regions, and in solution in some natural waters known as "sulphur waters." The oxide $SO_2$ is likewise found issuing from the earth in volcanic regions. Compounds of sulphur with metallic elements, as with iron, copper, lead, zinc, are very abundant. Such compounds are iron pyrites, $FeS_2$; copper pyrites, $CuFeS_2$; galenite, PbS; and zinc blende, ZnS. Some sulphates are widely distributed and occur in large quantities; for example, gypsum and calcium sulphate, $CaSO_4 + 2H_2O$; barium sulphate, or heavy spar, $BaSO_4$; lead sulphate, $PbSO_4$. Finally sulphur occurs in a few animal and vegetable products in combination with carbon, hydrogen, and, generally, with nitrogen.

**Extraction of Sulphur from its Ores.**—By far the largest quantity of sulphur found in the market is taken from the mines in Sicily. Of these mines there are between 250 and 300. When taken from the mines it is mixed with many earthy substances, from which it must be separated. In Sicily the separation is generally effected by piling the ore so as to leave passages for air, covering the piles with earthy matter to prevent free access of air and then setting fire to them. A part of the sulphur burns, and this causes the rest of it to melt. The molten sulphur runs down to the bottom of the pile, and by a proper arrangement it is drawn off from time to time. If the pile of ore were not covered up, and the air were allowed to enter freely, the sulphur would burn up, and be converted into the gas, sulphur dioxide. The "crude brimstone" obtained in the manner described is afterwards refined by distillation, and it is this refined or distilled sulphur which is met with in the market under the names "roll brimstone" and "flowers of sulphur."

The distillation is carried on in retorts made of earthen-

ware, and these are connected with large chambers of brick-work. When the vapor of sulphur first comes into the condensing-chamber it is suddenly cooled, and hence deposited in the form of a fine powder. This is called "flowers of sulphur." After the distillation has continued for some time the vapor condenses in the form of a liquid, which collects at the bottom of the chamber. This is drawn off into slightly conical wooden moulds, and takes the form of "roll brimstone" or "stick sulphur."

Some sulphur is obtained from iron pyrites by heating in closed vessels. The change which takes place on heating iron pyrites is analogous to that which takes place on heating manganese dioxide in preparing oxygen. A sulphur compound of the formula $Fe_3S_4$ and free sulphur are formed in the former case, as the compound of manganese and oxygen, $Mn_3O_4$, and free oxygen are formed in the latter:

$$3FeS_2 = Fe_3S_4 + S_2;$$
$$3MnO_2 = Mn_3O_4 + O_2.$$

**World's Production of Sulphur.**—In 1901, 603,483 tons of sulphur were produced, of which Italy produced 563,096 tons and the United States only 6,976 tons. In 1906, owing to the development of the Louisiana deposits, 298,859 tons were produced in the United States. The Louisiana sulphur is obtained by the ingenious method of forcing superheated steam through pipes into the deep-lying sedimentary deposits, thus melting the sulphur and forcing the molten sulphur in *pure condition* through pipes to the surface.

**Properties.**—Sulphur is a yellow, brittle substance which at 50° is almost colorless. If heated rapidly it melts at 114.5°, forming a thin, straw-colored liquid. When heated to a higher temperature it becomes darker in color, and at 200° to 250° it is so viscid that the vessel in which it is contained may be inverted without danger of its running out. Finally, at 448.4° it boils, and is then converted into a brownish-yellow vapor. When molten sulphur solidifies, or when it is deposited

from a solution, it takes the form of crystals. But the crystals formed from molten sulphur are entirely different from those deposited from cold solutions of sulphur. The latter belong to the rhombic system. They are octahedrons with a rhombic base. And this is the form of the sulphur found in nature. The former are honey-yellow needles and belong to an entirely different system—the monoclinic.

The rhombic crystals of sulphur can be made by dissolving "roll brimstone" in carbon bisulphide and allowing the solution to stand. The formation of the needles or monoclinic crystals may be shown by melting a considerable quantity, say a pound or two, of roll brimstone in a sand or Hessian crucible, and allowing the liquid mass to cool slowly. When a thin crust has formed on the surface this should be perforated, and the remainder of the liquid sulphur poured off. The crucible will then be found lined with long, dark-yellow, lustrous needles. If the monoclinic needles are allowed to lie unmolested they gradually undergo change spontaneously. They lose their lustre and become lighter in color; and now they consist of minute crystals like those found in nature. They have changed to the rhombic form. It is evident, therefore, that the arrangement of the particles in the monoclinic crystals of sulphur is not a stable one at ordinary temperatures, whereas it has been shown that it is stable at temperatures above 100°. The change from the monoclinic to the rhombic form is accompanied by a considerable evolution of heat. Monoclinic sulphur melts at 119.25°.

At temperatures above 96.5° and below 119.25° sulphur crystallizes in the monoclinic form, at temperatures below 96.5° in the rhombic form. The temperature 96.5° is the *transition* temperature at which both forms can exist side by side.

Substances that crystallize in two distinct forms are called *dimorphous*. Carbon also crystallizes in two different forms, and this kind of relation is not uncommon. The difference between the two varieties of sul-

phur suggests that observed between the two forms of oxygen. Whether the explanation is the same in the two cases is doubtful.

Sulphur can also be obtained in the amorphous, or uncrystallized, condition. If sulphur is heated considerably above its melting-point and then quickly cooled under water it remains for some time soft and dough-like, and while in this condition it is amorphous. If allowed to stand it gradually becomes hard and brittle.

When separated from certain compounds in solution in water, the sulphur appears in finely-divided condition, and gives the liquid the appearance of milk. This is seen on adding hydrochloric acid to a solution of sodium thiosulphate, or hyposulphite, as it is generally called.

Certain varieties of sulphur dissolve completely in carbon bisulphide. This is true, for example, of the natural crystals and of those made artificially by deposition from a solution in carbon bisulphide. On the other hand, sulphur in the form of "flowers of sulphur" is only partly soluble in the liquid. There are therefore two forms of sulphur to be distinguished between, the *soluble* and the *insoluble*. The cause of the difference between these modifications is not known. "Stick sulphur" is mostly soluble, while in the "flowers of sulphur" there is at times a considerable percentage of the insoluble variety. The brittle sulphur formed when the molten sulphur suddenly cooled by water has hardened is a mixture of the crystalline and the amorphous. The sulphur precipitated from sodium hyposulphite by acids is also amorphous. Amorphous sulphur is insoluble, crystalline sulphur soluble in carbon bisulphide.

Sulphur is insoluble in water, and slightly soluble in alcohol and ether.

Sulphur is a much less active element than the members of the chlorine group, and also less active than oxygen. Generally speaking, however, it conducts itself like oxygen. It combines directly though not easily with hydrogen, and it combines readily with most metals, forming compounds called *sulphides* which, so far

as their composition is concerned, are analogous to the oxides. Thus when heated with iron, copper, or lead, it combines with them readily with evolution of heat and light.

In its chemical conduct it differs markedly from the members of the chlorine group. When heated to a sufficiently high temperature in the air or in oxygen sulphur forms the compound sulphur dioxide, $SO_2$, and, under certain conditions to be described farther on, this combines with more oxygen to form the trioxide $SO_3$. Further, it combines with nearly all the acid-forming elements if heated with them to a sufficiently high temperature. It combines with most other elements less readily than oxygen and it forms less stable compounds. Thus, its compound with hydrogen is decomposed much more readily into its elements than water is; and the sulphides or its compounds with metals are decomposed when they are heated in oxygen, the oxygen displacing the sulphur, much as chlorine displaces bromine; though there is this difference, sulphur itself unites readily with oxygen, and this facilitates the decomposition of the sulphides by the action of oxygen.

When treated with powerful oxidizing agents in the presence of water, sulphur is converted into sulphuric acid.

The specific gravity of the vapor of sulphur varies with the temperature, and is such as to indicate that below the boiling point at atmospheric pressure the molecule consists of eight atoms, this molecule beginning to dissociate at the boiling point 114.5° until at a temperature of 800° or higher it is completely broken down into molecules of two atoms. The vapor density at temperatures not far above the boiling point and under strongly reduced pressure still indicates that the molecule contains eight atoms ($S_8$).

**Uses of Sulphur.**—Enormous quantities of sulphur are used in the manufacture of sulphuric acid, and of gunpowder. It is also used in the manufacture of fireworks of various kinds. Burning sulphur gives sulphur dioxide,

which is extensively employed for bleaching wool, silk, straw, etc. When caoutchouc is thoroughly mixed with sulphur or some sulphur compound it becomes vulcanized.

### Compounds of Sulphur with Hydrogen.

The principal compound of sulphur and hydrogen is analogous in composition to water. It is known as hydrogen sulphide or sulphuretted hydrogen, and has the formula $H_2S$. Besides this there is at least one other compound which contains a larger proportion of sulphur, and probably has the composition $H_2S_5$.

**Hydrogen Sulphide, Sulphuretted Hydrogen,** $H_2S$.— When hydrogen is passed over highly-heated sulphur the two elements combine to form hydrogen sulphide. The action is, however, quite incomplete and is not to be compared with that which takes place when hydrogen and oxygen are heated together. This compound of sulphur and hydrogen occurs in nature in solution in the so-called "sulphur waters," which are met with in many parts of the earth. It is formed by heating organic substances containing sulphur, just as water is formed by heating organic substances containing oxygen. It is formed, further, by decomposition of organic substances that contain sulphur, as, for example, the albumen of eggs. The odor of rotten eggs is partly due to the formation of hydrogen sulphide. It is formed by the action of acids upon sulphides or hydrosulphides, just as water is formed by the action of acids upon oxides or hydroxides. Thus hydrochloric acid and ferrous sulphide, FeS, give ferrous chloride, $FeCl_2$, and hydrogen sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S;$$

just as ferrous oxide, FeO, and hydrochloric acid give ferrous chloride and water:

$$FeO + 2HCl = FeCl_2 + H_2O.$$

In the laboratory, where the gas is extensively used, it is generally prepared from ferrous sulphide, FeS, and

dilute sulphuric acid, which are brought together at the ordinary temperature in a flask such as is used in making hydrogen or a Kipp's apparatus. The reaction is like that which takes place between ferrous sulphide and hydrochloric acid. It is represented by this equation:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Commercial ferrous sulphide contains metallic iron, hence the hydrogen sulphide made in this way contains free hydrogen. Pure hydrogen sulphide is made by the action of pure hydrochloric acid on barium sulphide.

**Properties.**—Hydrogen sulphide is a colorless, transparent gas of the specific gravity 1.178. It solidifies at $-86°$ and boils at $-62°$. It has an extremely disagreeable odor, somewhat suggestive of that of rotten eggs. It is poisonous, even small quantities causing headache, vertigo, nausea, and other bad symptoms. It burns with a blue flame, forming water and sulphur dioxide:

$$H_2S + 3O = H_2O + SO_2.$$

If, however, the air has not free access, as when the gas is burned in a cylinder open at one end, only a part of the sulphur is burned, the rest being deposited upon the walls of the vessel, while the hydrogen burns. The gas is soluble in water, about three volumes being taken up at ordinary temperatures. This solution is used to some extent in the laboratory instead of the gas, but, owing to the fact that it undergoes change in consequence of the action of the oxygen of the air, it is not as valuable as it would be if it were more stable. The change consists in the oxidation of the hydrogen and the separation of the sulphur. If a bottle containing a solution of hydrogen sulphide is allowed to stand for a few days, particularly if it is opened from time to time, the odor of the gas will disappear and a deposit of sulphur will be noticed in the bottle. The liquid is then nothing but water. When the solution is boiled it loses all the gas contained in it.

Hydrogen sulphide is easily decomposed into its elements. It requires a temperature of only a little above

400° to effect direct decomposition. In consequence of this instability it causes a number of changes which the analogous compound water cannot effect. The relations here are similar to those that exist between hydrochloric and hydriodic acids. Hydrochloric acid is very stable, while hydriodic acid breaks down readily into hydrogen and iodine. Therefore hydriodic acid acts as a reducing agent, while hydrochloric acid does not. So, also, hydrogen sulphide acts as a reducing agent. Thus, if it is passed into concentrated sulphuric acid this reaction takes place:

$$H_2SO_4 + H_2S = 2H_2O + S + SO_2.$$

The action is to be traced to the decomposition of the hydrogen sulphide into hydrogen and free sulphur, the hydrogen then acting upon the sulphuric acid thus:

$$H_2SO_4 + 2H = 2\,H_2O + SO_2.$$

With hydriodic acid the reduction may go farther, as has been seen; with hydrobromic acid, however, the action takes place practically in the same way as with hydrogen sulphide.

Chlorine, bromine, and iodine act upon hydrogen sulphide, setting the sulphur free and uniting with the hydrogen:

$$H_2S + Cl_2 = 2\,HCl + S.$$

The instability of hydrogen sulphide is further shown by the ease with which it is decomposed by metals with liberation of hydrogen and formation of sulphides. It will be remembered that at high temperatures several metals decompose water, but that at ordinary temperatures only a few decompose it easily. Hydrogen sulphide acts much more readily; a number of metals which do not act upon water even at high temperatures, as silver, gold, and mercury, decompose this gas at ordinary temperatures.

Hydrogen sulphide acts upon metallic oxides, converting them into sulphides, as, for example:

$$CuO + H_2S = CuS + H_2O.$$

**Action of Hydrogen Sulphide upon Solutions of Salts—Use in Chemical Analysis.**—Hydrogen sulphide is extensively used in every chemical laboratory as a reagent in chemical analysis. In order that its action may be understood a few words of explanation are necessary. Sulphur, as we have seen, readily unites with the metallic or base-forming elements, forming with them the sulphides. Some of the sulphides are insoluble in water and in dilute acids; others are soluble in dilute acids but insoluble in water and in ammonia; while still others are soluble in water. This plainly furnishes a basis for the classification of the base-forming elements into three groups for the purpose of analysis:

I. Metals whose sulphides are insoluble in water and are not decomposed by dilute acids. This is called *the hydrogen sulphide group.* It includes lead, bismuth, silver, mercury, copper, cadmium, gold, platinum, tin, antimony, and arsenic.

II. Metals whose sulphides are insoluble in water but are decomposed by dilute acids. They are therefore not precipitated by hydrogen sulphide, but are precipitated by soluble sulphides. As ammonium sulphide is used for the purpose of precipitating these, the group is known as *the ammonium sulphide group.* It includes iron, nickel, cobalt, manganese, thallium, zinc, and uranium. Further, the two elements aluminium and chromium are precipitated with the above, not as sulphides but as hydroxides, and they are therefore included in the group.

III. Metals whose sulphides are soluble in water. This group includes all the metals not included in the above two.

By taking advantage, then, of the properties of the sulphides of the metals they can be divided into these three groups, and the detection of any particular element is thus facilitated. If hydrogen sulphide is passed through a solution, and a precipitate formed, we know that this can contain only those metals which belong to the hydrogen sulphide group; and so on. Now, if the precipitate formed with hydrogen sulphide is treated with certain

other reagents other changes take place, and by further study it is quite possible, and indeed comparatively simple, to determine which of the members of the group are present.

According to the ionic theory (see p. 166), hydrogen sulphide is dissociated in aqueous solution, forming the ions HS and H, and also S and H,H. So, also, the metallic salts are dissociated. For example, silver nitrate, $AgNO_3$, in aqueous solution gives the ions Ag and $NO_3$. Now when hydrogen sulphide is passed into a solution of silver nitrate the reaction that takes place is to be represented thus:

$$2(\overset{+}{Ag},\overset{-}{NO_3}) + \overset{+}{H},\overset{+}{H},\overset{-}{S} = Ag_2S + 2(\overset{+}{H},\overset{-}{NO_3}).$$

The silver sulphide is removed from the solution and is obtained as a solid precipitate, while the ions of nitric acid are in the solution, forming, as we say, a dilute solution of nitric acid. This dilute nitric acid does not act upon the silver sulphide, so that the reaction is complete, all the silver ions being carried out of the solution by the sulphur ions provided enough hydrogen sulphide is passed into the solution.

When, however, hydrogen sulphide is passed into a solution of ferrous chloride, $FeCl_2$, the results are different. In this case, we should naturally expect to find that the reaction would take place as represented in the equation:

$$\overset{++}{Fe},\overset{-}{Cl},\overset{-}{Cl} + \overset{+}{H},\overset{+}{H},\overset{=}{S} \rightleftarrows FeS + 2(\overset{+}{H},\overset{-}{Cl}).$$

This reaction is completely reversible and in equilibrium. But the ferrous sulphide, FeS, is acted upon by hydrochloric acid in solution, giving hydrogen sulphide and ferrous chloride, so that the change above represented cannot take place.

If, however, a soluble sulphide is added to a solution of a salt of iron or of any metal that acts in the same way, the sulphide is precipitated. Thus, if instead of passing

hydrogen sulphide, a solution of potassium sulphide is added, reaction takes place thus:

$$\overset{+}{Fe},\overset{+}{H},\overset{-}{Cl},\overset{-}{Cl} + \overset{+}{K},\overset{+}{K},\overset{=}{S} = FeS + 2(\overset{+}{K},\overset{-}{Cl}).$$

In the resulting solution the hydrogen ions of hydrochloric acid are not present and the ions of potassium chloride which are present do not act upon the ferrous sulphide. Therefore the ferrous sulphide is precipitated.

**Hydrosulphides.**—The action of hydrogen sulphide shows that it belongs to the class of acids. When it acts upon an oxide the corresponding sulphide and water are formed. But just as there are sulphides that are derived from hydrogen sulphide by the substitution of metallic elements for both hydrogen atoms, so there are hydrosulphides that are derived from it by the replacement of only one of the two atoms of hydrogen in the molecule. The sulphides correspond to the oxides, and the hydrosulphides to the hydroxides. Thus the analogous oxygen and sulphur compounds of potassium are:

| | |
|---|---|
| $K_2O$ | $K_2S$ |
| KOH | KSH. |

Sulphides and hydrosulphides are regarded as salts of hydrogen sulphide. In consequence of this power to form salts in the same way in general that acids do, hydrogen sulphide is sometimes called *sulphydric acid* and the salts of the formula MSH, *sulphydrates*. The name sulphydrate is analogous to hydrate, which, as has been pointed out, is used by some to designate the compounds of the formula MOH or the hydroxides. Between the acid, hydrogen sulphide, and the neutral compound, water, there is no fundamental difference. The difference is simply one of degree. In the present system of chemistry, which is largely an oxygen system, water is regarded as the connecting link between acids and bases, as was shown on p. 171. But we might with equal right found our definitions and conceptions of acids and bases upon the conduct of sulphur compounds, and thus build up a

sulphur system. In such a system hydrogen sulphide would be the connecting link between acids and bases.

**Hydrogen Persulphide,** $H_2S_5$.—The sulphides of certain metals, particularly the so-called alkali metals, sodium and potassium, combine with sulphur to form the polysulphides, examples of which are $K_2S_2$, $K_2S_3$, $K_2S_4$, and $K_2S_5$. If a solution of these substances is poured into an excess of diluted hydrochloric acid a heavy yellow oil is formed which has the composition $H_2S_5$ even if the polysulphide used contained a smaller proportion of sulphur:

$$4K_2S_2 + 8HCl = 8KCl + H_2S_5 + 3H_2S.$$

Hydrogen persulphide has a penetrating odor, irritates the eyes and is an active reducing agent. It may also be considered to be perthiosulphuric acid $H_2SS_4$. It is a very unstable substance breaking down readily into sulphur and hydrogen sulphide.

**Compounds of Sulphur with Members of the Chlorine Group.**—Sulphur combines directly with chlorine and forms the compounds $S_2Cl_2$, $SCl_2$, and $SCl_4$. Of these the first is the most stable. This can be boiled without undergoing decomposition. The second, sulphur dichloride, $SCl_2$, undergoes decomposition into chlorine and sulphur monochloride at the boiling-point; while sulphur tetrachloride exists only at low temperatures. All these compounds are decomposed by water, yielding oxygen compounds. With iodine sulphur forms an unstable hexiodide, $SI_6$; with fluorine, a very stable hexafluoride, $SF_6$.

## Selenium, Se. (At. Wt. 79.2).

**Occurrence.**—Selenium occurs only in small quantity in nature. It was first found in the deposit formed in a sulphuric-acid chamber (see p. 241), and owed its origin to the presence of small quantities of selenides in the sulphides used in the operation. It was found to resemble tellurium, and for that reason was called selenium, from σελήνη, the moon, tellurium receiving its name from *tellus*, the earth. Selenium occurs in a number of the natural sulphides, such as iron pyrites, copper pyrites, zinc blende,

etc.; and when these are treated in a current of air to decompose them and convert the sulphur into sulphur dioxide, the selenium is also oxidized, and the selenium dioxide thus formed is carried into the flues and other parts of the apparatus. As it is a solid it is easily condensed, and gradually a considerable quantity collects in the flues. This flue-dust is the best material from which to make selenium.

**Properties.**—There are three modifications of selenium, corresponding to those of sulphur. I. Amorphous or vitreous selenium, sp. gr. 4.26 to 4.28, soluble in carbon bisulphide. II. Monoclinic selenium, sp. gr. 4.47, soluble in carbon bisulphide. III. Hexagonal *metallic* selenium, sp. gr. 4.8, insoluble in carbon bisulphide. Selenium I is precipitated from solutions, or in the vitreous form obtained by super-cooling fused selenium. Selenium II crystallizes from the warm solution of selenium I in carbon bisulphide; it crystallizes like monoclinic sulphur. If selenium I or II is heated for some time at about 100°, selenium III is formed with a sudden rise of temperature which may—with sufficient material—reach the melting point of selenium III, 217°. Selenium III is bluish gray, sensitive to light, and after exposure to a strong light, conducts the electric current. Selenium I and II do not conduct the electric current. Selenium boils at 690°, forming a dark yellow, heavy vapor which expands on heating and above 900° consists of molecules of the composition $Se_2$. Selenium burns as sulphur does, forming the oxide $SeO_2$, which has the odor of rotten horse-radish. Compounds of the composition $H_2SeO_4$ and $H_2Se$ are also known.

### Tellurium, Te (At. Wt. 127.6).

**Occurrence.**—Tellurium occurs in some gold ores in the native or uncombined condition, and also in combination with gold, silver, antimony, lead, and other metals. Tellurides occur, among other places in the United States, in California and Virginia. The general method of preparing tellurium from its ores is the same as that by

which selenium is made. The tellurium is oxidized to tellurous acid, $H_2TeO_3$, which is isolated, and then reduced by means of sulphurous acid.

**Properties.**—Tellurium is silver-white, and crystallizes easily. It melts at about 450° and boils at about 1400°. Heated in the air it burns, forming a thick white cloud of tellurium dioxide, $TeO_2$. Treated with sulphuric acid it is oxidized to tellurous acid, $H_2TeO_3$, the sulphuric acid being reduced. Nitric acid oxidizes it likewise to tellurous acid. Melted together with potassium nitrate it is converted into potassium tellurate, $K_2TeO_4$.

## EXPERIMENTS.

### Properties of Sulphur.

Experiment 100.—Distil about 10 grams roll sulphur from an ordinary glass retort. What changes in color and in condition take place? Collect the liquid sulphur formed by the condensation of the vapor in a beaker-glass containing cold water.

Experiment 101.—Treat some powdered roll sulphur with carbon bisulphide and filter. Does it all dissolve? Try the same experiment with flowers of sulphur. Does this all dissolve? Put the solutions together and allow to evaporate. Examine the crystals deposited. Compare them with some natural crystals of sulphur. See whether one of the crystals will completely dissolve in carbon bisulphide.

Experiment 102.—In a covered sand or Hessian crucible melt about 25 grams of roll sulphur. Let it cool slowly, and when a thin crust has formed on the surface make a hole through this and pour out the liquid part of the sulphur. What is left? Compare with the crystals formed in the last experiment. Lay the crucible aside, and in the course of a few days again examine the crystals. What changes, if any, have taken place?

Experiment 103.—Add hydrochloric acid to a solution of sodium thiosulphate. What takes place?

Experiment 104.—In a wide test-tube heat some sulphur to boiling. Introduce into it small pieces of copper-foil or sheet copper. Or hold a narrow piece of sheet copper so that the end just dips into the boiling sulphur.

Experiment 105.—Dissolve some sulphur in concentrated caustic soda. In what form is the sulphur in the solution?

### Hydrogen Sulphide.

Experiment 106.—Arrange an apparatus as shown in Fig. 48. Put a small handful of ferrous sulphide, FeS, in the flask, and

pour dilute sulphuric acid upon it. Pass the evolved gas through a little water contained in the wash-cylinder *A*. Pass some of the gas into water. [What evidence have you that it dissolves?] Collect some by displacement of air. Its specific gravity is 1.178. Set fire to some of the gas contained in a cylinder. In this case the air has not free access to the gas, and the combustion is not complete. The hydrogen burns to form water, while a part of the sulphur is deposited upon the inside walls of the cylinder. If there is free access of air, the sulphur burns to sulphur dioxide and the hydrogen to water.

Make a solution of the gas in water in the usual way. Put some of this in a bottle and set it aside, and in the course of a few days examine it again. Boil another portion for a time in a test-tube, and note the changes. Pass a little of the gas through concentrated sulphuric acid contained in a test-tube, and note the changes. Moisten strips of paper with dilute solutions of lead nitrate, copper sulphate, stannous chloride, antimony chloride, and mercuric chloride; and

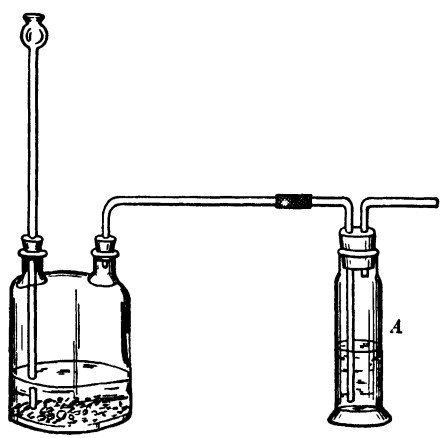



FIG. 43.

expose these papers in turn to the gas. What changes take place? Repeat Experiment 96, and see whether one of the gases given off produces similar changes.

EXPERIMENT 107.—Pass hydrogen sulphide successively through solutions containing a little *lead nitrate, cadmium nitrate,* and *arsenic chloride* prepared by dissolving a little white arsenic or arsenic trioxide, $As_2O_3$, in dilute hydrochloric acid. What action takes place in each case? The formula of lead nitrate is $Pb(NO_3)_2$; that of cadmium nitrate. $Cd(NO_3)_2$; and that of arsenic chloride in solution is $AsCl_3$. The corresponding sulphides are represented by the formulas PbS, CdS, and $As_2S_3$.

## CHAPTER XIV.

### COMPOUNDS OF SULPHUR, SELENIUM, AND TELLURIUM WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

**Introductory.**—It has already been stated that, when the three elements of the sulphur group are burned in the air, they are converted into the corresponding dioxides. Under certain conditions it is possible to convert sulphur dioxide and tellurium dioxide into the trioxides, $SO_3$ and $TeO_3$, while the corresponding compound of selenium has not been made. A lower oxide of sulphur, $S_2O_3$, and a higher one of the formula $S_2O_7$ have also been made. The dioxides dissolve in water, and from these solutions salts of the general formula $M_2SO_3$, $M_2SeO_3$, and $M_2TeO_3$ are obtained. The trioxide of sulphur dissolves in water with great evolution of heat, forming compounds $S(OH)_6$, $OS(OH)_4$, and $O_2S(OH)_2$.

Most of the salts obtained from this solution are derived from an acid of the formula $H_2SO_4$, and therefore this is generally called sulphuric acid. By treating sulphuric acid with reducing agents of various kinds it can be converted successively into other acids containing a smaller proportion of oxygen; and if the reduction is pushed far enough sulphur and hydrogen sulphide are obtained. The limit of reduction is reached in hydrogen sulphide; and, on the other hand, if hydrogen sulphide is oxidized the limit of oxidation is generally reached in sulphuric acid.

**Sulphuric Acid.** $H_2SO_4$.—Almost all the salts of sulphuric acid can be best explained on the assumption that the forms of sulphuric acid are derived from a compound $S(OH)_6$. This is called *normal sulphuric acid.* From normal sulphuric acid by loss of water, the compounds $H_4SO_5$, $H_2SO_4$, and $SO_3$ are formed:

$$S(OH)_6 = OS(OH)_4 + H_2O;$$
$$OS(OH)_4 = O_2S(OH)_2 + H_2O;$$
$$O_2S(OH)_2 = O_3S + H_2O.$$

While these compounds are all known, the salts of sulphuric acid are for the most part derived from the acid containing two hydrogen atoms, *viz.*, $O_2S(OH)_2$. In some salts two of the hydrogen atoms in normal sulphuric acid are replaced by metals, the others remaining. Salts of the general formula $S(OH)_4(OM)_2$ are thus formed. These are generally represented as containing two molecules of water of crystallization, thus, $M_2SO_4 + 2H_2O$. To decide between the two views is at present impossible. In the first place, the question as to the nature of water of crystallization must be answered before it can be said whether there is any conflict between the two views.

For the science as well as for the art of chemistry sulphuric acid is of fundamental importance. It is used daily in every chemical laboratory and in every chemical factory, and in some of the most important branches of chemical industry enormous quantities of it are used. In consequence of the large demand for the acid the process used in preparing it has been studied with great care, and it has reached a high state of perfection. As it furnishes an excellent example of the applications of the facts of science to the building up of an industry, it will be presented with some degree of fulness.

Sulphuric acid has been known for a long time. It was made in the eighteenth century by heating calcined iron vitriol (ferrous sulphate, $FeSO_4$) with sand, and was hence called *oil of vitriol*, a name which still survives. It was also prepared by treating sulphur with saltpetre (potassium nitrate, $KNO_3$). The acid was first prepared on the large scale in England with the use of comparatively large chambers lined with lead. It was known as English sulphuric acid, and is still called by this name.

Sulphuric acid occurs in nature in the form of salts or sulphates, such as calcium sulphate or gypsum, barium sulphate or heavy spar, and others. Although these salts occur in large quantity, the acid is not obtained from them, as there is no economical way of substituting hydrogen for the metal. The preparation of the acid by the substitution of hydrogen for the calcium in calcium

sulphate, $CaSO_4$, suggests itself, but this cannot be easily effected by any substance available in quantity. Hydrochloric and nitric acids are made from their salts which occur in nature, the former, as we have seen, from sodium chloride, NaCl, the latter from saltpetre or potassium nitrate, $KNO_3$, by treating with sulphuric acid. While phosphoric and boric acids act upon sulphates at temperatures above the boiling-point of sulphuric acid, as sulphuric acid acts on nitrates at temperatures above the boiling-point of nitric acid, sulphuric acid could not be made economically in this way.

The principal process that has until recently been employed in the manufacture of sulphuric acid is based upon the two fundamental facts that (1) when sulphur is burned it is converted into sulphur dioxide, $SO_2$; and (2) when sulphur dioxide is treated with an oxidizing agent in the presence of water it is converted into sulphuric acid:

$$\begin{aligned} SO_2 + H_2O + O &= H_2SO_4; \text{ or} \\ SO_2 + H_2O &= H_2SO_3; \text{ and} \\ H_2SO_3 + O &= H_2SO_4. \end{aligned}$$

The chief difficulty is, of course, experienced in effecting the oxidation of the sulphurous acid. It is accomplished by introducing the gas, sulphur dioxide, into large chambers together with compounds of nitrogen and oxygen, and steam. That which plays the chief part in effecting the transformation is a mixture of the two oxides NO and $NO_2$. This acts like the trioxide, $N_2O_3$, and it may be represented by this formula. Instead of starting with the trioxide, nitric acid is used in the manufacture of sulphuric acid. This at first reacts with sulphur dioxide and steam, as represented in the equation

$$2HNO_3 + 2SO_2 + H_2O = 2H_2SO_4 + N_2O_3.$$

After this the main reactions are (1) the formation of a compound of the formula $SO_2{<}^{NO_2}_{OH}$, called *nitrosyl-sulphuric acid;* and (2) the decomposition of the nitrosyl-

sulphuric acid by water. These reactions are represented in the two equations following:

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)(NO_2);$$

$$2SO_2{<}^{NO_2}_{OH} + H_2O = 2SO_2{<}^{OH}_{OH} + N_2O_3.$$

The nitrogen trioxide formed in the second reaction again enters into combination with sulphur dioxide, oxygen, and water to form nitrosyl-sulphuric acid, which again undergoes decomposition with water. It will be seen, therefore, that the trioxide is not lost, but that it serves the purpose of effecting the oxidation of the sulphur dioxide, and, theoretically, a small quantity of the gas should be capable of transforming an infinite quantity of sulphur dioxide into sulphuric acid.

Other reactions besides those mentioned above are undoubtedly involved in the manufacture of sulphuric acid, but, according to the most elaborate researches made on the subject in a factory in operation, those mentioned are the principal ones. Whatever the details may be, the oxidation is effected without difficulty, and the waste in nitrogen compounds is now but slight.

The large chambers in which the reactions are carried on are lined with lead, and known as the leaden chambers. The sulphur is burned in a special furnace so arranged that air has free access to it. The dioxide thus formed is then conducted through a tower so constructed that it presents a large surface to the action of the gas. Through this tower dilute sulphuric acid, taken from another tower at the end of the system, flows from above, and the hot gases coming in contact with this serve the purpose of concentrating it, while the gas itself is cooled before entering the leaden chamber. The general arrangement of the essential parts of a sulphuric-acid factory are shown in Fig. 44.

The sulphur dioxide passes through a large tube into the tower *G*, called the Glover tower. This is filled from *d* to *e* with pieces of fire-brick over which from the cistern

*b* a continual stream of dilute sulphuric acid flows. The gases are thus cooled down and the acid concentrated. From a second cistern there flows at the same time con-

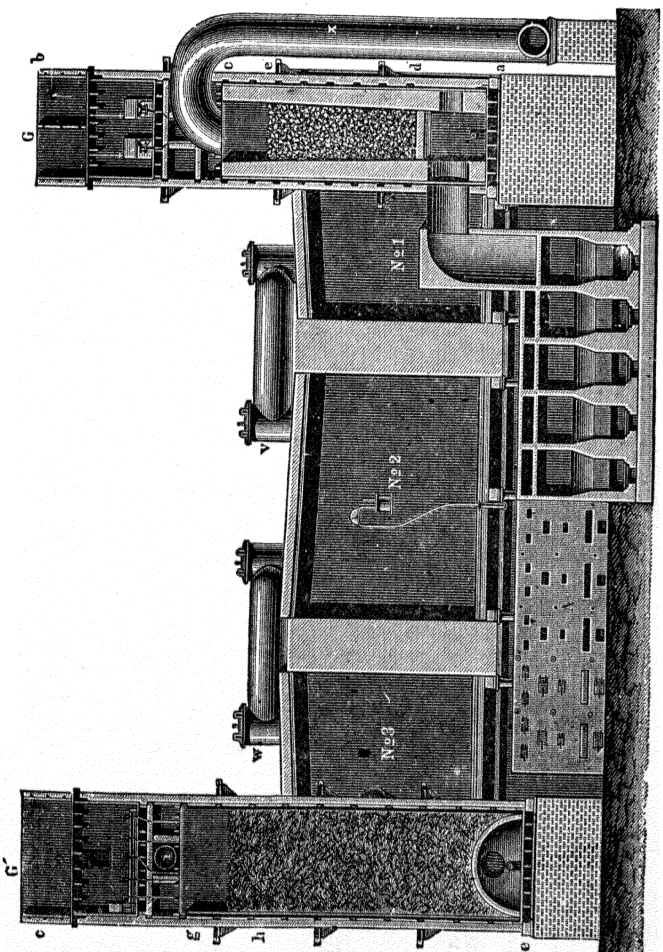



FIG. 44.

centrated sulphuric acid from the tower *G'*, or the Gay-Lussac tower. This stronger acid contains oxides of nitrogen in combination, and by contact with the dilute acid

the oxides are set free and are thus mixed with the sulphur dioxide. The nitric acid is introduced into the first chamber, No. 1, in the form of vapor, together with the oxides of nitrogen and sulphur dioxide, and here also the gases meet with water-vapor. The reactions above referred to now take place. From the first chamber the gases pass through the pipe *v* into the second, from this into the third at *w*, and finally, in order to prevent the escape of any unused oxides of nitrogen, the gases are passed through the Gay-Lussac tower *G'*. This contains coke over which is kept flowing concentrated sulphuric acid, which takes up the oxides of nitrogen and will give them up again when diluted. This liberation of the oxides of nitrogen is accomplished, as has been said, in the Glover tower. The concentrated acid collected at the bottom of the Glover tower is well adapted for use in the Gay-Lussac tower. The leaden chambers in some factories are nearly 100 feet long, 18 to 30 feet broad, and 15 feet high.

The acid taken from the chambers contains about 64 per cent of the compound $H_2SO_4$, and has the specific gravity 1.5. This is evaporated first in lead pans until it reaches the specific gravity 1.75. As stronger acid acts upon lead, the evaporation beyond this point is carried on in platinum, glass, or iron. The strong acid thus obtained, which has a specific gravity of about 1.830, is the concentrated sulphuric acid of commerce.

Instead of sulphur, iron pyrites is now extensively used for the preparation of sulphur dioxide in the manufacture of the sulphuric acid. This is a compound of iron and sulphur of the composition $FeS_2$. When it is heated in contact with the air it is converted into the oxide, and the sulphur passes off in the form of sulphur dioxide. If the sulphide used contains selenides the selenium dioxide formed in the roasting process is carried into the flues, and is there deposited with the flue-dust, as was stated in speaking of the source of selenium.

Commercial sulphuric acid prepared as above is a thick liquid, usually somewhat colored by impurities.

The nature of the impurities is dependent upon the substances used in the manufacture and upon the conditions. It often contains some lead sulphate in solution, and when it is diluted with water this separates, giving the liquid a more or less cloudy appearance. By standing, however, the liquid becomes clear, as the lead sulphate collects at the bottom. For obvious reasons, some oxides of nitrogen are also generally present. Among other impurities frequently met with in the commercial acid are arsenic from the pyrites, and a little selenium.

**Contact Process.**—This process consists in passing sulphur dioxide and air together over finely divided platinum, ferric oxide, or some other substance that has the power to effect the union of the sulphur dioxide and the oxygen of the air. The direct product of the union is sulphur trioxide, $SO_3$. This with water gives sulphuric acid. The reactions involved are:

$$SO_2 + O = SO_3;$$
$$SO_3 + H_2O = H_2SO_4.$$

The process perfected commercially by Knietsch is very interesting. Arsenious acid and other impurities contained in the pyrite must be removed completely, because traces of arsenic "poison" the catalyzer and render it inactive. The catalyzer or "contact agent" must be kept at 450°. With platinized asbestos as catalyzer, below 450° the action is too slow, above 450° incomplete because it is a reversible reaction and at temperatures above 450° it begins to work in the reverse direction.* The tubes containing the catalyzer are kept cool by passing the cold mixture of sulphur dioxide and air over their exterior before entering the interior, thus removing part of the heat of reaction which is indicated in the equation. By adding the sulphur trioxide to water or to sulphuric acid, absolutely pure acids of any concentration desired are obtained. In a recent year the Baden Aniline and Soda Factory in Germany made 116,000 tons

* If ferric oxide is used as catalyzer the temperature required is 600°.

of sulphur trioxide which was converted into " fuming sulphuric " acid.

**Pure Sulphuric Acid** is made by the method just described or from the commercial acid by treating it with such substances as will remove the oxides of nitrogen and arsenic, and by distilling. It is a colorless liquid at the ordinary temperature. The pure acid generally made has about the same concentration as the commercial crude acid. By taking special precautions in the distillation a product having very nearly the composition $H_2SO_4$ can be obtained. This is a thick, clear liquid of specific gravity 1.854 at 0°. When cooled down to a low temperature it forms large crystals which melt at 10.5°. When heated it gives off some sulphur trioxide in consequence of partial decomposition :

$$H_2SO_4 = H_2O + SO_3.$$

It finally boils, however, at the temperature 338°, and the distillate has the composition represented by the formula $H_2SO_4 + \frac{1}{2}H_2O$. Heated somewhat above its boiling-point it is completely decomposed into sulphur trioxide and water, according to the above equation. If the heating is carried to a higher temperature the sulphur trioxide breaks down into sulphur dioxide and oxygen.

Sulphuric acid has a strong tendency to absorb water, and to form compounds with it. In consequence of the formation of these compounds a great deal of heat is evolved when sulphuric acid is mixed with water. One molecule of sulphuric acid when mixed with about 1600 molecules of water gives 17,850 cal. Among the compounds thus formed are the so-called hydrates of the composition $H_2SO_4 + H_2O$ and $H_2SO_4 + 2H_2O$, which should probably be regarded as having the constitution $OS(OH)_4$ and $S(OH)_6$.

So strong is the tendency of the acid to combine with the elements of water that it abstracts them in the proportions to form water from many organic substances. Thus a piece of wood placed in sulphuric acid soon turns black and is completely disintegrated. The cause of this

is to be found in the fact that wood consists essentially of carbon, hydrogen, and oxygen; and the sulphuric acid abstracts the hydrogen and oxygen, leaving the carbon mainly in the uncombined state. Similarly it abstracts moisture from gases, and it is used extensively in the laboratory for this purpose. In contact with the skin it acts as it does upon wood, causing wounds which are painful and difficult to heal.

Sulphuric acid is often called a *strong acid*, a term which needs further explanation. As used here, it means simply that the acid has the power to decompose the salts of most other acids, appropriating the metals and setting the other acids free. This is illustrated by the formation of hydrochloric and nitric acids by treating sodium chloride and potassium nitrate respectively with sulphuric acid. We have seen, however, that the fact that sulphuric acid decomposes the salts of hydrochloric and nitric acids does not prove that it is a stronger acid than they are. There are other facts besides the strengths of the acids that determine whether such decompositions take place or not. (See Strength of Acids, p. 180.)

Sulphuric acid gives up its oxygen to other substances comparatively easily, and is generally reduced to sulphurous acid, which is decomposed into sulphur dioxide and water. Thus hydrogen sulphide and hydrobromic acid both act upon it, as we have seen; the products being, in the former case, sulphur dioxide, water, and sulphur; in the latter, sulphur dioxide, water, and bromine:

$$H_2SO_4 + H_2S = 2H_2O + SO_2 + S;$$
$$H_2SO_4 + 2HBr = 2H_2O + SO_2 + Br_2.$$

Generally, in acting upon metals it forms the corresponding salt and hydrogen is given off, but if the temperature is high and the acid concentrated the hydrogen acts upon the acid, reducing it. Thus, in making hydrogen by treating zinc with sulphuric acid, if the acid is dilute and is kept cool the reaction takes place in the simplest way; but if the acid is concentrated and is allowed to

get hot some hydrogen sulphide is always formed. Copper does not act upon sulphuric acid at ordinary temperatures. If it is heated with concentrated sulphuric acid, sulphur dioxide is the chief reduction-product. Even free hydrogen if passed into sulphuric acid heated to 160° reduces it, forming sulphur dioxide. The complete reduction of sulphuric acid to sulphur and hydrogen sulphide is beautifully shown by the action of hydriodic acid. As was stated in speaking of the action of sulphuric acid upon potassium iodide, four reactions may take place when these substances act upon each other. They are represented by the equations

$$2KI + H_2SO_4 = K_2SO_4 + 2HI;$$
$$H_2SO_4 + 2HI = 2H_2O + SO_2 + 2I;$$
$$H_2SO_4 + 6HI = 4H_2O + S + 6I;$$
$$H_2SO_4 + 8HI = 4H_2O + H_2S + 8I.$$

Carbon and sulphur also act upon sulphuric acid and reduce it to sulphur dioxide. With sulphur the action is represented thus:

$$2H_2SO_4 + S = 3SO_2 + 2H_2O.$$

Sulphuric acid is a dibasic acid (see p. 173) and forms two series of salts, normal salts of the general formula $M_2SO_4$, and acid salts of the formula $MHSO_4$. The sulphates are generally speaking stable. Those of the strongest bases are not decomposed by the highest heat. Those of weaker bases break down, giving up sulphur trioxide; or if the decomposition takes place at a temperature above that at which sulphur trioxide breaks down, this is decomposed into sulphur dioxide and oxygen.

**Tetrahydroxyl-Sulphuric Acid,** $OS(OH)_4$.—This compound has already been referred to as being formed by the addition of water to ordinary sulphuric acid. It is a crystallized compound which melts at 7.5°. No salts of this acid are known, or, rather, no salts derived from it by the replacement of all the hydrogen by metal are known. Only two of the hydrogen atoms appear to be

replaceable. This compound is generally represented by the formula $H_2SO_4 + H_2O$, and called a hydrate.

**Normal Sulphuric Acid,** $S(OH)_6$.—This is commonly represented by the formula $H_2SO_4 + 2H_2O$ and, like the preceding compound, is regarded as a hydrate. It appears to be formed by the action of water on sulphuric acid. On mixing sulphuric acid and water the maximum contraction takes place when the quantities necessary to form this compound are brought together, and there are other good reasons for believing that the compound exists in the solution. It is not a solid like the preceding compound. The acid forms no salts bearing simple relations to it.

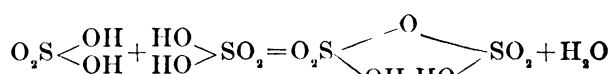
**Disulphuric Acid, Pyrosulphuric Acid,** $H_2S_2O_7$.—This compound is closely related to ordinary sulphuric acid, and is made from it by treating it with sulphur trioxide obtained in the contact process (p. 243), the two combining directly, as represented thus:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

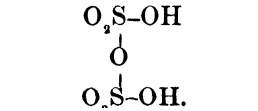
It crystallizes in prisms which melt at 35°, and is also called "solid sulphuric acid."

The "fuming" sulphuric acid commercially known as "oleum" is a mixture of sulphur trioxide and concentrated sulphuric acid in varying proportion. A fuming acid containing 80 per cent of the trioxide and 20 per cent of the compound, $H_2SO_4$, is preferred because its melting point is so low that it remains liquid in a warm room.

It is believed that the relation between disulphuric acid and ordinary sulphuric acid should be expressed by these formulas:



Or the formula of the acid may be written thus:



**Sulphurous Acid,** $H_2SO_3$.—While no acid of the formula $H_2SO_3$ is known in the free condition, a large number of salts which are derived from this acid are known. They are made by treating a water solution of sulphur dioxide with bases, and therefore it is believed that the solution contains the acid which is formed by the action of sulphur dioxide on water, thus:

$$SO_2 + H_2O = H_2SO_3.$$

It is, however, so unstable that it breaks down into the dioxide and water at every attempt to isolate it. The acid forms a number of unstable hydrates, apparently of complicated composition. Owing to their great instability, however, the investigation of these substances is extremely difficult and unsatisfactory.

Sulphurous acid takes up oxygen readily and is thus transformed into sulphuric acid. It is only necessary to allow a solution to stand for a time to find that the odor of the gas disappears and that sulphuric acid is then present in the solution. Sulphurous acid is frequently used in the laboratory as a reducing agent.

The sulphites take up oxygen to form sulphates, and they also take up sulphur to form thiosulphates. The two reactions appear to be analogous:

$$Na_2SO_3 + O = Na_2SO_4;$$
$$Na_2SO_3 + S = Na_2S_2O_3 \text{ (or } Na_2SO_3S).$$

Sulphurous acid forms two series of salts, the normal sulphites of the general formula $M_2SO_3$, and the acid sulphites of the general formula $MHSO_3$. These are unstable, though much more stable than the acid itself. When treated with most acids they are decomposed, yielding sulphur dioxide instead of sulphurous acid. The decomposition of sodium sulphite with hydrochloric acid is represented by the equation

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2;$$

with sulphuric acid thus:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

**Hyposulphurous Acid,** $H_2S_2O_4$.—This acid is also called hydrosulphurous acid, but the name hyposulphurous acid is more in accordance with the nomenclature adopted for the other acids, and is now preferred. But little is known of the compound. It is formed by reduction of a salt of sulphurous acid by zinc:

$$Zn + 2SO_2 = ZnS_2O_4.$$

The free acid cannot be obtained from this salt.

**Thiosulphuric Acid,** $H_2S_2O_3$.—This acid was formerly, and is still by many, called hyposulphurous acid. Its formation, or the formation of its salts by the addition of sulphur to the sulphites, has been mentioned, and the analogy between this reaction and that of the formation of sulphates by the addition of oxygen to sulphites has been commented upon. It may be regarded as sulphuric acid in which one atom of sulphur has been substituted for one atom of oxygen, and hence the name thiosulphuric acid is appropriate, whereas the name hyposulphurous acid suggests at once a compound similar to sulphurous acid, but containing less oxygen, and is therefore inappropriate.

The acid itself is unstable, breaking down into sulphur dioxide, sulphur, and water. By acids its salts are decomposed in a similar way with evolution of sulphur dioxide and separation of sulphur, which appears suspended in the liquid in a very fine state of division. With hydrochloric acid the decomposition takes place thus:

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

**Other acids of Sulphur.**—Of the other acids of sulphur but little need be said here. They form a series the members of which are closely related to one another as shown below:

| | |
|---|---|
| Dithionic acid | $H_2S_2O_6$ |
| Trithionic acid | $H_2S_3O_6$ |
| Tetrathionic acid | $H_2S_4O_6$ |
| Pentathionic acid | $H_2S_5O_6$ |

**Persulphuric Acid,** $HSO_4$, is formed by dissolving the oxide $S_2O_7$ in water, the oxide itself being formed by subjecting a mixture of sulphur dioxide and oxygen to the silent discharge in an ozone tube (see p. 118). The potassium salt of persulphuric acid is easily obtained by electrolysis of a saturated solution of acid potassium sulphate.

**Caro's Reagent.**—When potassium persulphate is added to moderately dilute sulphuric acid a solution is obtained that shows remarkable oxidizing powers. It has recently come into use in laboratories under the name of *Caro's reagent.* It contains an acid of the composition $H_2S_2O_9$. This acid, which is called Caro's acid, can also be obtained by pouring 5 parts concentrated sulphuric acid into 1 part 5 per cent hydrogen peroxide, or by electrolyzing concentrated sulphuric acid.

**Compounds of Sulphur with Oxygen.**—Sulphur combines with oxygen in two proportions, forming the oxides $SO_2$ and $SO_3$, or sulphur dioxide and sulphur trioxide. The trioxide is also known in the form of the hexoxide, $S_2O_6$. Besides these it forms a *sesquioxide*, $S_2O_3$, and a *heptoxide*, $S_2O_7$, but comparatively little is known in regard to the last two. The one best known is sulphur dioxide.

**Sulphur Dioxide,** $SO_2$.—This is formed when sulphur is burned in the air or in oxygen; and it is also easily formed by reduction of the higher oxides and acids of sulphur. Owing to the fact that with water it forms sulphurous acid, it is frequently called sulphurous anhydride. In the laboratory the methods most commonly employed are: (1) Heating sulphuric acid with copper; (2) heating the acid with carbon (charcoal); (3) heating the acid with sulphur; and (4) allowing concentrated sulphuric acid to drop into a 40 per cent solution of acid sodium sulphite or more conveniently by the action of commercial hydrochloric acid on lumps of acid sodium sulphite in a Kipp's apparatus:

$$H_2SO_4 + HNaSO_3 = HNaSO_4 + SO_2 + H_2O.$$

Sulphur dioxide is a colorless, transparent gas, with a

pungent, suffocating odor, familiar as the odor of burning sulphur matches. It solidifies at 73° and boils at 8°. It is poisonous, causing death when inhaled in quantity, and giving rise to bad symptoms even in comparatively small quantities. It does not readily give up its oxygen, so that burning bodies are extinguished when introduced into it. It acts something like water in this respect. It is more than twice as heavy as air, its specific gravity being 2.26. When sulphur is burned in oxygen gas the sulphur dioxide formed occupies the same volume as the oxygen used up, so that there is no change in the volume. This can be shown by the experiment here described. A piece of sulphur is placed in a bent glass tube, of the form shown in Fig. 45, and the tube then half filled with pure oxygen over mercury. On now heating the tube at the part where the sulphur is, this burns and is converted into sulphur dioxide. After the tube has cooled down to the ordinary temperature the gas is found to occupy the same volume as before. This will be readily understood by the aid of the following considerations: In the reaction

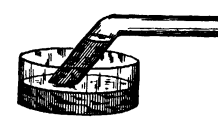


Fig. 45.

$$S + O_2 = SO_2$$

one molecule of sulphur dioxide is formed for every molecule of oxygen used up. But a molecule of sulphur dioxide in the form of gas occupies the same volume as a molecule of oxygen, so that, as the volume occupied by the sulphur in the experiment is insignificant, there is no change in volume occasioned by the above reaction.

Sulphur dioxide dissolves in water and forms a liquid in which sulphurous acid appears to be present.

The gas is easily liquefied by cold alone. It is only necessary for this purpose to pass the dry gas through a tube surrounded by a freezing mixture of ice and salt. The liquid changes rapidly into gas under ordinary pressure at the ordinary temperature. In this change so much heat is absorbed that a temperature of about — 60° can

be produced by means of it; and a portion of the liquid can thus be solidified.

Sulphur dioxide is very stable. If heated to 1200° under pressure, however, it gives sulphur trioxide and sulphur:

$$3SO_2 = 2SO_3 + S.$$

When conducted into solutions of bases or of carbonates the corresponding sulphites are formed:

$$2KOH + SO_2 = K_2SO_3 + H_2O;$$
$$K_2CO_3 + SO_2 = K_2SO_3 + CO_2.$$

Under certain conditions, as when the gas is passed into a hot solution of an alkali carbonate, a salt of the general formula $M_2S_2O_5$ is formed. This bears to the sulphite the same relation that the pyrosulphate bears to the sulphate:

$$2KHSO_3 = K_2S_2O_5 + H_2O;$$
$$\text{and } 2KHSO_4 = K_2S_2O_7 + H_2O.$$

**Uses.**—Sulphur dioxide is used extensively for the purpose of bleaching silk, wool, straw, and basket-ware. In order that it may bleach, however, water must be present, so that it appears that the true bleaching agent in this case is sulphurous acid and not the dioxide. When it is recalled that sulphur dioxide does not readily take up oxygen, while sulphurous acid does readily take it up, the necessity of having water present in the bleaching process at once becomes apparent. The bleaching in some cases certainly consists in abstracting oxygen from the colored substances, and thus converting them into colorless products. In other cases it is due to the formation of compounds of sulphurous acid with the dyestuffs.

Sulphur dioxide is not only a bleaching agent like chlorine, but like chlorine it is also a disinfectant. It has to some extent the power to destroy the organisms that cause changes in organic substances. It prevents fermentation and is therefore used as a preservative. Its

power to destroy the germs of disease, that is, to disinfect, is not as great as is frequently supposed. Much larger quantities are necessary for this purpose than are commonly used.

**Sulphur Trioxide,** $SO_3$.—This compound is made by passing sulphur dioxide and oxygen together over heated platinum in a finely-divided state (see p. 243). It is obtained most readily by heating disulphuric acid, which breaks up easily into sulphur trioxide and ordinary sulphuric acid according to the equation

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

Similarly, the acid sulphates of the alkali metals yield the corresponding normal sulphates and sulphur trioxide:

$$2NaHSO_4 = Na_2SO_4 + SO_3 + H_2O.$$

Sulphur trioxide crystallizes in transparent colorless prisms which melt at 14.8°, at ordinary temperatures it is a colorless oil which boils at 46.2°. Its molecular weight is represented by the formula $SO_3$. In contact with the air the oxide gives off thick fumes partly due to the great power of the compound to combine with water. Water acts with violence upon it, the heat evolved in the act being 39,170 cal. It also acts upon substances containing hydrogen and oxygen in much the same way that concentrated sulphuric acid does, charring them by abstracting the hydrogen and oxygen. It acts, however, more violently in this way than sulphuric acid does. With water it forms sulphuric acid, and it is, therefore, called sulphuric anhydride. The reaction involved in passing from sulphur trioxide to sulphuric acid is of a kind which, as we have seen, is frequently met with both with acidic oxides or anhydrides, and with basic or metallic oxides; and it is desirable that it should here be studied a little more carefully than it has yet been. What is known is that when sulphur trioxide acts upon water there is a great deal of heat evolved, and compounds of different composition are obtained. The composition of these compounds is represented by the formulas $SO_3 + H_2O$,

$SO_3 + 2H_2O$, and $SO_3 + 3H_2O$. So, too, when calcium oxide or lime, CaO, acts upon water, there is great evolution of heat, and a compound is formed the composition of which is represented by the formula $CaO + H_2O$. But in these formulas no attempt is made to give an account of what takes place in the chemical acts referred to. That the water is not present in the compounds as water is evident, in the first place from the conduct of the compounds, and in the second place from the amount of heat evolved in the act of combination. Now, taking the chemical conduct of the substances into consideration, they appear to contain hydrogen in combination with oxygen, and their conduct becomes comprehensible on the supposition that the group known as hydroxyl (–O–H) is present. This view has been found to be in accordance with a large number of facts, and it is of great assistance in dealing with these facts. The view is this: When an acidic oxide acts upon water it is converted into a hydroxyl compound which has acid properties, as shown in this equation:

$$O=S=O + \begin{matrix} H_2O \\ H_2O \\ H_2O \end{matrix} = S \begin{cases} OH \\ OH \\ OH. \\ OH \\ OH \\ OH \end{cases}$$

According to this, each molecule of water is decomposed and each hydrogen atom in the resulting compound is in combination with oxygen. The same kind of action takes place in the case of some basic oxides, as shown, for example, in the case of calcium oxide:

$$Ca=O + H_2O = Ca\begin{matrix} O–H \\ O–H \end{matrix}.$$

Just as sulphur trioxide acts upon water to form sulphuric acid, so it acts upon metallic oxides, to form sulphates. Thus with calcium oxide it forms calcium sulphate:

$$CaO + SO_3 = CaSO_4.$$

**Sulphur Hexoxide,** $S_2O_6$.—Sulphur trioxide is stable only at temperatures above 27°. Below this temperature it is changed to the polymeric form $S_2O_6$. Sulphur hexoxide crystallizes in fine white needles like asbestos, which remain solid up to 50°. Above this temperature it passes into the vapor of the trioxide which condenses to the liquid trioxide boiling at 46.2°. Its molecular weight shows that it is to be represented by the formula $S_2O_6$. It resembles the trioxide in its properties but is less active.

**Sulphuryl Chloride,** $SO_2Cl_2$, is formed by the direct action of chlorine upon sulphur dioxide in the sunlight, the action being similar to that which takes place when sulphur dioxide and oxygen unite to form the trioxide :

$$SO_2 + Cl_2 = SO_2Cl_2 ;$$
$$SO_2 + O = SO_3.$$

It is best prepared by heating the compound $SO_2{<}^{Cl}_{OH}$ to 170°–180°, when the following reaction takes place :

$$2SO_2{<}^{Cl}_{OH} = H_2SO_4 + SO_2Cl_2.$$

It is a liquid which is easily decomposed by water, as represented in the equation

$$SO_2Cl_2 + 2H_2O = SO_2(OH)_2 + 2HCl.$$

With half the quantity of water required to effect the above decomposition *chlorsulphuric acid*, $SO_2{<}^{Cl}_{OH}$, is formed :

$$SO_2{<}^{Cl}_{Cl} + H_2O = SO_2{<}^{Cl}_{OH} + HCl.$$

**Chlorsulphuric Acid, or Sulphuryl-hydroxyl Chloride,** $SO_2{<}^{Cl}_{OH}$, is formed by the direct action of hydrochloric acid upon sulphur trioxide :

$$SO_3 + HCl = SO_2{<}^{Cl}_{OH}.$$

Like sulphuryl chloride it is decomposed by water, yielding hydrochloric acid and sulphuric acid.

**Compounds of Selenium and Tellurium with Oxygen and with Oxygen and Hydrogen.**—In the introduction to this chapter it was stated that selenium and tellurium form compounds with oxygen corresponding to sulphur dioxide and sulphur trioxide. There is a third oxide of tellurium of the composition represented by the

formula, TeO, while only one oxide of selenium, the dioxide, $SeO_2$, is known. On the other hand, the acids of selenium and tellurium, corresponding to sulphurous and sulphuric acids, are known.

**Selenous Acid,** $H_2SeO_3$.—This compound is formed by oxidation of selenium in presence of water or by dissolving selenium dioxide in water. It is a crystallized solid, which attracts moisture from the air, and when heated breaks down into selenium dioxide and water. It forms two series of salts, the acid selenites, $MHSeO_3$, and the normal selenites, $M_2SeO_3$. While in composition the acid and its salts are analogous to sulphurous acid and the sulphites, in conduct there is a marked difference. Sulphurous acid tends, as we have seen, to take up more oxygen and form sulphuric acid, while selenous acid gives up its oxygen with great ease and yields selenium. When a solution of selenous acid is treated with sulphur dioxide the acid is reduced to selenium:

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

**Selenic Acid,** $H_2SeO_4$, is formed by the action of powerful oxidizing agents like saltpetre on selenium. Chlorine and bromine in water solution also serve the purpose. The action with chlorine is represented thus:

$$Se + 6Cl + 4H_2O = H_2SeO_4 + 6HCl.$$

**Selenium Dioxide,** $SeO_2$.—This is made by burning selenium, or by heating selenous acid. It is a solid crystallized substance that can be sublimed without undergoing decomposition and without melting. It dissolves readily in water, forming selenous acid. When it is sublimed particles of dust that may be present in the vessel effect partial reduction, and the product, instead of being white, as the oxide is when pure, is colored by particles of selenium.

**Tellurous Acid,** $H_2TeO_3$.—Tellurous acid is formed by treating tellurium tetrachloride with water. It is possible that the first action causes the formation of normal tellurous acid, $Te(OH)_4$, and that this then breaks down into tellurous acid, $H_2TeO_3$, and water:

$$TeCl_4 + 4H_2O = Te(OH)_4 + 4HCl;$$
$$Te(OH)_4 = TeO(OH)_2 + H_2O.$$

The potassium salt of the acid is formed by melting together tellurium dioxide and potassium carbonate:

$$K_2CO_3 + TeO_2 = K_2TeO_3 + CO_2.$$

If the salt thus formed is dissolved in water and nitric acid added to the solution, tellurous acid is thrown down:

$$K_2TeO_3 + 2HNO_3 = 2KNO_3 + H_2TeO_3.$$

It is a solid that easily loses water and is thus transformed into tellurium dioxide.

**Telluric Acid,** $H_2TeO_4$.—Salts of this acid are formed by melting tellurous acid with saltpetre and other oxidizing agents When the solution of the acid is evaporated to crystallization the solid compound deposited has the composition $H_6TeO_6$, and it appears probable that this is normal telluric acid, $Te(OH)_6$. This is soluble in water with neutral reaction. When normal telluric acid is heated to about 160°, it is decomposed into tellurium trioxide and water ·

$$Te(OH)_6 = TeO_3 + 3H_2O.$$

Although most of the tellurates are simple salts of the acid $H_2TeO_4$, others are derived from more complex forms of the acid. One of these is analogous to disulphuric acid.

**Oxides of Tellurium.**—*Tellurium monoxide* is formed by heating sulphur trioxide and tellurium together in a vacuum. *Tellurium dioxide* is formed by burning tellurium or by oxidizing it with nitric acid ; and, further, by the decomposition of tellurous acid by heat. It crystallizes and is but slightly soluble in water.

The *trioxide*, $TeO_3$, is formed by heating telluric acid to a high temperature. Its conduct is entirely different from that of sulphur trioxide. While the latter acts with violence upon water, and readily upon metallic oxides and hydrochloric acid, the former does not act readily upon any of these substances. It is insoluble in hot as well as cold water.

## Family VI, Group A.

Group A, Family VI, includes chromium, molybdenum, tungsten, and uranium. All of these show some resemblance to the elements of the sulphur group, but they also appear in entirely different characters, forming compounds of a kind unknown among the derivatives of sulphur and its analogues. The relations which these elements bear to sulphur is much like that which manganese bears to chlorine. The resemblance to sulphur is seen mainly in the formation of acids of the formulas $H_2CrO_4$, $H_2MoO_4$, $H_2WO_4$, and $H_2UO_4$, and the oxides $CrO_3$, $MoO_3$, $WO_3$, and $UO_3$. The common salts of chromic acid are derived from bichromic acid which is analogous to disulphuric acid. They have the general formula $M_2Cr_2O_7$ So, too, salts of molybdic acid are known which are derived from the simple form of the acid, $H_2MoO_4$, and others which are derived from a dimolybdic acid, $H_2Mo_2O_7$, and from more complicated forms. Tungsten has a wonderful power of forming complex acids. All of them, however, can be referred to the simple form $H_2WO_4$. And, finally, uranic acid forms salts which for the most part are derived from diuranic acid, $H_2U_2O_7$. The most important of these compounds will be taken up later.

When the acids of chromium, molybdenum, tungsten, and uranium lose oxygen they form compounds that have little or no acid character. The lower oxides of chromium form salts with acids, and these bear a general resemblance to the salts of aluminium, iron, and manganese. The chromates lose their oxygen quite readily when acids are present with which the chromium can enter into combination in its capacity as a base-forming element. Thus, when potassium chromate, $K_2CrO_4$, is treated with hydrochloric acid in the presence of something that can take up oxygen, decomposition takes place thus :

$$2K_2CrO_4 + 10HCl = 4KCl + 2CrCl_3 + 5H_2O + 3O.$$

With sulphuric acid the action takes place as represented in this equation :

$$2K_2CrO_4 + 5H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O + 3O.$$

In both these cases the chromium enters into combination as a trivalent base-forming element, taking the place of three atoms of hydrogen in hydrochloric acid in the first case, and of three atoms of hydrogen in the sulphuric acid in the second. Molybdenum and tungsten do not form salts of this character ; indeed they seem to be practically devoid of basic properties. Uranium, on the other hand, forms some curious salts. (See Uranium.)

## EXPERIMENTS.

### Manufacture of Sulphuric Acid.

Experiment 108.—The manufacture of sulphuric acid can be illustrated in the laboratory by means of the apparatus represented

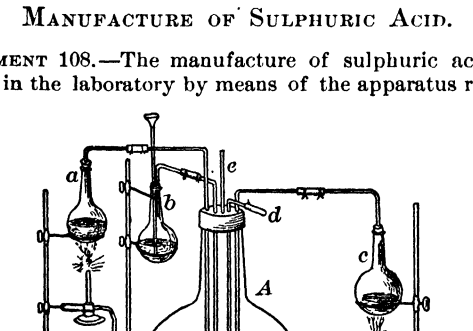



Fig. 46.

in Fig. 46. This consists of a large balloon-flask fitted with a stopper

having five openings. By means of tubes it is connected with three small flasks. One of these, *a*, contains water for the purpose of providing a current of steam ; another, *c*, contains copper-foil and concentrated sulphuric acid, which give sulphur dioxide when heated ; and the third, *b*, contains copper-foil and dilute nitric acid, which give oxides of nitrogen, mainly nitric oxide, NO. When the nitric oxide comes in contact with the air it combines with oxygen, forming nitrogen trioxide and nitrogen peroxide ; and when steam and sulphur dioxide are admitted to the flask the reactions involved in the manufacture of sulphuric acid take place. By means of a pair of bellows attached at *d* air is supplied. If air is not forced in, the gases become colorless, owing to complete reduction of the oxides of nitrogen to the form of nitric oxide, NO, which is colorless. If steam is not admitted the walls of the vessel become covered with crystals of nitrosyl-sulphuric acid. This is, however, decomposed by an excess of steam.

EXPERIMENT 109.—Into a vessel containing ordinary concentrated sulphuric acid introduce small sticks of wood, pieces of paper, and various other organic substances, and note the result. The charring effect is particularly well shown by adding the acid drop by drop to a concentrated solution of sugar, or to molasses, and stirring.

EXPERIMENT 110.—Sulphuric acid is detected in analysis by adding barium chloride to its solution, when insoluble barium sulphate is formed :

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl.$$

Other insoluble sulphates are those of strontium and lead ; and calcium sulphate is difficultly soluble. To a dilute solution of sulphuric acid or of any soluble sulphate, add in test-tubes barium chloride, strontium nitrate, and lead nitrate.

## SULPHUROUS ACID AND SULPHUR DIOXIDE.

EXPERIMENT 111.—Put eight or ten pieces of sheet copper, one or two inches long and about half an inch wide, in a 500 cc. flask ; pour 15 to 20 cc. concentrated sulphuric acid on it. On heating, sulphur dioxide will be evolved. The moment the gas begins to come off, lower the flame, and keep it at such a height that the evolution is regular and not too active.. Pass some of the gas into a bottle containing water. The solution in water is called sulphurous acid.

EXPERIMENT 112.—(See also Experiment 115). The most convenient method for making sulphur dioxide consists in letting moderately concentrated sulphuric acid drop into a water solution of acid sodium sulphite. Fit a flask with a stopper with two holes. Through one of the holes pass a dropping-funnel and through the other a convenient delivery-tube. In the funnel put a cooled mixture of equal volumes of concentrated sulphuric acid and water. In the

flask put a 40 per cent solution of acid sodium sulphite in water. By turning the stop-cock of the funnel so that the acid drops into the solution there will be a regular evolution of the gas.

EXPERIMENT 113.—Pass sulphur dioxide into a moderately dilute solution of potassium hydroxide, until the solution is saturated. What is then contained in the solution? To a little of it add hydrochloric acid. What takes place?

EXPERIMENT 114.—Try the effect of heating concentrated sulphuric acid with charcoal, and with sulphur.

EXPERIMENT 115.—Collect by displacement of air some of the gas made in Experiment 112. Does it burn? or does it support combustion?

EXPERIMENT 116.—Pass some of the gas through a bent glass tube surrounded by a freezing mixture of salt and ice. Tubes provided with glass stop-cocks are made for such purposes. They generally have the form represented in Fig. 47. If the tube is taken out of

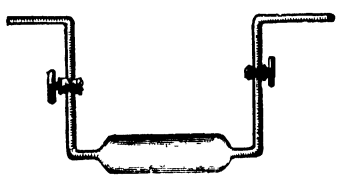


FIG. 47.

the freezing mixture, the liquid sulphur dioxide changes rapidly to gas, if the stop-cocks are opened.

EXPERIMENT 117.—Burn a little sulphur in a porcelain crucible under a bell-jar. Place over the crucible on a tripod some flowers. In the atmosphere of sulphur dioxide the flowers will be bleached.

### SULPHUROUS ACID IS A REDUCING AGENT.

EXPERIMENT 118.—To a dilute solution of potassium iodide in a test-tube gradually add chlorine water until the solution becomes clear and colorless. Now add a solution of sulphurous acid. At first iodine is deposited, but on further addition of sulphurous acid it dissolves again. Explain all the changes.

### SULPHUR TRIOXIDE.

EXPERIMENT 119.—Heat a little fuming sulphuric acid gently in a test-tube: What takes place? Put a little of the acid (5–10 cc.) in a small dry retort provided with a glass stopper and connect with a dry glass receiver. Heat the retort gently, and keep the receiver cool. By means of a dry glass rod take out some of the substance which collects in the receiver and put it in water. Lay a little of it on a piece of wood and on a piece of paper.

EXPERIMENT 120.—Prepare finely-divided platinum by moistening some fine asbestos with a solution of platinic chloride and heating to redness in a porcelain crucible. The substance thus obtained is known as platinized asbestos. Now arrange an apparatus so that both oxygen and sulphur dioxide can be passed together through a tube of hard glass as represented in Fig. 48.

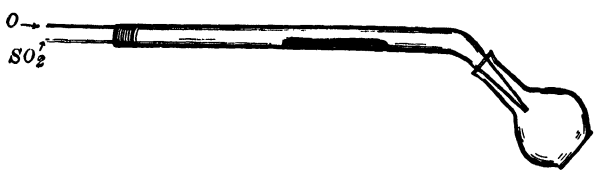



FIG. 48.

First pass the two dried gases together through the empty tube and heat a part of the tube by means of a burner. Is there any evidence of combination? Now stop the currents of the gases, let the tube cool down, and introduce a small layer of the platinized asbestos. Pass the dried gases over the heated asbestos. What takes place?

## CHAPTER XV

### NITROGEN.—THE AIR.—ARGON, ETC.

### Nitrogen, N (At. Wt. 14.01).

**General.**—Nitrogen bears to a group of elements relations very similar to those which oxygen bears to the sulphur group, and fluorine to the chlorine group. There are easily recognized resemblances between it and the members of the group, and yet there are some marked differences. Nitrogen is trivalent towards hydrogen, as shown in the compound $NH_3$, while it is both trivalent and quinquivalent towards oxygen, as appears to be shown in $N_2O_4$ and $N_2O_5$. The principal hydrogen compound, ammonia, is entirely different in character from those of chlorine and sulphur, for, while these are acid, the aqueous solution of ammonia has in a marked degree the character of a base. The two oxides above referred to are acidic, forming the acids $HNO_2$ and $HNO_3$, which are known as nitrous and nitric acids respectively.

**Occurrence of Nitrogen.**—It was discovered by Priestley and Scheele towards the end of the 18th century that the air consists of two gases, one of which is oxygen, and they showed that when the oxygen is removed the gas that is left has not the power to support combustion nor to support respiration. This gas was first called *azote* (from *α*, privative, and *ζωή*, life,) and this name is still retained in France, the symbol in use in that country being Az, whereas in all others the symbol is N. This is the only case in which there is a difference of usage in respect to the symbols of the chemical elements in different countries. The name *nitrogène* was given to it later, because it is a constituent of nitre or saltpetre, $KNO_3$ (*nitrum*, saltpetre, and *γένειν*, to produce), and this is the origin of the English name nitrogen. Not only is

nitrogen found free in the air, but it is found in combination in a large number of substances in nature. It is found in the nitrates, or salts of nitric acid, particularly as the potassium salt $KNO_3$, and the sodium salt $NaNO_3$, which occurs in enormous quantities in Chili, and is therefore known as Chili saltpetre. It is also found in the form of ammonia, which is a compound of nitrogen and hydrogen of the formula $NH_3$. Ammonia occurs in small quantity in the air, and is formed under a variety of conditions, which will be taken up later. Nitrogen occurs, further, in combination in many animal substances.

**Preparation.**—The most convenient way to prepare nitrogen is by burning in a closed vessel something that does not give a gaseous product of combustion; or by passing air over something that has the power to unite with oxygen. The best substance to use for the first purpose is phosphorus, which burns readily and yields a solid product, soluble in water. It is only necessary to place a piece of phosphorus in a floating vessel on the surface of water, set fire to it, and immediately place over it a closed bell-jar. As soon as the oxygen is used up the combustion stops, the vessel then contains nitrogen, and the walls are covered with a thin layer of phosphorus pentoxide, $P_2O_5$. This is soon converted by the water into phosphoric acid, which dissolves. Another convenient method for preparing nitrogen consists in passing air over copper heated in a tube. The copper takes up the oxygen readily, and the nitrogen passes on. Another good method consists in exposing to the air copper turnings partly covered with a solution of ammonia in a vessel so arranged as to allow free access of air while the escape of the gas from the vessel is prevented. This mixture absorbs oxygen slowly at the ordinary temperatures. Nitrogen can also be obtained from the air by cooling it below $-182.5°$ at which point the oxygen in the air liquefies, the nitrogen remaining a gas. The nitrogen prepared from the air is never pure, as other substances besides nitrogen and oxygen are always present in the air; and while some of these can be removed without

serious difficulty, others cannot. Pure nitrogen is obtained when chlorine is passed into a water solution of ammonia. This reaction takes place:

$$NH_3 + 3Cl = N + 3HCl;$$

but the hydrochloric acid combines at once with ammonia to form ammonium chloride, $NH_4Cl$:

$$NH_3 + HCl = NH_4Cl;$$

so that the only gaseous product is nitrogen. This experiment is more or less dangerous, for if all the ammonia should be used up, and the passage of chlorine continued, a compound of nitrogen and chlorine which is extremely explosive would be formed. Finally, nitrogen can be made by heating ammonium nitrite, $NH_4NO_2$, either dry or in solution. The hydrogen and oxygen of the compound unite to form water and the nitrogen is set free:

$$NH_4NO_2 = 2H_2O + N_2.$$

The simplest method of obtaining pure nitrogen practically is to heat a concentrated solution of ammonium sulphate mixed with a solution of sodium nitrite, passing the nitrogen generated through a wash-bottle filled with potassium bichromate and dilute sulphuric acid which removes accidental impurities:

$$2NaNO_2 + (NH_4)_2SO_4 = Na_2SO_4 + 4H_2O + N_2.$$

**Properties.**—Nitrogen is a colorless, tasteless, inodorous gas. At $-195.5°$ under the ordinary atmospheric pressure it is converted into a liquid; and this liquid solidifies at $-210.5°$. The critical temperature is $-146°$, and the critical pressure is 35 atmospheres. A liter of nitrogen under standard conditions weighs 1.2505 grams. Its specific gravity (air=1) is 0.967. It does not support combustion, nor does it burn. This latter fact is obvious, for, if nitrogen had the power to combine with oxygen when the temperature of the mixture is elevated, it is plain that this process of combustion would long ago have taken place, leaving one or the other of the two

gases and the product of combustion as the constituents of the air. Nitrogen not only does not combine with oxygen readily, but it does not combine readily with other elements except at high temperature. Lithium, however, burns freely in nitrogen, and combines slowly with it at ordinary temperatures forming a nitride.

The reason of the inertness of nitrogen lies in the stability of its molecule $N_2$, its atoms being held so firmly in the molecule that few substances can break down the molecule to combine with the atoms. This tendency of atomic nitrogen to form molecular nitrogen is the basis of the properties of all explosives in use, all of which yield nitrogen when exploded. Just as nitrogen does not support combustion, so also it does not support respiration. Animals would die in it, not on account of any active poisonous properties possessed by it, but for lack of oxygen. In the air it serves the useful purpose of diluting the oxygen. If the air consisted only of oxygen, all processes of combustion would certainly be much more active than they now are. What effect the continued breathing of oxygen would have upon animals it is impossible to say.

**The Air.**—The atmosphere of the earth, commonly called the air, consists essentially of the two elements nitrogen and oxygen in the proportion of 79 volumes of nitrogen to 21 volumes of oxygen, or, by weight, of 77 per cent of nitrogen and 23 per cent of oxygen. Dry air is a poor conductor of heat and of electricity. The weight of a liter of air under standard conditions is 1.293 grams. Wherever air has been collected and analyzed it has been found to have practically the same composition. Nevertheless very accurate analyses have shown that the composition of the air is subject to slight variations. To decide whether the air is a chemical compound or a mechanical mixture requires a careful examination of a number of facts. The evidence may be summed up as follows:

(1) If nitrogen and oxygen are mixed together the mixture conducts itself in exactly the same way as air.

The mixing is not attended by any phenomena indicating chemical action. Generally the chemical combination of two elements is accompanied by a change of temperature. When nitrogen and oxygen are brought together there is no change in the temperature of the gases, and no change of volume.

(2) The law of definite proportions is founded upon a very large number of observations, and in all cases in which we have independent evidence that chemical action takes place it is found that the substances combine in exactly the same proportions to form the same product Variation in the composition of a chemical compound is not known. The composition of the air varies slightly, according to circumstances, and this fact may be regarded as evidence that the air is not a chemical compound.

(3) Air dissolves somewhat in water. If air which is in solution in water is pumped out and analyzed, it is found to have a different composition from that of ordinary air. Instead of containing nearly 4 volumes of nitrogen to 1 of oxygen, it contains only 1.87 volumes of nitrogen to 1 of oxygen. The proportion of oxygen is much larger in the air that has been dissolved in water than it is in ordinary air. This is due to the fact that oxygen is more soluble than nitrogen in water. Therefore, when air is shaken with water, relatively more oxygen than nitrogen is dissolved. If the gases were in chemical combination we should expect the compound to dissolve as such and without change of composition.

The above evidence shows that nitrogen and oxygen are not combined chemically in the air, but that they are simply mixed together.

**Analysis of Air.**—The earliest examinations of Priestley, Lavoisier, and Scheele were made by burning substances in air contained in closed vessels. They concluded that the air is made up of $\frac{1}{5}$ oxygen and $\frac{4}{5}$ nitrogen by bulk. In order to determine the composition of the air to-day, we should proceed as follows: A qualitative examination would easily show the presence of nitrogen and oxygen.

If a solution of calcium hydroxide, $Ca(OH)_2$, known as lime-water, or a solution of barium hydroxide, $Ba(OH)_2$, is exposed to the air it becomes turbid, and a precipitate is formed. Neither nitrogen nor oxygen nor a mixture of the two gases can cause this change. It has been shown that the change is due to the presence in the air of a small quantity of the gaseous compound, carbon dioxide, $CO_2$. If calcium chloride or phosphorus pentoxide is exposed to the air it soon becomes moist and after a time turns liquid. This effect has been found to be due to the presence of water-vapor in the air. Nitrogen obtained from the air by passing the latter over copper, which abstracts the oxygen, has been shown to contain a small amount of an extremely inert gas, argon (which see). By other methods which need not be described here it can be shown that there are many other substances in the air besides those mentioned. Among them are ammonia, hydrogen dioxide, and organic matters of various kinds, including a large variety of germs the presence of which can be detected by the changes which exposure to the air produces in certain liquids, as milk and fruit-juices.

The next thing is to determine in what quantities these constituents are present, or to make a *quantitative analysis* of the air. For this purpose advantage may be taken of the fact that phosphorus when exposed to the air at ordinary temperatures combines slowly with the oxygen, leaving the nitrogen, argon, and minute quantities of other gases. If, therefore, a piece of ordinary phosphorus is inserted into a measured volume of air contained in a graduated glass tube over water or mercury, a diminution in volume will take place slowly. If, in the course of a few hours, the volume is again measured, the difference will give the volume of oxygen absorbed, while the gas remaining is chiefly nitrogen. Of course, in this case as in all others in which gas volumes are measured, corrections for temperature, pressure, and tension of aqueous vapor must be made.

Another method by which the ratio between the nitro-

gen and oxygen in air can be determined is that which was first employed by Dumas and Boussingault. It consists in passing air over heated copper, collecting and measuring the nitrogen, and weighing the copper oxide. The apparatus is arranged as shown in Fig. 49.

The copper is contained in the glass tube *ab* on the combustion furnace. At the ends of this tube are the stop-cocks *rr*. *V* is a glass globe provided with a stop cock *u*. Before the experiment the air is exhausted fron the globe and the tube *ab*, and the tube then carefully weighed. The tubes *B* and *C* and the apparatus *A* contain substances which have the power to absorb the car

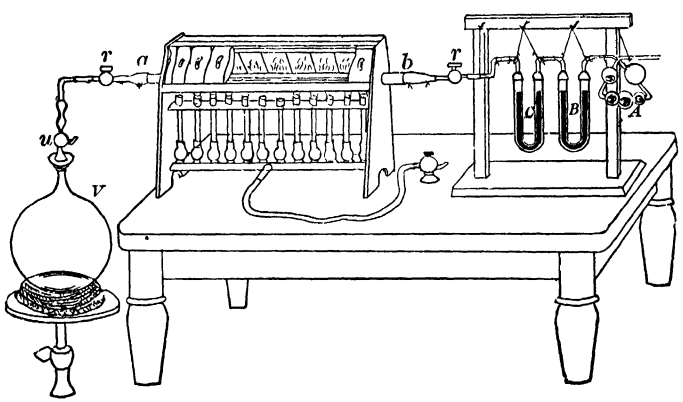



FIG. 49.

bon dioxide of the air. The tube *ab* is now heated and air admitted after passing through *C*, *B*, and *A*. The copper takes up the oxygen, and the nitrogen enters the globe *V*. After the globe is full it is weighed, then exhausted and weighed again, and the difference gives the weight of the nitrogen. The tube is also exhausted and weighed, and the difference between this weight and that of the exhausted tube before the experiment gives the weight of the oxygen.

The most refined method for the analysis of the air is the eudiometric method of Bunsen. This consists in adding some pure hydrogen to a measured volume of air

contained in a eudiometer (see p. 75) over mercury, and then exploding the mixture by means of an electric spark. If the conditions are right all the oxygen present will combine with hydrogen, and there will be a corresponding contraction in the volume of the gases. The amount of contraction will be equal to the volume of hydrogen and that of oxygen which have combined to form water. But from previous experiments on these two gases it is known that they combine in the ratio of one volume of oxygen to two of hydrogen. Consequently the volume of oxygen which was present is equal to one-third of the total contraction. Of course it is necessary that there should be enough hydrogen present to combine with all the oxygen. This method is capable of great exactness. The most accurate analyses made by this method by Bunsen and others have shown that in 100 volumes of air there are 20.9 to 21 volumes of oxygen.

The estimation of the quantity of water-vapor present in the air is an important problem. The quantity present depends upon a variety of causes, the temperature and the direction of the wind being the chief ones. A good chemical method of estimating the water consists in drawing a known volume of air over calcium chloride in a weighed tube. This substance has the power to take up water, as we have repeatedly seen. If the tube is weighed after a certain volume of air has been drawn through it, the increase in weight will show the weight of water contained in that volume of air.

The quantity of water-vapor present in the air varies between comparatively wide limits. At any given temperature the air can hold only a certain quantity. When it contains this quantity it is said to be *saturated*. If cooled below this temperature the vapor partly condenses, and appears as water. When a vessel containing ice is placed in the air, that which immediately surrounds the vessel is cooled down below the point at which the quantity of water-vapor present would saturate the air, and water condenses on the outside of the vessel. Every one has noticed that on a warm cloudy day more water

condenses on such a vessel than on a clear cool day. The water-vapor present in the air has an important effect on man. The inhabitants of countries with moist climates apparently have characteristics which are not generally met with in those who inhabit countries with dry climates. The difference between the effect of moist and that of dry air on an individual is well known.

When air which is charged with water-vapor comes in contact with cooler air, the vapor condenses and falls as rain.

The method employed for the purpose of estimating the quantity of carbon dioxide in the air consists in drawing a known volume of air over something that has the power to absorb the carbon dioxide, and then determining the increase in weight of the absorbing substance. Potassium or sodium hydroxide may be used. An apparatus has been constructed in which barium hydroxide, $Ba(OH)_2$, is used as the absorbent. When carbon dioxide is passed through a solution of this substance insoluble barium carbonate, $BaCO_3$, is precipitated according to the equation

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

This may be filtered off, dried, and weighed, and the quantity of carbon dioxide estimated from the results; or, if a known quantity of the hydroxide is taken, the quantity left unacted upon after the experiment can be determined by neutralizing with an acid, the neutralizing power of which has previously been determined with care. The quantity of carbon dioxide present in the air is relatively very small, being about 3 parts in 10,000 of air. It varies slightly according to the locality and season, being greater in cities and in summer than in the country and in winter; and greater in warm countries than in cold. It is essential to the life of plants, as oxygen is to the life of animals.

It has recently been shown that air always contains a minute quantity of free hydrogen.

It is not an easy matter to determine the quantities of the other constituents of the air, as the ammonia, organic

substances, etc., though there is no difficulty in determining that they are present in very small quantities.

*Composition of dry Air per Cubic Meter and per Kilogram.*

| | | | |
|---|---|---|---|
| 780.3 liters | nitrogen | = | 975.80 grams |
| 209.9 " | oxygen | = | 299.84 " |
| 9.4 " | argon | = | 16.76 " |
| 0.3 " | carbon dioxide | = | 0.59 " |
| 0 1 " | hydrogen | = | 0 01 " |
| 1000 liters | = 1 cubic meter air | = | 1293.00 grams |

| | | | |
|---|---|---|---|
| 755.14 grams | nitrogen | = | 603.81 liters |
| 231.47 " | oxygen | = | 162.03 " |
| 12.92 " | argon | = | 7.24 " |
| 0.46 " | carbon dioxide | = | 0.23 " |
| 0.01 " | hydrogen | = | 0.08 " |
| 1000.00 gr. | = 1 kil. air | = | 773.39 liters |

*Quantities of Rare Gases in 1 Cubic Meter Air.*

| | | |
|---|---|---|
| 0.015 liters | neon | = 0.01339 grams. |
| 0.0015 " | helium | = 0.00027 " |
| 0.00005 " | krypton | = 0.00018 " |
| 0.000006 " | xenon | = 0.00003 " |

**Air and Life.**—The relations of the air to the most important chemical changes that are taking place upon the earth form one of the most interesting subjects of study. We have had a glimpse of the action of oxygen, and of that of carbon dioxide; both are essential to the life of plants and animals. So, too, the water-vapor acts chemically upon plants, and probably to some extent in the respiration of animals. As regards the nitrogen, this element is frequently referred to as inert, and as serving the purpose of diluting the oxygen. Inert it undoubtedly is, and there is also no doubt that it dilutes the oxygen, but these statements give a very inadequate conception of the important part played by it in the processes of nature. Nitrogen in some form of combination is an essential constituent of plants and animals. The animals get their nitrogenous compounds from the plants, and the plants get theirs partly at least from the soil. By the growth of plants, therefore, nitrogenous compounds are constantly

being withdrawn from the soil. When plants and animals undergo decomposition in or on the soil, the nitrogen contained in them is gradually converted into salts of nitric acid or nitrates, and if the decomposition takes place in the air the nitrogen is converted principally into ammonia. Both in the form of nitrates and of ammonia the nitrogen can be utilized by plants, so that if the plants and animals which have received their nourishment from a certain tract of land should be allowed to decay upon this land after death, and the products thus formed should be uniformly distributed in the soil, the latter would not become exhausted. But the products of the soil are removed, and, therefore, the nitrogen required for the growth of other plants is removed, and the soil becomes unproductive. In order that it may be rendered fertile again, the lost nitrogen must be supplied. It has further been shown that some plants have the power to take up from the air a part of the nitrogen necessary for their development, and that in this absorption of nitrogen from the air certain minute organisms that exist in the soil play an important part.

**Pure and Impure Air.**—Pure air may be defined as air that consists of nitrogen, oxygen, and carbon dioxide in the proportions stated above, together with some water-vapor, ammonia, hydrogen dioxide, and argon, and nothing of an injurious nature. It is obvious that there is constant danger of contamination from natural causes. The most common cause of contamination is the breathing of human beings in rooms inadequately supplied with air. The breathing process involves the using up of oxygen and the giving off of carbon dioxide and small quantities of organic matter undergoing decomposition. If the quantity of oxygen is reduced below a certain limit the air becomes unfit for breathing purposes, and evil effects follow. An ordinary inhalation will not then be sufficient to supply the blood with the oxygen necessary to purify it, and the system will begin to suffer. Headache, drowsiness, and a general sense of discomfort follow. The ill effects of breathing

the air of a badly-ventilated room occupied by a number of human beings appear to be due for the most part to the presence of small quantities of decomposing organic matters which are given off from the lungs with the carbon dioxide and other gases. These act as poisons. They are given off from the lungs because they are unfit for use, and when they are taken back again the normal processes of the body are interfered with. The subject of ventilation has been so thoroughly discussed of late years that great improvement has been made in the arrangements for supplying pure air to dwelling apartments and audience halls, but there is still much room for improvement. Fortunately, in most buildings there is one source of supply of pure air that is independent of architects' plans. This is the diffusion of gases through the porous materials of which the buildings are constructed. This diffusion was referred to under the head of Hydrogen (see p. 58). There is also a good deal of ventilation through the cracks and other apertures that are always to be found in our buildings.

Under some conditions not thoroughly understood the air becomes contaminated by the decomposition of animal and vegetable matter. Air thus contaminated may cause specific diseases, and some of these are spoken of as being caused by *malaria*, a word which signifies simply bad air. It has been shown that there are in the air microscopic germs that have the power to develop in the body, and then to cause the symptoms which are referred to malaria. Disease germs and germs of other kinds are present in the air in great variety, and they play an important part in connection with the health and life of mankind.

**Liquid Air.**—Attention has been called to the fact that both oxygen and nitrogen can be liquefied. As air is a mixture of these two gases it follows that it can be liquefied. In brief the method employed consists in subjecting the air to a pressure of from 2000 to 2500 pounds to the square inch and cooling this compressed air down to the ordinary temperature by water. It is then passed through a tube that ends in a needle-valve. It is

allowed to escape through this valve into another tube that surrounds the one from which it has just escaped In expanding it is cooled down below the temperature at which the compressed air in the inner tube becomes liquid. This liquid escapes with the gaseous air and is easily collected.

Liquid air is a turbid, colorless liquid. The turbidity is due to the presence of solid water (ice) and solid carbon dioxide. By passing the liquid through a paper filter the solids are removed, and a transparent liquid is thus obtained. This consists mostly of nitrogen and oxygen in the proportion of about four-fifths of the former to one-fifth of the latter. This mixture has no constant boiling point; it begins to boil at $-195°$. As the nitrogen boils at a lower temperature (195.5°) than oxygen ($-182.5°$), more nitrogen than oxygen is converted into gas in a given time, and after a time, if suitable apparatus is used, the liquid that is left is nearly pure oxygen.

**Argon.**—Lord Rayleigh has shown that a liter of nitrogen prepared from the air by abstracting the oxygen and the small quantities of other substances known to be present weighs 1 2572 grams, while a liter of nitrogen made from some chemical compound, such as ammonia, weighs 1.2505 grams. Chemically-prepared nitrogen is lighter than that obtained from the air. This observation led Lord Rayleigh and Ramsay to a more thorough chemical examination of the air, the result of which was the discovery of a constituent previously unknown. This is the gas argon. It can be obtained by either of two methods: (1) By passing air over heated copper until all the oxygen is abstracted, and then over heated magnesium, or better, over lithium, which unites with the nitrogen but leaves the argon; (2) by mixing air with oxygen and passing electric sparks through the mixture. The oxygen and nitrogen combine and the product can easily be removed. After all the nitrogen has thus been removed argon remains. Argon is an element with the atomic weight 39.9. It is present in the air to the extent of about 1 per cent of the nitrogen. It also occurs in a number of mineral-water springs. It

cannot be made to combine with any other element. Indeed the argon atom is so inert that it does not combine with another argon atom to form the molecule, i. e. the molecule is monatomic. Argon solidifies at — 188° and boils at — 186°.

**Other Gases in the Air.**—By allowing the greater part of liquid air to evaporate and examining the residue Ramsay has discovered another gaseous substance in the air which he calls *krypton*. By liquefying argon by means of liquid air, and collecting the gas given off from it at successive stages, Ramsay has shown, further, that two other gases, which he calls *neon* and *xenon*, are present in the air in very small quantities. The atomic weights of these elements deduced from their specific gravities are: krypton 81.8, neon 20, xenon 128. Krypton melts at — 169° and boils at — 152°. Neon has been solidified but its melting point has not been exactly determined. Neon boils at about — 243°. Xenon melts at — 140°, and boils at — 109°. All of these gases are inactive and monatomic.

**Helium.**—When cleveite and some other rare minerals are treated with acids a gas is given off. This was at first held to be nitrogen, but a careful spectroscopic examination by Ramsay has shown that it contains a hitherto unknown gas. The spectrum contains lines which are identical with lines that have been observed in the solar spectrum. These have been ascribed to an unknown element, *helium*. Helium is also contained in the air in minute quantity. The atomic weight of helium is 4, and it is the only gas known that has not been liquefied. It remains a gas at — 259° under a pressure of 60 atmospheres. It is inert and monatomic. One liter water dissolves 14 cc. helium. Concerning the relations of helium to radium, see Radium.

## EXPERIMENTS.

### Preparation of Nitrogen.

**Experiment 121.—Place a good-sized stoppered bell-jar over water in a pneumatic trough. In the middle of a flat cork about three inches in diameter fasten a small porcelain crucible, and place**

this on the water in the trough. Put in it a piece of phosphorus about twice the size of a pea, and set fire to it. Quickly place the bell-jar over it At first some air will be driven out of the jar. The burning will continue for a short time, and then gradually grow less and less active, finally stopping. On cooling, it will be found that the volume of gas is less than four-fifths the original volume, for the reason that some of the air was driven out of the vessel at the beginning of the experiment Before removing the stopper of the bell-jar see that the level of the liquid outside is the same as that inside Try the effect of introducing successively several burning bodies into the nitrogen, as, for example, a candle, a piece of sulphur, phosphorus, etc.

EXPERIMENT 122.—Pass air slowly over copper contained in a tube heated to redness and collect the gas which passes through. Does it act like nitrogen?

EXPERIMENT 123.—Bring 7 grams dry sodium nitrite into a flask of 250 cc capacity; add 1 cc dilute ammonia, and a concentrated lukewarm solution of 20 grams ammonium sulphate. Warm gently. An abundant current of nitrogen is given off To purify the nitrogen conduct it through a wash-bottle containing a mixture of potassium bichromate and dilute sulphuric acid. Collect the gas over water as you collected oxygen The gas is pure nitrogen The formation of nitrogen in this case is due to the formation of ammonium nitrite which then breaks down into nitrogen and water (see p. 264).

### ANALYSIS OF AIR.

EXPERIMEMT 124.—Arrange an apparatus as in Fig. 11. Instead of a plain tube, use one graduated in cubic centimeters. Enclose 60 to 80 cc air in the tube over water. Arrange the tube so that the level of the water inside and outside is the same. Note the temperature of the air and the height of the barometer. Reduce the observed volume to standard conditions. Now introduce a piece of phosphorus, as in Experiment 26, and allow it to stand for twenty-four hours. Draw out the phosphorus. Again arrange the tube so that the level of the water inside is the same as that outside. Make the necessary corrections for temperature, pressure, and the pressure of aqueous vapor. It will be found that the volume has diminished considerably, but that about four-fifths of the gas originally put in the tube is still there If the work is done properly, the volume of the gas left in the tube will be to the total volume used as 79 to 100. In other words, of every 100 cc. air used 21 cc. are absorbed by phosphorus, and 79 cc are not. The gas absorbed is oxygen The gas left over has no chemical properties in common with oxygen Carefully take the tube out of the vessel of water, closing its mouth with the thumb or some suitable object to prevent the contents from escaping. Turn it with the mouth upward, and

introduce into it a burning stick. Does it support combustion? Is it oxygen?

EXPERIMENT 125.—Expose a few pieces of calcium chloride on a watch-glass to the air. It gradually becomes liquid by absorbing water from the air.

EXPERIMENT 126.—Expose some clear lime-water to the air. It soon becomes covered with a white crust. A similar change takes place if baryta-water is exposed in the same way. Lime-water is made by putting a few pieces of quicklime in a bottle and pouring water upon it. The mixture is well shaken up and allowed to stand. The undissolved substance settles to the bottom, and with care a clear liquid can be poured off the top. This is lime-water, which is a solution of calcium hydroxide, $Ca(OH)_2$, in water. Baryta-water is a solution of a similar compound of the element barium When these solutions are exposed to nitrogen or oxygen, or to an artificially prepared mixture of the two gases, no change takes place. Further, if air is first passed through a solution of caustic soda it no longer has the power to cause the formation of a crust on lime-water or baryta-water.

EXPERIMENT 127. Arrange an apparatus as shown in Fig. 50. The wash-cylinders *A* and *B* are half filled with a solution of ordi-

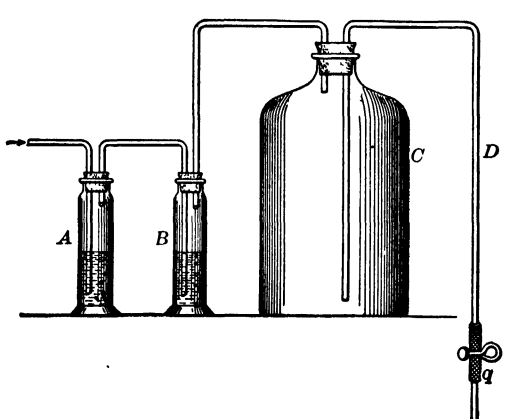



FIG. 50.

nary caustic soda. The bottle *C* is filled with water. The tube *D*, which should be filled with water and provided with a pinch-cock, acts as a siphon. Open the pinch-cock and let the water flow slowly out of the bottle As it flows out air will be drawn in through the caustic soda in the wash-cylinders. When the bottle is a quarter

filled with air pour some water in again until it is full. Then draw all the water off. Now remove the stopper from the bottle, pour in 20 to 30 cc. lime-water and cork the bottle. The crust formed on the lime-water will now be hardly, if at all, perceptible. There is, therefore, something present in the air under ordinary circumstances which has the power to form a crust on lime-water or baryta-water, and which can be removed by passing the air through caustic soda. Thorough examination has shown that this is the compound which chemists call *carbon dioxide*, and which is commonly known as *carbonic-acid gas*. It is the substance which was obtained by burning charcoal in oxygen.

EXPERIMENT 128.—Into the bottle containing the air from which the carbon dioxide has been removed hold a burning stick or taper for a moment. Notice whether a crust is now formed on the lime-water. Wood and the material from which the taper is made contain carbon. Explain the formation of the crust on the lime-water after the stick of wood or taper has burned for a short time in the vessel.

EXPERIMENT 129.—Arrange an apparatus as shown in Fig. 51. The bottle *A* contains air; *B* contains concentrated sulphuric acid; *C* contains granulated calcium chloride; *D* is carefully dried and

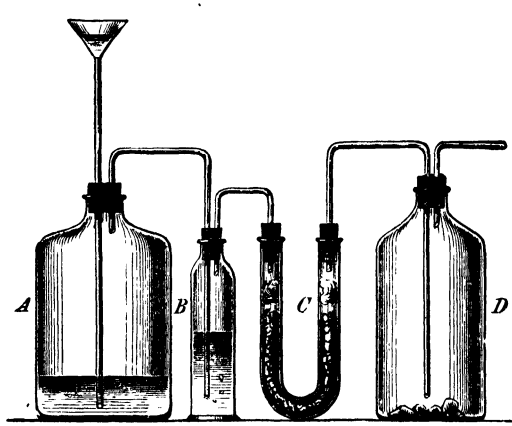



FIG 51

contains a few pieces of granulated calcium chloride and air. Pour water through the funnel-tube into *A*, when the air will be forced through *B* and *C* and into *D*. But in passing through *B* and *C* the moisture contained in it will be removed, and the air which enters *D* will be dry. After *A* has once been filled with water, empty it and fill it again, letting the dried air pass into *D*. This operation may be repeated any number of times. The calcium chloride in *D* will not grow moist.

## CHAPTER XVI

### COMPOUNDS OF NITROGEN WITH HYDROGEN.—WITH HYDRO GEN AND OXYGEN.—WITH OXYGEN, ETC.

**General Conditions which give Rise to the Formation of the Simpler Compounds of Nitrogen.**—It has been shown that at ordinary temperatures nitrogen is an inactive element. It is nevertheless easy to get compounds of nitrogen with many other elements, and among these compounds, some of those which it forms with hydrogen and oxygen are of high importance.

When a compound that contains carbon, hydrogen, and nitrogen, and is not volatile, is heated in a closed vessel, so that the air does not have access to it, the nitrogen passes out of the compound, not as nitrogen, but partly in combination with hydrogen, in the form of the compound *ammonia*. Nearly all animal substances contain carbon, hydrogen, oxygen, and nitrogen in many forms of combination, some of which are quite complicated. Many of these give off ammonia when heated. Similarly, compounds containing carbon, oxygen, and hydrogen, even though they may be thoroughly dry, when heated give off oxygen in combination with hydrogen in the form of water. Both these kinds of decomposition, that which gives ammonia and that which gives water, are to be ascribed to the fact that the compounds of carbon employed are unstable at high temperatures, and when they are decomposed the elements contained in them combine in stable forms, such as the comparatively simple compounds, water and ammonia. An illustration of this kind of action was referred to in describing the preparation of nitrogen by heating ammonium nitrite. This compound breaks down very easily under the influence of heat, the hydrogen and oxygen combining to form the

stable compound water, while the nitrogen remains uncombined. Some animal substances, as, for example, urine, give off ammonia when they undergo decomposition in the air. This decomposition is generally, if not always, due to the action of minute organisms, the germs of which are in the air. These germs develop when they come in contact with urea. The coal which is used for making illuminating-gas contains some hydrogen and nitrogen in chemical combination, and when the coal is heated ammonia is given off with the other products.

When animal substances undergo decomposition in the presence of basic compounds where the temperature is comparatively high, the nitrogen combines with oxygen and with the metal of the base. Either a salt of nitric acid, $HNO_3$, or of nitrous acid, $HNO_2$, is formed. In some countries where the conditions are favorable to the process, immense quantities of nitrates are found, chiefly potassium nitrate, $KNO_3$, and sodium nitrate, $NaNO_3$. Nitrates are, however, found everywhere in the soil. The change of animal and vegetable nitrogenous substances to nitrates is caused by the action of minute organisms, which are found everywhere, and serve an important purpose in converting the waste animal and vegetable matter into simple compounds that can be utilized by plants. How they effect the change is not known. From the salts of nitric acid found in nature, nitric acid itself can easily be made.

Nearly all the compounds of nitrogen with which we have to deal are made either from ammonia or from nitric acid.

Ammonia is formed by the weathering or decomposition of rocks containing nitrogen, and is therefore found in volcanic gases. The nitrogen in these rocks is probably in the form of nitrides (which see).

**Relations between the Principal Compounds of Nitrogen.**—It has been shown that whenever a compound of sulphur is oxidized with a strong oxidizing agent the final product of the action is sulphuric acid; and that, on the

other hand, under the influence of strong reducing agents these compounds yield hydrogen sulphide as the final product. So, also, the limit of oxidizing action in the case of chlorine is perchloric acid, and of reducing action, hydrochloric acid. Most of the other compounds of sulphur with hydrogen and oxygen are products intermediate between the two limits, sulphuric acid and hydrogen sulphide, as the other compounds of chlorine with hydrogen and oxygen are intermediate between hydrochloric acid and perchloric acid. The limit of reduction of nitrogen compounds is ammonia, $NH_3$, and of oxidation, nitric acid, $HNO_3$. As has been pointed out, the valence of nitrogen towards oxygen is greater than it is towards hydrogen, but the difference is not as marked as in the case of the members of the chlorine group, and in that of the sulphur group. Its hydrogen valence is 3, its maximum oxygen valence is 5.

A tabular list of the oxides of nitrogen and the acids formed by it is here given:

| *Oxides.* | | *Acids.* |
|---|---|---|
| Nitrous oxide, $N_2O$ | | Hyponitrous acid, $N_2(OH)_2$ |
| Nitric oxide, $NO(N_2O_2)$ | | Nitrous acid, $NO(OH)$ |
| Nitrogen trioxide, (Nitrous anhydride), | $N_2O_3$ | Nitric acid, $NO_2(OH)$ |
| Nitrogen peroxide, $NO_2(N_2O_4)$ | | |
| Nitrogen pentoxide, (Nitric anhydride), | $N_2O_5$ | |

In addition to these there are the basic compounds, *hydroxylamine*, $NH_2(OH)$, *ammonia*, $NH_3$, and *hydrazine*, $N_2H_4$; and with water ammonia probably forms the hydroxide $NH_4(OH)$, which is a base. In addition to these there is a compound of nitrogen with hydrogen of the formula $N_3H$. This is an acid. (See Triazoic Acid.) There is another acid of the same composition as hyponitrous acid but differing from it in properties, the relation of which to hyponitrous acid is not quite clear.

With the members of the chlorine group nitrogen forms a few compounds that are characterized by marked instability. So unstable are they that they explode violently when simply touched. The chloride of nitrogen explodes with great violence when the direct rays of the sun are allowed to shine upon it. With sulphur, nitrogen forms two compounds. With sulphur, hydrogen, and oxygen, however, nitrogen forms a number of compounds, one of which has already been referred to in connection with the manufacture of sulphuric acid. This is the so-called nitrosyl-sulphuric acid formed by the action of a mixture of the peroxide, $NO_2$, and the monoxide, NO, on sulphurous acid, oxygen, and water.

In studying the compounds of nitrogen, it will be best to begin with the end products, ammonia and nitric acid.

**Ammonia,** $NH_3$.—The conditions under which ammonia is formed have been mentioned. The chief source at present is the "ammoniacal liquor" of the gas-works. This is the water through which the gas has been passed for the purpose of removing the ammonia, and it contains ammonia, or ammonium hydroxide, $NH_4(OH)$, in solution. By adding hydrochloric acid to this solution the salt *ammonium chloride*, $NH_4Cl$, is formed. This is the well-known substance *sal ammoniac*. It appears that this name had its origin in the fact that common salt or sodium chloride, NaCl, was formerly called *sal armeniacum*, and that afterward, through a misunderstanding, ammonium chloride came to be known by the same name which underwent change to the form *sal ammoniacum*, or *sal ammoniac*. When the ammoniacal liquor is treated with sulphuric acid, *ammonium sulphate* is formed. To obtain ammonia from either of these salts it is only necessary to treat the salt with some strongly basic compound, as, for example, potassium or sodium hydroxide, or calcium hydroxide. Thus, when a solution of potassium hydroxide is poured on ammonium chloride or sulphate the strong penetrating odor of ammonia is noticed. The first

reaction probably results in the formation of ammonium hydroxide, thus:

$$\begin{aligned} NH_4Cl + KOH &= NH_4OH + KCl; \\ (NH_4)_2SO_4 + 2KOH &= 2NH_4OH + K_2SO_4; \\ 2NH_4Cl + Ca(OH)_2 &= 2NH_4OH + CaCl_2; \\ (NH_4)_2SO_4 + Ca(OH)_2 &= 2NH_4OH + CaSO_4. \end{aligned}$$

But the ammonium hydroxide breaks down very readily into water and ammonia, which escapes as a gas:

$$NH_4OH = NH_3 + H_2O.$$

In the laboratory ammonia is prepared by treating ammonium chloride with slaked lime or calcium hydroxide. The two are mixed in the proportion of two parts by weight of slaked lime to one of ammonium chloride, placed in a flask, and gently heated, when the ammonia is given off at once.

It is frequently more convenient to heat a strong aqueous solution of ammonia, such as is found in every chemical laboratory. Such a solution when gently heated readily gives off ammonia.

**Properties.**—Ammonia is a colorless, transparent gas with a very penetrating, characteristic odor. In concentrated form it causes suffocation. Its specific gravity is 0.59; that is to say, it is but little more than half as heavy as air. A liter of the gas under standard conditions weighs 0.7635 gram. It can easily be compressed to the liquid form by pressure and cold. It becomes solid at $-78°$, and boils at $-32.5°$.

When at ordinary temperatures the pressure is removed from liquefied ammonia it is converted into gas, and absorbs a great deal of heat. These facts are taken advantage of for the artificial preparation of ice. This application will be clear from the following explanation and Fig. 52.

An aqueous solution of ammonia saturated at 0° is brought into the strong iron cylinder *A*, and then gently warmed, while the vessel *B* is cooled by cold water. The

gas given off from *A* passes through the bent tubes into *B*, where it is condensed to a liquid. The cylinder *A* is now placed in a vessel of cold water, and the water which is to be frozen is placed in a cylinder *D*, and this into the hollow space *E* in the vessel *B*. The liquid ammonia passes rapidly into the form of gas which is absorbed in the water in *A*, while at the same time so much heat is absorbed that the water in *D* is frozen.

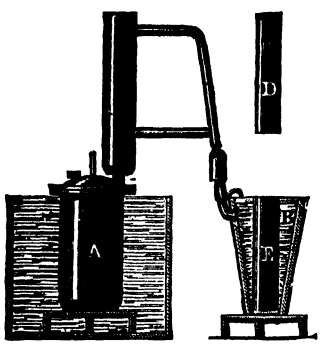


FIG. 52.

Ammonia does not burn in the air, but does burn in oxygen with a pale yellowish flame. It is absorbed by water in very large quantity. One volume of water at the ordinary temperature dissolves about 600 volumes of ammonia gas, and at 0° about 1000 volumes. The substance with which we commonly have to deal under the name of ammonia is a solution of ammonia in water. The solution has the odor of the gas. It loses all its gas when heated to the boiling temperature. The solution shows a strong alkaline reaction, and has the power to neutralize acids and form salts. The conduct of the solution is, in fact, strikingly like that of sodium and potassium hydroxides, and it is believed that in the solution there are present the ions of a compound of the formula $NH_4(OH)$, known as ammonium hydroxide, and formed by the direct action of ammonia upon water. If this is true, then the action of ammonia upon acids is to be explained as follows: Ammonium hydroxide is analogous to potassium hydroxide, but differs from it in that it contains the group of atoms $NH_4$ in place of the atom K. In some way this group plays in the salts formed by ammonia the same part that the elementary atom potassium plays in the salts of potassium, and just as the latter are called potassium salts so the former are called *ammonium*

*salts.* According to this the ammonium salts are salts containing the group $NH_4$, known as the *ammonium group*, in place of the hydrogen of the acids. They are formed by direct combination of ammonia with the acids, or by the action of ammonium hydroxide upon acids. The analogy between the action of ammonium hydroxide and that of potassium hydroxide upon acids is clearly shown by the aid of the following equations:

$$\begin{aligned}
K(OH) &+ HCl = KCl + H_2O;\\
NH_4(OH) &+ HCl = NH_4Cl + H_2O;\\
K(OH) &+ HNO_3 = KNO_3 + H_2O;\\
NH_4(OH) &+ HNO_3 = NH_4NO_3 + H_2O;\\
2K(OH) &+ H_2SO_4 = K_2SO_4 + 2H_2O;\\
2NH_4(OH) &+ H_2SO_4 = (NH_4)_2SO_4 + 2H_2O.
\end{aligned}$$

The formation of the ammonium salts by direct action of ammonia, $NH_3$, upon acids is represented in the following equations:

$$\begin{aligned}
NH_3 &+ HCl = NH_4Cl;\\
NH_3 &+ HNO_3 = NH_4NO_3;\\
2NH_3 &+ H_2SO_4 = (NH_4)_2SO_4.
\end{aligned}$$

The strong tendency of ammonia to combine directly with acids is shown by bringing two uncovered vessels, one containing a solution of ammonia, and the other a solution of hydrochloric acid, near each other. A dense cloud will at once be formed, if the solutions are concentrated. This is due to the direct combination of the gases escaping from the solutions.

While the assumption of the existence of the group ammonium, $NH_4$, in the ammonium salts is of great service in dealing with these salts, and while this assumption appears to be entirely justified by the facts, no compound of this composition has as yet been isolated. The name ammonium is given to the hypothetical compound for the reason that it evidently plays the part of a metallic element, and it is customary to give such elements names ending in *ium*. While, further, it is generally believed that the ions of the compound ammonium hydroxide,

$NH_4(OH)$, are formed when ammonia dissolves in water, the compound itself has not been isolated, owing to its instability and tendency to break down into ammonia and water. On the other hand, some very interesting derivatives of this hydroxide have been isolated. There is one which is derived from the hydroxide by the replacement of the four hydrogen atoms of the ammonium by groups of carbon and hydrogen atoms. This compound is stable and can be isolated as a hydroxide of the formula $NR_4(OH)$, in which $R_4$ represents the groups of carbon and hydrogen atoms. In solution it acts almost exactly like potassium hydroxide.

**Nitrides.**—Nitrides may be regarded as derived from ammonia by the substitution of metallic atoms for the hydrogen, just as the sulphides may be regarded as derived from hydrogen sulphide by the substitution of metallic atoms for the hydrogen of this substance. Compounds closely related to the nitrides are formed when dry ammonia gas is conducted over a number of metals when heated. For example, sodium gives the compound $NH_2Na$ thus:

$$Na + NH_3 = NH_2Na + Na.$$

The compound $NH_2Na$ is called sodamide and belongs to the class known as *metal amides*, in which metal takes the place of *one* hydrogen atom of ammonia. Liquid ammonia reacts with a number of the metals dissolving them and forming colored solutions.

So, too, aqueous ammonia dissolves other metals like zinc and copper, and also dissolves many metal oxides. Hence its technical and domestic use for cleaning tarnished metal articles.

**Composition of Ammonia.**—By oxidation it is possible to convert the hydrogen of ammonia into water and leave the nitrogen in the free state. As water and nitrogen are the only products formed, and the quantity of oxygen used in the oxidation is equal to the quantity of oxygen found in the water formed, it follows that nitrogen and hydrogen are the only elements contained in ammonia.

When electric sparks are passed for some time through a mixture of nitrogen and hydrogen, some ammonia is formed. Conversely, when electric sparks are passed for a time through ammonia, nitrogen and hydrogen are obtained. Hence it is not possible to obtain much ammonia in this way as the action is reversible and a condition of equilibrium occurs:

$$N_2 + 3H_2 \rightleftarrows 2NH_3.$$

If, in the oxidation of a known weight of ammonia, the water formed and the nitrogen left uncombined are accurately determined, it will be found that in ammonia the elements are combined very nearly in the proportion of 14 *parts by weight of nitrogen to* 3 *parts by weight of hydrogen.* Further, the molecular weight determined by the method of Avogadro is approximately 17. Therefore, the molecular formula of ammonia is $NH_3$, the atomic weight of nitrogen being 14.

The proportion by volume in which the two elements combine can be determined by the following method: A glass tube closed at one end and provided with a glass stop-cock at the other is filled with pure chlorine gas. By means of a small funnel attached to the open end a little of a strong aqueous solution of ammonia is slowly introduced into the tube. Reaction takes place at once between the chlorine and the ammonia, according to the equation

$$NH_3 + 3Cl = N + 3HCl;$$

and the hydrochloric acid unites with ammonia to form ammonium chloride:

$$3HCl + 3NH_3 = 3NH_4Cl.$$

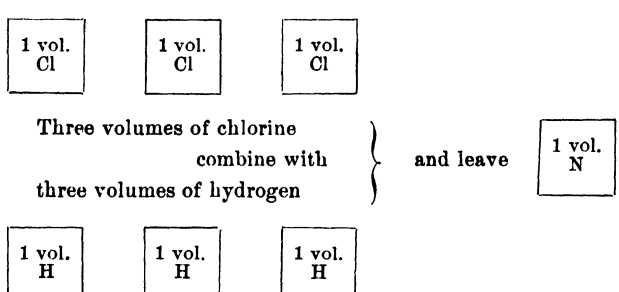
The entire change is therefore represented by the equation

$$4NH_3 + 3Cl = N + 3NH_4Cl.$$

Hydrogen and chlorine combine in equal volumes, as has already been shown. Now, if we start with a measured volume of chlorine, and add ammonia to it until it is all

used up, we know that the volume of hydrogen that has been extracted from ammonia is equal to the volume of chlorine with which we started. If we measure the volume of nitrogen left over, we know the volume of the nitrogen which was in combination with a volume of hydrogen equal to that of the chlorine originally taken. This experiment has been tried repeatedly, and it has been found that the ratio of the volume of nitrogen to that of the hydrogen with which it was combined is as 1 to 3. The tube being full of chlorine at the beginning of the experiment, it will be found to be one-third full of nitrogen at the end. *Therefore, in ammonia* 1 *volume of nitrogen is combined with* 3 *volumes of hydrogen.*

The experiment just referred to will perhaps be better understood by the aid of the accompanying diagram. The chlorine in the tube may be represented as made up of three equal parts or volumes. Each volume of chlorine combines with an equal volume of hydrogen, leaving the nitrogen uncombined. The volume of nitrogen left is only one-third of that of the chlorine, or for three volumes of chlorine there is one volume of nitrogen:




Therefore in ammonia the gases nitrogen and hydrogen are combined in the proportion of 1 volume of nitrogen to 3 volumes of hydrogen.

When nitrogen and hydrogen unite in the proportions above stated, how many volumes of ammonia gas do the four volumes of the constituents form? It is not possible to determine this by direct combination of the two gases,

but ammonia can be decomposed into its constituents by continued passage of electric sparks through it. When this is done it is found that after the decomposition the gases accupy twice the volume which was occupied by the ammonia. It appears, therefore, that when hydrogen and nitrogen combine to form ammonia the volume is reduced to one-half, or, what is the same thing, when three volumes of hydrogen combine with one volume of nitrogen the four volumes form two volumes of ammonia gas.

The above facts have already been commented upon in speaking of the combination of gases in general; and it has been shown that chlorine, oxygen, and nitrogen combine with hydrogen in entirely different ways:

(1) 1 volume of chlorine combines with 1 volume of hydrogen to form 2 volumes of hydrochloric acid gas.

(2) 1 volume of oxygen combines with 2 volumes of hydrogen to form 2 volumes of water-vapor.

(3) 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia gas.

What the cause of these differences is we do not know. In some way these facts are directly connected with the law of Avogadro that equal volumes of all gases contain the same number of molecules, and with the power of the atoms of chlorine, oxygen, and nitrogen to combine with one, two, and three atoms of hydrogen respectively. When one atom of chlorine unites with one atom of hydrogen the result is a molecule. So also when one atom of oxygen unites with two atoms of hydrogen, and when one atom of nitrogen unites with three atoms of hydrogen, the result in each case is a molecule, and, according to the law of Avogadro, a gaseous molecule, whether it consists of one atom or a hundred atoms, occupies the same space.

**Ammonium Amalgam.**—A very curious substance which appears to consist of mercury and ammonium is formed when a solution of ammonium chloride is treated with a compound of sodium and mercury known as sodium amalgam. The action is thought to take place thus:

$$2NH_4Cl + Na_2Hg = 2NaCl + (NH_4)_2Hg.$$

The product, ammonium amalgam, is unstable, breaking down readily into ammonia, hydrogen, and mercury. It will be referred to again and somewhat more fully under Mercury.

**Hydrazine,** $N_2H_4$.—A compound closely related to ammonia and ammonium has been prepared by a complicated method that cannot be explained here. This is known as hydrazine. Its composition and molecular weight are represented by the formula $N_2H_4$. A large number of derivatives of hydrazine are known.

Hydrazine is a liquid that boils at 113.5° in a current of hydrogen and melts at 1.4°. It acts upon acids much as ammonia does, forming the hydrazine salts.

**Hydroxylamine,** $NH_2(OH)$.—This compound is prepared by reducing nitric acid :

$$NO_2(OH) + 6H = NH_2(OH) + 2H_2O.$$

It can also be prepared by reducing nitric oxide :

$$2NO + 6H = 2NH_2(OH).$$

It is a solid consisting of leaflets or hard needles. It melts at 33.05°, and boils at 58° under a pressure of 22 mm. When the water solution is evaporated, both ammonia and hydroxylamine pass over with the water. Its salts are easily obtained by treating the solution with acids :

$$NH_2(OH) + HCl = NH_3(OH)Cl ;$$
$$NH_2(OH) + HNO_3 = NH_3(OH)NO_3.$$

From the method of formation and the composition it appears that these salts are ammonium salts in which hydroxyl is substituted for one hydrogen of the ammonium. They should therefore be called *hydroxyl-ammonium salts.* One of the most characteristic properties of hydroxylamine is the ease with which it breaks down into ammonia, nitrogen, and water :

$$3NH_2OH = N_2 + NH_3 + 3H_2O.$$

If brought in contact with compounds capable of reduction, it reduces them, the nitrogen in these cases generally combining with oxygen to form nitrous oxide, $N_2O$. The reduction of cupric oxide, CuO, takes place according to the equation

$$2NH_2(OH) + 4CuO = N_2O + 2Cu_2O + 3H_2O.$$

By nascent hydrogen hydroxylamine is reduced to ammonia.

**Triazoic Acid,** $N_3H$.—This compound, which is also called *hydrazoic* and *hydronitric acid,* can be made by a number of reactions in-

volving the use of complex organic substances. A simpler method consists in passing ammonia gas over heated metallic sodium, and then passing nitrous oxide, $N_2O$, over the sodamide thus formed. The following reaction takes place :

$$NH_2Na + N_2O = N_3Na + H_2O.$$

By dissolving in water the sodium salt, $N_3Na$, treating it with dilute sulphuric acid, and distilling, a solution of the acid is obtained. The compound is a colorless liquid that boils at 37°. It has a very penetrating odor, and produces bad effects upon one who inhales it. It is an acid resembling hydrochloric acid. It, as well as some of its salts, is extremely explosive. Its ammonium salt formed by direct union with ammonia is interesting as it has the composition $N_3NH_4$ or $N_4H_4$.

**Nitric Acid,** $HNO_3$.—This important compound was first made, though not in pure condition, about the thirteenth century, by distilling saltpetre, copper sulphate, and alum. The name nitric acid has its origin in the fact that the compound is formed from nitre. It has already been stated that the salts of this acid, especially the potassium and sodium salts, occur widely distributed in the earth, and that there is a great accumulation of the sodium salt in Chili, South America, whence the name Chili saltpetre. Wherever organic matter, particularly that of animal origin, undergoes spontaneous decomposition in the presence of basic substances, nitrates are formed, in consequence of the action of an organism known as the *nitrifying ferment.* This process of nitrification has already been referred to in a general way. It is one of great importance for the welfare of the human race, and indeed of most living beings, as by its aid the useless nitrogenous substances of dead plants and animals are converted into the useful nitrates which in the soil aid the process of plant growth.

Nitric acid can be formed by the action of electric sparks on nitrogen and oxygen in the presence of water. It is also formed by the action of oxidizing agents on ammonium compounds.

Nitric acid is generally prepared by treating potassium or sodium nitrate with concentrated sulphuric acid.

When sodium nitrate is treated with sulphuric acid action takes place thus:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

The salt formed in this way is *primary* or *acid* sodium sulphate. If sufficient saltpetre is present and the temperature is raised, a second reaction takes place, resulting in the formation of *normal* sodium sulphate:.

$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3.$$

But the temperature required for this reaction is so high (220°) that a considerable part of the nitric acid is decomposed. In the preparation of nitric acid, therefore, the first reaction is the one used, and for this purpose the substances are brought together in retorts in the proportion of their molecular weights (about equal weights), and the retort gently heated. The nitric acid distils over slowly, and is condensed by cooling the receiver.

On the large scale the acid is made by bringing Chili saltpetre and concentrated sulphuric acid together in cast-iron cylinders or retorts.

**Nitric Acid and Nitrates from Atmospheric Nitrogen.**—The world's supply of nitric acid and nitrates is drawn at present mostly from the Chili saltpetre deposits. According to recent official statistics the deposits will be exhausted in twenty years. Although still more recently (1907) the discovery of new deposits of large extent is announced, this will only postpone the time of exhaustion, as 1,400,000 tons was consumed—largely as fertilizer—in 1905, and the demand is increasing rapidly.

Of many attempts to obtain oxides of nitrogen directly and nitric acid indirectly from the air by the action of electric sparks or the electric arc, the one which is of greatest promise commercially is that of Birkelund and Eyde now in use on a large scale in Norway.

It should first be stated that the action is purely thermal, i. e. it is the heat of the arc that produces the result, and that the reaction $N_2 + O_2 \rightleftarrows 2NO$ becomes reversible if the product is not cooled rapidly.

The process utilizes the action of the magnetic field on the arc. With a powerful alternating current forming arcs, and powerful electro-magnets, glowing electric discs are produced built up of arcs deflected from the terminals by the magnetic field. In practice these discs are six feet in diameter, and have a temperature of over 2000°. The discs are enclosed in a circular furnace (like a wheel set on edge) and a rapid current of air passes across its diameter. The gas leaving the furnace is a mixture of nitric oxide, nitrogen and unchanged air. This passes into granite towers filled with porous material over which water drips, where the following reactions occur:

$$2NO + O_2 = 2NO_2, \quad \text{and} \quad 3NO_2 + H_2O = 2HNO_3 + NO.$$

When all of the nitric oxide is changed into acid, the latter is treated with lime and gives calcium nitrate. This is now the market product. It is said to be a better fertilizer than Chili saltpetre.

Another commercial fertilizer made from atmospheric nitrogen is calcium cyanamide (which see).

**Properties of Nitric Acid.**—Nitric acid is a colorless volatile liquid. It begins to boil at 86°, but at this temperature it undergoes partial decomposition into nitrogen peroxide, water, and oxygen:

$$2HNO_3 = 2NO_2 + H_2O + O.$$

It undergoes the same change slowly when exposed to the direct rays of the sun. In consequence of this decomposition the distillate collected in the manufacture of nitric acid, and, in general, whenever the acid is distilled, always contains a considerable percentage of water, and is colored more or less yellow by the nitrogen peroxide present. In order to abstract the water from ordinary nitric acid it is mixed with concentrated sulphuric acid and slowly distilled; but even under these circumstances the product is colored in consequence of slight decomposition, and it also contains some water. By conducting carbon dioxide gas through the gently warmed acid the nitrogen peroxide can be removed, and in this way an

acid containing about 99.5 per cent of the compound $HNO_3$ has been obtained.

Pure nitric acid is a very active substance chemically. It gives up its oxygen readily and is itself thus reduced to other compounds of nitrogen and oxygen, or of nitrogen, oxygen, and hydrogen. When it acts upon the metals it forms nitrates, metal atoms being substituted for the hydrogen. According to the conditions, nitrogen peroxide, $NO_2$, nitrous acid, $HNO_2$, nitric oxide, NO, nitrous oxide, $N_2O$, nitrogen, hydroxylamine, $NH_2(OH)$, and, finally, ammonia are formed by reduction of the acid. Of these reactions, that which gives nitric oxide, NO, is the one that commonly takes place on treating metals with nitric acid. The oxides $NO_2$ and $N_2O_5$ are themselves readily reduced to nitric oxide.

If the element upon which the acid acts has not the power to take the place of the hydrogen, the action is oxidation. This is shown in the action of strong nitric acid upon tin, phosphorus, carbon, sulphur, etc. In each case the highest oxidation-product is formed. Tin is converted into normal stannic acid, $Sn(OH)_4$; phosphorus into phosphoric acid, $PO(OH)_3$; carbon into carbon dioxide, $CO_2$; and sulphur into sulphuric acid, $SO_2(OH)_2$. It disintegrates carbon compounds very readily, converting them into their final products of oxidation. In contact with the skin it causes bad wounds.

Under no conditions does nitric acid acting on metals or on anything else, give off free hydrogen.

The acid mostly used in the laboratory has the specific gravity 1.2 and contains 32 per cent nitric acid, $HNO_3$. The commercial acid contains about 68 per cent of the acid.

When a mixture of nitric acid and water is boiled under the ordinary atmospheric pressure it loses either water or nitric acid until it contains 68 per cent of the acid and then it distils over. This does not correspond to any definite hydrate of nitric acid, though it approximates the composition required by normal nitric acid, $N(OH)_5$, or $HNO_3 + 2H_2O$, and it is probable that this hydrate is the chief constituent of the mixture.

Nitric acid is a strong monobasic acid, forming salts of the general formula $MNO_3$, all of which are soluble in water. Because nitric acid is a strong acid, and all normal nitrates are soluble in water, it is one of the best solvents.

**Red Fuming Nitric Acid** is formed in the manufacture of nitric acid from saltpetre and sulphuric acid if the temperature is raised to a sufficient extent to cause the acid sulphate to act upon the nitrate:

$$NaNO_3 + HNaSO_4 = Na_2SO_4 + HNO_3.$$

At this temperature the nitric acid undergoes considerable decomposition. The nitrogen peroxide formed is absorbed by the nitric acid, and the product thus obtained is the red fuming acid. It acts more energetically than nitric acid, and finds some applications in the laboratory and in the arts. When heated it gives off nitrogen peroxide, and if diluted with water it is changed to ordinary nitric acid, as nitrogen peroxide is decomposed by water, forming nitric acid and nitric oxide or nitrous acid, according to the temperature of the water.

*Nitro-hydrochloric Acid* or *Aqua Regia* is a liquid formed by mixing concentrated nitric and hydrochloric acids. It was called *aqua regia* because it can dissolve gold, the king of the metals. The active power of this liquid as a solvent of metallic substances is due to the fact that it gives off chlorine, and a compound of nitrogen, oxygen, and chlorine which readily gives up its chlorine. This compound has the composition represented by the formula NOCl, and is called *nitrosyl chloride.* The product of the action of nitrohydrochloric acid upon a metal is a chloride of the metal.

**Nitrous Acid,** $HNO_2$.—When certain salts of nitric acid are reduced they yield the corresponding nitrites. Thus, when potassium nitrate is heated with metallic lead this reaction takes place:

$$KNO_3 + Pb = KNO_2 + PbO.$$

Indeed, if potassium nitrate is heated alone it loses oxygen and is converted into the nitrite:

$$2KNO_3 = 2KNO_2 + O_2;$$

but the reaction is not complete, and the salt thus obtained always contains more or less nitrate.

Nitrous acid is known only in solution. If an attempt is made to isolate it from a nitrite the product is the anhydride, nitrogen trioxide, $N_2O_3$. Thus, if sulphuric acid is added to potassium nitrite the following reaction takes place:

$$2KNO_2 + H_2SO_4 = N_2O_3 + H_2O + K_2SO_4.$$

It may be that the first action is the liberation of nitrous acid, and that this then breaks down by loss of water. The two reactions are represented thus:

$$2KNO_2 + H_2SO_4 = 2HNO_2 + K_2SO_4;$$
$$2HNO_2 = N_2O_3 + H_2O.$$

The trioxide, $N_2O_3$, however, breaks down into the two gases nitrogen tetroxide, $NO_2$, and nitric oxide, NO.

A certain analogy will be observed between this action and that which takes place in the action of potassium hydroxide upon an ammonium salt, when ammonium hydroxide is probably first given off, and then breaks down into ammonia and water.

Salts are known which are derived from *normal nitrous acid*, $N(OH)_3$, but most of the nitrites are derived from the acid of the formula NO(OH), which is to be regarded as formed from the normal acid by loss of one molecule of water:

$$N(OH)_3 = NO(OH) + H_2O.$$

**Hyponitrous Acid,** $H_2N_2O_2$.—The sodium salt of this acid is made by reducing sodium nitrite in solution by means of sodium amalgam:

$$2NaNO_2 + 8H = Na_2N_2O_2 + 4\,H_2O.$$

The acid can also be made by oxidation of hydroxylamine.

It is a solid consisting of white crystalline plates. It is very explosive when freed from water. In water solution it is much more stable, but at the ordinary temperature it breaks down gradually, the principal products being nitrous oxide and water:

$$H_2N_2O_2 = N_2O + H_2O.$$

**Nitrous Oxide,** $N_2O$.—This compound can be obtained by reduction of nitric acid, and is sometimes formed in considerable quantity when copper is treated with the concentrated acid, though when made in this way it is always mixed with a large proportion of nitric oxide. The best way to make it is to heat ammonium nitrate, $NH_4NO_3$, which breaks down into nitrous oxide and water:

$$NH_4NO_3 = N_2O + 2H_2O.$$

It has been shown that when ammonium nitrite is heated it breaks down in the same way into free nitrogen and water:

$$NH_4NO_2 = N_2 + 2H_2O.$$

In these reactions the tendency of hydrogen and oxygen to combine at elevated temperatures is exhibited. At ordinary temperature this tendency is not strong enough to cause a disturbance of the equilibrium of the parts of the compound. As the temperature is raised and the equilibrium thus disturbed, the affinity of the hydrogen for the oxygen asserts itself. The two elements combine to form water, and the decomposition above represented takes place.

Nitrous oxide is a colorless, transparent gas of sweetish taste and odor. Its specific gravity is 1.53; it becomes solid at $-100°$, and boils at $-89.5°$. It is somewhat soluble in water; one volume of water at 0° dissolving somewhat more than its own volume of the gas. It supports combustion almost as well as pure oxygen. Some substances that burn in oxygen do not, however, burn in nitrous oxide. Sulphur which burns in oxygen is extinguished in nitrous oxide, unless it is previously heated to a high temperature.

When inhaled, nitrous oxide causes a kind of intoxication, that is apt to show itself in the form of hysterical laughing. Hence the gas is called *laughing gas.* Inhaled in larger quantity it causes unconsciousness and insensibility to pain. It is therefore used extensively to prevent

pain in some surgical operations, particularly in extracting teeth.

The gas is easily liquefied, and enclosed in properly constructed metallic cylinders the liquid is now obtainable in the market. In order to get the gas it is only necessary to open the stop-cock of the cylinder. When the liquid comes in contact with the air it rapidly turns to gas, and the temperature is very much lowered in consequence. This under proper conditions causes a part of the liquid to solidify.

**Nitric Oxide,** NO.—This is the most stable compound of nitrogen and oxygen, and is the most common product of the reduction of nitric acid. Thus, when nitric acid acts upon copper and other metallic elements the chief product is generally nitric oxide, though, as we have seen, the reduction may be carried farther. The principal action in the case of copper is represented thus:

$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

Considering the ease with which nitric acid gives up its oxygen, and the ease with which copper takes up oxygen, it is probable that the copper abstracts oxygen directly from the acid as represented thus:

$$2HNO_3 + 3Cu = 3CuO + H_2O + 2NO.$$

In this case the copper oxide would at once form copper nitrate with the excess of nitric acid:

$$6HNO_3 + 3CuO = 3Cu(NO_3)_2 + 3H_2O.$$

Or, combining the two equations, the total action is represented in the same way as it is above. The nitric acid must not have a specific gravity higher than 1.2, and the temperature must be kept down, otherwise the reduction of the nitric acid is carried farther and considerable nitrous oxide is formed.

It is possible that to some extent the hydrogen liberated from the acid may act as a reducing agent, thus causing the formation of the lower oxides of nitrogen, as, for example,

$$2HNO_3 + 6H = 2NO + 4H_2O.$$

Nitric oxide is a colorless, transparent gas. It solidifies at $-167°$ and boils at $-150°$. Its most remarkable property is its power to combine directly with oxygen when the two are brought together. The act of combination is not accompanied by the ap-

pearance of light, though heat is evolved. In the reaction which takes place at ordinary temperatures nitrogen peroxide, $NO_2$, is formed:

$$NO + O = NO_2.$$

The product is a colored gas, and the change of the colorless nitric oxide to this colored product can therefore easily be recognized. This reaction is, further, the chief cause of the reddish-brown fumes seen when nitric acid acts upon metals and other elements. At a low temperature some nitrogen trioxide is formed when oxygen acts upon nitric oxide.

From what has already been said, it will appear that in nitric oxide the oxygen and nitrogen are more firmly united than in the other oxides. Most burning substances are extinguished when introduced into it, though a few when heated in it to a high temperature extract all or a part of the oxygen. Zinc and iron extract half the oxygen and convert nitric oxide into nitrous oxide. Potassium and sodium decompose it, leaving the nitrogen free.

**Nitrogen Trioxide,** $N_2O_3$.—This oxide is formed by addition of oxygen to nitric oxide at low temperatures; by decomposition of the nitrites by means of acids; and by the combination of nitric oxide with the peroxide at a temperature below $-21°$. The gas given off when nitric acid is reduced with starch or arsenious oxide, $As_2O_3$, appears to be a mixture of nitric oxide and the peroxide. Pure nitrogen trioxide is a liquid of an indigo-blue color. It solidifies at $-111°$ and boils at $-2°$. At $-10°$ it begins to lose its color and at $-2°$ it undergoes partial decomposition into nitrogen peroxide and nitric oxide:

$$N_2O_3 = NO + NO_2.$$

With cold water nitrogen trioxide undergoes decomposition accompanied by an evolution of nitric oxide. Possibly this reaction takes place:

$$3N_2O_3 + H_2O = 2HNO_3 + 4NO.$$

By treating the oxide with a solution of sodium hydroxide or potassium hydroxide the corresponding nitrite is formed:

$$2KOH + N_2O_3 = 2KNO_2 + H_2O.$$

**Nitrogen Peroxide,** $NO_2$.—When nitric oxide and oxygen are brought together in the proportion of 2 volumes of the former to 1 volume of the latter they combine completely to form nitrogen peroxide. These relations will be readily understood when it is borne in mind that 2 molecules of nitric oxide require 1 molecule of oxygen to effect the change, as is shown in the equation

$$2NO + O_2 = 2NO_2.$$

The compound is most easily obtained by heating lead nitrate, when nitrogen peroxide and oxygen are given off, and lead oxide remains behind in the vessel·

$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$

If the gases are passed through a tube surrounded by a freezing mixture the peroxide is condensed to the form of liquid, while the oxygen passes on. When perfectly dry the peroxide is easily solidified, melting at $-10°$ and boiling at 26°. It acts energetically upon compounds that have the power to take up oxygen. When treated with water it undergoes decomposition. If the temperature is low, nitrous and nitric acids are formed:

$$2NO_2 + H_2O = HNO_2 + HNO_3.$$

If the water is hot, however, the products are nitric acid and nitric oxide:

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The nitric oxide thus formed will take up oxygen from the air and yield nitrogen peroxide again, and this, in contact with hot water, will be decomposed, forming nitric acid and nitric oxide, until all the peroxide is converted into nitric acid.

The determinations of the specific gravity of the gas from the peroxide show that at low temperatures the molecular formula is $N_2O_4$, but that when the temperature 150° is reached the molecule is represented by the formula $NO_2$. The compound appears therefore to undergo gradual decomposition or dissociation by heat, so that until the temperature 150° is reached the gas is a mixture of the compounds $N_2O_4$ and $NO_2$.

**Nitrogen Pentoxide,** $N_2O_5$.—This compound, which bears to nitric acid the relation of an anhydride, is formed by passing chlorine over silver nitrate and condensing the product. The reaction takes place thus:

$$2AgNO_3 + Cl_2 = N_2O_5 + 2AgCl + O.$$

It is also formed by treating nitric acid with phosphorus pentoxide, $P_2O_5$, a compound that has a very marked power to unite with water. The action is represented thus:

$$2HNO_3 = N_2O_5 + H_2O.$$

The pentoxide is a crystallized substance, that readily decomposes into nitrogen peroxide and oxygen. It melts at 30° and boils with decomposition between 45° and 50°. In consequence of the ease with which it gives up its oxygen it acts violently upon many oxidizable substances. With water it forms nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

**Compounds of Nitrogen with the Elements of the Chlorine Group.**—Notwithstanding the ease with which chlorine combines with most elements, and the stability of the compounds which it forms with them, its compound with nitrogen is extremely unstable. It can be made by the action of chlorine on ammonia, and by decomposing a solution of ammonium chloride by means of an electric current. In the latter case chlorine is liberated at one of the poles and then acts upon the ammonium chloride:

$$NH_4Cl + 6Cl = 4HCl + NCl_3.$$

It appears that when chlorine acts upon ammonia different products are formed by the substitution of chlorine for the hydrogen atom for atom, thus:

$$\begin{aligned} NH_3 &+ Cl_2 = NH_2Cl + HCl\,; \\ NH_2Cl &+ Cl_2 = NHCl_2 + HCl\,; \\ NHCl_2 &+ Cl_2 = NCl_3 + HCl. \end{aligned}$$

According to this, the trichloride of nitrogen is the final product of the substituting action of chlorine upon ammonia. The compound is an oil, that undergoes decomposition very readily. It is, indeed, one of the most explosive substances known. It is decomposed by heat, and especially by contact with certain substances, among which are oil of turpentine and caoutchouc. It is slowly decomposed by water. Direct sunlight causes explosion of the chloride.

When ammonia is treated with iodine reactions take place similar to those which take place with chlorine. The product is the iodide of nitrogen, $N_2H_3I_3$. This compound, like the chlorine compounds, is extremely explosive. The simplest way to prepare it is to place a little powdered iodine on a filter and pour concentrated ammonia over it. The substance should be made in only very small quantities at a time. When dried it decomposes with violent explosion by contact even with soft substances.

## EXPERIMENTS.

### Preparation and Properties of Ammonia.

Experiment 130.—To a little ammonium chloride on a watch-glass add a few drops of a strong solution of caustic soda, and notice the odor of the gas given off. Do the same thing with caustic potash. Mix small quantities of ammonium chloride and lime in a mortar, and add a few drops of water.

Experiment 131.—Mix 20 parts iron filings, 1 part potassium nitrate, and 1 part solid potassium hydroxide, and heat the mixture in a test-tube. Is there any evidence of the formation of ammonia?

Experiment 132.—Arrange an apparatus as shown in Fig. 37

omitting, however, the funnel-tube ; a cork with one hole will therefore serve. Weigh 100 grams quicklime in the flask, and add just enough water to slake it without making it moist; then add 50 grams ammonium chloride, and mix by shaking. Heat on a sand-bath. After the air is driven out, the gas will be completely absorbed by the water in the first Woulff's flask if shaken from time to time. Disconnect the delivery-tube from the series of Woulff's flasks, and connect with another tube bent upward. Collect some of the gas by displacement of air, *placing the vessel with the mouth downward.* (Why?) The arrangement is shown in Fig. 53. The vessel in which the gas is collected should be dry, as water absorbs ammonia very readily. Hence, also, it cannot be collected over water. In the gas collected introduce a burning stick or taper. Ammonia does not burn in air, nor does it support combustion. In working with the gas great care must be taken to avoid inhaling it in any quantity. After enough has been collected in cylinders to exhibit the chief properties, connect the delivery-tube again with the series of Woulff's flasks, and pass the gas over the water as long as it is evolved.

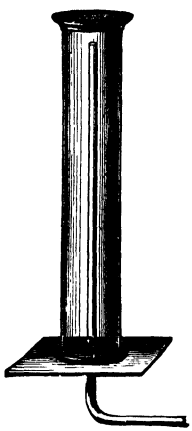


FIG. 53.

### AMMONIA BURNS IN OXYGEN.

EXPERIMENT 133.—Put a little of a concentrated solution of ammonia in a flask placed upon a tripod. Heat gently and, from a gasometer, pass a rapid current of oxygen through a bent tube into the liquid. Apply a light to the mouth of the vessel, when the ammonia will be seen to burn.

### AMMONIA FORMS AMMONIUM SALTS WITH ACIDS.

EXPERIMENT 134.—Put 100 cc. of a *dilute* solution of ammonia in an evaporating-dish. Try its effect on red litmus paper. Slowly add dilute hydrochloric acid until the alkaline reaction is destroyed and the solution is neutral. Evaporate to dryness on a water-bath. Compare the substance thus obtained with sal-ammoniac, or ammonium chloride. Taste. Heat on a piece of platinum-foil. Treat with a caustic alkali. Treat with a little concentrated sulphuric acid in dry test-tubes. Do they appear to be identical? Similarly sulphuric acid and ammonia yield ammonium sulphate ; nitric acid and ammonia yield ammonium nitrate; etc.

EXPERIMENT 135.—Fill a dry cylinder with ammonia gas, and

another of the same size with hydrochloric acid gas. Bring them together with their mouths covered. Quickly remove the covers, when a dense white cloud will appear in and about the cylinders. This will soon settle on the walls of the vessels as a light white solid. It is ammonium chloride. Thus, from two colorless gases we get a solid substance by an act of chemical combination. Heat is evolved in the act of combination.

## Composition of Ammonia.

Experiment 136.—*This experiment should be performed by a person experienced in the use of chemical apparatus.* A glass tube, such as represented in Fig. 54, provided with a glass stop-cock is needed. Fill this tube with chlorine free from air over a saturated solution of sodium chloride. After it is filled let it stand for some time mouth downward in the solution of sodium chloride to let the liquid drip out of it. Close the stop-cock and remove the tube from the solution. Hold it mouth upward, and pour a concentrated solution of ammonia into the funnel-like projection above the stop-cock; put in the glass-stopper, and now by slightly opening the stop-cock let the ammonia pass drop by drop into the tube. Reaction between the chlorine and the ammonia takes place, accompanied by a marked evolution of heat, and in a partly-darkened room light is seen. Great care must be taken not to admit air with the ammonia. After nearly all the ammonia has passed in from the funnel, pour into the funnel about two-thirds as much ammonia as has already been used, and let this in gradually. Leave the stop-cock closed, and fill the funnel with dilute sulphuric acid. Fit a bent tube into a cork; fill this tube with dilute sulphuric acid; put the cork in the funnel, and the other end of the tube in a small beaker containing dilute sulphuric acid, and, after immersing

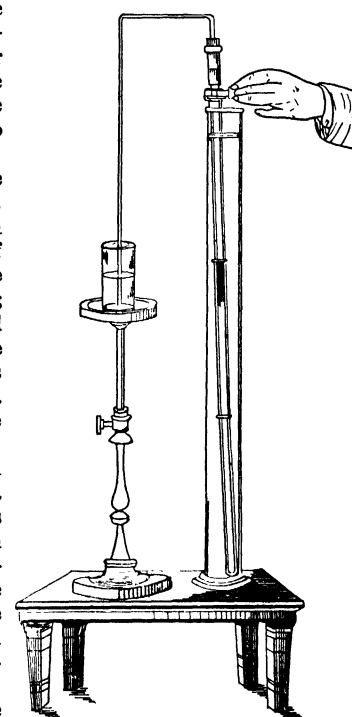


Fig. 54.

the long tube in water of the ordinary temperature, open the stop-cock. If the operation has been carried out as it should be, the dilute acid will flow into the tube until it is two-thirds full, and will then stop. The residual gas is nitrogen. What evidence in regard to the composition of ammonia is furnished by this experiment?

The arrangement of the apparatus in the last stage of the experiment is shown in Fig. 54.

## Preparation and Properties of Nitric Acid.

Experiment 137.—Arrange an apparatus as shown in Fig. 55. In the retort put 20 grams sodium nitrate (Chili saltpetre) and 20

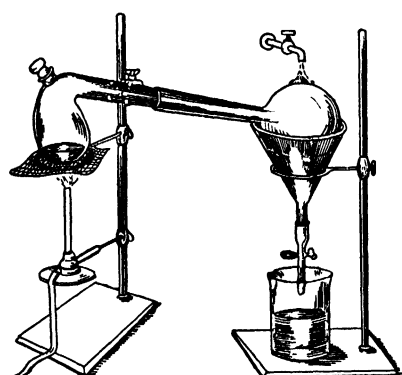


Fig. 55.

grams concentrated sulphuric acid. On gently heating, nitric acid will distil over, and be condensed in the receiver.—What reaction takes place?—After the acid is all distilled off, remove the contents of the retort. Recrystallize the substance from water, and compare it with the sodium sulphate obtained in the preparation of hydrochloric acid. (See Experiment 75.) In the latter stage of the operation the vessels become filled with a reddish-brown gas. The acid collected has a yellowish color.

Experiment 138.—*This and Experiments 139, 140, 141, should be performed only by experienced persons.* Mix together 400 grams concentrated sulphuric acid and 80 grams ordinary concentrated nitric acid. Pour the sulphuric acid into the nitric acid. Distil the mixture from a retort arranged as in the preceding experiment, taking care to keep the neck of the retort cool by placing filter-paper moistened with cold water on it. Use the acid thus obtained for the purpose of studying the properties of pure nitric acid.

## Nitric Acid gives up Oxygen readily, and is hence a good Oxidizing Agent.

Experiment 139.—Pour concentrated nitric acid into a wide test-tube, so that it is about one-fourth filled. Heat the end of a stick of charcoal of proper size, and, holding the other end with a forceps, introduce the heated end into the acid. It will continue to burn with a bright light, even though it is placed below the surface of

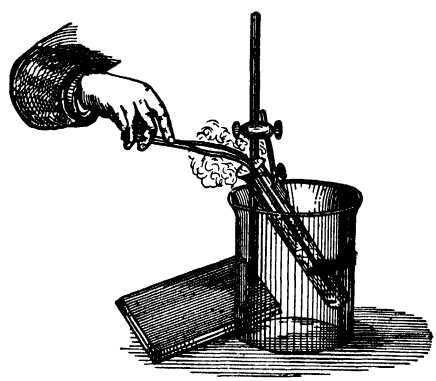


Fig. 56.

the liquid. The action is oxidation. The charcoal in this case finds the oxygen in the acid and not in the air. Great care must be taken in performing this experiment. The charcoal should not come in contact with the sides of the test-tube. A large beaker-glass should be placed beneath the test-tube, so that in case it breaks the acid will be caught and prevented from doing harm. The arrangement of the apparatus is shown in Fig. 56.

The gases given off from the tube are offensive and poisonous. Hence this experiment as well as all others with nitric acid should be carried on under a hood in which the draught is good.

Experiment 140.—Boil a little strong nitric acid in a test-tube in the upper part of which some horse-hair (or woollen yarn) has been introduced in the form of a stopper. The horse-hair (or yarn) will take fire and burn, and leave a white residue. Hold the test-tube with forceps over a vessel to catch the contents should the tube break.

Experiment 141.—In a small flask put a few pieces of granulated tin. Pour on this just enough strong nitric acid to cover it. Heat gently over a small flame. Soon action will take place. Colored gases will be evolved, the tin will disappear, and in its place will be

found a white powder. This consists mostly of tin and oxygen. (See Experiment 13.)

### Metals dissolve in Nitric Acid, forming Nitrates.

Experiment 142.—Dissolve a few pieces of copper-foil in ordinary commercial nitric acid diluted with about half its volume of water. The operation should be carried on in a good-sized flask and under an efficient hood. When the copper has disappeared, pour the blue solution into an evaporating dish, and evaporate down to crystallization. Compare the substance thus obtained with copper nitrate. Heat specimens of each Treat small specimens with sulphuric acid. What evidence have you that the two substances are identical?

### Nitrates are decomposed by Heat.

Experiment 143.—Heat some potassium nitrate in a test-tube. Introduce a piece of wood with a spark on it. Heat also lead nitrate, copper nitrate, and any other nitrates that may be available. What difference do you observe between the decomposition of potassium nitrate and that of lead nitrate?

### Nitrates are Soluble in Water.

Experiment 144.—Try the solubility in water of the nitrates used in the last experiment.

### Nitric Acid is reduced to Ammonia by Nascent Hydrogen.

Experiment 145.—In a good-sized test-tube treat a few pieces of granulated zinc with dilute sulphuric acid. Now add drop by drop dilute nitric acid. The hydrogen ceases to be given off. Pour the contents of the tube into an evaporating-dish and evaporate the liquid. Put the residue into a test-tube and add a solution of caustic soda, when the smell of ammonia will be noticed. Try the action of the gas on red litmus paper. Moisten the end of a glass rod with a little hydrochloric acid, and hold it in the tube. White fumes are seen. What are they? Do the same with nitric acid. What are the fumes in this case?

### Nitrous Acid.

Experiment 146.—Melt 25 grams potassium nitrate in a shallow iron plate and gradually add 50 grams metallic lead cut in small pieces. Stir them together as thoroughly as possible. After the mass is cooled down, break it up, and treat with water in a flask.

The potassium nitrite will dissolve, while the lead oxide and unused lead will not dissolve. Filter. Add a little sulphuric acid to some of the solution. A colored gas will be given off. See whether a solution of potassium nitrate acts in the same way. Treat with sulphuric acid a little of the residue left after heating potassium nitrate alone in a test-tube as in Experiment 143.

## Nitrous Oxide.

Experiment 147.—In a retort heat 10 to 15 grams crystallized ammonium nitrate until it has the appearance of boiling. Do not heat higher than is necessary to secure a regular evolution of gas. Connect a wide rubber tube directly with the neck of the retort and collect the evolved gas over water, as in the case of oxygen. It supports combustion almost as well as pure oxygen. Try experiments with wood, a candle, and a piece of phosphorus.

## Nitric Oxide.

Experiment 148.—Arrange an apparatus as shown in Fig. 57. In the flask put a few pieces of copper-foil. Cover this with water. Now add slowly, waiting each time for the action to begin, *ordinary* concentrated nitric acid. When enough nitric acid has been added gas will be evolved. If the acid is added rapidly, it not infrequently happens that the evolution of gas takes place too rapidly, so that the liquid is forced out of the flask through the funnel-tube. This can be avoided by not being in a hurry. At first the vessel becomes filled with a reddish-brown gas, but soon the gas evolved becomes colorless. Collect over water two or three vessels full. The gas collected is principally nitric oxide, NO, though it is frequently mixed with a considerable quantity of nitrous oxide.

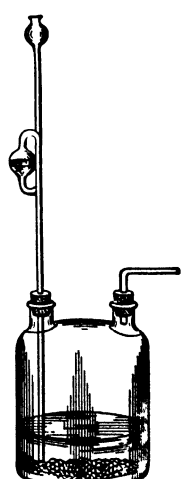


Fig. 57.

Experiment 149.—Turn one of the vessels containing colorless nitric oxide with the mouth upward, and uncover it. The colored gas is at once seen, presenting a very striking appearance. Do not inhale the gas. Perform the experiments with nitric oxide where there is a good draught.

Experiment 150.—Pass nitric oxide into a concentrated solution of ferrous sulphate. Afterwards heat the solution and collect the gas. What do you conclude that the gas is?

## Nitrogen Trioxide.

Experiment 151.—In a flask fitted with a safety-funnel and a delivery-tube pour nitric acid of specific gravity 1.30–1.35 upon coarsely-granulated arsenious oxide, $As_2O_3$. Heat gently, and conduct the gases through a tube surrounded by a freezing mixture, as in Experiment 116.

## Nitrogen Peroxide.

Experiment 152.—Admit a little air to nitric oxide contained in a bell-jar over water, and let the vessel stand. Almost immediately the color will disappear, showing that the nitrogen peroxide formed is decomposed. Again admit air, and let the vessel stand. The same changes will be noticed as in the first instance. If oxygen is used instead of air the above changes can be repeated over and over again. Devise an experiment for the purpose of determining whether the nitric oxide is gradually used up or not.

## CHAPTER XVII.

### ELEMENTS OF FAMILY V, GROUP B: PHOSPHORUS.—ARSENIC.—ANTIMONY.—BISMUTH. THE ELEMENTS AND THEIR COMPOUNDS WITH HYDROGEN AND OXYGEN.

**General.**—The elements of this group bear to nitrogen much the same relations that the members of the sulphur group bear to oxygen, and those of the chlorine group to fluorine. In general they form compounds of the same character and of similar composition. At the same time gradations in properties are noticed in passing from one end of the group to the other. Like nitrogen, the elements of the group are strongly marked acid-formers, though this character grows less marked from nitrogen to bismuth. Antimony is both an acid-forming and a base-forming element, while bismuth is more basic than acid. The stability of the hydrogen compounds decreases from nitrogen to antimony; while bismuth does not form a compound with hydrogen. Ammonia is strongly basic; the corresponding compound of phosphorus has weak basic properties, while those of arsenic and antimony have no basic properties. These hydrogen compounds correspond in composition to ammonia. They are:

$$NH_3 \quad PH_3 \quad AsH_3 \quad SbH_3.$$

Like nitrogen, phosphorus, arsenic, and antimony unite with metals to form binary compounds, called phosphides, arsenides and antimonides, which when decomposed by dilute acids yield the hydrogen compounds.

With chlorine they all form compounds corresponding to nitrogen trichloride, and phosphorus and antimony form compounds in which they are quinquivalent, while

bismuth forms a chloride, $Bi_2Cl_4$, in addition to the trichloride. The compounds referred to are:

| | | | | |
|---|---|---|---|---|
| | | | | $Bi_2Cl_4$ |
| $NCl_3$ | $PCl_3$ | $AsCl_3$ | $SbCl_3$ | $BiCl_3$ |
| | $PCl_5$ | | $SbCl_5$ | |

They all form two oxides corresponding to nitrogen trioxide and pentoxide:

| | | | | |
|---|---|---|---|---|
| $N_2O_3$ | $P_2O_3$ | $As_2O_3$ | $Sb_2O_3$ | $Bi_2O_3$ |
| $N_2O_5$ | $P_2O_5$ | $As_2O_5$ | $Sb_2O_5$ | $Bi_2O_5$ |

None of the elements of the group forms as great a variety of compounds with oxygen as nitrogen does. Antimony, however, forms the oxide $Sb_2O_4$, corresponding to nitrogen peroxide, $N_2O_4$; and bismuth forms the oxide $Bi_2O_2$ or BiO, corresponding to nitric oxide, NO.

The hydroxyl compounds or acids, like those of nitrogen, are related to the maximum hydroxyl compounds of the elements with the valence 5, and to the maximum hydroxyl compounds of the elements with the valence 3. That is to say, they may be regarded as derived from a hydroxide of the general formula $M(OH)_5$, and another of the formula $M(OH)_3$. Where M is nitrogen these acids break down to the forms $NO_2(OH)$ and $NO(OH)$ by loss of one or two molecules of water. In the case of the elements of the phosphorus group, however, the breaking down is not generally carried as far as with nitrogen. The rule is the same as in the sulphur and chlorine groups: the normal acid breaks down to form compounds containing the same number of hydrogen atoms as the hydrogen compounds of the elements. Thus the hydroxyl derivatives of chlorine generally break down to form compounds containing one atom of hydrogen, or the same number that is contained in the hydrogen compound, hydrochloric acid, thus: $Cl(OH)_7$ yields $ClO_3(OH)$; $Cl(OH)_5$ yields $ClO_2(OH)$, etc. So, also, in the sulphur group, $S(OH)_6$ yields $SO_2(OH)_2$, etc., the number of

hydrogen atoms in the common form of the acid being the same as that in the hydrogen compound of sulphur, $SH_2$.

The product of the direct action of oxygen upon phosphorus is the pentoxide $P_2O_5$. Arsenic, antimony, and bismuth, however, form the trioxides $As_2O_3$, $Sb_2O_3$, and $Bi_2O_3$. It is possible to obtain a compound of arsenic and oxygen of the formula $As_2O_5$, one of antimony, $Sb_2O_4$, and another, $Sb_2O_5$, and, finally, two oxides of bismuth, $Bi_2O_3$ and $Bi_2O_5$. Phosphorus, further, forms the oxides $P_4O$, $P_2O_3$, and $P_2O_4$. The table below contains the formulas of the above-mentioned compounds systematically arranged:

| | | | |
|---|---|---|---|
| $P_4O$ | —— | —— | $Bi_2O_2$ |
| $P_2O_3$ | $As_2O_3$ | $Sb_2O_3$ | $Bi_2O_3$ |
| $P_2O_4$ | —— | $Sb_3O_4$ | —— |
| $P_2O_5$ | $As_2O_5$ | $Sb_2O_5$ | $Bi_2O_5$ |

The final products of the oxidation of the elements of this group, if water is present, are phosphoric, arsenic, antimonic, and bismuthic acids. All of these are well-marked acids except the last. They may all be regarded as derived from the normal acids of the general formula $M(OH)_5$ by loss of one or two molecules of water. The common forms of phosphoric, arsenic, and antimonic acids are those which are formed from the normal acids by loss of one molecule of water:

$$\underset{\text{Normal phosphoric acid}}{P(OH)_5} = \underset{\text{Orthophosphoric acid}}{P\begin{cases} O \\ (OH)_3 \end{cases}} + H_2O;$$

$$\underset{\text{Normal arsenic acid}}{As(OH)_5} = \underset{\text{Orthoarsenic acid}}{As\begin{cases} O \\ (OH)_3 \end{cases}} + H_2O;$$

$$\underset{\text{Normal antimonic acid}}{Sb(OH)_5} = \underset{\text{Orthoantimonic acid}}{Sb\begin{cases} O \\ (OH)_3 \end{cases}} + H_2O.$$

Bismuthic acid appears, however, to be formed from the normal acid by loss of two molecules of water, just as

the so-called *metaphosphoric*, *metarsenic*, and *metantimonic* acids are:

$$\underset{\text{Normal bismuthic acid}}{Bi(OH)_5} = \underset{\text{Bismuthic acid}}{Bi\begin{cases} O \\ OH \end{cases}} + 2H_2O;$$

$$P(OH)_5 = \underset{\text{Metaphosphoric acid}}{P\begin{cases} O_2 \\ OH \end{cases}} + 2H_2O;$$

$$As(OH)_5 = \underset{\text{Metarsenic acid.}}{As\begin{cases} O_2 \\ OH \end{cases}} + 2H_2O;$$

$$Sb(OH)_5 = \underset{\text{Metantimonic acid}}{Sb\begin{cases} O_2 \\ OH \end{cases}} + 2H_2O.$$

From the ordinary or *ortho acids* and from the *meta acids* more complex forms are derived by loss of different quantities of water. The most common form besides those mentioned is that of the so-called *pyro acids*, of which pyrophosphoric acid is the best known example. It is formed from the ortho acid by loss of one molecule of water from two molecules of the acid, just as pyrosulphuric or disulphuric acid is formed from two molecules of ordinary sulphuric acid by loss of one molecule of water. The formation of pyrophosphoric acid from orthophosphoric acid takes place according to the equation

$$\begin{matrix} OP(OH)_3 & OP(OH)_2 \\ & = \quad >O \\ OP(OH)_3 & OP(OH)_2 \end{matrix} + H_2O.$$

$$\underset{\text{Orthophosphoric acid}}{2H_3PO_4} = \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} + H_2O.$$

Pyroarsenic and pyroantimonic acids bear the same relation to the ortho acids that pyrophosphoric acid bears to orthophosphoric acid.

By partial oxidation of phosphorus in the presence of water, phosphorous acid, $H_3PO_3$, is formed. The same acid is formed by the action of phosphorus trichloride on water. According to the latter method of formation we should

expect to find that this acid is normal phosphorous acid, $P(OH)_3$. It appears probable, however, that the acid has the constitution $OP\begin{cases}H\\OH\\OH\end{cases}$. The acids of arsenic and antimony of similar composition seem to be the normal acids $As(OH)_3$ and $Sb(OH)_3$. The hydroxyl derivative of bismuth corresponding to these acids has no acid properties, but is basic. Hypophosphorous acid has the composition $H_3PO_2$. It is monobasic, and it appears therefore that it contains but one hydroxyl, as represented in the formula $H_2OP(OH)$. It is probable that the relations between phosphoric, phosphorous, and hypophosphorous acids should be represented by the formulas

$$OP\begin{cases}OH\\OH\\OH\end{cases} \qquad OP\begin{cases}H\\OH\\OH\end{cases} \qquad OP\begin{cases}H\\H\\OH\end{cases}.$$

Phosphoric acid — Phosphorous acid — Hypophosphorous acid

The fundamental compound, then, from which these may be regarded as derived is the unknown oxyphosphine $OPH_3$. By oxidation we should expect phosphine to yield in successive stages the three products above named:

$$P\begin{cases}H\\H\\H\end{cases} \quad OP\begin{cases}H\\H\\H\end{cases} \quad OP\begin{cases}H\\H\\OH\end{cases} \quad OP\begin{cases}H\\OH\\OH\end{cases} \quad OP\begin{cases}OH\\OH\\OH\end{cases}.$$

Unknown — Hypophosphorous acid — Phosphorous acid — Phosphoric acid

The oxidation of hydrogen sulphide takes place similarly, as has been shown:

$$S\begin{cases}H\\H\end{cases} \quad O_2S\begin{cases}H\\H\end{cases} \quad O_2S\begin{cases}H\\OH\end{cases} \quad O_2S\begin{cases}OH\\OH\end{cases}$$

Unknown — Sulphurous acid — Sulphuric acid

With oxygen and chlorine the elements of the phosphorus group form a number of compounds called oxychlorides. Towards chlorine as well as towards oxygen all these elements except bismuth are quinquivalent. A part or all of the oxygen of the oxygen compounds can be replaced by chlorine. Starting with the chlorine compound on the one hand, oxychlorides can be obtained from it, until oxygen

is substituted for all the chlorine, and the limit is reached in the oxide. So, also, hydroxyl can be substituted for the chlorine and the acids thus obtained.

With sulphur phosphorus apparently forms a large number of compounds. Among them are two having the formulas $P_2S_3$ and $P_2S_5$ These are plainly analogous to the two oxides $P_2O_3$ and $P_2O_5$.

Arsenic forms several compounds with sulphur, the principal of which are the *disulphide*, $As_2S_2$, the *trisulphide*, $As_2S_3$, and the *pentasulphide*, $As_2S_5$. The principal sulphides of antimony are those of the formulas $Sb_2S_3$ and $Sb_2S_5$, and of bismuth those of the formulas $Bi_2S_2$ and $Bi_2S_5$.

Of the elements of this group phosphorus occurs most abundantly in nature, arsenic and antimony next, and bismuth least abundantly. Arsenic, antimony, and bismuth occur to some extent in the uncombined condition. Phosphorus occurs in combination. All the elements of the group find application in the arts.

## Phosphorus, P (At. Wt. 31).

**Occurrence.**—The name phosphorus is derived from the Greek φῶς, light, and φόρος, carrier, on account of the fact that it gives light and takes fire very easily. The element occurs in nature in the form of phosphates derived from orthophosphoric acid, $H_3PO_4$, and in the form of organic compounds of phosphorus in the brain and nerve substance of man and animals, in eggs, in albumen, and in plants, especially in the seeds of plants. Phosphorus is also contained in the so-called basic slags from the basic steel processes. These slags are used as fertilizers on account of the phosphate contained in them. The chief natural salt of phosphoric acid is calcium phosphate, $Ca_3(PO_4)_2$, which is the principal constituent of the minerals *phosphorite* and *apatite*, and of the ashes of bones. The phosphates, like the nitrates, are widely distributed in the soil and are of fundamental importance in the process of plant life, especially with grain to develop the kernels. The phosphates found in the bones are taken into the animal body in the food. All plants used as food contain small quantities of the phosphates which

they get from the soil. The phosphates taken into the body are partly given off in the excrement and urine, and it was in an examination of urine made in the hope of finding the philosopher's stone that phosphorus was discovered in 1669. At present phosphorus is made almost entirely from bones.

The molecular weight of phosphorus is 124, the molecule being represented by the symbol $P_4$.

**Preparation.**—In addition to the phosphates, organic materials are contained in bones. When the bones are burned the organic materials pass off for the most part in the form of carbon dioxide, water, and volatile compounds containing nitrogen, and the so-called mineral or earthy portions, the chief constituent of which is tertiary calcium phosphate, $Ca_3(PO_4)_2$, or phosphoric acid in which calcium has been substituted for all the hydrogen, remain behind. The tertiary phosphate is insoluble in water, and there is no simple way by which the phosphorus can be set free from it. When it is treated with sulphuric acid calcium sulphate which is difficultly soluble is deposited and primary calcium phosphate, $Ca(H_2PO_4)_2$, is in the solution. The reaction is represented thus:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4.$$

The calcium sulphate, or gypsum, is allowed to settle and is then filtered off and washed. The solution is evaporated to dryness and heated. The primary calcium phosphate is by this means converted into calcium metaphosphate:

$$Ca(H_2PO_4)_2 = Ca(PO_3)_2 + 2H_2O.$$

This metaphosphate is then mixed with charcoal and generally with sand, when the reaction represented by the following equation takes place:

$$2Ca(PO_3)_2 + 2SiO_2 + 10C = 2CaSiO_3 + 10CO + 4P.$$

If an electric furnace is used for the heating it is not necessary to convert the ordinary or tertiary phosphate

into the primary phosphate, as the former can be reduced directly by charcoal and sand:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 3CaSiO_3 + 10CO + 4P.$$

The phosphorus passes over in the form of vapor, and is collected under water. The crude phosphorus thus obtained must be subjected to a cleansing process before it can be used. For this purpose it is pressed, while in the molten condition under water, through chamois leather, or it is distilled again from iron retorts; or, still better, it is treated with chromic acid as follows: It is fused under water, then a little potassium or sodium bichromate in solution is added, and afterwards an equivalent quantity of sulphuric acid, and the whole allowed to stand for two hours or more. The phosphorus is then washed with hot water, and after being siphoned off it is filtered through canvas bags. The phosphorus is then cast into sticks in tin tubes. In this form it generally comes into the market.

At the time of the last report available about 3000 tons of phosphorus was manufactured in one year in England and in France and Germany. Quite recently phosphorus has been manufactured to some extent in Sweden.

**Properties.**—Ordinary phosphorus is colorless or slightly yellowish, translucent, and at ordinary temperatures it can be cut like wax, but it becomes hard and brittle at low temperatures. It melts at 44°, and boils at 290°. It is insoluble in water. When kept under water for some time in diffused light it becomes opaque, crystalline on the surface, and yellow. It is soluble in carbon bisulphide, and crystallizes when deposited from this solution. It gives off fumes in contact with the air, and emits a pale light known as *phosphorescence.* It is very poisonous, the inhalation of the vapor in small quantities causing serious disturbances of the system. The workmen in the factories where phosphorus is made or used are frequently affected by phosphorus-poisoning. Among the prominent symptoms is gradual decomposition of the

bones. When taken into the stomach phosphorus also acts as a poison and causes death. When heated in the air it takes fire at 50°. It also takes fire by rubbing, and it must be handled with the greatest care, as wounds caused by it are dangerous and difficult to heal. When it burns in the air it is converted into the pentoxide, $P_2O_5$, which is also the product of its combustion in oxygen. It combines further with other elements directly, frequently with evolution of light. Thus, when it is brought together with chlorine, bromine, and iodine, it forms the compounds $PCl_3$, $PBr_3$, and $PI_3$. It also combines with sulphur. When a piece is put in water and the water boiled, a part of the phosphorus passes over, and if the water-vapor is condensed in a glass tube in a dark room, it is seen to be phosphorescent. This furnishes a convenient method for its detection, as, for example, in a case of suspected poisoning by phosphorus.

Treated with oxidizing agents, as, for example, nitric acid, phosphorus is slowly converted into phosphoric acid, just as sulphur is converted into sulphuric acid under the same conditions.

**Red Phosphorus.**—When phosphorus is left for a long time under water in the light, it becomes at first yellow, then reddish, and finally red. The same change takes place when it is heated for a time in an atmosphere free from oxygen; and rapidly when it is heated to 300° in an hermetically sealed tube. The red substance thus obtained has properties entirely different from those of ordinary phosphorus. It is a red powder, that frequently has a crystalline structure. It does not emit light. It does not melt at a low temperature. It is not poisonous, and cannot be easily ignited. Further, it is insoluble in carbon bisulphide. In every respect this red modification of phosphorus conducts itself as a much less active substance chemically than ordinary phosphorus. In an atmosphere of carbon dioxide it is converted into ordinary phosphorus when heated to 261°, and if heated to this temperature in the air it takes fire, and then forms

the same product that ordinary phosphorus does in burning.

**Applications of Phosphorus.**—Phosphorus is used principally in the manufacture of matches and as a poison for vermin. Various mixtures are used for making matches. Nearly all of them contain phosphorus together with some oxidizing compound, and some neutral substance to act as a medium for holding the constituents together. An example is a mixture consisting of 2 parts phosphorus, 1 part manganese dioxide, 3 parts chalk, $\frac{1}{8}$ part lamp-black, and 5 parts glue. The mixture used in the manufacture of the so-called "safety matches" consists of potassium chlorate, potassium bichromate, minium, and antimony trisulphide. This will not ignite by simple friction, but will ignite when drawn across a paper upon which is a mixture of red phosphorus and antimony pentasulphide.

**Compounds of Phosphorus with Hydrogen.**—There are three compounds of phosphorus with hydrogen, a gaseous compound of the formula $PH_3$, corresponding to ammonia; a liquid of the formula $PH_2$, or $P_2H_4$, corresponding to hydrazine; and a solid of the formula $P_2H$, or $P_4H_2$.—

**Phosphine, Gaseous Phosphuretted Hyrdogen**, $PH_3$.—This compound is formed:

(1) By treating a strong solution of potassium hydroxide with phosphorus, when reaction takes place as follows:

$$3KOH + 4P + 3H_2O = 3KH_2PO_2 + PH_3.$$

The compound $KH_2PO_2$ is known as potassium hypophosphite, being derived from hypophosphorous acid, $H_3PO_2$.

(2) By treating zinc phosphide with dilute hydrochloric acid. Assuming that zinc phosphide has the composition represented by the formula $Zn_3P_2$, the reaction with hydrochloric acid takes place according to the equation

$$Zn_3P_2 + 6HCl = 3ZnCl_2 + 2PH_3.$$

(3) By treating phosphonium iodide, $PH_4I$, with water or a dilute solution of potassium hydroxide:

$$PH_4I + H_2O = PH_3 + HI + H_2O;$$
$$PH_4I + KOH = PH_3 + KI + H_2O.$$

When made from phosphorus and potassium hydroxide it always

contains a considerable proportion of hydrogen, for the reason that potassium hypophosphite gives off hydrogen when heated with a solution of potassium hydroxide. From zinc phosphide and from phosphonium iodide it can be obtained in pure condition.

Phosphine is a colorless gas with an unpleasant, garlic-like odor. It is insoluble in water, and is poisonous. It burns, but does not take fire spontaneously when pure.

Although pure phosphine does not take fire spontaneously when brought in contact with the air, the gas made by any one of the methods above referred to contains some of the liquid compound of phosphorus and hydrogen, $P_2H_4$, which is spontaneously inflammable, and therefore the gas takes fire. If it is collected in a glass vessel over water, and allowed to stand so that the light acts upon it, the liquid phosphine is decomposed into the gaseous and solid varieties, and the residual gas no longer has the property of taking fire spontaneously.

**Compounds of the Members of the Phosphorus Group with the Members of the Chlorine Group.**—In the introduction to this chapter it was stated that the elements of the phosphorus group combine with chlorine in two proportions, forming compounds of the general formulas $MCl_3$ and $MCl_5$. Arsenic, however, forms only one compound with chlorine, $AsCl_3$, while bismuth forms one of the formula $BiCl_3$, and another, $Bi_2Cl_4$. The compounds of phosphorus and chlorine are the best known, and a brief study of these will give a fair idea of the methods of preparation and the conduct of the analogous compounds of the other members of the group.

**Phosphorus Trichloride,** $PCl_3$, is made by conducting dry chlorine gas upon phosphorus in a retort connected with a receiver. Action takes place at once with evolution of heat. The trichloride distils over and is condensed as a liquid into the receiver. Or it can be made somewhat more conveniently by dissolving ordinary phosphorus in a little phosphorus trichloride, cooling the vessel by placing it in cold water, and passing dry chlorine into the solution until the increase in weight shows that all the phosphorus in solution has been transformed into the trichloride. It is purified by distillation on a water-bath. It is a clear, colorless liquid, that boils at 76° and solidifies at − 112°. In contact with air it fumes in consequence of

the action of the water-vapor. It has a disagreeable odor of its own mixed with that of hydrochloric acid. Its most characteristic decomposition is that which it undergoes with water, resulting in the formation of phosphorous and hydrochloric acids.

The trichloride shows a strong tendency to take up chlorine, bromine, iodine, oxygen, and sulphur, and thus to become saturated. With chlorine it forms the pentachloride, $PCl_5$, with oxygen the oxychloride, $POCl_3$, and with sulphur the sulphochloride, $PSCl_3$.

**Phosphorus Pentachloride,** $PCl_5$, is formed by treating phosphorus or the trichloride with dry chlorine. It is best prepared by passing chlorine through a wide tube upon the surface of the trichloride, contained in a vessel which is kept cool. It is a white solid, but it generally has a yellowish or greenish color in consequence of a slight decomposition into the trichloride and free chlorine. It sublimes below 100° without melting. When heated to boiling it undergoes partial decomposition into chlorine and the trichloride, and this decomposition is complete at about 300°. As the temperature is raised from the apparent boiling-point to the point at which the decomposition is complete, the color of the vapor is seen to grow darker in consequence of the increased quantity of free chlorine present. The decomposition is gradual, and, for any given temperature, the amount of decomposition is constant. This kind of decomposition, called *dissociation*, has been studied carefully, and is found to be capable of explanation by the aid of the kinetic theory of gases. In a later chapter this subject will be discussed, and a number of other examples will be given. Owing to this decomposition under the influence of heat the specific gravity of the vapor of phosphorus pentachloride is not what it should be, if the formula is $PCl_5$. On the other hand, the specific gravity of the vapor of the trichloride leads to the formula $PCl_3$ and that of the oxychloride to the formula $POCl_3$. The apparent anomaly presented by the pentachloride is easily understood. When a molecule of the compound is converted

into vapor, or is heated to a sufficiently high temperature, it is broken down in accordance with this equation:

$$PCl_5 = PCl_3 + Cl_2.$$

From the one molecule, therefore, two gaseous molecules are obtained. Consequently the vapor formed occupies twice as much space as it would if there were no decomposition. It follows that the specific gravity of the vapor must be only half what it would be if there were no decomposition. When the compound is converted into vapor in an atmosphere of phosphorus trichloride, the decomposition referred to does not take place, and, under these circumstances, the specific gravity is found to be in accordance with Avogadro's law, and with the formula $PCl_5$. This case is a particularly interesting one, as it has played an important part in the discussions in regard to the validity of Avogadro's law.

Treated with water phosphorus pentachloride first gives the *oxychloride* and hydrochloric acid, thus:

$$PCl_5 + H_2O = POCl_3 + 2HCl;$$

and by further action the oxychloride is converted into phosphoric acid, thus:

$$POCl_3 + 3H_2O = PO(OH)_3 + 3HCl.$$

Phosphorus oxychloride is a colorless liquid boiling at 107.5° and solidifying at 1.8°.

**Phosphoric Acid, Orthophosphoric Acid,** $H_3PO_4$.—The compound known as phosphoric acid, from which the best known phosphates are derived, is that which has the formula $H_3PO_4$. To distinguish it from the other varieties it is called *orthophosphoric acid.* It is the final product of oxidation of phosphorus in the presence of water. Thus, when phosphorus is boiled with nitric acid it is converted into orthophosphoric acid; and also when phosphorus is burned in the air, and the product dissolved in water, this same substance is formed. In this case the first product of the oxidation is the pentoxide $P_2O_5$, also known

as phosphoric anhydride, and when this is treated with water it is converted into phosphoric acid:

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The occurrence of phosphoric acid in nature has already been referred to in connection with the occurrence of phosphorus, which is found in nature almost exclusively in the form of phosphates, principally as calcium phosphate, $Ca_3(PO_4)_2$, in phosphorite, apatite, and the ashes of bones.

In order to prepare the acid two ways suggest themselves: (1) by oxidizing phosphorus with nitric acid; and (2) by extracting it from one of the natural phosphates, as phosphorite or bone-ash. The first of these methods is well adapted to the preparation of pure phosphoric acid, such as is needed for medicinal purposes; the latter is used where absolute purity of the product is not required.

The preparation of phosphoric acid from a phosphate is not a simple matter. If the acid were volatile or insoluble there would be no difficulty in separating it. In the former case it would only be necessary to proceed as in preparing hydrochloric and nitric acids. By adding an acid that is not volatile except at a high temperature, such, for example, as sulphuric acid, and heating, the non-volatile acid drives out the volatile. On the other hand, if phosphoric acid were insoluble in water, it could be separated by adding a soluble acid to one of its soluble salts. When, for example, nitric acid is added to a solution of potassium tellurite, $K_2TeO_3$, tellurous acid, being insoluble, is thrown down:

$$K_2TeO_3 + 2HNO_3 = 2KNO_3 + H_2TeO_3.$$

But phosphoric acid is not volatile and is soluble, so that neither of these methods can be used. By treating the calcium salt with sulphuric acid the calcium can be completely separated in the form of calcium sulphate, which is difficultly soluble in water and insoluble in alcohol. The

ideal reaction to be accomplished is that represented in the following equation:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

But when sulphuric acid is added to calcium phosphate, only a part of the calcium is precipitated as sulphate, the rest remaining in the form of primary calcium phosphate:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

The phosphate thus formed is soluble in water, and the calcium is not easily precipitated from it. By evaporation and addition of sufficient sulphuric acid and alcohol the precipitation can be effected, and a solution of phosphoric acid thus obtained. This acid is not pure, as there are substances in bone-ash which are not removed by the method described.

Phosphoric acid for medicinal purposes is often made by dissolving the pentoxide in water.

**Properties.**—When evaporated to the proper consistency the acid forms a thick syrup which slowly solidifies in the form of large crystals. The crystals melt at 41.8°, and are deliquescent. When heated to a sufficiently high temperature the acid loses water, as already explained, and yields, first, pyrophosphoric, and then metaphosphoric acid. It is a tribasic acid, capable of yielding three classes of salts of the general formulas

$$OP\begin{cases} OH \\ OH, \\ OM \end{cases} \quad OP\begin{cases} OH \\ OM, \\ OM \end{cases} \quad \text{and} \quad OP\begin{cases} OM \\ OM, \\ OM \end{cases}$$

which are known respectively as the *primary*, *secondary*, and *tertiary phosphates*. The primary and secondary phosphates are also known as *acid phosphates*, and the tertiary salts as *neutral* or *normal phosphates*. In these salts it is not necessary that all the hydrogen should be replaced by the same metal. There are salts in which two or three metals take the place of the hydrogen atoms. A phosphate much used in the laboratory, for example, is one in which one hydrogen atom of phosphoric acid is

replaced by a sodium atom, and another by ammonium, $NH_4$. This salt has the formula $OP\begin{cases} OH \\ ONa \\ ONH_4 \end{cases}$, and is called *ammonium sodium phosphate.* Another phosphate commonly met with is *ammonium magnesium phosphate*, $OP\begin{cases} ONH_4 \\ O \\ O \end{cases}>Mg'$, which is derived from the acid by replacement of two hydrogen atoms in the molecule by one bivalent magnesium atom, and one by the ammonium group.

The changes which these three classes of phosphates undergo when heated are of special interest. The tertiary phosphates are stable. The primary and secondary phosphates give up all their hydrogen, which passes off in the form of water. Thus, primary sodium phosphate, $H_2NaPO_4$, loses one molecule of water from each molecule of the salt, and is converted into the *metaphosphate*, $NaPO_3$:

$$OP\begin{cases} OH \\ OH \\ ONa \end{cases} = O_2P(ONa) + H_2O.$$

In general *the primary phosphates are converted into metaphosphates by heat.*

When a secondary phosphate is heated the product is a pyrophosphate. Thus when secondary sodium phosphate is heated to a sufficiently high temperature it is converted into sodium pyrophosphate:

$$\begin{matrix} OP\begin{cases} ONa \\ ONa \\ OH \end{cases} \\ OP\begin{cases} OH \\ ONa \\ ONa \end{cases} \end{matrix} = \begin{matrix} OP\begin{cases} ONa \\ ONa \\ O \end{cases} \\ OP\begin{cases} ONa \\ ONa \end{cases} \end{matrix} + H_2O,$$

or

$$2\ Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

In general, *a secondary phosphate is converted into a pyrophosphate by heat.*

**Pyrophosphoric Acid,** $H_4P_2O_7$.—When phosphoric acid is heated to 200°–300° until a specimen neutralized with ammonia gives a pure white precipitate with silver nitrate, it is completely transformed into pyrophosphoric acid by loss of water. The white precipitate referred to is the silver salt of pyrophosphoric acid. The silver salt of orthophosphoric acid is yellow. This difference in color led, many years ago, to a careful investigation of the change in composition which phosphoric acid undergoes when heated, and to the recognition of the existence of pyrophosphoric acid as distinct from orthophosphoric acid; and the study of the relations existing between these acids and metaphosphoric acid has had a strong influence in shaping the views of chemists in regard to the relations between other similar acids. The views at present held in regard to the relations between the common forms of oxygen acids and the so-called normal acids of maximum hydroxides are simply an extension of the ideas first introduced into chemistry by Graham in connection with the three varieties of phosphoric acid. The modifications of sulphuric acid seen in the normal acid, $S(OH)_6$, the ordinary acid, $SO_2(OH)_2$, and the pyro-acid, $H_2S_2O_7$, are examples of the same kind of relations.

*Pyrophosphates* are formed, as we have seen, when the secondary phosphates, like disodium phosphate, $HNa_2PO_4$, are heated.

**Metaphosphoric Acid,** $HPO_3$.—This acid is formed by dissolving phosphorus pentoxide, $P_2O_5$, in cold water:

$$P_2O_5 + H_2O = 2HPO_3.$$

It is also formed by heating phosphoric acid to 400°:

$$H_3PO_4 = HPO_3 + H_2O.$$

Further, the metaphosphates are formed by heating the primary phosphates like primary sodium phosphate, $H_2NaPO_4$. The acid is a vitreous translucent mass, known as *glacial phosphoric acid* (*Acidum phosphoricum glaciale*). It is the more common commercial form of

phosphoric acid. It is a monobasic acid, and in composition is analogous to nitric and chloric acids:

$HPO_3$ . . . . . Metaphosphoric acid.
$HNO_3$ . . . . . Nitric acid.
$HClO_3$ . . . . . Chloric acid.

When boiled with water in which there is a little nitric acid metaphosphoric acid is readily converted into orthophosphoric acid:

$$HPO_3 + H_2O = H_3PO_4.$$

This transformation is effected also by simply allowing the solution of the meta-acid in water to stand for a time, and by boiling the solution.

**Polyphosphoric Acids.**—Salts of more complex acids of phosphorus are known. One example will suffice; the slags from the Thomas-Gilchrist process (which see) for removing phosphorus from iron, contain a compound $P_2O_9Ca_4$, which is the calcium salt of an acid, $P_2O_9H_8$.

**Phosphorous Acid,** $H_3PO_3$.—This acid is formed when phosphorus trichloride is treated with water. It is also formed together with phosphoric and hypophosphoric acids when phosphorus is allowed to stand in contact with moist air. The acid can be obtained from its solutions by evaporation, when it is deposited in transparent crystals.

Phosphorous acid is only dibasic, its salts having the general formula $HM_2PO_3$. This fact has led to the belief that in the acid two of the hydrogen atoms are in combination with oxygen in the form of hydroxyl, while the third is in combination with phosphorus as represented in the formula $OP\begin{cases} H \\ OH \\ OH \end{cases}$. This conclusion finds further support in the conduct of some derivatives of phosphorous acid.

**Hypophosphoric Acid,** $H_4P_2O_6$, is formed together with phosphoric and phosphorous acids when sticks of ordinary phosphorus placed in glass tubes drawn out to a small opening at one end are exposed to the action of moist air.

**Hypophosphorous Acid,** $H_3PO_2$, has already been referred to, as its potassium salt is formed in the preparation of phosphine by the action of phosphorus upon a solution of potassium hydroxide:

$$8KOH + 4\,P + 3H_2O = 3K_2HPO_2 + PH_3.$$

The acid is monobasic, and this has led to the belief that only one of the hydrogen atoms in the molecule of the acid is in combination with oxygen as hydroxyl, and that the two others are in combination with phosphorus as represented in the formula $OP\begin{cases} H \\ H. \\ OH \end{cases}$ The relation between this acid and phosphorous and phosphoric acids has already been commented upon (see page 313).

**Phosphorus Pentoxide, Phosphoric Anhydride,** $P_2O_5$.—This highest oxidation-product of phosphorus is formed by burning the element in air or in oxygen. It is a white powder that attracts moisture from the air and becomes liquid. This power to combine with water is its most characteristic property. It forms first, as we have seen, metaphosphoric acid and, by further action, orthophosphoric acid. Its action towards water is strongly suggestive of the action of sulphur trioxide or sulphuric anhydride towards water. Owing to this power to combine with water, phosphorus pentoxide is used for the purpose of drying gases and as a dehydrating agent in general.

**Phosphorus Trioxide, or Phosphorous Anhydride,** $P_2O_3$ (or $P_4O_6$), is formed by burning phosphorus so that the air does not have free access to it, as by putting a piece of phosphorus in a glass tube drawn out to a fine opening, drawing air over the phosphorus, and warming it gently. In this way not enough air can get access to the phosphorus to convert it into the pentoxide. The trioxide has such a strong tendency to pass over into the pentoxide that when brought into the air it takes fire and burns, forming the higher oxide. It is converted into phosphorous acid by water at about 15°. Warm water acts differently.

## Arsenic, As (At. Wt. 75).

**Occurrence.**—Arsenic occurs in nature to some extent in the uncombined condition or native. Compounds of the metals with arsenic, or the *arsenides*, occur very widely distributed, and they frequently accompany, and

are similar to, the sulphides. The most common compound of this kind is the so-called *arsenical pyrites*, which has the composition FeAsS, and may therefore be regarded as iron pyrites, $FeS_2$, in which one atom of arsenic has been substituted for one atom of sulphur. Among other arsenic compounds deserving special mention are the two arsenides of iron of the formulas $FeAs_2$ and $Fe_2As_3$, which are apparently analogous to the sulphides $FeS_2$ and $Fe_2S_3$; and, further, the sulphides of arsenic, orpiment, $As_2S_3$, and realgar, $As_2S_2$. The oxide $As_2O_3$ occurs in considerable quantity, and also salts of arsenic acid, or the arsenates, which in composition are analogous to the phosphates.

**Preparation.**—The arsenic which comes into the market is either that which occurs native or is made from arsenical pyrites by heating:

$$FeAsS = FeS + As.$$

**Properties.**—Arsenic has a metallic lustre and steel color. It is very brittle. When heated it volatilizes without melting. At red heat it burns with a bluish flame, and the vapor given off has the odor of garlic. This odor produced under such circumstances is characteristic of arsenic, and furnishes one of the means for detecting it. Arsenic combines with most elements directly, the action being accompanied in some cases, as in that of chlorine, by an evolution of light. As an element it is not poisonous, but when oxidized to the form of the oxide $As_2O_3$ it is extremely poisonous. As it is easily oxidized, the element itself may act as a poison.

Arsenic like phosphorus is tetratomic. Its molecular weight is 300 corresponding to the symbol $As_4$. Like phosphorus arsenic is known in two different modifications. The common form is the so-called "metallic arsenic" described above. By rapidly cooling its vapor a yellow variety is obtained, crystalline, soluble in carbon bisulphide, and volatile with steam, resembling ordinary or white phosphorus in these respects.

**Arsine, Arseniuretted Hydrogen, $AsH_3$.**—This compound

is analogous to ammonia and to gaseous phosphine. It is made by reducing compounds of arsenic containing oxygen, as arsenic trioxide or arsenic acid; and also by treating a compound of zinc and arsenic with dilute sulphuric acid. The reactions involved in the first method are

$$As_2O_3 + 6H_2 = 2AsH_3 + 3H_2O;$$
$$H_3AsO_4 + 4H_2 = AsH_3 + 4H_2O.$$

That involved in the second method is:

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4.$$

Arsine is a colorless gas with an odor suggestive of garlic. It is extremely poisonous, even very small quantities being capable of producing bad effects, and it requires but little to cause death. When ignited in the air it takes fire and burns with a pale blue flame, the products of the combustion being arsenic trioxide, $As_2O_3$, and water. The gas is so unstable that, when it is passed through a glass tube heated to redness, it is decomposed into arsenic and hydrogen, the former being deposited just in front of the heated portion of the tube as a thin, almost black, layer with a high metallic lustre.

**Arsenic Acid,** $H_3AsO_4$.—The compound of arsenic and oxygen which is most readily obtained is the trioxide, $As_2O_3$, and this is formed by direct combination of the two elements. When this is oxidized either with *aqua regia* or by passing chlorine into water in which the trioxide is suspended it is converted into arsenic acid:

$$As_2O_3 + 3H_2O + 2O = 2H_3AsO_4.$$

From its solutions it is obtained in crystallized form. According to the temperature to which it is heated the deposit has the composition of the ortho-acid, $H_3AsO_4$, of the pyro-acid, $H_4As_2O_7$, or of the meta-acid, $HAsO_3$. Perfect analogy with the phosphorus compounds is here observed. When the pyro- and meta-acids are dissolved in water they are converted into the ortho-acid. Arsenic acid, like phosphoric acid, is a strong tribasic acid, form-

ing three series of salts which under the influence of heat conduct themselves like the corresponding phosphates, the primary salts yielding metarsenates, and the secondary salts yielding pyro-arsenates.

**Arsenious Acid,** $H_3AsO_3$, is not known in the free state, but salts derived from it are formed by treating arsenic trioxide with bases.

**Arsenic Trioxide,** $As_2O_3$ ($As_4O_6$).—This compound is commonly called arsenic or white arsenic. It is the most important of all the compounds of the element arsenic. It finds applications for many purposes, and is manufactured in large quantities. It occurs in small quantity in nature, but that which comes into the market is manufactured by roasting natural arsenides, especially arsenical pyrites, FeAsS. The products of roasting this compound are ferric oxide, $Fe_2O_3$, sulphur dioxide, $SO_2$, and arsenic trioxide, $As_2O_3$. Of these, the first is a non-volatile solid, the second a gas, and the third a volatile solid. By passing the volatile products through properly constructed canals the arsenic trioxide is condensed on the walls. Some of the powder thus obtained must be subjected to a second process of distillation to make it pure enough for the market. In a recent year over 6000 tons of this substance were produced in England and Saxony.

**Properties.**—Arsenic trioxide is a colorless, amorphous, vitreous mass. Gradually it becomes opaque and crystalline, with an appearance like that of porcelain. It crystallizes in two forms, the common one being that of regular octahedrons. Under exceptional conditions it crystallizes in the form of rhombic prisms. When heated it sublimes, and is deposited on a cold surface in the form of octahedrons. Arsenic trioxide is difficultly soluble in water, but more easily in hydrochloric acid.

The trioxide is easily reduced. When heated with potassium cyanide, KCN, or with charcoal in a dry glass tube arsenic is deposited above the flame in the form of a dark lustrous layer. When brought into a vessel from which hydrogen is being evolved it is reduced to arsine.

The specific gravity of the vapor of the oxide shows that it has the formula $As_4O_6$, and not $As_2O_3$; as, however, most of its reactions can be more conveniently expressed by the aid of the simpler formula, the latter is commonly used.

Arsenic trioxide has a weak, disagreeable, sweet taste, and is an active poison. A dose of from two to three grains is sufficient to cause death unless it is ejected by vomiting, or rendered harmless by conversion into an insoluble compound. It is possible, by beginning with small doses, and gradually increasing them, to accustom the human body to considerably larger doses than that mentioned. It strengthens the power of the respiratory organs, and consequently facilitates mountain-climbing The peasants in some mountain regions are said to use it habitually. It is much used in medicine, especially in skin diseases. It is also used extensively as a rat-poison. The most efficient antidote is a mixture of ferric hydroxide, $Fe(OH)_3$, and magnesia, which forms with arsenic trioxide an insoluble compound.

**Arsenic Pentoxide,** $As_2O_5$, is formed by igniting arsenic acid. If heated too high the pentoxide breaks down into arsenic trioxide and oxygen. A marked difference will be observed between the conduct of the oxides of phosphorus and that of the corresponding oxides of arsenic. While phosphorus trioxide takes up oxygen spontaneously when exposed to the air, and the pentoxide is not decomposed by heat, the trioxide of arsenic does not under any circumstances take up oxygen directly, and the pentoxide easily breaks down into the trioxide and oxygen when heated.

**Sulphides.**—There are three compounds of arsenic with sulphur—the disulphide, $As_2S_2$, the trisulphide, $As_2S_3$, and the pentasulphide, $As_2S_5$.

**Arsenic Disulphide,** $As_2S_2$, occurs in nature and is known as *realgar*. It can also be obtained by melting arsenic and sulphur together in the right proportions. It forms an orange-red powder. It was formerly used as a pigment.

**Arsenic Trisulphide,** $As_2S_3$, is found in nature and is called *orpiment* or king's yellow. It can be prepared by melting together arsenic and sulphur in the proper proportions, and by precipitating a solution of arsenic trioxide in hydrochloric acid with hydrogen sulphide. It melts, forming a red liquid. The natural substance, as well as that which is precipitated by means of hydrogen sulphide, is yellow. It dissolves in soluble sulphides, forming salts of sulpharsenious acid, $H_3AsS_3$, or $HAsS_2$. The salts are, for the most part, derived from the acid of the latter formula. There is, therefore, perfect analogy between the oxygen and sulphur compounds, for, as has been seen, when arsenic trioxide is dissolved in potassium hydroxide a salt of the formula $KAsO_2$ is formed. The analogy is clearly shown by means of the equations

$$As_2O_3 + 2KOH = 2KAsO_2 + H_2O;$$
$$As_2S_3 + 2KSH = 2KAsS_2 + H_2S.$$

**Arsenic Pentasulphide,** $As_2S_5$, is formed by melting sulphur and arsenic together in the proper proportions, and by precipitating a solution of sodium sulpharsenate with hydrochloric acid:

$$2Na_3AsS_4 + 6HCl = 6NaCl + As_2S_5 + 3H_2S.$$

**Arsenic Trichloride,** $AsCl_3$, is the only compound which arsenic forms with chlorine. It is easily made by passing chlorine into a retort containing powdered arsenic.

## Antimony, Sb (At. Wt. 120.2).

**Occurrence.**—Antimony occurs in nature in small quantity in the free state, but chiefly in the form of stibnite, which is the trisulphide, $Sb_2S_3$. This also occurs widely distributed in nature in combination with sulphides of various metals, as copper, lead, and silver. The element is made from the sulphide either by heating it with iron, with which the sulphur combines, leaving the antimony free; or by roasting it, that is, heating it in combination with the air, thus converting the antimony into the tetroxide $Sb_2O_4$, and the sulphur into the dioxide $SO_2$,

and then treating the oxide of antimony with reducing agents, as, for example, carbon:

$$Sb_2O_4 + 4C = 2Sb + 4CO.$$

**Properties.**—Antimony is hard and brittle; has a silver-white color, and a high metallic lustre. It melts at 625°. It can be distilled at white heat. At ordinary temperature it is not changed by contact with the air. When heated to a sufficiently high temperature in the air it takes fire and burns, forming the white oxide $Sb_2O_3$. It combines directly with chlorine, forming the chloride $SbCl_5$. Nitric acid oxidizes it either to antimony oxide, $Sb_2O_3$, or antimonic acid, $H_3SbO_4$. *Aqua regia* dissolves it. Hot concentrated sulphuric acid dissolves it, forming antimony sulphate, and sulphur dioxide escapes.

Like arsenic antimony has been obtained in a yellow non-metallic modification, soluble in carbon bisulphide. This very unstable form is obtained by conducting oxygen at 90° through stibine.

**Applications of Antimony.**—Antimony is used as a constituent of several alloys (which see). These will be discussed later on. The value of antimony as a constituent of alloys consists in the fact that it renders them hard. The fact that liquid antimony like water expands on solidifying makes it valuable for type-metal as the expanding metal fills the matrix. Among the soluble alloys of antimony are type-metal, from which type is made, and britannia metal. The former consists of lead and antimony, and the latter of tin and antimony. There are a number of other alloys that contain antimony. These will be referred to under the other constituents.

**Stibine,** $SbH_3$.—This analogue of ammonia, phosphine, and arsine is more like arsine than it is like the others. It is made by the same methods as those used in making arsine, i. e., by treating an alloy of zinc and antimony with sulphuric acid, or by reducing oxides of antimony by means of nascent hydrogen. The latter method gives a gas containing a large percentage of hydrogen, but for

most purposes this is not objectionable. It is only necessary to introduce into a flask containing zinc and dilute sulphuric acid a little of a solution of some oxygen compound of antimony, when the reduction at once takes place, and the escaping hydrogen contains stibine.

Stibine is a colorless, inodorous gas, that burns with a greenish-white flame. In general, it conducts itself much like arsine. It is unstable and breaks down when the tube through which it is passing is heated to about 150°. It then leaves a deposit resembling that formed from arsine. When a cold object, as a piece of porcelain, is held for a moment in a flame of stibine a dark deposit is formed resembling that formed with arsine.

**Methods of distinguishing between Arsenic and Antimony.**—As arsenic is sometimes used in cases of poisoning, the question of deciding whether it is present in a given liquid or mixture may be of great importance. One of the chief difficulties encountered is the similarity of the two elements arsenic and antimony. The method commonly employed in examining a substance for arsenic is known as *Marsh's test.* This consists in getting the substance in solution, and then pouring some of the liquid into a vessel containing pure zinc and pure dilute sulphuric acid. If arsenic is present in the solution it will, under these circumstances, be converted into arsine, the presence of which can be recognized by heating the tube through which the gas is passing, and by holding a piece of porcelain in the flame. If deposits are not formed in the tube or on the porcelain, arsenic is not present; but if deposits are formed, the only conclusion that can be drawn is that *either* arsenic *or* antimony is present, or possibly both may be present. For the purpose of distinguishing between the two elements, advantage is taken of the following differences between the spots: The antimony spots are darker than those formed by arsenic, and they have a smoky appearance, while those of arsenic have not; further, the arsenic deposits are quite volatile, and can therefore be driven before the flame in the tube or upon the porcelain, while those of

antimony are not volatile; again, the deposits of arsenic are easily soluble in a solution of sodium hypochlorite or hypobromite, while the antimony deposits are insoluble in these solutions. There are other differences, but those mentioned will suffice to enable a careful worker and observer to distinguish between the two without any possibility of doubt. Another difficulty always encountered in examining for arsenic is the fact that the sulphuric acid, the zinc, and the glass of which the vessels are made may contain arsenic. It is quite possible to overcome all the difficulties and to decide positively whether arsenic is present or not. If it is found that on heating the tube through which the hydrogen is passing no deposit is formed, even after continued heating, and that the hydrogen flame gives no deposit upon a piece of porcelain introduced into it, then it is safe to proceed with the examination of the suspected liquid. If the substance which is to be examined for arsenic has to be treated with chemical compounds in order to prepare it for analysis, every compound used in this part of the process must, of course, be separately examined for arsenic.

**Antimonic Acid,** $H_3SbO_4$.—This acid is the final product of the oxidation of antimony when treated with *aqua regia*. It need only be said that it is very similar to phosphoric and arsenic acids; and that, like these, it yields a meta- and a pyro-acid of the formulas $HSbO_3$ and $H_4Sb_2O_7$. The acid of the formula $OSb(OH)_3$, or orthoantimonic acid, is known in the free state, and is formed by treating a soluble salt of antimonic acid with sulphuric or nitric acid:

$$OSb(OK)_3 + 3HNO_3 = 3KNO_3 + OSb(OH)_3.$$

An acid $Sb_2O(OH)_8$ is also known in the free state, being formed by the action of antimony pentachloride upon water. The lower oxides of antimony, the trioxide, $Sb_2O_3$, and the tetroxide, $Sb_2O_4$, are not strongly acidic; that is to say, they do not readily form salts when treated with bases. In this respect the trioxide of antimony differs markedly from the corresponding oxides of phosphorus and arsenic.

**Antimony Trioxide,** $Sb_2O_3(Sb_2O_6)$.—Although the molecular weight of this compound shows that it has the composition represented by the formula $Sb_2O_6$, it is still called the trioxide. It is found in nature

as white ore of antimony, and is easily formed by burning antimony in the air and by oxidizing it with nitric acid or saltpetre That formed by burning antimony in the air always contains some of the tetroxide, and by heating it long enough in the air and to a temperature high enough it is completely transformed into the tetroxide. When the trioxide is dissolved in caustic soda a salt of the formula $NaSbO_2$ is formed. This is plainly derived from an acid of the formula $HSbO_2$, which bears a simple relation to normal antimonious acid. Towards most bases, however, antimony trioxide does not conduct itself as an acid. On the other hand, towards the stronger acids it acts as a base

**Salts of Antimony.**—The salts of antimony are derived either from the hydroxide $Sb(OH)_3$ or from the hydroxide SbO.OH. The salts of the first class are called *antimony salts;* those of the second class are called *antimonyl salts.* In the salts formed when the trihydroxide of antimony is completely neutralized by acids, the antimony takes the place of three atoms of hydrogen. Thus, the nitrate has the formula $Sb(NO_3)_3$; the sulphate has the formula $Sb_2(SO_4)_3$; etc. Besides these normal salts there are, however, basic salts. Thus there are two basic nitrates possible. These have the formulas $Sb\begin{cases}OH\\OH\\NO_3\end{cases}$ and $Sb\begin{cases}OH\\NO_3\\NO_3\end{cases}$.

The formation of antimonyl salts is illustrated by the sulphate. This may be regarded as formed by the action of sulphuric acid upon the hydroxide SbO.OH, which is analogous in composition to the acid of arsenic of the formula AsO.OH:

$$2SbO.OH + \begin{matrix}HO\\HO\end{matrix}\!>\!SO_2 = \begin{matrix}SbO.O\\SbO.O\end{matrix}\!>\!SO_2 + 2H_2O.$$

The product is *antimonyl sulphate.* The weak basic character of the hydroxides of antimony is shown by the fact that many of its salts are decomposed by water (hydrolyzed). The salt of antimony most commonly met with is the so-called *tartar emetic.* This appears to be an antimonyl potassium salt of tartaric acid. Tartaric acid is a dibasic acid of the formula $C_4H_4O_4\begin{cases}OH\\OH\end{cases}$. When one of its acid

hydrogen atoms is replaced by potassium, and the other by the antimonyl group SbO, the salt thus formed is tartar emetic, $C_4H_4O_4\begin{cases}OSbO\\OK\end{cases}$.

Antimony trioxide dissolves in hydrochloric acid, forming the trichloride, and this, as has been stated, is decomposed by water yielding oxychlorides.

**Antimony Tetroxide,** $Sb_2O_4$.—This compound is most easily obtained by igniting antimonic acid, $H_3SbO_4$. Two reactions are involved:

$$2H_3SbO_4 = Sb_2O_5 + 3H_2O;$$
$$Sb_2O_5 = Sb_2O_4 + O.$$

It is also formed by igniting the trioxide in the air. At ordinary temperatures the tetroxide is white, but it becomes yellow when heated. Towards strong acids this oxide acts like a weak base. A potassium salt of the formula $K_2Sb_2O_5$ is known, which is derived from the acid $H_2Sb_2O_5$, and this in turn from the simpler acid $SbO(OH)_3$ by loss of water. The oxide itself is regarded by some as an antimonyl salt of metantimonic acid, $SbO_2.OH$, of the formula $SbO_2.O.SbO$.

**Antimony Pentoxide,** $Sb_2O_5$.—Antimony tetroxide does not combine with oxygen to form the pentoxide. The latter can be obtained only by gentle ignition of antimonic acid, care being taken not to raise the temperature high enough to decompose the pentoxide into the tetroxide and oxygen. The fact that the pentoxide readily yields salts of antimonic acid when treated with basic solutions was mentioned under Antimonic Acid.

**Antimony Trisulphide,** $Sb_2S_3$.—This compound occurs in nature in considerable quantity and is the chief source of antimony. It is known as *stibnite* and *antimony blende.* In some localities, especially in Japan, it occurs in large crystals of great beauty. When heated in the air, or roasted, it is converted into the trioxide, and finally into the tetroxide, while the sulphur escapes as the dioxide. Hydrochloric acid dissolves the trisulphide in the form of the chloride with evolution of hydrogen sulphide:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Nitric acid converts it into the oxide with separation of sulphur. When a solution of antimony chloride is treated with hydrogen sulphide, the trisulphide is thrown down.

This artifically-prepared trisulphide has an orange-red color, while that which occurs in nature is black or gray. The sulphide dissolves in solutions of metallic sulphides, forming salts of sulphantimonious acid, either SbS.SH or $Sb(SH)_3$.

**Antimony Pentasulphide,** $Sb_2S_5$, is formed by passing hydrogen sulphide into a solution of antimonic acid or by decomposing a salt of sulphantimonic acid by means of an acid. The action takes place thus:

$$2H_3SbO_4 + 5H_2S = Sb_2S_5 + 8H_2O;$$
$$2Na_3SbS_4 + 6HCl = 6NaCl + Sb_2S_5 + 3H_2S.$$

It is, when dry, a golden-yellow powder known as *sulphur auratum*. It dissolves easily in solutions of metallic sulphides, forming the *sulphantimonates*, of which the sodium salt, $Na_3SbS_4$, known as Schlippe's salt, is a good example. The action is represented by this equation:

$$Sb_2S_5 + 6NaSH = 2Na_3SbS_4 + 3H_2S.$$

When heated in the air the pentasulphide gives off enough sulphur to form the trisulphide; while when the pentoxide is heated it is converted into the tetroxide. The sulphantimonates are decomposed when treated with acids and the pentasulphide is thrown down.

**Compounds of Antimony and Chlorine** — Antimony forms two compounds with chloride, analogous in composition to the two chlorides of phosphorus. These are *antimony trichloride* $SbCl_3$, and *antimony pentachloride*, $SbCl_5$ The trichloride is formed by direct treatment of the element with chlorine. It is also formed by dissolving antimony in hydrochloric acid with addition of nitric acid, and when this solution is distilled the chloride of antimony passes over. At the ordinary temperatures it is a solid, colorless, crystalline, soft substance, which, on account of its consistency, has received the common name "butter of antimony" (*butyrum antimonii*).

Antimony chloride has a caustic action and is used in medicine. It is also used for the purpose of burnishing iron-ware, as gun-barrels. When treated with the chloride they acquire a brownish, bronze-like color.

*Antimony pentachloride* in general resembles phosphorus pentachloride. It gives up its chlorine, however, somewhat more readily.

**Oxychlorides of Antimony.**—Antimony trichloride is decomposed by cold water as represented in the equation

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

If, however, hot water is used, the composition of the product approximates that represented by the formula $Sb_4O_5Cl_2$. This complex mixture of oxychlorides is known as the "*powder of algaroth.*" It may be regarded as derived from the simple oxychloride by loss of antimony trichloride, thus:

$$5SbOCl = Sb_4O_5Cl_2 + SbCl_3.$$

Many other oxychlorides besides the two mentioned have been obtained, but they are all more or less closely related to the simple compound SbOCl.

## BISMUTH, Bi (At. Wt. 208).

**Occurrence, etc.**—Bismuth is not abundant nor widely distributed in nature. It occurs for the most part native in veins of granite and clay slate. Among the compounds of bismuth found in nature are the oxide $Bi_2O_3$ and the corresponding sulphide $Bi_2S_3$.

The ores are roasted and then treated with appropriate reducing agents. In different places different methods of extraction are employed. As the chief applications of bismuth are for pharmaceutical purposes, it is necessary that the element should be especially pure; above all, that it should not be contaminated with arsenic. In order to remove the last traces of this element, the powdered bismuth is generally melted with saltpetre.

Bismuth is a hard, brittle, reddish-white substance with a metallic lustre. It melts at 269°. It looks very much like antimony, but is distinguished from it by its reddish tint. At ordinary temperatures it remains unchanged in the air. When heated to redness it burns with a bluish flame, forming the yellow oxide $Bi_2O_3$.

Hydrochloric acid scarcely acts upon it; concentrated sulphuric acid forms *bismuth sulphate*, $Bi_2(SO_4)_3$, in which the bismuth evidently plays the part of a base-forming element; nitric acid gives *bismuth nitrate*, $Bi(NO_3)_3$, which is partly decomposed by water, forming so-called

basic nitrates difficultly soluble in water. These salts will be briefly treated of below.

Some bismuth is used in the preparation of alloys that are easily fusible, as, for example, Newton's metal, which contains bismuth, lead, and tin; Rose's metal, which consists of the same constituents in slightly different proportions; and Wood's metal, which consists of bismuth, lead, tin, and cadmium.

Bismuth possesses in a still greater degree than antimony the property of expansion on passing from the liquid to the solid state. This in connection with the low melting point of its alloys renders it valuable for making plates for printing drawings and pictures.

Bismuth does not combine with hydrogen.

**Oxides of Bismuth.**—The principal compound of bismuth and oxygen is the trioxide, $Bi_2O_3$, which is formed when bismuth is burned in the air. It is a yellow powder. It is basic and forms salts which in composition correspond to the salts of antimony. Like the latter, they are of two classes—the *bismuth salts* and the *bismuthyl salts*. The former are derived from the triacid base, $Bi(OH)_3$, the latter from the monacid base, $BiO(OH)$.

**Salts of Bismuth.**—The best known salts of bismuth are those which it forms with sulphuric and with nitric acids. There is a sulphate of the formula $BiH(SO_4)_2$ formed by dissolving bismuth oxide in dilute sulphuric acid. The sulphate which is most stable in the presence of water is the bismuthyl salt, $(BiO)_2SO_4$. When bismuth is dissolved in nitric acid and the solution evaporated to dryness the salt $Bi(NO_3)_3+10H_2O$ is obtained. This salt is decomposed when heated, and by water, forming *basic nitrates of bismuth*. The composition of the basic nitrate obtained by decomposing the neutral nitrate with water differs according to the conditions. Hot and cold water produce different results. A solution containing much nitric acid does not give the same result as one containing little, etc. As basic bismuth nitrate is used in medicine it is necessary that specific directions should be given for its preparation, in order that a substance of the

same composition should always be obtained. The basic nitrate of bismuth, or the *subnitrate*, as it is frequently called in pharmacy, is much used in medicine as a remedy in dysentery and cholera. It is also used as a cosmetic.

**Bismuth Dioxide,** $Bi_2O_2$, is formed as a brown precipitate when potassium hydroxide is added to a solution of bismuth chloride and stannous chloride, $SnCl_2$.

**Bismuth Peroxide,** $BiO_2$, is formed by heating bismuth pentoxide to 160°, and is used as an energetic oxidizing agent.

**Bismuth Pentoxide,** $Bi_2O_5$, is formed by oxidizing the trioxide, by means of chlorine, in alkaline solution. Although some experimenters appear to have obtained salts of bismuthic acid, as, for example, $KBiO_3$, others have failed to obtain them. In any case it is evident that the acid properties of the oxide are very weak.

**Bismuth Trisulphide,** $Bi_2S_3$, occurs in nature, and is formed by precipitating bismuth from solutions of its salts with hydrogen sulphide. It dissolves in hot concentrated hydrochloric acid and in nitric acid. It does not dissolve in solutions of the sulphides as the sulphides of arsenic and antimony do.

**Bismuth and Chlorine.**—Bismuth differs from the other members of the phosphorus group in its conduct towards chlorine. It forms the chloride, $Bi_2Cl_4$, of which there is no analogue among the compounds of the other elements of the group with chlorine. The compound may, however, be regarded as analogous to the hydrogen compounds hydrazine, $N_2H_4$, and liquid phosphine, $P_2H_4$. *Bismuth trichloride,* $BiCl_3$, is formed by treating bismuth with chlorine, and by dissolving bismuth oxide, $Bi_2O_3$, in hydrochloric acid. From this solution a crystallized compound of the formula $BiCl_3+H_2O$ is deposited, and it is impossible to drive all the water off from this compound without causing decomposition. Treated with water the chloride is decomposed, forming the oxychloride, BiOCl:

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

## Family V, Group A.

As the members of Group A, Family VII, are related to Group B of the same family; and as the members of Group A, Family VI, are related to the members of Group B of the same family, so the members of Group A, Family V, are related to the members of Group B, which have just been studied. The members of Group A are vanadium, columbium, tantalum, and didymium, all of

which are rare. Of these vanadium has been most thoroughly investigated, and columbium next.

**Vanadium,** V (At. Wt. 51.2).—This element occurs in nature in the form of vanadates or salts of vanadic acid, $H_3VO_4$, which is analogous to phosphoric acid.

**Vanadic Acid,** $H_3VO_4$, is the most important and best known of the compounds of vanadium It is the final product of the oxidation of vanadium, and bears to this element the same relation that phosphoric, arsenic, and antimonic acids bear to phosphorus, arsenic, and antimony. The vanadates are derived from ortho-, meta-, and pyrovanadic acids, though the most stable ones are the metavanadates, $MVO_3$. The free *metavanadic acid* is known. It is a beautiful golden-yellow compound, which may be used as a substitute for gold bronze

**Columbium,** Cb (At. Wt. 94).—This element, which is also called niobium, occurs in the mineral columbite.

**Tantalum,** Ta (At Wt 181).—Tantalum occurs in the minerals columbite and tantalite, accompanied by columbium.

**Didymium,** consists of two very similar elements, *neodymium* and *praseodymium*. In some of their compounds they show a resemblance to the members of this group. They form, for example, an oxide of the formula $Di_2O_5$. On the other hand, they seem to be more closely related to cerium and lanthanum, which are also very rare elements, occurring associated with didymium. These will be further treated of in connection with lanthanum and cerium.

## Boron, B (At. Wt. 11).

**General.**—Although the element boron is not a member of the family to which nitrogen and phosphorus belong, it nevertheless resembles the members of this family in some respects. It belongs to the same family as aluminium, and in the composition of its compounds it is undoubtedly similar to aluminium; but, on the other hand, its oxide is distinctly acidic, while that of aluminium is basic.

**Occurrence.**—Boron occurs in nature chiefly in the form of boric acid, or as salts of this acid, especially a sodium salt known as borax and the calcium salts colemanite and borocalcite.

**Preparation.**—From borax and the other borates the acid can easily be obtained. When heated, water is given off, and boron trioxide, $B_2O_3$, is left:

$$2B(OH)_3 = B_2O_3 + 3H_2O.$$

By heating the oxide with potassium, amorphous boron is obtained. By melting the oxide with aluminium, boron is formed and is dissolved in the molten aluminium, from which, on cooling, it is deposited in crystals. Amorphous boron in almost pure form is obtained by heating borax with magnesium powder. One of the chief difficulties encountered in preparing boron is the marked tendency of the element to combine with the nitrogen of the air. At the high temperature at which the reduction takes place the two elements combine very readily to form boron nitride, BN. The crystals obtained in the process described are not pure boron, but contain aluminium, or carbon and aluminium, apparently in combination with the boron. The crystals are very hard, and some of them have a high lustre.

**Properties.**—Amorphous boron is a greenish-brown powder. It burns when heated in the air or in oxygen, the product being the trioxide $B_2O_3$. Strong oxidizing agents, like nitric acid and saltpetre, oxidize it, forming boric acid. It combines readily also with many other elements, as with chlorine, nitrogen, and sulphur. When it is brought into the melting hydroxides or carbonates of potassium or sodium, it forms borates of the corresponding metals.

**Boron Hydride,** $BH_3$, is an unstable gas. It also occurs in a more stable solid modification. It is obtained as a by-product in the reduction of borates, and by decomposition of the borides.

**Boron Trichloride,** $BCl_3$.—This compound is formed by heating boron in a current of dry chlorine, and by heating a mixture of boron trioxide and charcoal in chlorine:

$$2B_2O_3 + 3C + 6Cl_2 = 4BCl_3 + 3CO_2.$$

This reaction is especially interesting on account of its double character. Carbon alone could not reduce the boron trioxide at the temperature employed; nor could the chlorine alone displace the oxygen and form the chloride, but when both chlorine and carbon act together these changes take place, one aiding the other.

The chloride is a liquid that boils at 17°. Like phosphorus trichloride, it is easily decomposed by water, forming boric acid, which, as will be seen, is analogous in composition to phosphorous acid and arsenious acid:

$$BCl_3 + 3H_2O = B(OH)_3 + 3HCl.$$

**Boric Acid,** $B(OH)_3$.—Boric acid occurs free in nature and in the form of salts, of which the principal one is borax. Besides borax, which is a sodium salt derived from tetraboric acid, $H_2B_4O_7$, there are other natural borates, as boracite, which is a magnesium salt combined with magnesium chloride; datholite, which is made up of silicic acid, boric acid, and the element calcium; colemanite, $Ca_2B_6O_{11}$, a salt of the acid $H_4B_6O_{11}$ ($6B(OH)_3 - 7H_2O = H_4B_6O_{11}$); and borocalcite, $CaB_4O_7$, which is analogous to borax. One of the most interesting natural forms of boric acid is that given off from the earth with steam. Such jets of steam are met with in many volcanic regions, and are called fumaroles. In Tuscany many of the fumaroles are charged with small quantities of boric acid. Those at Monte Cerboli and Monte Rotundo in Tuscany are utilized for the purpose of obtaining the boric acid. For this purpose basins are built over the fumaroles and filled with water, so that the steam is condensed and the boric acid dissolved in the water. The solutions formed at the higher levels flow into basins at lower levels, and finally become charged with a considerable quantity of the acid. The most concentrated solution thus obtained is evaporated to crystallization by the aid of the heat furnished by the fumaroles. The acid obtained in this way is not pure, but it can be purified by recrystallization.

Boric acid can also be made from borax by treating the salt in solution with dilute sulphuric acid:

$$Na_2B_4O_7 + H_2SO_4 + 5H\,O = Na_2SO_4 + 4B(OH)_3.$$

If the solution is sufficiently concentrated the boric acid crystallizes out on cooling.

Boric acid is easily soluble in water, and crystallizes from the solution. It is also soluble in alcohol, and this solution burns with a characteristic green flame. The acid is quite volatile with water-vapor. When heated at 100° orthoboric acid, $B(OH)_3$, loses one molecule of water, and is converted into *metaboric acid*, $HBO_2$; at 160° it yields *tetraboric acid*, $H_2B_4O_7$; and at a higher tempera-

ture it is converted into boron trioxide or boric anhydride, $B_2O_3$. These changes are represented thus:

$$H_3BO_3 = HBO_2 + H_2O;$$
$$4H_3BO_3 = H_2B_4O_7 + 5H_2O.$$

The most stable salts are the tetraborates and metaborates. Borax is the sodium salt of tetraboric acid, $Na_2B_4O_7$. The salts of orthoboric acid are unstable. They break down (are hydrolyzed) when treated with water, forming free boric acid and either metaborates or tetraborates.

Most of the boric acid obtained from Tuscany is used in the manufacture of borax, a salt that finds extensive application.

The most important source of boric acid is colemanite, which occurs in California. About 2500 tons are mined monthly.

**Salts of Boron.**—Although the most characteristic compounds of boron are those in which it acts as an acid-forming element, it forms some compounds in which its power as a base-former is shown. Thus, with concentrated sulphuric acid the trioxide forms a compound which appears to be pyrosulphuric acid, $H_2S_2O_7$, in which the group BO, analogous to antimonyl, SbO, is substituted for one hydrogen. It has the composition $(BO)HS_2O_7$. Further, when concentrated phosphoric acid acts upon crystallized boric acid, *boron phosphate*, $BPO_4$, is formed. This compound is characterized by great stability. Concentrated acids, for example, do not decompose it. It also forms a salt that appears to be analogous to tartar emetic, which, as has been pointed out, is probably antimonyl potassium tartrate, $C_4H_4O_6\left\{\begin{matrix}SbO\\K\end{matrix}\right.$. This is the salt represented by the formula $C_4H_4O_6\left\{\begin{matrix}BO\\K\end{matrix}\right.$, which may be called boryl potassium tartrate.

**Nitrogen Boride, BN.**—This compound has been mentioned in connection with the preparation of boron. It is easily obtained by igniting a mixture of dehydrated borax and ammonium chloride. It forms a white powder, insoluble in water, and characterized by great stability. At red heat it is decomposed by water-vapor into ammonia and boric acid:

$$2BN + 6H_2O = 2B(OH)_3 + 2NH_3.$$

## EXPERIMENTS.

### Phosphorus.

**Experiment 153.**—[This, as well as the other experiments with phosphorus, should be performed only by an experienced person.] Arrange an apparatus as shown in Fig. 58. The neck of the retort is somewhat drawn out and bent downward and fitted air-tight by means of a cork to the wide glass tube *B*. Some small pieces of ordinary phosphorus are now carefully slipped into the retort—as much as is obtained by cutting up two sticks three to four inches long. The apparatus is then adjusted as shown in the figure, so that the end of the tube *B* dips below the surface of the water in the beaker *C*. The whole is then allowed to stand for some hours. The oxygen is absorbed from the air contained in the vessel, and the water rises in *B*. Without uncovering the end of *B*, replace the water in *C* by some that has a temperature of about 50°. Now heat the retort gradually and the phosphorus will distil over and condense in *C* in the molten condition. By lowering the heat gradually at the end of the operation it can finally be stopped without danger of breaking the vessel.

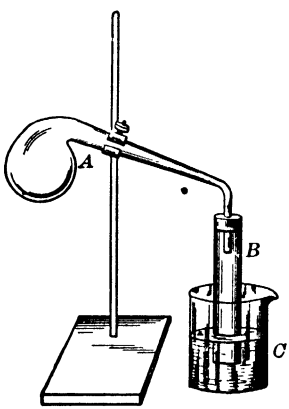


Fig. 58.

**Experiment 154.**—Dissolve a little ordinary phosphorus in carbon bisulphide. Pour some of this solution on a strip of filter-paper, and let this hang in the air or wave it gently in the air. After the carbon bisulphide has evaporated the phosphorus will take fire.

**Experiment 155.**—Bring together in a porcelain crucible or evaporating-dish a little phosphorus and iodine. It will be seen that simple contact is sufficient to cause the two substances to act upon each other. Direct combination takes place, and the action is accompanied by light and heat.

### Phosphorus Abstracts Oxygen from other Substances.

**Experiment 156.**—Add a little of a solution of phosphorus in carbon bisulphide to a solution of copper sulphate. What change takes place?

**Experiment 157.**—Put a few small pieces of ordinary phosphorus

in a glass tube and seal it. Heat gradually to 300°. Open the tube and examine the product. See whether it takes fire as readily as ordinary phosphorus does; whether it dissolves in carbon bisulphide; whether it melts easily when put in water heated to between 45° and 50°.

## Phosphine.

Experiment 158.—*Caution!* Arrange an apparatus as shown in Fig. 59. In the small flask *B* put about 5 grams caustic potash dissolved in 10–15 cc. water, and *when the solution is cold* add a few small pieces of phosphorus the size of a pea. Pass hydrogen for

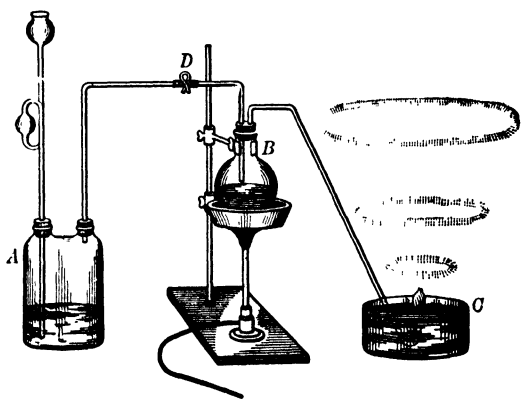



Fig. 59.

some time through the apparatus from the generating-flask *A* until all the air is displaced; then disconnect at *D*, leaving the rubber tube, closed by the pinch-cock, on the tube which enters the flask. *Gently* heat the contents of the retort, when gradually a gas will be evolved, and will escape through the water in *C*. As each bubble comes in contact with the air it takes fire, and the products of combustion arrange themselves in rings, which become larger as they rise. They are extremely beautiful, particularly if the air of the room is quiet. Both the phosphorus and the hydrogen combine with oxygen in the act of burning. Collect some of the gas in a tube over water, and then place the tube mouth upward. What difference is there between the burning of the gas under these circumstances, and that noticed when the rings are formed? Collect another tubeful of the gas, and let this stand for some time. Then open the vessel by taking it out of the water. Has any change taken place in the gas?

## Phosphoric Acid.

Experiment 159.—In a flask connected with an inverted condenser, as shown in Fig. 60, boil 10 to 15 grams ordinary phos-

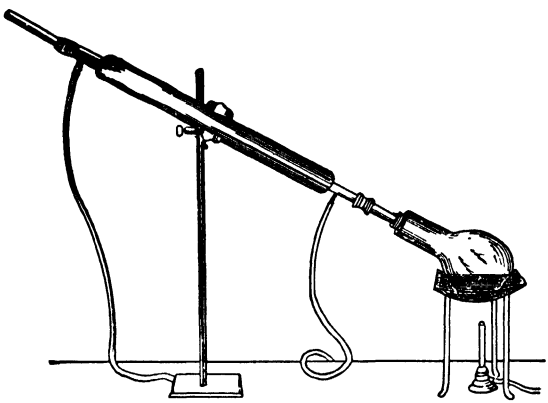


Fig. 60.

phorus with 250 cc. ordinary commercial nitric acid. The most concentrated acid must not be used. If necessary, add more acid after a time. Boil gently until the phosphorus disappears. Evaporate the solution to complete dryness, so as to get rid of all the nitric acid.

Experiment 160.—Try the action of a solution of ordinary sodium phosphate on a solution of silver nitrate. Heat a little of the phosphate in a porcelain crucible to redness. After cooling, try the action of the salt left in the crucible on silver nitrate.

## Phosphorus Trichloride.

The experiments with the chlorides of phosphorus must be carried on under a hood or out-of-doors.

Experiment 161.—Arrange an apparatus as shown in Fig. 61. The tube *A* is arranged so that it can be raised or lowered in the retort. Put 50 to 100 grams ordinary phosphorus in the retort, taking precautions to prevent it from taking fire during the operation. This is best accomplished by fitting corks in both openings of the retort; placing the retort in a vessel of cold water; removing the cork from *B*; throwing in a piece of phosphorus, and quickly putting the cork in. The pieces must not be put in in too rapid succession. After all the phosphorus is in the retort, adjust the ap-

paratus as represented, placing the receiver *D* in a dish of cold water. Now connect by means of the rubber tube *E* with an

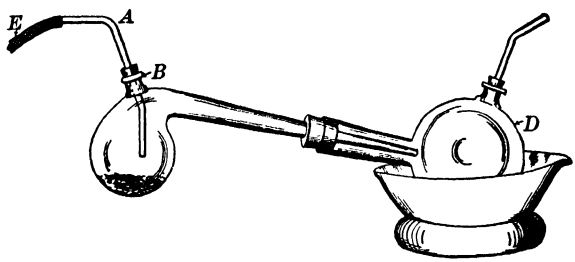



FIG 61.

apparatus furnishing chlorine, dried by means of concentrated sulphuric acid and calcium chloride. As soon as the chlorine comes in contact with the phosphorus action begins, and the product, which is phosphorus trichloride, distils over into the receiver. If the action is taking place too rapidly, the inside of the retort will become covered with a coating of red phosphorus. In this case raise the tube *A* a little and the red coating will gradually disappear. If the tube is raised too high, not enough heat is generated, and the trichloride in the retort is converted into the pentachloride, which is deposited as a white coating. By raising and lowering the tube according to the indications, the retort can be kept clear, and all the phosphorus converted into the trichloride. This manipulation of the tube is much facilitated by fitting into the cork a somewhat larger tube, through which the smaller one can pass easily; letting this project about an inch and a half above the cork and passing over it a piece of rubber tubing of such size that while the smaller tube moves through it readily, the two form a gas-tight joint. This is shown in Fig. 62. After the operation is finished, pour the liquid from the receiver into a clean dry flask, and distil on a water-bath. Try the action of a little of the compound on water.

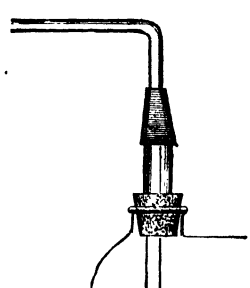


FIG. 62.

## PHOSPHORUS PENTACHLORIDE.

**EXPERIMENT 162.**—Put the trichloride of phosphorus obtained in the last experiment in a wide-mouthed bottle surrounded by cold

water. Through a wide glass tube pass dry chlorine upon the surface of the liquid, and as the action advances, and a solid begins to make its appearance, stir the contents of the bottle. Continue the passage of the chlorine until the product is a perfectly dry solid. The arrangement of the bottle containing the trichloride, and that of the delivery-tube, is shown in Fig. 63. The bottle is put in a larger vessel containing cold water, which is renewed from time to time during the process.

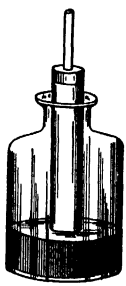


FIG 63.

Try the action of a little phosphorus pentachloride on water. In a large dry flask heat a little of the pentachloride.

## ARSENIC.

EXPERIMENT 163.—Heat a small piece of arsenic on charcoal in the flame of the blowpipe.

## ARSINE.

EXPERIMENT 164.—Arrange an apparatus as shown in Fig. 64. Put some pure granulated zinc in the flask and pour dilute sulphuric acid on it. The calcium-chloride tube serves to dry the gas. When

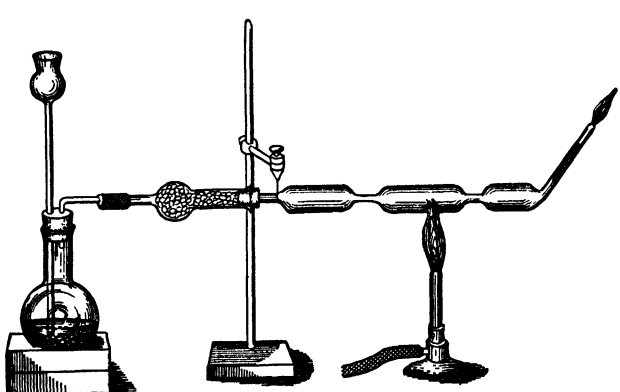


FIG. 64.

the air is all out of the vessel and the hydrogen is lighted, add slowly a little of a solution of arsenic trioxide, $As_2O_3$, in dilute hydrochloric acid. The appearance of the flame will soon change. It will become paler, with a slightly bluish tint, and give off white fumes. *See next Experiment.*

### Marsh's Test for Arsenic.

Experiment 165.—Into the flame of the burning hydrogen and arsine produced in the last experiment introduce a piece of porcelain, as the bottom of a small porcelain dish or a crucible, and notice the appearance of the spots. Heat by means of a Bunsen burner the tube through which the gas is passing, which should be of hard glass. Just beyond the heated place there will be deposited a thin layer of metallic arsenic, commonly called a *mirror of arsenic*. This deposit is due to the direct decomposition of the arsine into arsenic and hydrogen by heat. [Compare ammonia, phosphine, and arsine with reference to their stability.]

### Arsenic Acid.

Experiment 168.—Pass chlorine into water containing arsenic trioxide in suspension, until the oxide is dissolved. Evaporate to crystallization. Into a dilute solution of a very little of the product thus obtained, to which some hydrochloric acid has been added, pass hydrogen sulphide. Explain the changes.

### Reduction of Arsenic Trioxide.

Experiment 167.—In the bottom of a dry tube of hard glass of the form represented in Fig. 65 put a minute piece of arsenic trioxide, and just above it a small bit of charcoal. Heat gently. Explain the change.



Fig. 65.

### Sulphides of Arsenic.

Experiment 168.—Pass hydrogen sulphide into a dilute solution of arsenic trioxide in hydrochloric acid.—Filter off the precipitate, and try the action of ammonium sulphide on some of it.

### Antimony.

Experiment 169.—Heat a small piece of antimony on charcoal in the blowpipe flame. Try the action of dilute and of concentrated hydrochloric acid, of dilute and of concentrated nitric acid, and of a mixture of the two acids on a small piece of antimony.

### Stibine.

Experiment 170.—Stibine is made by the same method as that used in making arsine. Make some, using a solution of tartar emetic. Introduce a piece of porcelain in the flame, and afterwards heat the tube through which the gas is passing. Compare the anti-

mony spots with the arsenic spots. Color? Volatility? Conduct towards a solution of sodium hypochlorite or hypobromite?

### Sulphides of Antimony

Experiment 171.—Pass hydrogen sulphide into a solution of antimonic acid made by treating antimony with *aqua regia* and diluting with water. Pass hydrogen sulphide into a solution of antimony trichloride made by dissolving stibnite or antimony trisulphide in hydrochloric acid. Try the action of ammonium sulphide on the precipitates after filtering.

### Oxychlorides of Antimony.

Experiment 172.—Treat a solution of antimony trichloride with water.

### Bismuth.

Experiment 173.—Heat a piece of bismuth on charcoal in the blowpipe flame. See how it conducts itself towards hydrochloric acid; towards nitric acid. If a solution is obtained in either case, add water to it. Explain what takes place.

### Basic Nitrates of Bismuth.

Experiment 174.—Dissolve a little bismuth in nitric acid and evaporate. Add water.

### Boron.

Experiment 175.—Make a hot solution of 30 grams crystallized borax in 120 cc. water. Add *slowly* 10 grams concentrated sulphuric acid. On cooling, the boric acid will crystallize out. What evidence have you that the substance which crystallizes out of the solution is not borax? Try the solubility in alcohol of specimens of each. Is there any difference? Treat a few crystals of borax with about 10 cc. alcohol; pour off the alcohol and set fire to it. Treat a few crystals of the boric acid in the same way. What difference do you observe? Distil an aqueous solution of boric acid, and determine whether any of the acid passes over with the water-vapor.

## CHAPTER XVIII.

### CARBON (C, At. Wt. 12) AND ITS SIMPLER COMPOUNDS WITH HYDROGEN AND CHLORINE.

**Introductory.**—Carbon bears to Family IV relations similar to those which nitrogen, oxygen, and fluorine bear to Families V, VI, and VII. Towards hydrogen, as well as towards chlorine and oxygen, carbon is quadrivalent, and towards oxygen it is also bivalent. In this family the maximum oxygen-valence coincides with the hydrogen-valence, while, as has been seen, in Families V, VI, and VII, the oxygen-valence is higher than the hydrogen-valence, the difference becoming greater from Family V to VII. While the higher oxygen compounds of Family IV are acidic, forming acids which are derived from the normal acid, $R(OH)_4$, the lower oxides are not generally acid. The hydrogen compounds of the general formula $MH_4$, of which there are but two, those of carbon and silicon, have neither acid nor basic properties. Carbon is distinguished by the large number of the compounds into which it enters, all of which are more or less closely related to a comparatively small number of fundamental forms. Silicon also forms a large number of compounds, as we shall see; but these are of a different kind from those obtained from carbon.

**Occurrence of Carbon.**—In general, substances that are obtained from the vegetable or animal kingdom *blacken* when heated to a sufficiently high temperature, and afterwards, if they are heated in the air, they burn up, as we say. Considering the great variety of substances found in living things, it appears remarkable that nearly all have this property in common. It is due to the fact that *nearly all animal and vegetable substances contain the element carbon.* When they are heated the other ele-

ments present are first driven off in various forms of combination, while the carbon is last to go. Hydrogen and oxygen pass off as water; hydrogen and nitrogen as ammonia; and much of the carbon also passes off in combination with hydrogen, with hydrogen and oxygen, and with nitrogen and hydrogen. If the heating is carried on in the air, the carbon finally combines with oxygen to form a colorless gas—it burns up. Carbon is the central element of organic nature. There is not a living thing, from the minutest microscopic animal to the mammoth, from the moss to the giant tree, that does not contain this element as an essential constituent. The number of the compounds which it forms is almost infinite, and they present such peculiarities that they are commonly treated of under a separate head, "Organic Chemistry." There is no good reason for this, except the large number of the compounds. For our present purpose it will suffice to consider the chemistry of the element itself, and of a few of its more important simple compounds.

From what has already been said, it will be seen that the principal form in which carbon occurs in nature is in combination with other elements. It occurs not only in living things, but in their fossil remains, as in coal. Coal-oil, or petroleum, consists of a large number of compounds which contain only carbon and hydrogen. Most products of plant-life contain the elements carbon, hydrogen, and oxygen. Among the more common of these products may be mentioned sugar, starch, and cellulose. Most products of animal life contain carbon, hydrogen, oxygen, and nitrogen. Among them may be mentioned albumin, fibrin, casein, etc. Carbon occurs in the air in the form of carbon dioxide. It also occurs in the form of salts of carbonic acid; the carbonates, which are very widely distributed, forming whole mountain ranges. Limestone, marble, and chalk are varieties of calcium carbonate.

Uncombined, the element occurs pure in two very different forms in nature: (1) as *diamond;* and (2) as *graphite* or *plumbago.*

**Diamond.**—The diamond occurs in few places on the earth, and but little is known as to the conditions which have given rise to its formation. The celebrated diamond beds are in India, Borneo, Brazil, and South Africa. When found, diamonds are generally covered with an opaque layer, which must be removed before its beautiful properties are apparent. The crystals are sometimes regular octahedrons, though usually they are somewhat more complicated, and the faces are frequently curved. It is the hardest substance known. For use as a gem it must be cut and polished. The object in view is to bring out as strikingly as possible its brilliancy by exposing the faces favorably to the action of the light. If heated to a very high temperature without access of air, it swells up and is converted into a black mass resembling coke. The change takes place without loss in weight. Heated to a high temperature in oxygen, it burns up, yielding only carbon dioxide. It is insoluble in all known liquids at ordinary temperatures. It dissolves, however, in molten cast iron and in some other molten metals. Small diamonds have been made by Moissan by dissolving carbon in cast iron with the aid of an electric furnace, and suddenly cooling the mass. Under these conditions the carbon in the inner parts of the mass is under great pressure while passing into the solid form from solution.

**Graphite.**—Graphite, or plumbago, is found in nature in large quantities. Sometimes it is crystallized, but in forms entirely different from those assumed by the diamond. It can be prepared artificially by dissolving charcoal in molten iron, from which solution, on cooling, graphite is deposited. It can also be prepared by heating charcoal to a high temperature in the electric furnace. This variety differs in some of its properties from that which crystallizes from iron. Both varieties are found in nature. It has a grayish-black color and a metallic lustre. It is quite soft, leaving a leaden-gray mark on paper when drawn across it, and it is hence used in the manufacture of so-called *lead*-pencils. It is sometimes called black-lead. When heated without access of air it remains un-

changed. Heated to a very high temperature in the air, or in oxygen, it burns up, forming only carbon dioxide. Like the diamond, it is insoluble in all known liquids at ordinary temperatures.

The name graphite is given to different modifications of carbon. Between the soft, light Siberian graphite and the dense, heavy and very hard graphite used to make arc-light terminals, there are various modifications, differing in their physical properties. An artificial graphite is now prepared at Niagara Falls by distilling carborundum (silicon carbide, SiC). The silicon distils off in the electric furnace leaving a very pure and hard graphitic carbon. In the actual process (Acheson's) anthracite coal is mixed with sand and heated in an electric furnace.

**Amorphous Carbon.**—All forms of carbon that are not diamond, nor graphite, are included under the name *amorphous carbon.* The name signifies simply that it is not crystallized. The most common form of amorphous carbon is ordinary charcoal.

*Charcoal* is that form of carbon which is made by the *charring process.* This consists simply in heating wood without a sufficient supply of air to effect complete combustion. The substance almost exclusively used in the manufacture of charcoal is wood. As has already been stated, wood is made up of a large number of substances, nearly all of which, however, consist of the three elements carbon, hydrogen, and oxygen. One of the chief constituents of all kinds of wood is cellulose. Now, when wood is heated to the temperature at which oxygen begins to act on it, it burns, if air is present. Under ordinary circumstances the chemical changes that take place are complex; but if care is taken, the combustion can be made complete, and then all the carbon is converted into carbon dioxide, and all the hydrogen into water. If, on the other hand, the air is prevented from coming in contact with the wood, as by heating it in a closed vessel, or if it is prevented from coming in contact with it to a sufficient extent to effect complete combustion, the hydrogen is given off partly as water and partly in the form of

volatile products containing carbon and oxygen, as *wood spirits* or *methyl alcohol*, *pyroligneous* or *acetic acid*, *acetone*, etc. The carbon, however, is for the most part left behind as charcoal, as there is not enough oxygen to convert it into carbon dioxide. Such a process as that just described, when carried on in closed vessels, is known as *destructive distillation* or *dry distillation*. It is also known as the charring process. It is a complex example of a kind of change already dealt with. Whenever chemical compounds are heated the constituents tend to arrange themselves in forms that are stable at the higher temperature. Sulphites become sulphates; phosphites become phosphates; chlorates become perchlorates; ammonium salts break down into the acids and ammonia; ammonium nitrite is decomposed giving nitrogen and water; ammonium nitrate yields nitrous oxide and water; primary phosphates yield metaphosphates; secondary phosphates yield pyrophosphates, etc., etc. Carbon compounds are, in general, more sensitive to the influence of heat than the compounds of other elements, and most of them are decomposed even at comparatively low temperatures.

The above statements will make it possible to understand the working of a charcoal-kiln. This consists essentially of a pile of wood so arranged as to leave spaces between the pieces, and covered with some rough material through which the air will not pass easily, as, for example, a mixture of powdered charcoal, turf, and earth. Small openings are left in this covering, so that after the wood is kindled it will continue to burn slowly. The process is sometimes carried on in structures of brickwork with the necessary openings in the walls. The changes above mentioned take place. The gases or volatile substances pass out of the top of the kiln, and appear as a dense cloud. In due time the holes through which the air gains access to the wood, thus making the burning possible, are closed, and the burning ceases. Charcoal, which is impure amorphous carbon, is left behind. As wood always contains some incombustible substances

in small quantity, these are, of course, found in the charcoal. When the wood or charcoal is burned, these substances remain behind as the ash.

Ordinary charcoal is a black, comparatively soft substance. It burns in the air, though not easily, unless the gases that are formed are constantly removed and fresh air supplied,—conditions which are brought about by a good draught, or by blowing upon the fire with a pair of bellows. It burns readily in oxygen. The product of the combustion in the air and in oxygen, when the conditions are favorable, is carbon dioxide, $CO_2$. In the air, when the draught is bad, another compound of carbon and oxygen, carbon monoxide, CO, is formed. Heated without access of air, charcoal remains unchanged. Charcoal is insoluble in liquids generally, though it is soluble in molten iron, and it crystallizes from the solution, as has been seen, in the form of graphite, and sometimes as diamond.

*Coke.*—Besides wood charcoal, there are other forms of amorphous carbon, which are manufactured for special purposes, or are formed in processes carried on for the sake of other products. Coke is a form of amorphous carbon made by heating ordinary gas-coal without access of air, as is done on the large scale in the manufacture of illuminating gas. Coke bears to coal much the same relation that charcoal bears to wood.

*Lamp-black* is a very finely-divided form of charcoal which is deposited on cold objects placed in the flames of burning oils. The oils consist almost exclusively of carbon and hydrogen. When burned in the air they yield carbon dioxide and water. If the flame is cooled down by any means, or if the supply of air is partly cut off, the carbon is not completely burned, the flame "smokes," as we say, and deposits soot. This process is chemically analogous to the deposit of metallic arsenic from a flame of arsine. The soot obtained from the flames of burning oils is made up largely of fine particles of carbon, though some of the unchanged oil is contained in it. Lamp-black is used in the manufacture of printing-ink. As

carbon is acted upon directly by very few substances, and is not soluble, it is almost impossible to destroy the color of printing-ink without destroying the material upon which it is impressed.

*Bone-black*, or *Animal Charcoal*, is a form of amorphous carbon that is made by charring bones. Bones consist of about one-third organic matter and two-thirds incombustible matter, mostly calcium phosphate. When charred, the organic matter undergoes the changes briefly described under the head of Charcoal, while the incombustible constituents remain unchanged. As the organic matter is distributed through the substance of the bones the charcoal obtained in this way is in a very fine state of division, but it is mixed with several times its own weight of mineral matter. In order to remove the latter the bone-black must be treated with an acid, as hydrochloric acid, and afterwards thoroughly washed with water. An efficient variety of animal charcoal is made, further, by mixing blood with sodium carbonate, charring, and afterwards dissolving out the sodium carbonate with water.

Bone-black and wood-charcoal are very porous, and have the power to absorb gases. When placed in air containing bad-smelling gases these are absorbed, and the air is thus to some extent purified. When water containing disagreeable substances is treated with charcoal, these are wholly or partly absorbed, and the water is improved. Charcoal-filters are therefore extensively used. A charcoal-filter to be efficient should be of good size, and from time to time the charcoal should be taken out and renewed. The small filters which are screwed into faucets are of little value, as the charcoal soon becomes charged with the objectionable material present in the water, and is then a source of contamination rather than a means of purification. The power of charcoal to absorb gases depends upon its porosity. That from some varieties of wood is more porous than that from other varieties. Box-wood charcoal absorbs 90 times its own volume of ammonia gas, 35 times its volume of carbon dioxide, and nearly twice its volume of hydrogen. Charcoal from cocoa-nut

wood absorbs 172 times its volume of ammonia, and 68 times its volume of carbon dioxide.

Some coloring matters can be removed from liquids by passing the liquids through *bone-black filters*. On the large scale, this fact is taken advantage of in the refining of sugar. The solution of sugar first obtained from the cane or beet is highly colored; and, if it were evaporated, the sugar deposited from it would be dark-colored. If, however, the solution is first passed through bone-black filters, the color is removed, and now, on evaporating, white sugar is deposited. In the laboratory constant use is made of this method of decolorizing liquids. The action can easily be shown by adding a little bone-black to a solution containing some litmus or indigo. If the solution is digested for a short time with the bone-black, and then passed through a filter, it will be found that the coloring matter is removed.

Charcoal does not undergo decay in the air or under water nearly as readily as wood. That is another way of stating the chemical fact that the substances of which wood is made up are more susceptible to the action of other chemical substances than charcoal is. One good illustration of this, indeed, is seen in the relative ease with which charcoal and wood burn in the air. Piles that are driven below the surface of water are sometimes charred to protect them from the action of those substances which cause decay.

**Coal.**—Under this head are included a great many kinds of impure amorphous carbon that occur in nature. Although there is an almost infinite number of kinds of coal, for ordinary purposes they may be divided into *hard* and *soft coals*, or *anthracite* and *bituminous coals*. Then there are substances more nearly allied to wood called *lignite*, and those which represent a very early stage in the process of coal-formation, viz., *peat*. A close examination of all these varieties has shown that they have been formed by the gradual decomposition of vegetable matter in an insufficient supply of air. The process has been going on for ages. Sometimes the substances have, at

the same time, been subjected to great pressure, as can be seen from the position in which they occur in the earth. The products in the earlier stages of the coal-forming process are more closely allied to wood than those in the later stages. All forms of coal contain other substances in addition to the carbon. The soft coals are particularly rich in other substances. When heated they give off a mixture of gases and the vapors of volatile liquids. The gases are, for the most part, useful for illuminating purposes. The liquids form a black, tarry mass, known as *coal tar*, from which many valuable compounds of carbon are obtained. The gases are passed through water for the purpose of removing certain impurities. This water absorbs ammonia, and forms the *ammoniacal liquor* of the gas-works, which, as has been stated, is the principal source of ammonia.

**Diamond, Graphite, and Charcoal are Different Forms of the Element Carbon.**—It has been shown that oxygen presents itself in two forms—ordinary oxygen and ozone. Ozone is made from oxygen, and oxygen from ozone, without any increase or decrease in weight; and in general the compounds obtained by the combination of other elements with oxygen are identical with those obtained by the combination of the same elements with ozone. So, also, there are several varieties of sulphur, two of which crystallize in different forms. There are, further, at least two different modifications of the element phosphorus, and these differ from each other markedly. The explanation of the difference between oxygen and ozone is that the molecule of the former is made up of two atoms, while that of ozone is made up of three, which are in a state of unstable equilibrium. This explanation is reached through a study of the specific gravity of the two gases. At present no satisfactory explanation can be given of the difference between the varieties of phosphorus and between the varieties of sulphur. It will probably be shown to be due to the way in which the atoms are grouped together in the molecules, and also to the way in which the molecules

are grouped together to form the masses. It is difficult to conceive that the black, porous charcoal, and the dull, gray graphite are chemically identical with the hard, transparent, brilliant diamond. Yet this is undoubtedly the case, as can be shown by a simple experiment. Each of the substances when burned in oxygen yields carbon dioxide. Now, the composition of carbon dioxide is known, so that, if the weight of the carbon dioxide formed in a given experiment is known, the weight of the carbon in it is also known. When a gram of pure charcoal is burned it yields $3\frac{2}{3}$ grams carbon dioxide, and in this quantity of carbon dioxide there is contained exactly one gram of carbon. Further, when a gram of graphite is burned the same weight ($3\frac{2}{3}$grams) of carbon dioxide is obtained as in the case of charcoal; and the same thing is true of diamond. It follows from these facts that the three forms of matter known as charcoal, graphite, and diamond consist only of the element carbon. What the difference is due to is not known. What has been said in regard to the difference between the modifications of sulphur and those of phosphorus will probably hold good for the case of carbon.

Notwithstanding the marked difference in their appearance and in many of their physical properties, the three forms of carbon have some properties in common. They are insoluble in all known liquids at ordinary temperatures. They are tasteless, inodorous, and infusible. When heated without access of air they remain unchanged, unless the temperature is very high, when the diamond swells up and is converted into a mass resembling coke.

**Chemical Conduct of Carbon.**—At ordinary temperatures carbon is an inactive element. If it is left in contact with any one of the elements, no chemical change takes place. It will not combine with any of them unless the temperature is raised. At higher temperature, however, it combines with several of them with great ease, especially with oxygen. Under proper conditions it combines also with nitrogen, with hydrogen, with sulphur,

and with many other elements. It combines with oxygen either directly, as when it burns in the air or in oxygen; or it abstracts oxygen from some of the oxides. The direct combination of oxygen and carbon has already been shown in the burning of charcoal in oxygen, and is familiar to every one in the fire in a charcoal furnace. That carbon dioxide is formed can be shown by passing the gas through lime-water or baryta-water, when insoluble calcium or barium carbonate will be thrown down. The reason why lime-water or baryta-water is used is simply that an insoluble compound is formed, and this can be seen, and it can be separated from the liquid and examined. The reaction that takes place is represented thus:

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Carbon dioxide}}{CO_2} = \underset{\text{Calcium carbonate}}{CaCO_3} + H_2O;$$

$$\underset{\text{Barium hydroxide}}{Ba(OH)_2} + \underset{\text{Carbon dioxide}}{CO_2} = \underset{\text{Barium carbonate}}{BaCO_3} + H_2O.$$

No other common gas acts in this way on these solutions. Hence, when, under ordinary circumstances, a gas is passed into lime-water and an insoluble compound is formed, it may be concluded that the gas is carbon dioxide, though this conclusion may require further proof.

The abstraction of oxygen from compounds by means of carbon may be illustrated in a number of ways. Thus, when powdered copper oxide, CuO, is mixed with powdered charcoal, and the mixture heated in a tube, carbon dioxide is given off, and can be detected as in the last experiment mentioned. Copper is left behind, and, if the proportions are properly selected, all the carbon will pass off as carbon dioxide, and only the copper be left behind:

$$2CuO + C = 2Cu + CO_2.$$

In a similar way, arsenious oxide, $As_2O_3$, gives up its oxygen to carbon. This fact furnishes indeed a delicate method for the detection of the substance. If a little is placed in the bottom of a small tube, and above it a small

piece of charcoal, then when heat is applied the arsenious oxide sublimes, and as its vapor passes the heated charcoal the oxygen is abstracted, and the element arsenic, being also somewhat volatile, is deposited just above the charcoal in the form of a lustrous mirror on the walls of the tube. The reaction is

$$2As_2O_3 + 3C = 4As + 3CO_2.$$

As has already been explained, the abstraction of oxygen from a compound is known as *reduction*. Hence, carbon is called a reducing agent. It is indeed the reducing agent most extensively used in the arts. Its chief use is in extracting metals from their ores, which are the forms in which they occur in nature. Thus, iron does not occur in nature as iron, but in combination with other elements, especially with oxygen. In order to get the metal the ore must be reduced, or, in other words, the oxygen must be extracted. This is invariably accomplished by heating it with some form of carbon, either coke or charcoal.

The elements chlorine, oxygen, nitrogen, and hydrogen being gases, and the products formed when the first three combine with hydrogen being also gaseous or convertible into vapor, it is a comparatively easy matter to study the relations between the volumes of the combining gases and the volumes of the products formed. It is, however, impossible to determine the ratio between the volume of carbon in the form of gas and that of other gases with which it combines.

**Compounds of Carbon with Hydrogen, or Hydrocarbons.**—Carbon forms a large number of compounds with hydrogen. These so-called *hydrocarbons*, among which may be mentioned *marsh-gas* or *methane*, $CH_4$, *olefiant gas* or *ethylene*, $C_2H_4$, *acetylene*, $C_2H_2$, and *benzene*, $C_6H_6$, will be treated of in a later chapter together with some other typical compounds of carbon. Marsh-gas burns with a non-luminous flame. Ethylene, acetylene, and benzene with smoky luminous flame. (See Luminosity of Flames.)

## EXPERIMENTS.

### Carbon.—Bone-black Filters

Experiment 176.—Make a filter of bone-black by fitting a paper filter into a funnel 12 to 15 mm. (5 to 6 inches) in diameter at its mouth. Half fill this with bone-black. Pour a dilute solution of indigo through the filter. If the conditions are right the solution will pass through colorless. Do the same thing with a dilute solution of litmus. If the color is not completely removed by one filtration, filter again. The color can also be removed from solutions by putting some bone-black into them and boiling for a time. Try this with half a liter each of the litmus and indigo solutions used in the first part of the experiment. Use about 4 to 5 grams bone-black in each case. Shake the solution frequently while heating.

### Charcoal absorbs Gases.

Experiment 177.—Collect over mercury in glass tubes some ammonia gas, and some carbon dioxide. Introduce into each a

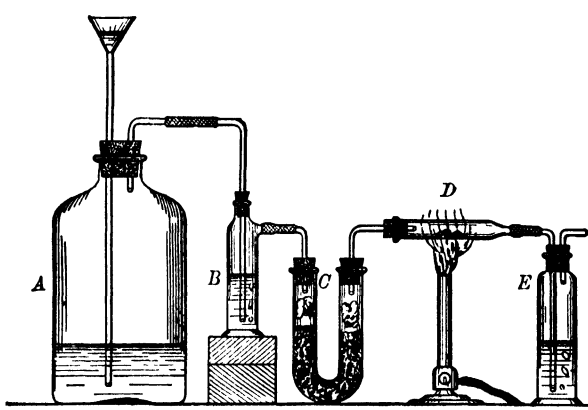



Fig. 66.

piece of charcoal, that has been heated in a Bunsen-burner flame in order to drive out gases that may be contained in the pores.

### Carbon combines with Oxygen to form Carbon Dioxide.

Experiment 178.—Put a small piece of charcoal in a piece of hard-glass tube. Heat the tube, and pass oxygen through it. Pass

the gases into clear lime-water. Arrange the apparatus as shown in Fig. 66.

*A* is a large bottle containing oxygen; *B* is a cylinder containing sulphuric acid; *C* is a U-tube containing calcium chloride; *D* is the hard-glass tube containing the charcoal; *E* is the cylinder with clear lime-water. What takes place?

### Carbon reduces some Oxides when heated with them.

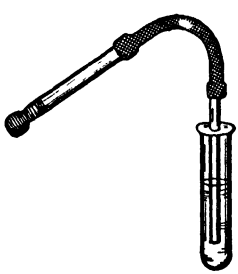


Fig. 67.

Experiment 179.—In a small hard-glass tube closed at one end put a little of a mixture of about equal parts of powdered copper oxide and powdered charcoal. Attach a short piece of rubber tubing to the open end of the glass tube, as shown in Fig. 67. Heat the tube and pass the gas which is given off into lime-water contained in a small test-tube. Is it carbon dioxide? What evidence have you that oxygen has been extracted from the copper oxide? Compare the substance left in the tube with metallic copper. Treat both with nitric acid; with sulphuric acid.

Experiment 180.—Repeat Experiment 167 with somewhat larger quantities of the substances and examine the gas given off.

### Hydrocarbons.

Experiment 181.—Make marsh-gas by heating in a retort a mixture of 20 grams sodium acetate, 20 grams potassium hydroxide, and 30 grams slaked lime. Collect some of the gas over water. Is it a combustible gas?

Experiment 182.—Make ethylene as follows: In a flask of 2 to 3 liters capacity put a mixture of 25 grams alcohol and 150 grams ordinary concentrated sulphuric acid. Heat to 160° to 170°, and add gradually through a funnel-tube about 500 cc. of a mixture of 1 part of alcohol and 2 parts of concentrated sulphuric acid. Pass the gas through three wash-bottles containing, in order, concentrated sulphuric acid, caustic soda, and concentrated sulphuric acid. Collect some of the gas over water. Is it combustible?

## CHAPTER XIX.

### SIMPLER COMPOUNDS OF CARBON WITH OXYGEN, AND WITH OXYGEN AND HYDROGEN.

**General.**—The final product of oxidation of carbon is carbon dioxide, and the final product of reduction is marsh-gas, but between these two limits there are a number of interesting derivatives, just as there are a number of compounds of sulphur between hydrogen sulphide and sulphuric acid; a number of compounds of nitrogen between ammonia and nitric acid; and a number of compounds of phosphorus between phosphine and phosphoric acid. Some of these will be treated of in a later chapter.

**Carbon Dioxide,** $CO_2$.—The principal compound of carbon and oxygen is carbon dioxide, $CO_2$, commonly known as *carbonic-acid gas*. Under the head of The Air attention was called to the fact that this gas is a constant constituent of the air, though its relative quantity is small—about 3 parts in 10,000. It issues from the earth in many places, especially in the neighborhood of volcanoes. Many mineral waters, prominent among which are the waters of Pyrmont, Selters, and the Geyser Spring of Saratoga, contain it in large quantity. In small quantity it is present in all natural waters. In combination with bases it occurs in enormous quantities, particularly in the form of calcium carbonate, $CaCO_3$, varieties of which are ordinary limestone, chalk, marble, and calc-spar. Dolomite, which forms mountain-ranges, being particularly abundant in the Swiss Alps, is a compound containing calcium carbonate and magnesium carbonate, $MgCO_3$.

Carbon dioxide is constantly formed in many natural processes. Thus, all animals that breathe in the air give off carbon dioxide from the lungs. That the gases from the lungs contain carbon dioxide can easily be shown by

passing them through lime-water, when a precipitate of calcium carbonate is formed.

That carbon dioxide is formed in the combustion of charcoal and wood has already been shown. In a similar way it can be shown that the gas is formed whenever any of our ordinary combustible substances are burned. From our fires, as from our lungs, and from the lungs of all animals, then, carbon dioxide is constantly given off. Further, the natural processes of decay of both vegetable and animal matter tend to convert the carbon of this matter into carbon dioxide, which then finds its way principally into the air. The process of alcoholic fermentation, and some other similar processes, also give rise to the formation of carbon dioxide. Sugar is contained in all fruit-juices. When the fruits ripen, fall to the earth, and undergo spontaneous change, the sugar is converted into alcohol and carbon dioxide. It is thus evident that there are many important sources of supply of carbon dioxide, and it will be readily understood why the gas should be found everywhere in the air.

**Preparation.**—The easiest way to get carbon dioxide not mixed with other substances is by adding an acid to a salt of carbonic acid, or a carbonate. In the decomposition of the carbonates by acids the same principle is illustrated as that involved in setting nitric acid free from a nitrate, or hydrochloric acid from sodium chloride by sulphuric acid, and more especially in the liberation of sulphur dioxide from a sulphite. In all these cases the products are volatile, and therefore, when a non-volatile acid is added to the salts, decomposition takes place. Sulphites do not yield the acid from which they are derived, but this breaks down into water and the anhydride:

$$\begin{cases} 2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3; \\ 2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl. \end{cases}$$

$$\begin{cases} Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2SO_3; \\ H_2SO_3 = SO_2 + H_2O. \end{cases}$$

$$\begin{cases} Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2CO_3; \\ H_2CO_3 = CO_2 + H_2O. \end{cases}$$

Any acid that is not volatile at the ordinary temperature will decompose a carbonate and cause an evolution of carbon dioxide. The action between sodium carbonate and hydrochloric acid is represented thus:

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O;$$

that between nitric acid and sodium carbonate thus:

$$Na_2CO_3 + 2HNO_3 = 2NaNO_3 + CO_2 + H_2O.$$

For the purpose of preparing carbon dioxide in the laboratory, calcium carbonate, in the form of marble or limestone, and hydrochloric acid are commonly used. The reaction involved is represented thus:

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

The apparatus used is the same as that used in making hydrogen from zinc and sulphuric acid. As the gas is somewhat soluble in water, it is best for ordinary purposes to collect it by displacement of air, the vessel being placed with the mouth upward, as the gas is considerably heavier than air.

Commercially, the carbon dioxide that escapes from mineral springs, or is obtained as a by-product in chemical processes, is compressed in steel cylinders to the liquid form, and then placed on the market. Germany alone produced 11000 tons in a recent year. "Sparklets" are little steel capsules containing 2–4 grams liquid carbon dioxide, enough to make a bottle of soda water.

**Properties.**—Carbon dioxide is a colorless gas at ordinary temperatures. When subjected to a low temperature and high pressure it is converted into a liquid that boils at $-57°$. Liquid carbon dioxide is now manufactured on the large scale for use as a fire-extinguisher, and for the purpose of charging liquids with the gas. When some of the liquid is exposed to the air, evaporation takes place so rapidly that a great deal of heat is absorbed, and some of the liquid becomes solid. Solid carbon dioxide melts at $-79°$. Its critical temperature is $31°$. The gas has a slightly acid taste and smell. It is not combustible, nor does it support combustion. It is not com-

bustible for the same reason that water is not: because it already holds in combination all the oxygen it has the power to combine with. Before it can burn again it must first be decomposed. As regards the statement that it does not support combustion, it should be remarked that this is only relatively true. The compound does not easily give up oxygen, but to some substances it does give it up, and some such substances burn in it. For example, the element potassium, which as we have seen, has the power to decompose water, has also the power to decompose carbon dioxide if heated in it to a sufficiently high temperature, and when the decomposition once begins, it proceeds with brilliancy, the act being accompanied by a marked evolution of heat and light. Carbon dioxide is much heavier than air, its specific gravity being 1.529. A liter of the gas under standard conditions of temperature and pressure weighs 1.977 grams. It dissolves in water, one volume of water dissolving about one volume of the gas at the ordinary temperature. As is the case with all gases, when the pressure is increased the water dissolves more gas, and when the pressure is removed the gas again escapes. The so-called "soda-water" is simply water charged with carbon dioxide under pressure. The escape of the gas when the water is drawn is familiar to every one. The name soda-water has its origin in the fact that the carbon dioxide used in charging the water is frequently made from primary or acid sodium carbonate, $NaHCO_3$, which is also called soda or "bicarbonate of soda."

**Relations of Carbon Dioxide to Chemical Energy.**— Carbon has the power to combine with oxygen, and in so doing a definite quantity of heat is evolved. One gram carbon burns to form carbon dioxide generating 8000 cal. heat: $C + O_2 = CO_2 + 8000$ cal. A kilogram of carbon represents a certain quantity of chemical energy, which can be obtained from it first in the form of heat, and by transformation, in other forms of energy, as motion, electrical energy, etc. After the kilogram of carbon has been burned it no longer represents the energy it did in the form of carbon. A body of water elevated ten or fifteen

feet represents a certain quantity of energy that can be obtained by allowing the water to fall upon the paddles of a water-wheel connected with the machinery of a mill. After the water has fallen, however, it no longer has the power to do work, or it has none of the energy which it possessed by virtue of its position. In order that it may again do work it must again be lifted. So, too, in order that the carbon in carbon dioxide may again do work the compound must be decomposed.

**Respiration.**—It was stated above that carbon dioxide is given off from the lungs just as it is from a fire. It is a waste-product of the processes taking place in the animal body. Just as it cannot support combustion, so also it cannot support respiration. It is not poisonous any more than water is; but it cannot supply the oxygen needed for breathing purposes, and hence animals die when placed in it. They die by suffocation, very much as they do in drowning. Any considerable increase in the quantity of carbon dioxide in the air above that which is normally present is objectionable, for the reason that it decreases the proportion of oxygen in the air breathed. If, however, pure carbon dioxide is introduced into the air, it has been found that as much as 5 per cent may be present without serious results to those who breathe it. In a badly-ventilated room in which a number of people are collected, and lights are burning, it is well known that in a short time the air becomes foul, and bad effects, such as headache, drowsiness, etc., are produced on the occupants of the room. These effects appear to be due, not to the carbon dioxide, but largely to other waste-products given off from the lungs in the process of breathing (see p. 272). As carbon dioxide is given off from the lungs at the same time, the quantity of this gas present is roughly proportional to the quantity of the organic impurities. Hence, by determining the quantity of carbon dioxide it is possible to form an opinion as to whether the air of a room occupied by human beings is fit for use or not.

As carbon dioxide is formed in the earth wherever an acid solution comes in contact with a carbonate, the gas is

often given off from fissures in the earth. It is hence not infrequently found in old wells that have not been in use for some time, and deaths have been caused by descending into these wells for the purpose of repairing them. The gas is also frequently met with in mines, and is called *choke-damp* by the miners. The miners are aware that after an explosion caused by fire-damp there is danger of death from choke-damp. The cause of the presence of this gas after an explosion is clear. When fire-damp, or marsh-gas, explodes with air the carbon is oxidized to choke-damp, or carbon dioxide, and the hydrogen to water. Air in which a candle will not burn is not fit for breathing purposes.

**Carbon Dioxide and Life.**—The *rôle* played by carbon dioxide in nature is extremely important and interesting. The carbon contained in living things is obtained from carbon dioxide, and generally returns to this form when life ceases. All living things contain carbon as an essential constituent. Whence comes this carbon? Animals eat either the products of plant-life or other animals which derive their sustenance from the vegetable kingdom. The food of animals comes, then, either directly or indirectly from plants. But plants derive their sustenance largely from the carbon dioxide of the air. The plants have the power to decompose the gas with the aid of the direct light of the sun, and they then build up the complex compounds of carbon which form their tissues, using for this purpose the carbon of the carbon dioxide which they decompose. Many of these compounds are fit for food for animals; that is to say, they are of such composition that the forces at work in the animal body are capable of transforming them into animal tissues, or of oxidizing them, and thus keeping the temperature of the body up to the necessary point. That part of the food which undergoes oxidation in the body plays the same part as fuel in a stove. It is burned up with an evolution of heat, the carbon being converted into carbon dioxide, which is given off from the lungs. From fires and from living animals carbon dioxide is returned to the air, where

it again serves as food for plants. When the life-process stops in the animal or the plant, decomposition begins; and the final result of this, under ordinary circumstances, is the conversion of the carbon into the dioxide.

**Energy Stored up in Plants.**—It will thus be seen that under the influence of life and sunlight carbon dioxide is constantly being converted into compounds containing carbon which are stored up in the plants. These compounds are capable of burning, and thus giving heat; or some of them may be used as food by animals, when they assume other forms under the influence of the life-process of the animals. As long as life continues, plants and animals are storehouses of energy. When death occurs, the carbon compounds begin to pass back to the form of carbon dioxide, and the chemical energy is transformed partly into heat, and is thus, as we say, dissipated. The power to do work, which the carbon compounds of plants and animals possess, comes from the heat of the sun. It takes a certain quantity of this heat, operating under proper conditions, to decompose a certain quantity of carbon dioxide, and elaborate the compounds contained in the plants. When these compounds are burned they give out the heat which was absorbed in their formation during the growth of the plants. These compounds are said to possess chemical energy. This has its origin in heat, and is capable of reconversion into heat. The transformation of the energy of the sun's heat into chemical energy lies at the foundation of all life. As the heat of the sun acting upon the great bodies of water and on the air gives rise to the movements of water which are essential to the existence of the earth as it is, so the action of the sun's rays on carbon dioxide, under the influence of the delicate and inexplicable mechanism of the leaf of the plant, gives rise to those changes in the forms of combination of the element carbon which accompany and are of fundamental importance to the wonderful process of life.

**Carbonic Acid and Carbonates.**—When carbon dioxide is passed into water the solution has a slightly acid reaction. The solution acts upon bases and forms salts.

The formula of the sodium salt formed in this way is $Na_2CO_3$; that of the potassium salt, $K_2CO_3$; etc. These salts are plainly derived from an acid, $H_2CO_3$, and this is called carbonic acid. It is probable that this acid is contained in the solution of carbon dioxide in water. It is, however, so unstable that it breaks down into carbon dioxide and water:

$$H_2CO_3 = CO_2 + H_2O.$$

The formation of a salt by the action of carbon dioxide on a base takes place as shown in the following equations:

$$2KOH + CO_2 = K_2CO_3 + H_2O;$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

With the acid the action would take place as represented thus:

$$2KOH + H_2CO_3 = K_2CO_3 + 2H_2O;$$
$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O.$$

There is complete analogy between the action of carbon dioxide and that of sulphur dioxide on solutions of bases. With potassium hydroxide and calcium hydroxide, sulphur dioxide acts as represented in the following equations:

$$2KOH + SO_2 = K_2SO_3 + H_2O;$$
$$Ca(OH)_2 + SO_2 = CaSO_3 + H_2O.$$

The products formed are sulphites or salts of sulphurous acid.

Like sulphurous acid, carbonic acid is dibasic, and forms two series of salts, the *primary* and *secondary*, or the *acid* and *normal salts*. The primary or acid salts have the general formula $HMCO_3$, and the secondary or normal salts have the general formula $M_2CO_3$. Examples of the former are $HKCO_3$, $HNaCO_3$, $CaH_2(CO_3)_2$, etc.; and of the latter $K_2CO_3$, $Na_2CO_3$, $CaCO_3$, $BaCO_3$, etc.

The secondary or normal salts formed by carbonic acid with the most strongly marked metallic elements, viz., potassium and sodium, are not decomposed by heat, but all other carbonates are decomposed by heat more or

less easily, according to the strength of the base. Calcium carbonate when ignited loses carbon dioxide, and lime, or calcium oxide, remains behind:

$$CaCO_3 = CaO + CO_2.$$

**Carbon Monoxide,** CO.—When a substance containing carbon burns in an insufficient supply of air,—as, for example, when the draught in a furnace is not strong enough to remove the products of combustion and supply fresh air,—the oxidation of the carbon is not complete, and the product, instead of being carbon dioxide, is carbon monoxide, CO. This compound can also be made by extracting oxygen from carbon dioxide. It is only necessary to pass the dioxide over heated carbon, when reaction takes place as represented thus:

$$CO_2 + C = 2CO.$$

This method of formation is illustrated in coal-fires, and can be well observed in an open grate. The air has free access to the coal, and at the surface complete oxidation takes place. But that part of the carbon dioxide which is formed at the lower part of the grate is drawn up through the heated coal, and is partly reduced to carbon monoxide. When the monoxide escapes from the upper part of the grate it again combines with oxygen, or burns, giving rise to the characteristic blue flame noticed above a mass of burning anthracite coal.

The monoxide is also formed by passing steam over highly-heated carbon, when this reaction takes place:

$$C + H_2O = CO + H_2.$$

This is the reaction involved in the manufacture of "water-gas." The gas thus obtained is largely a mixture of hydrogen and carbon monoxide. The gas is "enriched" by passing it through a furnace in which it is mixed with highly-heated vapors of hydrocarbons from petroleum. The main reaction, the decomposition of water by heated carbon, is effected in large furnaces filled with anthracite coal. The coal is first heated to a high temperature by

setting fire to it, the products of combustion being allowed to escape. When it is hot enough, the air is shut off and steam passed rapidly in, when the decomposition of the water by the carbon takes place. Soon the mass becomes so much cooled that the reaction stops. The steam is then cut off and air turned on again, and so on.

The easiest way to make carbon monoxide is by heating oxalic acid, a compound of carbon, hydrogen, and oxygen, of the formula $C_2H_2O_4$, with five to six times its weight of concentrated sulphuric acid. The change is represented thus:

$$C_2H_2O_4 = CO_2 + CO + H_2O.$$

Both the dioxide and monoxide of carbon are formed. Both are gases. In order to separate them the mixture is passed through a solution of sodium hydroxide. This takes up the carbon dioxide, forming sodium carbonate, and allows the monoxide to pass.

Carbon monoxide is a colorless, tasteless, inodorous gas, insoluble in water. It solidifies at $-207°$ and boils at $-190°$. It burns with a pale-blue flame, forming carbon dioxide. It is exceedingly poisonous when inhaled because its affinity for blood is 130 times as great as that of oxygen, and it decomposes the blood. Air becomes poisonous when it contains 0.05 per cent carbon monoxide. Hence it is very important that it should not be allowed to escape into rooms occupied by human beings. Deaths are sometimes caused by the gases from coal-stoves. The most dangerous of these is carbon monoxide. A pan of smouldering charcoal gives off this gas, and the fact that it is poisonous is well known. It has been used to a considerable extent for the purpose of suicide. The poisonous character of carbon monoxide has led to a great deal of discussion and to some legislation on the subject of "water-gas." The question has been repeatedly raised whether governments should allow the manufacture of the gas. There is no doubt of the fact that it is a dangerous substance, and that it should not be allowed to escape into the air is obvious. Wherever it is used special

precautions should be taken to guard against leaking. There is no doubt that it is more poisonous than coal-gas.

**Thermochemistry of the Combustion of Carbon.**—One gram carbon burned to carbon dioxide yields 8000 cal. heat. One gram carbon burned to carbon monoxide yields 2400 cal. In terms of gram-molecular-weights these facts are expressed as below:

$$C + 2O = CO_2 + 12 \times 8000 \text{ cal.} = 96000 \text{ cal.}$$
$$C + O = CO + 12 \times 2400 \text{ cal.} = 28800 \text{ cal.}$$
$$67200 \text{ cal.}$$
$$CO + O = CO_2 + 67200 \text{ cal.}$$

It will thus be seen that when carbon is burned to carbon monoxide, the product still contains more than two-thirds of the energy of the carbon. Hence the value of carbon monoxide in "fuel gases" (which see) and in metallurgical processes as a reducing agent.

In the reduction of iron from its ores, the carbon monoxide formed in the blast-furnace plays an important part. At ordinary temperatures the gas does not combine readily with oxygen. When passed over some substances rich in oxygen, as, for example, chromic anhydride, $CrO_3$, and potassium permanganate, $KMnO_4$, in acid solution, it takes up oxygen even at the ordinary temperature. It unites with chlorine in the direct sunlight, and forms the compound known as *carbonyl chloride* or *phosgene*, $COCl_2$.

**Fuel Gases.**—The use of gaseous fuel is constantly on the increase in metallurgical and technical-chemical processes, because higher temperatures can be obtained by the rapid combustion of gas than by the slower combustion of coal or coke, and because both the temperature and the nature of the flame can be readily regulated.

While illuminating gas obtained by the distillation of coal, has a high heat-value (calorimetric value), only a small portion of the coal distils, the greater part remaining as coke. It is an important problem to convert coal or coke completely into gas in such a way that the gas

shall retain as much as possible of the heat-energy of the coal or coke. This is accomplished by making water-gas, air-gas, Dowson-gas, generator-gas, etc.

As an example take the formation of water-gas:

$$C + H_2O = CO + H_2$$

Gram mol wts. 12 18 28 2

This process is endothermic, i. e. outside heat is required to decompose the water in excess of that formed by the partial combustion of the carbon. As the heat absorbed by the decomposition of 18 grams water is exactly the same as the heat of combustion of 2 grams hydrogen the only final loss of heat is that expended in burning 12 grams carbon to 28 grams carbon monoxide: $12 \times 2400$ cal. = 28000 cal. to be deducted from the 96000 cal. total heat-energy of 12 grams carbon. But this heat is only lost when the gas is cooled to ordinary temperatures for transportation through pipes. If the hot gas is burned as fast as it is made, the loss of heat is not great; practically about 92 per cent of the fuel value of the coal is obtained from the gas.

"Air-gas" is made by conducting heated air over hot coke, and is a mixture of carbon monoxide and nitrogen. This process is exothermic, i. e. heat is given off.

**Siemens Regenerative Apparatus.**—The name refers to the regeneration of heat. The process consists in principle in utilizing waste heat to heat up cold air or gas before combustion, and in practice is applied in various ways. It is of great technical importance and is utilized in making gas, steel, glass, bricks, lime and many other products.

If in such an apparatus a *mixture* of air and steam in suitable proportions is passed over heated coal, the heat of the partial combustion of the coal in the air of the mixture is sufficient to decompose the steam without using other heat than that formed in the reaction. "Dowson-gas" and "generator-gas" are products formed in this way and contain carbon monoxide, hydrogen, and some

hydrocarbons as valuable constituents, and nitrogen and carbon dioxide as worthless constituents.

"Oil gas" is made by dripping liquid by-products of the petroleum and paraffin industries into hot iron retorts. It has a high fuel value but is generally used as illuminant.

**Methods for obtaining High Temperatures.**—The *calorimetric* value or amount of heat obtainable from a given substance must be distinguished from the *pyrometric* value or obtainable temperature. For example, a temperature sufficient to melt platinum (1700°) cannot be reached by burning coal or fuel gas, but platinum is readily melted by the heat of the oxy-hydrogen blowpipe, about 2000°. Temperatures of 2500°–3000° degrees can be obtained by the Goldschmidt process (which see), and much higher temperatures by the electric furnace which utilizes the heat of the electric arc.

## EXPERIMENTS.

### Carbon Dioxide is formed when a Carbonate is treated with an Acid.

Experiment 177.—In test-tubes add successively dilute hydrochloric, sulphuric, nitric, and acetic acids to a little sodium carbonate. In each case pass the gas given off through lime-water, and insert a burning stick in the upper part of each tube. Perform the same experiments with small pieces of marble.

### Preparation and Properties of Carbon Dioxide.

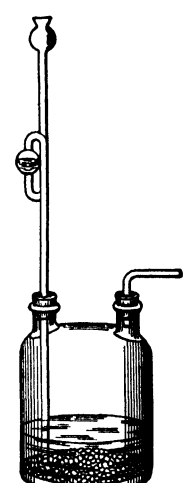


Fig. 68.

Experiment 183.—Arrange an apparatus as shown in Fig. 68. In the flask put some pieces of marble or limestone, and pour ordinary hydrochloric acid on it. The gas should be collected by displacement of air, the vessel being placed with the mouth upward. Collect several cylinders or bottles full of the gas. Into one introduce successively a lighted candle, a burning stick, a bit of burning phosphorus. With another proceed as if pouring water from it. Pour the invisible gas upon the flame of a burning candle. Pour

some of the gas from one vessel to another, and show that it has been transferred. Balance a beaker on a good-sized pair of scales, and pour carbon dioxide into it. If the balance is at all sensitive, the pan on which the beaker is placed will sink.

### Carbon Dioxide is given off from the Lungs.

Experiment 184.—Force the gases from the lungs through some lime-water by means of an apparatus arranged as shown in Fig. 69.



Fig. 69.

### Formation of Carbonates.

Experiment 185.—Pass carbon dioxide into a solution of potassium hydroxide to saturation. Determine whether a carbonate is in solution or not.

Experiment 186.—Pass carbon dioxide into 50 to 100 cc. clear lime-water. Filter off the white insoluble substance. Try the action of a little acid on it. What evidence have you that it is a carbonate?

Experiment 187.—Pass carbon dioxide first through a little water to wash it, and then into 50 to 100 cc. clear dilute lime-water. Continue to pass the gas for some time after the precipitate is formed. The precipitate dissolves. Heat the solution. What happens? Explain these reactions.

### Preparation and Properties of Carbon Monoxide.

Experiment 188.—Put 10 grams crystallized oxalic acid and 50 to 60 grams concentrated sulphuric acid in an appropriate flask. Connect with two Woulff's flasks containing a solution of caustic soda. Heat the contents of the flask gently. Collect some of the gas over water. Set fire to some, and notice the characteristic blue flame.

### Carbon Monoxide is a good Reducing Agent.

Experiment 189.—Pass carbon monoxide over some heated copper oxide contained in a hard glass tube. Is the oxide reduced? How do you know? Is carbon dioxide formed? What evidence have you? Was the carbon monoxide used free of carbon dioxide? If not, what evidence have you that carbon dioxide is formed in this experiment?

Experiment 190.—Pass carbon dioxide over heated charcoal in a hard-glass tube. What is formed?

## CHAPTER XX.

### ILLUMINATION.—FLAME.—BLOWPIPE.

### COMPOUNDS OF CARBON WITH NITROGEN AND SULPHUR.

**Introduction.**—As the substances used for illumination contain carbon, and the chemical processes involved consist largely in the oxidation of the carbon of these compounds, this is an appropriate place to treat briefly of the subject of illumination from a chemical point of view, as well as that of flame, and the blowpipe, which gives a useful form of flame much used in the laboratory.

In all kinds of illumination, except the electric light, we are dependent upon flames for the light. Whether we use illuminating gas, a lamp, or a candle, the light comes from a flame. In the first case, the gas is burned directly; in the case of the lamp, the oil is first drawn up the wick, then converted into a gas, and this burns; while, finally, in the case of the candle, the solid material of the candle is first melted, then drawn up the wick, converted into gas, and the gas burns, forming the flame. In each case the flame is a burning gas.

**Illuminating Gas, Coal-gas.** — Illuminating gas is sometimes made from coal by heating it in closed retorts. As has already been explained, coal, especially the softer kinds, contains compounds of carbon and hydrogen, together with some nitrogen and other elements. When it is subjected to destructive distillation, as in the manufacture of coal-gas, the hydrogen passes off partly in combination with carbon, as hydrocarbons, and partly in the free state. The nitrogen passes off as ammonia, and a large percentage of the carbon remains behind in the retort in the uncombined state as *coke*. The gases given off are purified, and form illuminating gas. One ton of coal yields on an average 10,000 cubic feet of gas. The value of a gas depends upon the amount of light given by the burn-

ing of a definite quantity. This is measured by comparing it with the light given by a candle burning at a certain rate. The standard candle is one made of spermaceti, which burns at the rate of 120 grains per hour; that is to say, a candle which, burning under ordinary conditions, loses 120 grains in one hour. The standard burner used for the gas is one through which five cubic feet of gas pass per hour. Now, to determine the illuminating power of a gas, it is passed through the standard burner at the rate mentioned, and the light given by it is compared with the light given by the standard candle. This comparison is easily made by means of an instrument called the *photometer*. The illuminating power of the gas is then stated in terms of the standard candle. The statement that the illuminating power of a gas is fourteen candles, signifies that, when burning at the rate of five cubic feet per hour, its flame gives fourteen times as much light as that of the standard candle.

**Flames.**—A flame is the phenomenon produced at the surface where two gases meet and combine with evolution of light and heat. Ordinarily a flame is a gas that is combining with oxygen. The hydrogen flame is simply the phenomenon accompanying the act of combination of the two gases hydrogen and oxygen. Owing to the fact that we are surrounded by oxygen, we speak of hydrogen as the burning gas. How would it be if we were surrounded by an atmosphere of hydrogen? Plainly, oxygen would then be spoken of as a burning gas. If a jet of oxygen is allowed to escape into a vessel containing hydrogen, a flame will appear where the oxygen escapes from the jet, if a light is applied. This is an experiment which requires special precautions, and, as the principle can be illustrated as well by means of illuminating gas, this may be used instead. Just as illuminating gas burns in an atmosphere of oxygen, so oxygen "burns" in an atmosphere of illuminating gas.

**Kindling Temperature of Gases.**—In studying the action of oxygen upon other substances, we learned that it is necessary that each of these substances should be raised to

a certain temperature before it will readily combine with oxygen. This statement is as true of gases as of other substances. When a current of hydrogen is allowed to escape into the air, or into oxygen, no action takes place unless it is heated up to its burning temperature, when it takes fire and continues to burn, as the burning of one part of the gas heats the part that follows it, and hence it is heated to the burning temperature as fast as it escapes into the air. If the gas is cooled even very slightly below this temperature, it is extinguished. This can easily be shown by bringing down upon the flame of a Bunsen burner a piece of wire gauze. There will be no flame above the gauze, but gas will pass through unburned, and this will burn if it is lighted above the gauze. In this case, by simply passing through the thin wire gauze, the gases are cooled below their burning temperatures, and the flame does not pass through. So, also, if the gas is turned on and not lighted, and the gauze held an inch or two above the outlet, the gas will burn above the gauze if lighted above, and will not pass downward through the gauze, unless this becomes very hot.

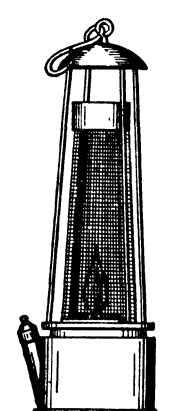


FIG. 70.

**Miner's Safety-lamp.**—The principle illustrated in the experiments referred to in the last paragraph is utilized in the miner's *safety-lamp*. One of the dangers which the coal-miner has to encounter is the occurrence in the mines of fire-damp, or methane, $CH_4$, which with air forms an explosive mixture. The explosion can only be brought about by contact of flame with the mixture. In order to avoid the contact, the flame of the safety-lamp is surrounded by wire gauze, as shown in Fig. 70. When a lamp of this kind is brought into an explosive mixture of marsh-gas and air, the mixture passes through the wire gauze and comes in contact with the flame, and a small explosion or a series of small explosions inside the gauze

occurs, but the flame of the burning gas inside the wire gauze cannot pass through and raise the temperature of the gas outside to the burning temperature. Hence no serious explosion can take place. The flickering of the flame of the lamp, and the occurrence of small explosions inside, give the miner the necessary warning. While the safety-lamp does undoubtedly afford much protection, still explosions occur. Some of these have been shown to be caused by the presence of coal-dust in the mines, and by the commotion of the air produced in blasting. By the aid of the coal-dust, and by sudden and violent movements of the air, it is possible for a flame surrounded by wire gauze to explode a mixture of marsh-gas and air on the other side of the gauze.

**Structure of Flames.**—The hydrogen flame consists of a thin envelope of burning hydrogen enclosing unburned gas, and surrounded by water-vapor, which is the product of the combustion. The structure of other flames depends upon the complexity of the gases burned, and the conditions under which the burning takes place. In general, a flame consists of an outer envelope of gas combining with oxygen, and hence hot, and an inner part containing unburned gas, which is comparatively cool. A part of the unburned gas is, however, quite hot, and it would combine with oxygen were it not for the fact that it is surrounded by an envelope that prevents access of air. The *outer hot part* of the flame is called the *oxidizing flame*, because it presents conditions favorable to the oxidation of substances introduced into it. The *inner hot part* is called the *reducing flame*, because it consists of highly-heated substances that have the power to combine with oxygen; and hence many compounds containing oxygen lose it, or are reduced, when introduced into this part of the flame. The hottest part of the flame is about half-way between the bottom and the top. Here oxidation is taking place most energetically. The hottest part of the unburned gases is at the tip of the dark central part of the flame. In the flame of a Bunsen burner the two parts can be easily distinguished. The dark central part

of the flame extends for some distance above the outlet of the burner. If the holes at the base of the burner are partly closed, the tip of the central part of the flame becomes luminous. This luminous tip is most efficient for the purpose of reduction. The principal parts of the flame are those marked in Fig. 71. The part marked *b* is the central cone of unburned gases; that marked *c* is the luminous tip, the best part of the flame for reduction. *A* is the envelope of burning gas. The hottest part of the flame is at *a*; that which is most efficient in causing oxidation is at *d*. This is further surrounded by a non-luminous envelope consisting of the products of combustion carbon dioxide and water-vapor. Certain metals placed in the upper end of the flame take up oxygen, because they are highly heated in the presence of oxygen. Certain oxides lose their oxygen when placed in the tip of the central cone, because the gases are here heated to the temperature at which they have the power to combine with oxygen.

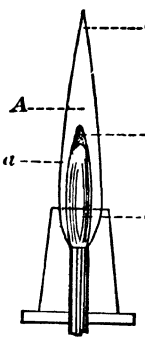


FIG. 71.

**Blowpipe.**—The oxidizing and reducing flames are much used in the laboratory. For the purpose of increasing their efficiency a *blowpipe* is used. This is a tube with a convenient mouth-piece and a nozzle with a small opening through which air is blown into a flame. The blowpipe may be used with the flame of a candle, an alcohol-lamp, or a gas-lamp. It is commonly used with a gas-lamp. By regulating the current of air and slightly changing the position of the tip of the blowpipe a good oxidizing flame or a good reducing flame can be produced. Some oxides are very easily reduced when heated in the reducing blowpipe flame. Others are not. It is often possible to judge of the composition of a substance by heating it in the blowpipe flame, and noticing its conduct. Some metals are easily oxidized in the oxidizing flame. Some form characteristic films, or thin layers of oxides, on the substance upon which they are heated, which is

usually charcoal; and, in some cases, it is possible to detect the presence of certain substances by the color of the film of oxide. The blowpipe is therefore of value as affording a method for the detection of the presence of certain elements in mixtures or compounds of unknown composition. The chemical principles involved in its use will be clear from what has already been said.

**Causes of the Luminosity of Flames.**—It is evident that flames differ greatly in their power to give light. The hydrogen flame, for example, though extremely hot, gives practically no light. This is also the case with the flame of the Bunsen burner; while, on the other hand, the flame of coal-gas, burning under ordinary circumstances, and that of a candle, etc., give light. To what is the difference due? This subject has been studied very thoroughly, and it has been found that there are several causes that operate to make a flame luminous and *vice versa*. In the first place, if a solid substance which does not burn is introduced into a non-luminous flame, a part of the heat appears as light. This is seen when a spiral of platinum wire is introduced into a hydrogen flame. It is also seen when a piece of lime is introduced into the hot, non-luminous flame of the oxy-hydrogen blowpipe. A similar cause operates in ordinary gas-flames to make them luminous. Particles of unburned carbon are always present, as can be shown by putting a piece of porcelain or any solid substance into the flame, when there will be deposited on it a layer of soot, consisting mainly of finely-divided carbon. The particles of unburned carbon are formed by the dissociation of some of the constituents of the burning gas into carbon and hydrogen, or carbon and hydrocarbon, at the tip of the inner cone. Constituents which dissociate in this way are present in all gases that give luminous flames. In the flame such particles are heated to incandescence, or to the temperature at which they give light. Again, it has been found that a candle gives more light at the level of the sea than it does when at the top of a high mountain, as Mount Blanc, on which the experiment

has actually been performed. This is partly due to a difference in the density of the gases. Naturally, the denser the gas the more active the combustion, the greater the heat, and the brighter the light. This last statement ceases to be true when the oxidation becomes sufficient to burn up all the solid particles in the flame. If gases, which in burning give light, are cooled down before they are burned, the luminosity is diminished, and, conversely, non-luminous flames may be rendered luminous by heating the gases before burning them. Gases that otherwise give luminous flames give non-luminous flames when diluted to a sufficient extent with neutral gases, such as nitrogen and carbon dioxide, which neither burn nor support combustion. Lewes has shown that acetylene (which see) is always formed in flames, and his work makes it appear probable that the luminosity of most, if not of all, flames is due to the formation and decomposition of this gas.

**Bunsen Burner.**—All the statements made in regard to the causes of the luminosity of flames are based upon carefully performed experiments. These experiments, however, cannot, for the most part, be readily repeated by the student in the laboratory in a satisfactory way. One constant reminder of the possibility of rendering a luminous flame non-luminous, and *vice versa*, is furnished by the burner universally used in chemical laboratories, and called, after the inventor, the *Bunsen burner*. The construction of this burner is easily understood. It consists of a base and an upper tube. The base is connected by means of a rubber tube with the gas-supply. The gas escapes from a small opening in the base, and passes upward through the tube. At the lower part of the tube there are two holes, which may be opened or closed by turning a ring with two corresponding holes in it. When the gas is turned on, it is lighted at the top of the tube. Air is at the same time drawn through the holes at the base. The result is that the flame is practically non-luminous. If the ring at the base is turned so that the air-holes are closed, the flame becomes luminous. The advantage of

the non-luminous flame for laboratory use consists in the fact that it does not deposit soot, and, at the same time, it is hot.

The non-luminosity of the flame of the Bunsen burner appears to be due to several causes: (1) Dilution of the gases by means of the nitrogen of the air; (2) Cooling of the gases by the entrance of the air; (3) Burning of the solid particles by the aid of the oxygen of the air admitted to the interior of the flame.

**Illuminants.**—These may be referred to three types: (A) Those in which the light is obtained from luminous flames; (B) Those in which the light is produced by heating solids to incandescence without combustion of the solid; (C) Those in which a solid becomes incandescent but burns without flame.

To class A belong candles, lamps burning oil or petroleum, ordinary flames of coal-gas, water-gas, acetylene, oil-gas (or Pintsch-gas), etc.

Class B includes the incandescent electric light—in which a carbon film or strip of metal is heated to incandescence in a vacuum by its resistance to the current—and the Welsbach light, in which a film of metallic oxides (see Thorium) is heated to incandescence by a non-luminous Bunsen flame from gas, alcohol, or petroleum.

Class C includes the different types of electric arc lamps, in which the glowing arc is formed between carbon terminals which glow and form carbon dioxide without flame.

The modern prodigal use of artificial light is noteworthy. More candles are manufactured now than at any former time. Indeed with the exception of animal and vegetable oils, every form of illuminant is in increasing demand in spite of the rapid increase in the number of illuminants.

### Compounds of Carbon with Nitrogen and with Sulphur.

**Cyanogen,** $C_2N_2$.—Carbon does not combine with nitrogen under ordinary circumstances. If, however, these

elements are brought together at very high temperatures in the presence of metals, they combine to form compounds known as *cyanides*. Thus, when nitrogen is passed over a highly-heated mixture of carbon and potassium carbonate, potassium cyanide, KCN, is formed. Carbon containing nitrogen, as animal charcoal, when ignited with potassium carbonate, reduces the carbonate, forming potassium, in presence of which carbon and nitrogen combine, forming potassium cyanide. When refuse animal substances, such as blood, horns, claws, hair, etc., are heated together with potassium carbonate and iron, a substance known as *potassium ferrocyanide*, or *yellow prussiate of potash*, $K_4Fe(CN)_6 + 3H_2O$, is formed. When this is heated to a sufficiently high temperature it is decomposed, yielding potassium cyanide:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

It is easy to make the mercury salt, $Hg(CN)_2$, from the potassium salt. By heating mercuric cyanide it breaks up, yielding metallic mercury and cyanogen gas:

$$Hg(CN)_2 = Hg + C_2N_2,$$

just as mercuric oxide yields mercury and oxygen when heated:

$$HgO = Hg + O.$$

Cyanogen (from κύανος, *blue*) owes its name to the fact that several of its compounds have a blue color. It is a colorless gas, which is easily soluble in water and alcohol, and is *extremely poisonous*. It burns with a purple-colored flame.

**Hydrocyanic Acid, Prussic Acid,** HCN.—This acid, commonly called *prussic acid*, occurs in nature in amygdalin, in combination with other substances, in bitter almonds, the leaves of the cherry, laurel, etc. It is prepared by decomposing metallic cyanides with hydrochloric acid. It is volatile and passes over. The action is represented thus:

$$KCN + HCl = KCl + HCN.$$

Hydrocyanic acid is a volatile liquid, boiling at 26.1°, and solidifying at − 14°. It has a characteristic odor suggestive of bitter almonds. *It is extremely poisonous.* It dissolves in water in all proportions. Such a solution is known as prussic acid. Pure hydrocyanic acid is very unstable. By standing, a brown substance is deposited from its solution.

**Cyanic Acid,** HCNO.—By gentle oxidation of a cyanide it is converted into a cyanate. Thus, by melting together potassium cyanide and lead oxide, potassium cyanate is formed:

$$KCN + PbO = KCNO + Pb.$$

Cyanic acid is a volatile, acrid, unstable liquid. It breaks down at once into carbon dioxide and ammonia in presence of water:

$$CONH + H_2O = NH_3 + CO_2.$$

The potassium salt is easily soluble in water, but is decomposed by it, yielding ammonia and acid potassium carbonate:

$$CONK + 2H_2O = KHCO_3 + NH_3.$$

These decompositions of cyanic acid and the cyanates further exemplify the tendency of cyanogen compounds to undergo decomposition in presence of water.

**Carbon Bisulphide,** $CS_2$.—Just as carbon combines directly with oxygen to form the dioxide, so it combines directly with sulphur to form the bisulphide; but there is a great difference in the ease with which carbon combines with the two elements. In order to effect combination with sulphur a very high temperature is necessary. The compound is prepared on the large scale by heating charcoal to a high temperature in an upright cast-iron cylinder, and adding sulphur in such a way that it enters the bottom of the cylinder. The product is passed through a series of tubes arranged so as to secure condensation.

Carbon bisulphide is a clear liquid of high refractive power. It boils at 46.2°. When pure it has a pleasant odor, but if kept for a time, especially if water is present

in the vessel, it undergoes slight decomposition, and products of extremely disagreeable odor are formed. It can generally be freed from these by shaking it with a little mercury and then redistilling. It burns readily, forming carbon dioxide and sulphur dioxide:

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

Carbon bisulphide is only slightly soluble in water, and is decomposed by it very slowly. The bisulphide is an excellent solvent for many substances which are not soluble in water, as, for example, fats, resins, iodine, and one of the modifications of sulphur and of phosphorus. The solution of iodine in it has a beautiful violet color; and when a water solution containing a little free iodine is shaken with carbon bisulphide the latter acquires a violet color and separates below the water.

Carbon bisulphide finds extensive application as a solvent, and it is also used for the purpose of destroying *phylloxera*, the insect which is so destructive to grape-vines, particularly in the wine districts of France.

**Sulphocyanic Acid,** HCNS.—Just as the cyanides take up oxygen and are converted into cyanates so also they take up sulphur and are converted into sulphocyanates:

$$KCN + S = KCNS.$$

**Constitution of Cyanogen and its Simpler Compounds.**—The compounds of cyanogen show, in general, a remarkable similarity to the compounds of the chlorine group. The hydrogen compound is a monobasic acid and forms a series of salts, the *cyanides*, which in general are analogous to the chlorides. Comparing the cyanides with the chlorides it is clear that in the former the group CN, or the cyanogen group, plays the same part that the atom chlorine plays in the chlorides:

| | |
|---|---|
| H(CN) | HCl |
| K(CN) | KCl |
| $Hg(CN)_2$ | $HgCl_2$. |

So, also, cyanic acid and hypochlorous acid are analogous:

HO(CN) HOCl.

This relation suggests that which is observed between the ammonium compounds and those of potassium and sodium. The cyanogen

group is evidently univalent, as it combines with one atom of hydrogen, one of potassium, etc.

## EXPERIMENTS.

### Coal-gas.

Experiment 191.—Heat some bituminous coal in a retort and collect over water the gases given off. Are these gases combustible?

### Oxygen "Burns" in an Atmosphere of a Combustible Gas.

Experiment 192.—Break off the neck of a good-sized retort; fit a perforated cork to the small end; pass a piece of glass tube through the cork, and connect by means of rubber hose with an outlet for coal-gas. Fix the apparatus in position, as shown in Fig. 72. Turn

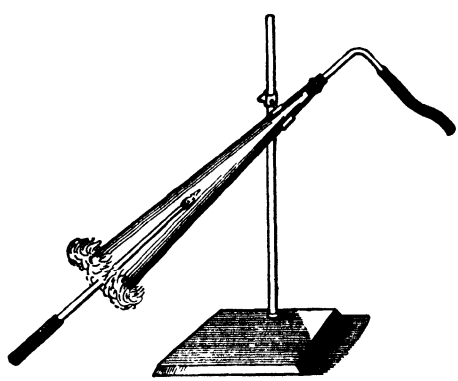


Fig. 72.

the gas on, and when the air is driven out of the retort-neck, light the gas. The neck is now filled with illuminating gas, and the gas is burning at the mouth of the vessel. If now a platinum jet from which oxygen is issuing is passed up into the gas the oxygen will take fire, and a flame will appear where the oxygen escapes from the jet. The oxygen "burns" in the atmosphere of coal-gas.

### Kindling Temperature of Gases.

Experiment 193.—Light a Bunsen burner. Bring down upon the flame a piece of brass or iron wire-gauze. There is no flame above the gauze. That the gas passes through unburned can be shown by

applying a light just above the outlet of the burner and above the gauze. The gas will take fire and burn. By simply passing through the thin wire-gauze, then, the gas is cooled down below its burning temperature, and does not burn unless it is heated up again. Turn on a Bunsen burner. Do not light the gas. Hold a piece of wire gauze about one and a half to two inches above the outlet. Apply a lighted match above the gauze, when the gas will burn above the gauze, but not below it. Here again the heat necessary to raise the temperature of the gas to the burning temperature cannot be communicated through the gauze. If in either of the above-described experiments the gauze is held in position for a time, it will probably become so highly heated that the gas on the side where there is no flame will be raised to the burning temperature. The instant that point is reached the flame becomes continuous.

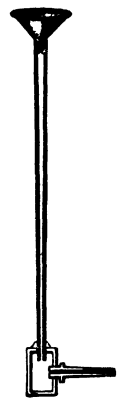


FIG. 73.

## THE BLOWPIPE AND ITS USES.

The blowpipe used in chemical laboratories is constructed as shown in Fig. 73.

When used with the Bunsen burner it is best to slip into the burner a brass tube ending above in a narrow slit-like opening, as shown in Fig. 74. The tube referred to, marked *a* in the figure, reaches to the bottom of the burner, and thus cuts off the supply of air which usually enters the holes at the base. The gas is now lighted, and the current so regulated that there is a small flame about 1½ to 2 inches long. The tip of the blowpipe is placed on the slit of the burner in the flame, as shown in Fig. 75. By blowing regularly and not violently through the pipe the flame is forced down in the same direction as the end-piece of the blowpipe, and the slant of the

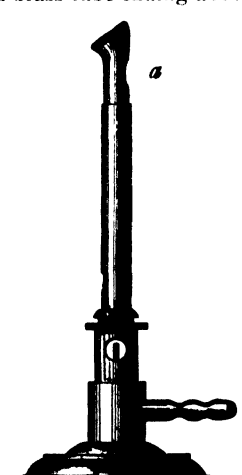



FIG. 74.

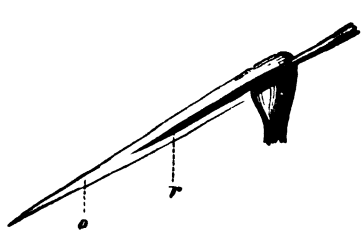



FIG. 75.

burner-slit. Under proper conditions the flame separates sharply into a central blue part and an outer part of another color. The direction and lines of division of the flame are indicated in Fig. 75. The outer part of the flame marked *o* is the *oxidizing flame;* the part marked *r* is the *reducing flame.*

EXPERIMENT 194.—Select a piece of charcoal about 4 inches long by 1 inch wide and 1 inch thick, with one surface plane.* Near the end of the plane surface make a cavity by pressing the edge of a small thin coin against it, and turning it completely round a few times. Mix together equal small quantities of dry sodium carbonate and lead oxide. Put a little of the mixture in the cavity in the charcoal, and heat it in the reducing flame produced by the blowpipe. In a short time globules of metallic lead will be seen in the molten mass. After cooling, scrape the solidified substance out of the cavity in the charcoal. Put it in a small mortar, treat it with a little water, and, after breaking it up and, allowing as much as possible to dissolve, pick out the metallic beads. Is it malleable or brittle? Is metallic lead malleable or brittle? Is it dissolved by hydrochloric acid? Is lead soluble in hydrochloric acid? Is it soluble in nitric acid? Is lead soluble in nitric acid? The action of the acids can be tried by putting a bead on a small dry watch-glass and adding a few drops of the acid. Does the substance act like lead? What has become of the oxygen with which the lead was combined in the oxide? Is there any special advantage in having a support of charcoal for this experiment?

EXPERIMENT 195.—Heat a small piece of metallic lead on charcoal in the oxidizing blowpipe flame Notice the formation of the oxide, which forms a coating or film on the charcoal in the neighborhood of the metal. Is there any analogy between this process and the burning of hydrogen? In what does the analogy consist? What differences are there between the two processes?

EXPERIMENT 196.—Repeat the experiments with arsenic, antimony, and bismuth. Notice the colors of the films formed on the charcoal.

EXPERIMENT 197.—Melt into a bit of glass tubing a piece of platinum wire 8 to 10 mm. (3 to 4 inches) long, and bend the end so as to form a small loop, as shown in Fig. 76. Heat the loop in the



FIG. 76.

flame of a Bunsen burner, and then dip it into some sodium-ammonium phosphate (microcosmic salt). Heat in the oxidizing flame of the blowpipe until a clear glass bead is formed in the loop. What

* Pieces of charcoal prepared for blowpipe work can be bought from dealers in chemical apparatus at small cost.

changes have taken place? and what is the clear glass? Bring a minute particle of a manganese compound in contact with the bead, and heat again. What change takes place? Try the same experiment, using successively a cobalt compound, a copper compound, and an iron compound. Now, instead of using microcosmic salt, use borax. Explain the changes in all the above-described experiments.

## CYANOGEN.

EXPERIMENT 198.—Make potassium cyanide by heating potassium ferrocyanide in an iron crucible

EXPERIMENT 199.—Make cyanogen by heating mercuric cyanide. *Cyanogen is poisonous.* Burn some of the gas.

EXPERIMENT 200.—Make potassium cyanate from some of the cyanide obtained in Experiment 198. This is done by melting it in an iron crucible, and, while the mass is liquid, adding about four times its weight of red lead, stirring during the operation. After this the crucible should again be put in the furnace for a little while, the metallic lead allowed to settle, and the contents poured out on a smooth stone. Break up the mass, and extract the cyanate with alcohol.

## CHAPTER XXI.

### ELEMENTS OF FAMILY IV, GROUP A: SILICON.—TITANIUM.—ZIRCONIUM.—CERIUM.—THORIUM.

**General.**—While in some respects the elements of this group resemble carbon and bear to it relations similar to those which the members of the chlorine group bear to fluorine, the members of the sulphur group to oxygen, and the members of the phosphorus group to nitrogen, yet between them and carbon there are some remarkable differences. All the members of the group except titanium combine with hydrogen. The compounds formed have the formulas $SiH_4$, $ZrH_2$, $CeH_2$, and $ThH_2$.

All the elements of the group form oxygen compounds analogous to carbon dioxide. They are:

$$SiO_2 \qquad TiO_2 \qquad ZrO_2 \qquad CeO_2 \qquad ThO_2.$$

The first three are acidic, and form salts which in composition are analogous to the carbonates. These are the silicates, titanates, and zirconates of the general formulas

$$M_2SiO_3, \qquad M_2TiO_3, \qquad M_2ZrO_3.$$

Cerium and thorium oxides are basic. These facts suggest the relations between the members of the phosphorus group. The oxides of the last two members, antimony and bismuth, are basic, although the oxide of antimony is also acidic in its conduct towards the stronger bases.

The compounds of silicon are very abundant in nature; those of the other members of the group are rare.

### Silicon, Si (At. Wt. 28.4).

**Occurrence.**—It has already been seen what an exceedingly important part carbon plays in animate nature. It is interesting to note that silicon, which in some respects

from a chemical point of view resembles carbon, is one of the most important constituents of the mineral or inorganic parts of the earth. It occurs chiefly in the form of the dioxide, $SiO_2$, commonly called silica, or silicon dioxide; and in combination with oxygen and several of the common metallic elements, particularly with sodium, potassium, aluminium, and calcium, in the form of *silicates*. Next to oxygen, silicon is the most abundant element in the earth. More than one-fourth of the crust of the earth is silicon. There are extensive mountain-ranges consisting almost entirely of the dioxide, $SiO_2$, in the form known as *quartz* or *quartzite*. Other ranges are made up of silicates, which are compounds formed by the combination of silicon dioxide and bases. The clay of the valleys and river-beds also contains silicon in large quantity, while the sand found so abundantly on the deserts and at the seashore is largely silicon dioxide.

**Preparation.**—Silicon does not occur in nature in the free state. The oxide, $SiO_2$, which is most abundant in the form of sand, is decomposed by heating it with potassium or magnesium, and silicon is thus set free. When magnesium is used the action is violent, and in addition to the silicon a compound of silicon and magnesium is formed. Silicon has also been made by heating the oxide with carbon in the electric furnace, and by decomposing the chloride with potassium:

$$SiCl_4 + 4K = Si + 4KCl.$$

The best way to make it is by heating together potassium fluosilicate, $K_2SiF_6$, sodium, and zinc:

$$K_2SiF_6 + 4Na = 4NaF + 2KF + Si.$$

The zinc melts and the silicon which separates dissolves in the molten zinc. On cooling, it is deposited from the solution in beautiful needle-shaped crystals, around which the zinc solidifies at a lower temperature. By treating the mass with hydrochloric acid the zinc is dissolved and the crystals of silicon are left behind. When obtained by reduction of the oxide or the chloride by means of

potassium, it is a brown amorphous powder. If made by decomposition of potassium fluosilicate by aluminium, it is deposited from the molten aluminium in crystals somewhat resembling graphite. Just as there are three forms of carbon, the amorphous, graphite, and diamond, so there are three corresponding forms of silicon, the amorphous brown powder, the graphitoidal, and the needles. The amorphous variety is converted into crystallized silicon by continued heating at a high temperature.

Amorphous silicon acts upon hydrofluoric acid, forming silicon tetrafluoride, $SiF_4$, and setting hydrogen free:

$$Si + 4HF = SiF_4 + 2H_2.$$

In this reaction it exhibits one of the properties of a base-forming element. Towards other acids, however, it is indifferent. It is not acted upon by sulphuric acid, nor by nitric acid, nor *aqua regia*. It dissolves, however, in potassium hydroxide, forming potassium silicate, in this case acting like an acid-forming element:

$$Si + 2KOH + H_2O = K_2SiO_3 + 2H_2.$$

This form of silicon also burns in the air, forming the dioxide.

Crystallized silicon, on the other hand, does not burn in oxygen at the highest temperatures. It reduces carbon dioxide, however, and decomposes carbonates at a high temperature. It is also oxidized by a melting mixture of potassium nitrate and the hydroxide or carbonate. It combines with nitrogen at a high temperature.

Both the graphitoidal and needle-formed crystals of silicon consist of regular octahedrons. Both forms have a blackish-gray color and a metallic lustre.

**Silicon Hydride, Silico-methane,** $SiH_4$.—This gas is obtained mixed with silico-ethane, $Si_2H_6$, when a compound of magnesium and silicon is treated with hydrochloric acid:

$$Mg_2Si + 4HCl = SiH_4 + 2MgCl_2.$$

It can be liquefied at $-11°$ and under a pressure of 50 atmospheres. Thus made, it takes fire when it comes in contact with the air, and the act is accompanied by explosion. The products of its combus-

tion are silicon dioxide and water. When pure it forms a colorless gas which does not take fire spontaneously in the air at the ordinary temperature. When it is diluted with hydrogen, or when heated, it does take fire. When burned in a cylinder or narrow tube, so that free access of air is not possible, amorphous silicon is deposited upon the walls of the vessel.

**Titanium,** Ti (At. Wt. 48.1).—Titanium occurs in nature as titanium dioxide, $TiO_2$, in three distinct forms, known as rutile, brookite, and anatase; in combination with iron, as titaniferous iron which contains ferrous titanate, $FeTiO_3$; and in a number of iron ores and rare minerals.

**Zirconium,** Zr (At. Wt. 90.6).—The principal form in which zirconium occurs in nature is as zircon, a silicate of the formula $ZrSiO_4$, derived from normal silicic acid, $Si(OH)_4$, by the substitution of an atom of zirconium for the four hydrogen atoms.

**Thorium,** Th (At. Wt. 232.5).—This element occurs principally in the mineral thorite, which is essentially a silicate of thorium, $ThSiO_4$, analogous to zircon.

**Cerium** so much resembles the two elements lanthanum and didymium that, although it falls in the same group as silicon and resembles the elements of this group in some respects, it seems advisable to postpone its study until lanthanum and didymium are taken up.

### Compounds of the Elements of the Silicon Group with those of the Chlorine Group.

**Silicon Tetrachloride,** $SiCl_4$.—This compound is formed when silicon is heated in a current of chlorine, and by passing a current of dry chlorine over a heated mixture of silicon dioxide and carbon. Under these latter circumstances the following reaction takes place:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

The tetrachloride is a colorless liquid, solidifying at $-89°$ and boiling at 58°. It is decomposed by water, silicic acid and hydrochloric acid being formed. The reaction probably takes place as represented in the following equation:

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$

The normal acid thus formed breaks down readily, however, forming the ordinary acid of the formula $SiO(OH)_2$ or $H_2SiO_3$, corresponding to carbonic acid, $H_2CO_3$.

**Silicon Hexachloride**, $Si_2Cl_6$, is formed when silicon tetrachloride is heated with silicon :

$$3SiCl_4 + Si = 2Si_2Cl_6.$$

It is a liquid boiling at 145.5° and solidifying at −1°. When heated to a sufficiently high temperature it is decomposed, yielding silicon and the tetrachloride:

$$2Si_2Cl_6 = 3SiCl_4 + Si.$$

Water decomposes it, forming the corresponding hydroxyl derivative, which loses water and forms the acid $Si_2O_2(OH)_2$ or $H_2Si_2O_4$:

$$Si_2Cl_6 + 6H_2O = Si_2(OH)_6 + 6HCl;$$
$$Si_2(OH)_6 = Si_2O_2(OH)_2 + 2H_2O.$$

The product is in some respects analogous to disulphuric acid.

**Silicon Tetrafluoride**, $SiF_4$.—This is one of the most interesting of the compounds that silicon forms with the members of the Chlorine Family. It is made by treating silicon dioxide with hydrofluoric acid. The action is secured by treating a mixture of silicon dioxide (sand) and calcium fluoride (fluor-spar) with concentrated sulphuric acid, when two reactions take place:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF;$$
$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

The tetrafluoride escapes as a colorless gas, and forms thick clouds in moist air on account of the action of water upon it. Silicon tetrafluoride solidifies at −77° and boils at − 65°.

Water decomposes the tetrafluoride, as it does the tetrachloride. The first action probably consists in the formation of normal silicic acid and hydrofluoric acid, the normal acid then breaking down by loss of water and yielding the ordinary form of silicic acid:

$$SiF_4 + 4H_2O = Si(OH)_4 + 4HF;$$
$$Si(OH)_4 = SiO(OH)_2 + H_2O.$$

The silicic acid thus formed separates as a gelatinous mass. At the same time the hydrofluoric acid acts upon some of

the silicon tetrafluoride, forming the compound *fluosilicic acid*, which has the formula $H_2SiF_6$:

$$SiF_4 + 2HF = H_2SiF_6.$$

The complete action may be represented in one equation, as follows:

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

The fluosilicic acid remains in solution in the water, and by treating this solution with carbonates or hydroxides of the metallic elements the salts known as the fluosilicates are obtained. The solution of the acid can be concentrated to a certain extent in a platinum vessel, but it breaks down into silicon tetrafluoride and hydrofluoric acid when it becomes concentrated. If more potassium hydroxide than is required to neutralize the acid is added to the solution, decomposition ensues, with formation of silicic acid:

$$H_2SiF_6 + 6KOH = 6KF + H_2SiO_3 + 3H_2O.$$

By water alone, however, the acid is not decomposed, and the salts are fairly stable. When heated, the salts give off silicon tetrafluoride, and fluorides are left behind:

$$K_2SiF_6 = 2KF + SiF_4.$$

### Compounds of the Members of the Silicon Group with Oxygen, and with Oxygen and Hydrogen.

**Silicon Dioxide,** $SiO_2$.—This compound occurs very abundantly in nature in many different forms, both crystallized and amorphous. Quartz is a form of crystallized silicon dioxide which is found very widely distributed. It crystallizes in the hexagonal system in prisms and pyramids, the crystals sometimes attaining great size and beauty. Another form of the crystallized compound is that known as tridymite. Like quartz it crystallizes in the hexagonal system, but the characteristic forms are not the same as those of quartz. Further, it nearly always occurs in triplet crystals. The finer crystals of

quartz are generally called *rock-crystal;* the crystalline variety in which the crystals are not well developed is called *quartzite.* The amorphous varieties of silicon dioxide frequently contain water in combination, or, rather, they are hydroxides of silicon. Examples of these forms are opal, agate, amethyst, carnelian, flint, sand, chalcedony. Some of these are colored by small quantities of other substances contained in them. Carnelian owes its color to a compound of iron, probably ferric oxide; flint contains small quantities of organic matter. The specific gravity of the crystallized varieties is higher than that of the amorphous varieties, and they also differ somewhat chemically.

**Properties.**—Silicon dioxide is insoluble in water and in most acids. It dissolves, however, in hydrofluoric acid, forming the tetrafluoride. It requires the temperature produced by the oxyhydrogen blowpipe or the electric arc to melt it. The amorphous varieties are more easily acted upon by other substances, as, for example, hydrofluoric acid, than the crystallized. When the amorphous compound is boiled with solutions of potassium or sodium hydroxide, or of the carbonates of these metals, it dissolves, forming the corresponding silicate:

$$K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2;$$
$$2KOH + SiO_2 = K_2SiO_3 + H_2O.$$

The crystallized varieties are not dissolved in this way. All forms of the dioxide act upon melting hydroxides or carbonates of potassium or sodium, and form the corresponding silicates.

**Uses.**—Plants take up silicon dioxide from the soil, and this being deposited in various parts of their tissues gives them the necessary firmness. Straw, for example, is rich in silicon dioxide. Horsetail, a plant of the genus *Equisetum*, is so rich in finely divided silicon dioxide that it is used for polishing. There are great natural deposits of finely-divided silicon dioxide known as *infusorial earth.* This consists of the remains of diatoms. And finally silicon dioxide is found in hair, in feathers,

and in egg albumin. Silicon dioxide finds extensive application in the manufacture of mortar, glass, and porcelain. Ordinary glass is a silicate of calcium and potassium or sodium, made by melting together sand and the carbonates of the metals mentioned.

**Quartz Glass.**—Silicon dioxide expands only one-twelfth as much as the best glass when heated. For this reason flasks and tubes are now made of fused silicon dioxide under the name quartz glass. Such flasks can be heated red hot and plunged into cold water or liquid air without injury, and can be heated to 1700° without softening. The fused quartz also differs optically from glass in that it gives free passage to the ultra-violet light rays. The necessarily high price of objects of quartz glass prevents its general substitution for glass for general laboratory use.

**Silicic Acid.**—There are many varieties of silicic acid, all of which can, however, be referred to the *normal acid*, $Si(OH)_4$. This normal acid is contained in the gelatinous precipitate formed when silicon tetrachloride or tetrafluoride is decomposed by water:

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$

The normal acid readily loses water and forms the acid of the formula $OSi(OH)_2$ or $H_2SiO_3$. From the latter most of the ordinary silicates are derived. It cannot be isolated, for when filtered off and exposed to the air it loses more water, and when heated to a sufficiently high temperature it is converted into silicon dioxide.

When potassium or sodium silicate in solution is treated with hydrochloric acid, most of the silicic acid separates in the form of a gelatinous mass if the solution is concentrated. If, however, the solution is dilute, a considerable part of the acid remains in solution. Further, when a concentrated solution of the silicate of potassium or sodium is poured quickly into hydrochloric acid, or the acid is poured quickly into the solution of the silicate, the silicic acid remains in solution. If, however, the solutions are brought together drop by drop the silicic acid separates. From these solutions of silicic

acid, ammonia or ammonium carbonate throws down the acid.

A solution of pure silicic acid can be obtained by means of *dialysis*. It has been found that solutions of different substances pass with different degrees of ease through porous membranes, just as gases differ as regards the ease with which they pass through porous diaphragms. This fact concerning gases was referred to in connection with hydrogen. Now, while some solutions pass readily through parchment paper, others pass through with difficulty, and some do not pass through at all. A *dialyser*, or an apparatus used in dialysis, may be made by tying a piece of parchment paper over the mouth of a ring-formed glass or rubber vessel, and placing this in another shallow vessel. Pure water is put in the outer vessel, and the solution for dialysis in the inner one. The arrangement is illustrated in Fig. 77.

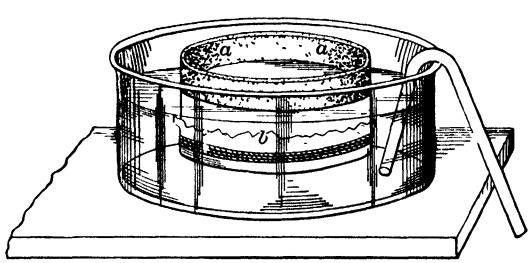



FIG. 77.

In the figure *aa* is the hoop of gutta-percha, and *b* is the parchment paper. When now the solution containing hydrochloric acid, sodium chloride, and silicic acid is put in the dialyser, the hydrochloric acid and sodium chloride pass readily through the membrane, while the silicic acid is left behind, and in the course of a few days, if the water in the outer vessel is renewed from time to time in the interval, the solution of silicic acid in the inner vessel will be found to be free from the other substances. This solution can be evaporated to some extent by boiling, but when a certain concentration is reached the acid

separates. In a vacuum such a solution can be evaporated further without the formation of a deposit. Finally, a transparent mass is left which has approximately the composition represented by the formula $H_2SiO_3$. The dialysed solution of silicic acid is coagulated by a very dilute solution of sodium or potassium carbonate, and by carbon dioxide itself.

The substance that passes through the membrane is called a *crystalloid*, and that which does not pass through is called a *colloid*. The solution of the colloid is called a *colloidal* solution.

When the solutions containing silicic acid are evaporated to complete dryness the acid is converted into silicon dioxide and insoluble hydrates. This residue is called *insoluble silicic acid*. When this is treated with hydrochloric acid and water it remains undissolved, and if filtered off and ignited it leaves a residue of silicon dioxide. To sum up: Whenever silicic acid is formed in a solution it is a more or less complex derivative of normal silicic acid, and is somewhat soluble in water, but by the processes just described the soluble acid is converted into insoluble silicon dioxide, as explained.

**Polysilicic Acids.**—Silicic acid is remarkable for the great number of derivatives which it yields. Most of these bear to the normal acid relations similar to those which the various forms of phosphoric acid bear to normal phosphoric acid. It has already been stated that salts of the acid $H_2SiO_3$ are more common than those of the normal acid. Among the salts of the normal acid are zircon, $ZrSiO_4$, and thorite, $ThSiO_4$. The ordinary silicates of potassium and sodium are derived from the acid $H_2SiO_3$; so also are wollastonite, $CaSiO_3$, and enstatite, $MgSiO_3$.

**Disilicic Acid,** $H_2Si_2O_5$, is derived from ordinary silicic acid by loss of one molecule of water from two molecules of the acid:

$$2SiO(OH)_2 = (SiO)_2O(OH)_2 + H_2O.$$

Its composition is, therefore, $H_2Si_2O_5$, which may be

written $O_3Si_2(OH)_2$. Another form of disilicic acid $H_6Si_2O_7$ is derived from two molecules of the normal acid by loss of one molecule of water:

$$2Si(OH)_4 = OSi_2(OH)_6 + H_2O.$$

The well-known mineral serpentine is apparently the magnesium salt of this acid. It is represented by the formula $Mg_3Si_2O_7$.

**Trisilicic Acids** are derived from three molecules of the normal acid or of the ordinary acid by loss of different numbers of molecules of water. Thus, by loss of two molecules the normal acid would yield a product $H_8Si_3O_{10}$. By loss of two molecules of water this trisilicic acid would yield an acid of the formula $H_4Si_3O_8$.

Orthoclase or ordinary feldspar is the aluminium-potassium salt of the second form of trisilicic acid, in which one atom of hydrogen is replaced by potassium, and three by an aluminium atom, as shown in the formula $AlKSi_3O_8$.

**Titanium Dioxide,** $TiO_2$.—As has been stated, this is one of the principal forms in which titanium is found in nature. There are three natural crystallized varieties—rutile, brookite, and anatase.

**Thorium Dioxide,** $ThO_2$.—This occurs in nature as the mineral thorite, but is obtained commercially from the mineral monazite which contains about 5 per cent thorium. *Welsbach mantles* are made by dipping a cylinder of cotton web in a solution of a mixture of thorium and cerium nitrates. When the cotton is burned away a web of thorium and cerium oxides remains which becomes incandescent and yields a strong light when heated with a comparatively small Bunsen flame. Mantles containing 99 per cent thorium oxide and 1 per cent cerium oxide are said to give the best light. The superior light emitted by the Welsbach mantle as compared with that emitted by the incandescent pure oxide of thorium is believed to be due to chemical action occurring and reoccurring constantly in the Bunsen flame between thorium oxide and the two oxides of cerium.

**Silicides** are compounds of silicon with other elements, bearing the same relation to the hydrides of silicon that sulphides have to hydrogen sulphide.

**Silicon Carbide, Carborundum.**—Thus carbon and silicon combine to form silicon carbide, CSi, which is now manufactured on the large scale and known as carborundum. It is to be observed that this substance may be regarded either as silicon carbide or as carbon silicide. It is made by heating a mixture of quartz sand, coke, and common salt, or sodium chloride, in the electric furnace to 3500°, when the reaction represented below takes place:

$$SiO + 2C = CSi + 2CO.$$

The product is in the main crystallized, the crystals being bluish or yellowish-green. They have the specific gravity 3.22 to 3.12. The compound is said to be colorless when perfectly pure. It scratches ruby and chrome-steel, and on account of its hardness it is much prized as a polishing agent, being used to a considerable extent in place of emery. Pure carbon silicide is insoluble in nearly all ordinary solvents, including hydrochloric, nitric, sulphuric, and hydrofluoric acids. It is, however, decomposed by fusing caustic alkalies or their carbonates.

## Family IV, Group B.

Allied to the members of the silicon group, yet differing from them in some important particulars, are the three elements germanium, tin, and lead. Of these the first two are more acidic in character than the last. They combine with chlorine in two proportions, forming the chlorides $GeCl_2$, $SnCl_2$, $PbCl_2$, $GeCl_4$, $SnCl_4$, $PbCl_4$. With oxygen they unite, forming the compounds $GeO_2$, $SnO_2$, and $PbO_2$. Stannic oxide, $SnO_2$, and lead peroxide, $PbO_2$, form salts with bases, and these have the composition represented by the general formulas $M_2SnO_3$ and $M_2PbO_3$, and are therefore analogous to the silicates and titanates. On the other hand, salts are known which are derived from the oxide PbO. These have the general formula $M_2PbO_2$, and are to be regarded as salts of an acid, $Pb(OH)_2$. These salts are not stable, and are not easily obtained. The principal derivatives of lead are those in which it plays the part of a base-forming element. It will therefore be better to postpone its study until it is taken up under the general head of the base-forming

elements. Notwithstanding, further, the marked analogy between some of the compounds of tin and those of the members of the silicon group, it appears on the whole advisable to treat of this element in company with lead, which it also resembles in many respects.

## EXPERIMENTS.

### Silicon.

Experiment 201.—Prepare sodium fluosilicate as directed in the next experiment. Mix 3 parts of the dry salt with 1 part of sodium cut in pieces. Throw this mixture all at once into a Hessian crucible heated to bright red heat in a furnace. Add immediately 9 parts granulated zinc, and a layer of sodium chloride previously heated to drive off water. The crucible is then covered and the fire allowed to burn down. After cooling, the regulus of zinc containing the silicon is separated from the slag, washed with water, and treated with hydrochloric acid. The zinc dissolves and leaves the silicon. This is again washed with water and then heated with nitric acid, and washed with water, when crystals of silicon, sometimes of great beauty, are obtained. Try the effect of heating a little of the silicon in the air. Try the action of acids and of alkalies upon it.

### Silicon Tetrafluoride and Fluosilicic Acid.

Experiment 202.—Arrange an apparatus as shown in Fig. 78. *A* is a bottle of about 2 liters capacity, such as are commonly used for transporting acids. This is about two-thirds filled with alternating

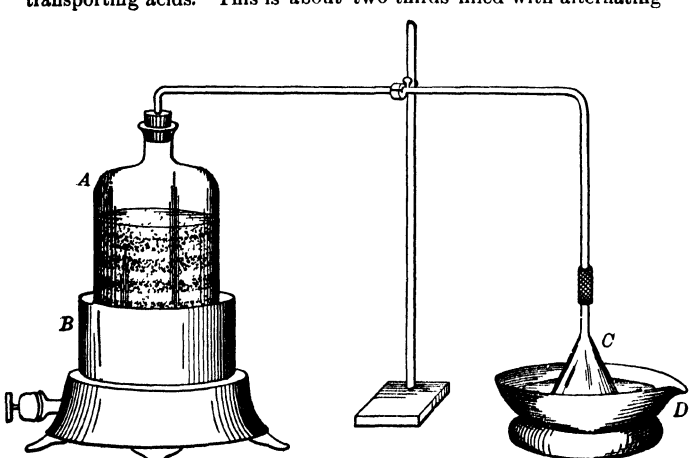



Fig. 78.

layers of sand and powdered fluor-spar, moistened with concentrated sulphuric acid. The bottle is put in the deep sand-bath *B*, and connected by means of a wide glass tube with the funnel *C*, which dips just below the surface of the water in the large evaporating dish *D*. The sand-bath is now gently heated, when silicon tetrafluoride passes over. Coming in contact with water, it is decomposed, silicic acid being deposited and fluosilicic acid passing into solution. In order to prevent clogging, the gelatinous silicic acid is from time to time removed from the mouth of the funnel by means of a bent glass rod. After the action is complete, filter the solution. Take out one-quarter and to the rest slowly add a solution of sodium carbonate until the whole just begins to show an alkaline reaction ; now add the other quarter of the acid, and filter. Explain all the reactions. Heat a little of the dried salt in a covered platinum crucible. What change takes place? What evidence have you that the change has taken place? To a little of the salt in water add a solution of potassium hydroxide. What change takes place? Dry the silicic acid formed in the first part of the experiment by decomposition of the silicon tetrafluoride.

## Silicic Acid.

Experiment 203.—Boil some of the silicic acid obtained in the last experiment in a solution of sodium hydroxide. Treat some of the solution with hydrochloric acid ; with ammonium chloride.

Experiment 204.—Fuse a mixture of equal weights of potassium and sodium carbonates in a platinum crucible in the flame of the blast-lamp and slowly add fine sand to the molten mass. Continue the heating until no more sand is dissolved. Pour the molten mass out on a stone, and when cooled break it up and treat it with water.

Experiment 205.—Treat a little of the solution containing sodium and potassium silicates, prepared in the last experiment, with a little sulphuric or hydrochloric acid. A gelatinous substance will be precipitated. This is silicic acid. Some of the acid remains in solution. By evaporating the solution to dryness and heating for a time on the water-bath, all the silicic acid is rendered insoluble.

## CHAPTER XXII.

### CHEMICAL ACTION.

**Retrospective.**—Thus far the principal elements of four families and the compounds which they form with one another have been presented for study. No matter how simple or how complex the chemical changes studied were, certain fundamental laws governing all cases of chemical action were found to hold good. These laws have been discussed, but it will be well to recall them here before taking up others which are intimately connected with them. The first great law of chemical change is

I. *The law of conservation of mass.*

According to this the *amount* of matter is not changed by a chemical act.

The second law is

II. *The law of definite proportions.*

According to this, the *composition* of any compound is always the same.

The third law is

III. *The law of multiple proportions.*

According to this, the different weights of any element that combine with a fixed weight of another or others bear simple relations to one another.

To account for the laws of definite and multiple proportions the *Atomic Theory* has been proposed.

According to this, each element is made up of particles of definite weight, which are chemically indivisible, and chemical action consists in union or separation of these particles. These hypothetical particles are called *atoms.*

The elements must combine in the proportion of their atomic weights or of simple multiples of these, if the atomic theory is true.

Further study showed that it is necessary to assume the existence of larger particles than the atoms, viz., the *molecules*. According to the theory of molecules, every chemical compound and element is made up of molecules, which are the smallest particles having the same chemical properties as the mass. These molecules are made up of atoms which, in the case of compounds, are of different kinds, and in the case of elements, of the same kind. In the case of a few elements the atom appears to be identical with the molecule.

From the study of gases the conclusion is reached that in equal volumes of all gases under standard conditions there is always the same number of molecules (Avogadro's hypothesis). This furnishes a means of determining the relative weights of molecules of gaseous substances; and from these molecular weights it is possible to draw conclusions in regard to the atomic weights of those elements which enter into the composition of the compounds thus studied.

The formulas of chemical compounds are intended to be *molecular* formulas. They are intended to tell of what atoms and of how many atoms the molecules represented are made up.

The method of determining molecular weights based upon Avogadro's hypothesis is applicable only to gaseous substances, or to such as can be converted into gas without undergoing decomposition. While many of the compounds with which we have had to deal are of this character, many of them are not, and in regard to the molecular weights of these we must be in doubt unless some other method applicable to liquids and soilds is available. So, too, the atomic weights of those elements which enter into the composition of gaseous compounds can be deduced from the molecular weights, but plainly those which do not enter into the composition of such compounds require some other method. For determining

the atomic weights of such elements an excellent method is based upon the study of specific heats; while for the determination of the molecular weights of solid substances that can be dissolved without decomposition a method has been worked out that is based upon the extent to which the compound raises the boiling-point or lowers the freezing-point of its solution. Both these methods will be briefly described in this chapter.

Next, it is found that there is a limit to the law of multiple proportions. While, according to this law, the weights of any element which unite with a given weight of another element bear simple relations to one another, the law is silent as to how many kinds of compounds are possible between any two elements. A careful examination of the composition of the compounds of the elements shows, however, that there is a limit to the number of atoms of one element that can combine with one atom of another element. This limit is determined by what is called the *valence* of the elements. Observations on the composition of compounds have led to the hypothesis of the *linking of atoms*—the linking taking place according to the laws of valence. The arrangement of the atoms in a molecule is, according to this, the *constitution* of a compound.

Valence, as we have seen, is not a constant property of the atoms. Towards oxygen the elements which we have thus far studied have the highest valence; towards hydrogen the lowest; and, in general, towards the members of the chlorine group they exhibit an intermediate valence. The valence towards hydrogen is in most cases constant, while the valence towards oxygen and towards the members of the chlorine group varies, in some cases between comparatively wide limits, as between 1 and 7 in the chlorine group, and between 2 and 6 in the sulphur group. Further, the variations in the valence of an element generally take place from odd to odd or from even to even. In the case of chlorine it appears to vary from 1 to 3 to 5 to 7; in that of sulphur, from 2 to 4 to 6; in that of phosphorus, from 3 to 5.

A comparison of the atomic weights finally led to the discovery that the properties of the elements are a *periodic function of these weights.* This is the *periodic law* of chemistry. This makes a systematic classification of the elements according to their atomic weights and their properties possible, and is full of suggestion as to the relations which the forms of matter we call elements bear to one another.

**Classification of Reactions of the Elements and Compounds Studied.**—While there is undoubtedly something confusing in the number of the compounds and their reactions which we have been studying, still, when these are interpreted in the light of the atomic theory, of the law of valence, and of the periodic law, the study is much simplified, and those things which seem to have little or no connection are found to form parts of a general system. In studying chemistry, one of the first things to be done is to learn how elements and compounds act upon one another, and what products are formed. The question of composition is one of the first that presents itself, and this must be studied before other questions can be intelligently discussed. What, then, are the most prominent facts which we have learned in studying the elements and compounds that have thus far been taken up?

**Kinds of Chemical Reactions.**—All chemical reactions may be classified under three heads:

(1) Those which consist in direct combination;

(2) Those which consist in direct decomposition; and

(3) Those which involve the interaction of two or more elements or compounds and the formation of two or more compounds. This is known as double decomposition or metathesis.

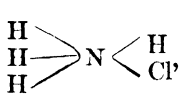
**Direct Combination.**—A number of examples of each of these kinds of reactions have been studied. As examples of the first kind the following may be mentioned: The combination of hydrogen and chlorine to form hydrochloric acid; the formation of ammonium chloride from ammonia and hydrochloric acid; the formation of calcium hydroxide from calcium oxide and water; the

formation of nitrogen peroxide from nitric oxide and oxygen; and the formation of carbon bisulphide from carbon and sulphur.

As regards the combination of hydrogen and chlorine, it should be remarked that this act is the same in principle as that of metathesis. Strictly speaking, it is not a case of direct combination. For according to the molecular theory, free chlorine and free hydrogen consist of molecules which are made up of two atoms each. Therefore, when these elements are brought together the molecules are first decomposed into atoms before the act of union can take place. The two acts are represented by these two equations:

$$Cl_2 + H_2 = Cl + Cl + H + H;$$
$$Cl + Cl + H + H = 2HCl.$$

In the case also of the union of hydrochloric acid and ammonia it appears probable that a serious disarrangement of the constituent atoms is necessary in order that the act of combination may take place. According to the ammonium theory, ammonium chloride is represented by the formula

 , which means that the atom of chlorine

and four atoms of hydrogen are in combination with the atom of nitrogen. But, in order that a compound of this constitution may be formed from ammonia and hydrochloric acid, it is necessary that the molecule of hydrochloric acid should be broken down into its constituent atoms. So that this case of apparent direct combination is, as far as we can judge, in reality more complicated than it appears, and should be represented by the two equations:

$$NH_3 + HCl = NH_3 + H + Cl;$$
$$NH_3 + H + Cl = NH_4Cl.$$

All other cases of apparent direct combination are probably of the same character, so that it is doubtful

whether a single case of simple direct combination is known.

**Direct Decomposition.**—As examples of direct decomposition the following cases may be cited: The decomposition of mercuric oxide by means of heat into mercury and oxygen; that of ammonium chloride into ammonia and hydrochloric acid by heat; that of potassium nitrate into potassium nitrite and oxygen by heat; that of phosphorus pentachloride into the trichloride and chlorine by heat; that of ammonia into hydrogen and nitrogen by continued action of electric sparks; and that of nitrogen iodide by contact with a solid substance.

On close examination of each of the above cases, which are fairly typical and as simple as any that can be chosen, it will be seen that no one of them is merely a case of decomposition; for even though it must be assumed that the first result in each case is the setting free of the atoms of one or two elements, it must also be assumed that these atoms unite again to form other molecules either of elements or compounds. Thus, when mercuric oxide is decomposed, mercury and oxygen are obtained. As far as can be determined, the mercury atoms do not unite with each other, but the oxygen atoms do, so that the total action involves decomposition and afterwards combination as represented in the equations

$$2HgO = Hg + Hg + O + O;$$
$$Hg + Hg + O + O = Hg + Hg + O_2.$$

In the case of the pentachloride of phosphorus, it is probable that the two atoms of chlorine are first given off from each molecule of the chloride, leaving a molecule of the trichloride, but the atoms of chlorine afterwards unite to form molecules as represented thus:

$$PCl_5 = PCl_3 + Cl + Cl;$$
$$PCl_3 + Cl + Cl = PCl_3 + Cl_2.$$

Similar statements hold good for all other cases of direct decomposition.

**Metathesis.**—This is the most common kind of chemi-

cal action, and indeed from what has been said in regard to direct combination and direct decomposition it will be seen that there is no essential difference between these and metathesis. Most of the reactions with which we have had to deal are examples of double decomposition or metathesis. Such are: The formation of salts by the action of bases upon acids; the formation of the sulphides of arsenic, antimony, and bismuth by the action of hydrogen sulphide upon solutions of compounds of these elements; the setting free of hydrochloric and nitric acids by the action of sulphuric acid upon chlorides and nitrates; of carbon dioxide and oxides of nitrogen by the action of acids upon carbonates and nitrites; and of ammonia by treating ammonium salts with lime. As simple an example of this kind of action as can be given is that of the formation of hydrogen and potassium chloride from potassium and hydrochloric acid gas. The molecular weight of potassium is not positively known, but, assuming its molecule to be made up of two atoms, the action must be represented in this way:

$$K_2 + 2HCl = 2KCl + H_2.$$

The next stage of complication is exhibited in the reaction following:

$$KI + HCl = KCl + HI.$$

Examples similar to the latter, but somewhat more complicated, are these:

$$2KOH + H_2SO_4 = K_2SO_4 + H_2O;$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl.$$

**The Cause of Chemical Reactions.**—The prime cause of chemical reactions is something that we conceive of as an attractive force exerted in different degrees between the different elements. When any elements or compounds are brought together under certain conditions the tendency is always towards the formation of the most stable compounds of those elements that can be formed under the given conditions. Thus, potassium sulphate and

water are more stable forms of combination of the elements hydrogen and oxygen, and potassium, sulphur and oxygen, than sulphuric acid and potassium hydroxide are under the conditions under which the action takes place. So also the system composed of potassium chloride and hydriodic acid is more stable than that composed of potassium iodide and hydrochloric acid under the conditions of the action. Why the one system is more stable than the other is not known, for it is not known what relations exist between the atoms in the molecules. It is convenient to conceive of that which causes the atoms to unite to form compounds as an attractive force. It is evident that this force is more strongly exerted between some elements than between others. That between chlorine and hydrogen is, for example, much stronger than that between chlorine and nitrogen or oxygen. Owing, however, to the complicated character of most chemical reactions, it is extremely difficult to make measurements of this force.

**An Ideal Chemical Reaction.**—In every case in which two compounds act upon each other to form two new ones, several forces must be at work. Suppose, for example, $AB$ and $CD$ act upon each other in the gaseous condition to form two compounds $BC$ and $AD$, also both gaseous. The normal course of such a reaction would lead to the formation not only of the two compounds $BC$ and $AD$, but $AB$ and $CD$ would also be present in the resulting system. For $A$ has the power to combine with $B$ as well as with $D$, and $C$ has the power to combine with $D$ as well as with $B$. In the system we should have operating the tendency of $A$ to combine with $B$, and that of $A$ to combine with $D$; that of $C$ to combine with $D$, and that of $C$ to combine with $B$. As these forces operate simultaneously, equilibrium is established when certain quantities of the four possible compounds are formed, the quantities depending in the first instance upon the relative strengths of the forces at work.

It is difficult to give an illustration of this kind of relation, because the study of chemical changes between gases

that give rise to the formation of gaseous products is difficult, and the study of changes in solution is complicated by the action of the solvent and, if the solvent is water and the substances are acids, bases, or salts, this action plays a controlling part.

**Influence of Mass.**—When hydrogen sulphide is passed into a solution of cadmium chloride, cadmium sulphide is precipitated, the reaction being represented by the equation

$$(1) \qquad CdCl_2 + H_2S = CdS + 2HCl.$$

On the other hand, when hydrochloric acid is added to cadmium sulphide the latter dissolves and the action is represented by the equation

$$(2) \qquad CdS + 2HCl = CdCl_2 + H_2S.$$

This action is plainly the reverse of that which takes place when hydrogen sulphide acts upon cadmium chloride in solution. The difference between the two cases is due to the relative masses of hydrogen sulphide and of hydrochloric acid that are brought into action. If the hydrochloric acid is very dilute and the hydrogen sulphide is present in excess, reaction (1) takes place and is complete. If the conditions are reversed, then reaction (2) takes place. If considerable hydrochloric acid is added to a solution of cadmium chloride, and hydrogen sulphide passed into the solution, all the cadmium will not be precipitated as sulphide, and the amount precipitated will depend upon the amount of hydrochloric acid present. A reaction that can take place in two directions or that is reversible (see p. 60) is commonly represented thus:

$$CdCl_2 + H_2S \rightleftarrows CdS + 2HCl.$$

Equilibrium is established in such cases under definite conditions, and the law governing the equilibrium has been discovered.

Guldberg and Waage were the first to formulate the *law of mass action.* The law is as follows:

*When two substances act upon each other, the action is proportional to the active mass of the substances taking part in the change.*

By active mass is meant the molecular concentration, or, in other words, the number of gram-molecules (see p. 164) per liter.

The following quotation from the memoir by Guldberg and Waage will make the subject somewhat clearer:

"When two substances $A$ and $B$ are transformed into two new substances $A'$ and $B'$, the chemical force with which $A$ and $B$ act upon each other is measured by the quantity of the new substances formed in unit time.

"The quantity of a substance in unit volume of the compound in which the chemical change takes place we call the active mass of the substance.

"The chemical force with which two substances $A$ and $B$ act upon each other is equal to the product of their active masses, multiplied by the *coefficients of affinity*.

"By coefficient of affinity a coefficient is understood which is dependent upon the chemical nature of the two substances and upon the temperature. If the active masses of $A$ and $B$ are represented by $p$ and $q$, and the coefficient of affinity by $k$, then the force acting between $A$ and $B$ is expressed by $kpq$.

"When in a chemical process $A$ and $B$ are transformed into $A'$ and $B'$, and $A'$ and $B'$ can at the same time be transformed into $A$ and $B$, equilibrium will be established when the force acting between $A$ and $B$ is equal to the force acting between $A'$ and $B'$.

"If the active masses of $A'$ and $B'$ are represented by $p'$ and $q'$ and their coefficient of affinity by $k'$, the chemical force acting between $A'$ and $B'$ is expressed by $k'p'q'$.

"The condition of equilibrium is therefore expressed by the equation $kpq = k'p'q'$."

**Reactions may be Complete if One of the Products formed is Insoluble or Volatile.**—When two substances which by interaction can form an insoluble product are

brought together, the reaction generally takes place and is complete. When the substances are brought together we may imagine that, owing to interaction, a small quantity of the insoluble compound is formed at once. If this product were soluble, the action would stop before it is complete, because this new product would itself exert its action upon the system. Being insoluble, however, it is removed from the sphere of action, and the same reaction which caused the formation of the first particles of it can now be repeated, and so on, until the reaction is complete. This is illustrated in the action of sulphuric acid upon barium chloride in solution. The two substances react as represented in this equation:

$$BaCl_2 + H_2SO_4 + Aq = BaSO_4 + 2HCl + Aq.$$

The symbol Aq is simply intended to indicate that the reaction takes place in solution. If barium sulphate were soluble, all four substances—barium chloride, sulphuric acid, barium sulphate, and hydrochloric acid—would be present in the solution after the establishment of equilibrium. But, being insoluble, it is removed, and new quantities are formed as long as the substances necessary for its formation are present in the solution; that is, until either all the barium chloride is decomposed or all the sulphuric acid is removed. Reactions involving the formation of insoluble compounds or precipitates are among the most common with which we have to deal, particularly in the various operations of analytical chemistry.

Again, when two substances that can form a volatile product are brought together, the reaction generally takes place and is complete. The reason why a reaction of this kind is complete is the same as that given in the case of the formation of an insoluble compound. Each successive portion of the volatile product formed is removed, and the reaction which gave rise to it proceeds as long as the necessary substances are present. This kind of action has been repeatedly illustrated. It is that, for example, which is seen in the liberation of hy-

drochloric acid from a chloride by the action of sulphuric acid; of carbon dioxide by the action of an acid upon a carbonate; and of ammonia by the action of lime upon ammonium chloride.

An interesting example of the combined influence of mass and the volatility of the product is seen in the action of heated iron upon an excess of steam, and of the oxide of iron upon an excess of hydrogen. (See p 60).

**Dissociation.**—When water-vapor is heated to a sufficiently high temperature it is decomposed into the two gases hydrogen and oxygen. This decomposition does not take place suddenly when a certain temperature is reached, but it begins at a comparatively low temperature and increases as the temperature is raised. For any given temperature and pressure the amount of decomposition is definite. On cooling a mixture of water-vapor and hydrogen and oxygen, the two elements combine to a greater and greater extent as the temperature is lowered. A condition of equilibrium is established under each new set of conditions. The gradual decomposition of a substance into its constituents which reunite when the temperature is lowered is called dissociation. All cases of dissociation are examples of reversible reactions, and they also illustrate the phenomena of equilibrium. Other examples besides that mentioned are the change of nitrogen peroxide from the form $N_2O_4$ to that of $NO_2$. This may be represented thus:

$$N_2O_4 \rightleftarrows NO_2 + NO_2.$$

The dissociation of hydriodic acid into hydrogen and iodine may also be mentioned:

$$2HI \rightleftarrows H_2 + I_2.$$

In all these cases the substances taking part are gaseous.

When, however, calcium carbonate breaks down into lime and carbon dioxide two of the three substances are solids and one is a gas:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

Again, the dissociation of ammonium chloride into ammonia and hydrochloric acid involves the interaction of three substances, two of which are gases and one a solid:

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

It would lead too far to discuss these reactions in detail here.

The explanation of the phenomena of dissociation of gases is found in the kinetic theory of gases (see p. 42). According to this theory, the molecules of a gas at a given temperature are moving with different velocities, though the average velocity of all the molecules is the same at the same temperature. Now, it is highly probable that the motion of the atoms within the molecules partakes of that of the molecules themselves, so that the motion of the atoms in the molecules with the greatest velocity is probably the greatest, and, in these, decomposition will take place first. When a compound gas is heated, it is clear that even at a comparatively low temperature the motion of some of the molecules will be sufficient to cause their decomposition, and, as the average motion of all the molecules is constant for a given temperature, the amount of decomposition will be constant for that temperature. As the molecules are, however, moving in every direction and constantly colliding, a molecule that is decomposed at one instant may be re-formed at the next, and one that is not decomposed may acquire motion enough to cause its decomposition. Though, as is believed, these changes are constantly taking place at every temperature, still the number of molecules that will be decomposed in a given mass at a given temperature and pressure will always be the same. The higher the temperature, then, the greater the number of molecules in the condition that cause decomposition, and the smaller the number of those in the condition favorable to formation. At each temperature and pressure an equilibrium is established, the number of molecules decomposed being equal to the number formed. It is obvious that, if one of the products of decomposition is removed, the conditions are entirely changed. Then

the possibility of recombination will not exist, and total decomposition can be effected at a lower temperature than that required for total decomposition in the process of dissociation proper.

**Electrolytic Dissociation and Electrolysis.**—The action of an electric current upon the so-called electrolytes and the theory of electrolytic dissociation have already been discussed (see p. 166) and it has been pointed out that in water solutions of electrolytes the substances are to a greater or less extent in the condition of *ions*. This is recalled here because it has an important bearing on the subject treated of in the next paragraph.

**Raoult's Methods for the Determination of Molecular Weights.**—One great difficulty encountered in the study of chemical compounds is the determination of the molecular weights of those which are not gases or cannot be converted into vapor by heat. From studies on the freezing-points of solutions, it appears that quantities of compounds proportional to their molecular weights cause the same lowering of the freezing-points, provided the solvent does not act chemically upon the compound. This fact makes it possible to determine the molecular weights of substances that cannot be converted into vapor, but can be dissolved. The application of the method is simple. Suppose water to be the solvent used. It is known that this liquid solidifies or freezes at 0°. Now, it is found that by dissolving a certain quantity of some substance in a certain quantity of water the freezing-point is lowered say 0.5°. Further, the quantities of other substances necessary to lower the freezing-point of the same quantity of water to the same extent can be determined. These quantities are proportional to the molecular weights according to the law of Raoult. If, therefore, among the substances studied there is one the molecular weight of which is known, it is possible to determine the molecular weights of all by the method of Raoult.

So, also, it has been shown that quantities of compounds proportional to their molecular weights cause the same raising of the boiling-points, provided the solvent does not

act chemically upon the compounds or cause them to break down into their ions. Convenient methods have been devised for the determination of molecular weights of dissolved substances, the methods being based upon observations on the boiling-points and freezing-points. It should be noted that, when the molecular weight of a substance in solution has been determined, it does not follow that the substance has the same molecular weight when in the solid condition. This is a matter in regard to which we have little knowledge. It is probable that the molecules of solid substances consist of aggregates of the simple molecules that exist in solutions or in vapors. In some cases this has been proved.

**Determination of the Extent of Dissociation of a Dissolved Substance.**—The effect upon the boiling-point or freezing-point of a solution caused by the presence of a dissolved substance is proportional to the number of molecules in the solution or the number of individual particles, whether these are undecomposed molecules or the ions formed as a result of dissociation. Any substance that is dissociated in solution will give abnormal results if the attempt is made to determine its molecular weight by observations on the boiling-point or the freezing-point of its solutions. This method is therefore not applicable to solutions of electrolytes. On the other hand, the study of such solutions has shown that there is an increased lowering of the freezing-point for the same weight of solvent as the dilution becomes greater, a fact that points clearly to the conclusion that as the solution is diluted there is greater and greater dissociation, and advantage can be taken of this fact for the purpose of determining the extent to which dissociation has taken place in a solution of an electrolyte in water.

The methods of Raoult are now extensively used in the study of the compounds of carbon, simple forms of apparatus having been devised for this purpose. The recognition of the fact that electrolytes do not obey the law that holds good in the case of non-electrolytes led Arrhenius to the idea that the former are dissociated in

solution—an idea which has proved of great service to the science, and is likely to revolutionize the views of chemists in regard to the action of chemical substances upon each other in solution.

**Osmotic Pressure.**—During the last century it was observed that, when a vessel is filled with alcohol and the vessel tightly covered by tying a bladder over its mouth, and the whole then immersed in water, the bladder is stretched outward, showing that the liquid from without has found its way into the vessel through the bladder. For many years investigations on phenomena of this kind were carried on, but no results of a general character of special importance from the chemical point of view were reached until 1877, when Pfeffer, the botanist, gave an account of a large number of experiments, and laid the foundation of our present knowledge of the laws of osmotic phenomena. The simplest phenomenon of this kind is seen when a wide glass tube, tightly closed with a piece of bladder at the lower end, is partly filled with alcohol and then placed in a vessel of water, so that the level of the liquids inside and outside the tube is the same. If the tube is fixed in this position, the liquid will soon be found to rise in the tube. There is pressure from without inward. This is called *osmotic pressure*. Pfeffer's investigations had to do with the measurement of the pressure exerted by different substances under different conditions of temperature and dilution. Instead of using a bladder, which is not capable of much resistance, he used membranes made by precipitating copper ferrocyanide in the pores of clay cells. Somewhat later Van't Hoff showed that the results obtained by Pfeffer lead to the following remarkable laws governing osmotic pressure :

1. *The pressure is proportional to the concentration, or it is inversely proportional to the volume in which a definite quantity of the dissolved substance is contained.*

2. *The pressure increases for constant volume, proportionally to the absolute temperature.*

3. *Quantities of dissolved substances which are in the*

*ratio of the molecular weights of these substances exert equal pressures at the same temperatures.*

These laws are analogous to the well-known laws of gas-pressure, the third being plainly analogous to the law of Avogadro. Another form of the third law, together with an extension of it, is this:

*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.*

Morse and Frazer have succeeded in making practically perfect cells by means of which osmotic pressure can be measured with great accuracy. The results obtained by them with cane sugar and with glucose lead to the conclusion that *cane sugar and glucose dissolved in water exert an osmotic pressure equal to that which they would exert if gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.*

**Relations between Specific Heat and Atomic Weights.**— When equal weights of different elements are exposed to exactly the same source of heat, they require different periods of time to become heated to the same temperature. Given the same source of heat, it requires 32 times as long to raise the temperature of a pound of water 10, 20, or 30 degrees as it does to raise the temperature of a pound of mercury the same number of degrees; or it takes 32 times as much heat to raise a pound of water 10, 20, or 30 degrees as it does to raise a pound of mercury the same number of degrees. Starting at the same temperature, the quantity of heat required to raise the temperature of a certain weight of a substance one degree, as compared with the quantity of heat required to raise the temperature of the same weight of water one degree, is called the specific heat of the substance. Thus, from what was said above, the specific heat of mercury is $\frac{1}{32}$, or, in decimals, 0.03125. Similarly it can be shown that the specific heat of gold is 0.03244; of zinc, 0.0955; of silver, 0.057; of copper, 0.0952.

A simple relation is found to exist between the numbers expressing the specific heats of solid elements and

those expressing their atomic weights. This relation will be made clear by a consideration of a few cases:

| Element. | Specific Heat. | Atomic Weight. |
|---|---|---|
| Silver . . . . . | 0.0570 | 107.93 |
| Zinc . . . . . | 0.0955 | 65.4 |
| Cadmium . . . . | 0.0567 | 112.4 |
| Copper . . . . . | 0.0952 | 63.6 |
| Tin . . . . . | 0.0562 | 119. |

An examination of this table will show that the atomic weights are inversely proportional to the specific heats. We have

$$107.93 : 65.4 :: 0.0955 : 0.0570;$$
$$112.4 : 63.6 :: 0.0952 : 0.0567;$$
$$107.93 : 119. :: 0.0562 : 0.0570; \text{ etc.}$$

These proportions are only approximately correct; but it must be remembered that the means for the determination of atomic weights and specific heats are not perfect, and in both sets of figures there are undoubtedly small errors. Hence such slight variations from absolute agreement in these proportions should occasion no surprise. The agreement is sufficient to indicate a close connection between the two sets of figures. This connection may be stated in another way: *The product of the atomic weight by the specific heat is a constant.* Thus, in the above cases:

$$107.93 \times 0\ 057 = 6.16;$$
$$65.4 \times 0.0955 = 6.24;$$
$$112.4 \times 0.0567 = 6.37;$$
$$63.6 \times 0.0952 = 6.05;$$
$$118.5 \times 0.0562 = 6.70.$$

From this it appears that the quantity of heat necessary to raise weights of the elements proportional to their atomic weights the same number of degrees is essentially the same in all cases. Suppose two elements have the atomic weights 2 and 4. Their specific heats would be to each other as 2 to 1. That is to say, it would

require twice as much heat to raise the temperature of a given weight of the element with the atomic weight 2 a certain number of degrees, as it would require to raise the temperature of the same weight of the element with the atomic weight 4 the same number of degrees. But to raise the temperature of weights of these two elements proportional to their atomic weights would require the same quantity of heat. This fact may be stated thus:

*The atoms of all elements have the same capacity for heat.* This is only another way of stating that, to raise the temperature of an atom one degree, the same quantity of heat is always necessary.

Now, if it be assumed that the constant obtained by multiplying the specific heats by the atomic weights is 6.4, which is about the average of the different values found, then it is plain that, by dividing this number by the specific heat of an element, a number very near the atomic weight will be obtained. If the atomic weight is represented by $A$, and the specific heat by $H$, the following equation expresses the relation:

$$A = \frac{6.4}{H}.$$

If this law is without exceptions, it is plain that, in order to determine the atomic weight of an element, it is only necessary to determine its specific heat, and divide this into 6.4. The result will be very nearly the atomic weight. Knowing thus very nearly what the atomic weight is, it is a comparatively simple matter to determine it with accuracy by means of chemical analysis. Unfortunately for this purpose there are some marked exceptions to the law.

**Exceptions to the Law of Specific Heats.**—The elements glucinum, carbon, boron, and silicon form exceptions to the law of specific heats as this law has been stated above. At ordinary temperatures they do not follow the law. As the temperature is raised, however, the specific heat of these elements changes markedly, until finally, in the cases of carbon and silicon, a point is

reached beyond which there is only slight change. Thus, at 600° the specific heat of diamond is 0.441, and at 985° it is 0.440. That of silicon is 0.201 at 185°, and 0.203 at 332°. At these temperatures the elements obey the law. From elaborate studies on this subject, it appears that the law should be modified to read as follows:

*The specific heats of the elements vary with the temperature; but for every element there is a temperature, T, above which variations are very slight. The product of the atomic weight by the constant value of the specific heat is nearly a constant, lying between 5.5 and 6.5.*

Notwithstanding the irregularities referred to, the law of specific heats, commonly called, from the discoverers, *the law of Dulong and Petit*, has been of great value in the determination of atomic weights.

It has been shown that when the specific heats are determined at the melting-points of the elements the law is much more satisfactory than it now appears to be. The constant obtained lies between 9 and 10 for all elements thus far investigated.

## CHAPTER XXIII.

### BASE-FORMING ELEMENTS.—GENERAL CONSIDERATIONS.

**Introductory.**—The elements thus far studied belong for the most part to the class of acid-forming elements, or those whose compounds with oxygen and hydrogen have acid properties. All the members of Family VII, Group B, are acid-forming, while the single member of Group A of the same family is both acid-forming and base-forming. All the members of Family VI, Group B, are acid-forming, while the members of Group A of this family are both acid-forming and base-forming. In Family V, Group B, a gradation of properties is observed, the group beginning with strongly marked acid-forming elements and ending with an element, bismuth, which is more basic than acid in character. The elements of Group A, Family V, are both acid-forming, and base-forming, but they have not as sharply marked characteristics as the elements of Families VI and VII. Passing now to Family IV, it was found that the two most important members, carbon and silicon, belong to Group A. These two elements always act as acid-formers. A gradation of properties is observed in passing from silicon to thorium. The members of Group B of this family have the properties of the base-forming elements much more strongly marked than those of the acid-formers. There are still four families to be studied. These are Families I, II, III, and VIII, the members of which are almost exclusively base-forming elements. The compounds of these elements with hydrogen and oxygen are bases, or, in other words, have the power to neutralize acids. Their oxides are for the most part basic. An exception to this is found in the case of boron, already treated of, which forms a weak acid—boric acid. Its oxide is only slightly basic. The most strongly marked examples of

base-forming elements are those which occur in Family I, Group A; then follow in order those of Group A, Family II, and Group A, Family III. The resemblance between the members of Group B, Family I, and those of Group A of the same family is less striking than the resemblance between the two groups of any other family. Between the members of Group B, Family II, and those of Group A of the same family there is a general resemblance, while there are also differences. A similar remark applies to the relations between Groups A and B, Family III. The members of Family VIII occupy a somewhat exceptional position, as has already been pointed out. Each group of which this family consists is made up of three very similar elements with atomic weights that differ but little from one another.

**Metallic Properties.**—It has long been customary to divide the elements into two classes—the *metals* and the *non-metals*. This classification was originally based upon differences in the physical properties of the elements, the name *metal* being applied to those elements which have what is known as a metallic lustre, are opaque, and are good conductors of heat and electricity. All those elements which do not have these properties were called *non-metals*. Gradually the name *metal* came to signify an element which has the power to take the place of the hydrogen of acids and form salts, and the name *non-metal* to signify an element which has not this power. This classification, as will be seen, is practically the same as that which divides the elements into acid-forming and base-forming. The latter are the metals, the former are the non-metals. The imperfection of this classification has already been commented upon, the imperfection being due to the fact that some elements belong to both classes.

**Order in which the Base-forming Elements will be Taken Up.**—In studying the base-forming elements, it appears best to begin with those which have the most strongly marked character. These are the members of Family I, Group A. It further appears best to adhere as

closely as possible to the arrangement of the periodic system. Accordingly, the following order will be observed in the presentation of the elements yet to be studied:

1. Elements of Family I, Group A, or the *Potassium Group*, consisting of lithium, sodium, potassium, rubidium, and cæsium.

2. Elements of Family II, Group A, or the *Calcium Group*, consisting of glucinum, magnesium, calcium, strontium, barium, and erbium.

3. Elements of Family III, Group A, or the *Aluminium Group*, consisting of aluminium, scandium, yttrium, lanthanum, and ytterbium.

4. Elements of Family I, Group B, or the *Copper Group*, consisting of copper, silver, and gold.

5. Elements of Family II, Group B, or the *Zinc Group*, consisting of zinc, cadmium, and mercury.

6. Elements of Family III, Group B, or the *Gallium Group*, consisting of gallium, indium, and thallium.

7. Elements of Family IV, Group B, or the *Tin Group*, consisting of germanium, tin, and lead.

8. Elements of Family V, Group A, or the *Vanadium Group*, consisting of vanadium, columbium, didymium, and tantalum.

9. Elements of Family VI, Group A, or the *Chromium Group*, consisting of chromium, molybdenum, tungsten, and uranium.

10. Elements of Family VII, Group A, or the *Manganese Group*, of which manganese is the only representative.

11. Elements of Family VIII, of which there are three groups:

(A) The *Iron Group*, consisting of iron, nickel, and cobalt;

(B) The *Palladium Group*, consisting of ruthenium, rhodium, and palladium; and

(C) The *Platinum Group*, consisting of osmium, iridium, and platinum.

**Occurrence of the Metals.**—One of the first questions that suggests itself in connection with each element is,

In what forms of combination does it occur in nature? The chemical compounds which occur ready-formed in nature are called *minerals;* and the minerals, and mixtures of minerals from which the metals are extracted for practical purposes are called *ores.* The most common ores are oxides and sulphides. Examples of these are the ores of iron, tin, copper, lead, and zinc. The carbonates also occur in large quantity in nature, and are used for the purpose of preparing some of the metals. The carbonate of zinc, for example, is a valuable ore of zinc.

**Extraction of the Metals from their Ores.**—The detailed study of the methods used in the extraction of the metals from their ores is the object of *metallurgy.* Besides the methods used on the large scale, there are others which are only used in the laboratory. The most common method of extracting metals from their ores is that used in the case of iron, which consists in heating the oxides with charcoal. If the ores used are not oxides, they must first be converted into oxides before this method is applicable. This can generally be accomplished by heating the ores in contact with the air (*roasting*). Under these circumstances the natural carbonates, sulphides, and hydroxides, are converted into oxides. These changes are illustrated by the following equations:

$$FeCO_3 = FeO + CO_2;$$
$$2\,FeO + O = Fe_2O_3;$$
$$2\,FeS_2 + 11O = Fe_2O_3 + 4SO_2;$$
$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

By heating metallic oxides with carbon at the high temperatures attainable by means of powerful electric currents in the electric furnace some oxides are easily reduced that cannot be reduced by other means.

A second method consists in reducing the oxide by heating it in a current of hydrogen. This has been illustrated in the action of hydrogen upon copper oxide, when the following reaction takes place:

$$CuO + H_2 = H_2O + Cu.$$

The method is efficient for many oxides, but is expensive and is not used on the large scale.

Another method of extraction consists in treating the chloride of a metal with sodium. This is illustrated in the preparation of magnesium, which may be made by heating together magnesium chloride and sodium:

$$MgCl_2 + 2Na = 2NaCl + Mg.$$

Such a method is employed only in case it is impossible or extremely difficult to reduce the oxide.

The methods of electrolysis are in practical use at the present time as the best and simplest method of obtaining some metals. With some other metals, however, this method cannot be employed advantageously, is not practical as compared with other methods. Metals obtained from their salts by electrolysis are generally pure.

Besides the above methods, there are others which will be described under the individual metals.

**The Properties of the Metals.**—The metals differ very markedly from one another. Some are light, floating on water, as lithium, sodium, etc.; some are extremely heavy, as lead, platinum, etc. Some combine with oxygen with great energy; others form very unstable compounds with oxygen. Some form strong bases; others form weak bases. In general, those elements which are lightest, or which have the lowest specific gravity, are the most active chemically, while those which have the highest specific gravity are the least active. Among the former are lithium, sodium, and potassium; among the latter are lead, gold, and platinum.

**Compounds of the Metals.**—The principal compounds of the metals may be conveniently classified as:

*A. Binary Compounds, or Compounds containing two Elements.*

*a. Halides* or the compounds with fluorine, chlorine, bromine, and iodine; as the *fluorides*, *chlorides*, *bromides*, and *iodides*.

*b.* Compounds with oxygen; or the *oxides.*

*c.* Compounds with sulphur; or the *sulphides.*

*d.* Compounds with nitrogen; or the *nitrides.*

*e.* Compounds with carbon and with silicon; or the *carbides* and *silicides.*

*f.* Compounds with hydrogen; or the *hydrides.*

*g.* Compounds with boron, arsenic or antimony; or the *borides*, *arsenides*, and *antimonides.*

*B. Ternary Compounds or Quaternary Compounds, or Compounds containing three or four Elements.*

*a.* Compounds with oxygen and hydrogen; or the *hydroxides.*

*b.* Compounds with the acids of nitrogen; or the *nitrates* and *nitrites.*

*c.* Compounds with the acids of chlorine, bromine, and iodine; or the *chlorates*, *bromates*, *iodates*, *hypochlorites*, etc.

*d.* Compounds with the acids of sulphur, selenium, and tellurium; or the *sulphates*, *sulphites*, etc.

*e.* Compounds with carbonic acid; or the *carbonates.*

*f.* Compounds with the acids of phosphorus, arsenic, and antimony; or the *phosphates*, *arsenates*, etc.

*g.* Compounds with silicic acid; or the *silicates.*

*h.* Compounds with boric acid; or the *borates.*

It is more important to become acquainted with the *general* methods of preparation and the *general* properties of the more important compounds than to learn details concerning many individual members of each class. Only those compounds which illustrate general principles, or which, owing to some application, happen to be of special interest, need be dealt with in this book.

The acids of which the salts are derivatives are already known to us, and in dealing with the acids frequent reference has been made to the methods of making the salts, and to some of their more important properties. It will be well, before taking up the metals systematically, briefly to treat of the general methods of preparation, and the general properties of the different classes of

metallic compounds. It must be borne in mind, however, that the only way to become familiar with these substances and their conduct is by working with them in the laboratory.

**Chlorides.**—The chlorides, as well as the fluorides, bromides, and iodides, may be regarded as the salts of hydrochloric, hydrofluoric, hydrobromic, and hydriodic acids or simply as compounds of the metals with the members of the chlorine family. The most important of these compounds are the chlorides, and these well illustrate the conduct of the others.

The chlorides are made by treating a metal with chlorine, or with hydrochloric acid; by treating an oxide or a hydroxide with hydrochloric acid; by treating an oxide with chlorine and a reducing agent, like carbon; by treating a salt of a volatile acid with hydrochloric acid; by treating a salt of an insoluble acid with hydrochloric acid; by adding hydrochloric acid or a soluble chloride to a solution containing a metal with which chlorine forms an insoluble compound; and by adding to a solution of a chloride a salt, the acid of which forms with the metal of the chloride an insoluble salt, while the metal contained in it forms with chlorine a soluble chloride.

Only two of the above methods are peculiar to chlorides. These are the treatment of the metals with chlorine, and the treatment of oxides with chlorine and a reducing agent. The others involve principles which are also involved in the preparation of all salts, and they may therefore be treated of in a general way.

The formation of chlorides by direct treatment of the metals with chlorine is the simplest method of all. It has been illustrated in studying chlorine. It was found that chlorine combines with other elements with great ease. Thus, iron, copper, and tin combine with it, as represented in the following equations:

$$Cu + Cl_2 = CuCl_2;$$
$$2Fe + 3Cl_2 = 2FeCl_3;$$
$$Sn + 2Cl_2 = SnCl_4.$$

The preparation of chlorides by treating oxides with chlorine and a reducing agent has been illustrated in the making of boron trichloride. It is also used in making aluminium trichloride. For this purpose, chlorine is passed over a heated mixture of aluminium oxide and charcoal, when reaction takes place according to the following equation:

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

The other methods for preparing chlorides are, as has been said, general in character and are applicable to most salts.

## Formation of Salts in General.

1. *By treating a metal with an acid.*—This is the simplest method. It has been illustrated in the preparation of zinc sulphate by the action of zinc on sulphuric acid:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Other common examples are those represented in the following equations:

$$Fe + H_2SO_4 = FeSO_4 + H_2;$$
$$Zn + 2HCl = ZnCl_2 + H_2O.$$

2. *By treating an oxide or a hydroxide with an acid.*—This is of more general application than the preceding method. As it has been studied in some detail in connection with the subject of salts (see pp. 168–171), it need not be further treated of here.

3. *By treating the salt of a volatile acid with another acid.*—This method has been repeatedly illustrated in the decomposition of carbonates and nitrites by acids in general. While carbonic acid and nitrous acid themselves are perhaps not formed in these reactions, and we cannot say that the carbonates and nitrites are salts of volatile acids, yet the decomposition products of these acids are volatile at ordinary temperatures. The decomposition of carbonates by acids has been pretty fully studied, though attention was not directed to the fact that this kind of

action may be utilized for the purpose of making salts. As some carbonates occur in large quantity in nature or in the market, salts are frequently made by treating these with acids. Thus, magnesium sulphate is made by treating magnesium carbonate with sulphuric acid:

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2;$$

and calcium chloride is made by dissolving calcium carbonate in hydrochloric acid:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2; \text{ etc.}$$

These reactions proceed to the end for the reason that one of the products is volatile and is carried out of the field of action (see p. 420).

4. *By treating a salt of an insoluble acid with another acid.*—This case does not occur practically, as there are no common, insoluble acids. The principle involved is illustrated to some extent by the decomposition of a soluble silicate. Sodium silicate, for example, is soluble. When its solution in water is treated with an acid the silicic acid is partly precipitated:

$$Na_2SiO_3 + 2HCl + H_2O = Si(OH)_4 + 2NaCl.$$

The silicic acid formed is, however, somewhat soluble in water, so that the reaction is not complete. In any case the reaction is not one that is used for the preparation of salts.

5. *By the action of two salts upon each other.*—This method can be best described by means of an example. Suppose it is desired to prepare copper chloride by the action of two salts upon each other. Copper chloride is soluble. If copper sulphate and barium chloride are brought together in solution, the products are insoluble barium sulphate and soluble copper chloride:

$$CuSO_4 + BaCl_2 = BaSO_4 + CuCl_2.$$

By filtering off the barium sulphate, a solution of copper chloride is obtained.

6. *By precipitation.*—This method is illustrated in the formation of barium sulphate referred to in the last paragraph. Obviously, it is applicable only to difficultly soluble or insoluble salts. Many carbonates and phosphates can be made in this way.

**General Properties of the Chlorides.**—Most of the chlorides of the metals are soluble in water without decomposition, though many of them are decomposed when heated to a sufficiently high temperature with water. It will be remembered that the chlorides of the non-metallic or acid-forming elements are decomposed by water, yielding the corresponding oxides or hydroxides. The chlorides of some elements which are partly basic and partly acid are only partly decomposed. This is illustrated by the chloride of antimony, which with water forms an oxychloride:

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

The chlorides of the most strongly marked metals, like potassium, sodium, etc., are not decomposed by water. Calcium chloride dissolves with great ease, and, if the solution is evaporated, the chloride is again obtained. If, however, the attempt is made to drive off all the water by heat, some of the chloride is converted into the oxide as represented in the equation

$$CaCl_2 + H_2O = CaO + 2HCl.$$

Magnesium chloride is completely decomposed, when its solution in water is evaporated to dryness, the action being the same in character as that which takes place in the case of calcium chloride. The chlorides of iron and aluminium and of many other metals act in the same way. Silver chloride and mercurous chloride, HgCl, are insoluble in water. Lead chloride is difficultly soluble in water. If, therefore, on adding hydrochloric acid or a soluble chloride to a solution, a precipitate is formed, the conclusion is generally justified that one or more of the three metals—silver, lead, or mercury—is present. By taking into account the differences between these chlo-

rides, it is not difficult to decide of which of them a precipitate consists.

The chlorides are for the most part decomposed when treated with sulphuric acid, as has been shown in the action of sulphuric acid upon sodium chloride. Under these circumstances hydrochloric acid is given off, and the sulphate of the metal with which the chlorine was in combination is formed. In general, the reaction is represented by such equations as the following:

$$2MCl + H_2SO_4 = M_2SO_4 + 2HCl;$$
$$M''Cl_2 + H_2SO_4 = M''SO_4 + 2HCl; \text{ etc.}$$

Under ordinary circumstances, chlorides are not decomposed by any acid except sulphuric acid.

**The So-called Double Chlorides and Similar Compounds of Fluorine, Bromine, and Iodine.**—Many chlorides combine with the chlorides of the stronger metals, like sodium and potassium, forming well-characterized compounds. Generally, these double chlorides are analogous to the oxygen salts in composition, differing from them only by containing two atoms of chlorine in the place of each of the oxygen atoms. As examples of these salts of the *chloro-acids* those which are formed by the chlorides of platinum, antimony, chromium, and gold may be mentioned. Platinic chloride, $PtCl_4$, combines with other chlorides, forming salts of the general composition expressed by the formula $PtCl_4 + 2MCl$, or $M_2PtCl_6$.

**Different Chlorides of the Same Metal.**—Just as sulphur, selenium, phosphorus, and the other acid-forming elements combine with chlorine and the other members of the chlorine group in more than one proportion, so many of the metals combine with the members of the chlorine group in more than one proportion. Thus, mercury forms the two chlorides, $HgCl_2$ and $HgCl$, known respectively as mercuric and mercurous chlorides; iron forms the two chlorides $FeCl_3$ and $FeCl_2$, known as ferric and ferrous chlorides; and tin forms stannic chloride, $SnCl_4$, and stannous chloride, $SnCl_2$. The conversion of a higher chloride into a lower one is called an act of re-

duction. The change can generally be effected by means of nascent hydrogen:

$$SnCl_4 + 2H = SnCl_2 + 2HCl.$$
$$FeCl_3 + H = FeCl_2 + HCl.$$

The conversion of a lower chloride into a higher one is generally spoken of as an act of oxidation, for the reason that it is commonly effected by the action of oxygen. Thus the convenient way to transform ferrous chloride into ferric chloride is to treat it in solution in hydrochloric acid with an oxidizing agent, when a double action takes place, as represented in the following equation:

$$2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O.$$

The same change can be effected by the direct action of chlorine:

$$FeCl_2 + Cl = FeCl_3.$$

In this case it would obviously be incorrect to speak of the process as one of oxidation.

Another method of reduction, besides that referred to above involving the action of nascent hydrogen, is that illustrated in the equation

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4.$$

In this case mercuric chloride is changed to mercurous chloride by the action of stannous chloride. The latter unites with chlorine so readily that it extracts it from some other chlorides, and is itself transformed into stannic chloride. While, therefore, we say that the stannous chloride reduces the mercuric chloride, it is equally true to say that the mercuric chloride *chlorinates* the stannous chloride.

**Oxides.**—The oxides occur extensively in nature, and are among the most common ores of some of the important metals. The oxides of iron, tin, and manganese, for example, occur in nature. They can be made by oxidizing the metals, by heating nitrates, carbonates, and hydroxides, and by heating some sulphides in contact with the air.

When magnesium is burned it is converted into magnesium oxide:

$$Mg + O = MgO.$$

When lead nitrate is heated it gives off oxygen and an oxide of nitrogen, and lead oxide is left behind:

$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$

When calcium carbonate is heated it yields calcium oxide and carbon dioxide:

$$CaCO_3 = CaO + CO_2.$$

When aluminium hydroxide, $Al(OH)_3$, is heated it loses water, and aluminium oxide is left behind:

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

The sulphide of iron, when heated in contact with the air, or "roasted," is converted into ferric oxide and sulphur dioxide.

Most of the oxides of the metals are insoluble in water. Those of Group A, Family I, are soluble, but are converted by water into the corresponding hydroxides.

The oxides are generally acted upon by acids forming the corresponding salts. If the salt with a certain acid is insoluble, the salt is not formed by the action of that acid on the oxide unless the acid or its anhydride is fusible and not volatile, when by fusing them together the salt is formed.

**Different Oxides of the Same Metal.**—Just as there are different chlorides of the same metal, so there are different oxides, and indeed there is greater variety among these than among the chlorides. Iron forms three oxides, ferric oxide, $Fe_2O_3$, ferroso-ferric oxide, $Fe_3O_4$, and ferrous oxide, FeO; mercury forms the two oxides HgO and $Hg_2O$; etc. The lower oxides are converted into the higher by oxidation, and the higher into the lower by reduction. The higher oxides of several of the metals are acidic. This is markedly so in the case of chromium and manganese.

**Hydroxides.**—The hydroxides of the alkali metals and of barium, calcium, and strontium are formed by treating oxides with water, all hydroxides can be made by decomposing salts by adding soluble hydroxides to their solutions. In general, whenever a salt is decomposed by a strong base, the base of the salt separates in the form of the hydroxide. The formation of a hydroxide by the action of water on an oxide is well illustrated by the action of water on lime or calcium oxide, a process familiarly known as *slaking:*

$$CaO + H_2O = Ca(OH)_2.$$

Most of the hydroxides of the metals are insoluble in water. When a soluble hydroxide is added to a solution containing a metal whose hydroxide is insoluble, the latter is precipitated. Thus, when a solution of sodium hydroxide is added to a solution of a magnesium salt, magnesium hydroxide is precipitated:

$$MgSO_4 + 2NaOH = Na_2SO_4 + Mg(OH)_2.$$

So, also, when a solution of a ferric salt is treated with sodium hydroxide, a precipitate of ferric hydroxide is formed:

$$FeCl_3 + 3NaOH = 3NaCl + Fe(OH)_3.$$

Only the hydroxides of the members of the potassium family, and some of the members of the calcium family, are soluble in water. The hydroxides of sodium and potassium are called *alkalies.* The solution of ammonia in water acts like a soluble hydroxide, and probably contains ammonium hydroxide, $NH_4(OH)$, formed by the action of water on ammonia:

$$NH_3 + H_2O = NH_4(OH).$$

Now, when any one of the soluble hydroxides is added to a salt containing any metal that does not belong to the potassium or calcium family, an insoluble compound is formed.

**Decomposition of Salts by Bases.**—The decomposition

of salts by bases is analogous to the decomposition by acids. When a soluble base acts upon a salt, there are four kinds of action possible:

1. The base from which the salt is derived may be volatile, or may break up, yielding a volatile product.

In this case, decomposition takes place and the volatile base is given off. This is not a common case except among the compounds of carbon. The one illustration which we have had is the decomposition of ammonium salts by calcium hydroxide and sodium hydroxide, when the volatile compound ammonia, $NH_3$, is given off.

2. The hydroxide, or base from which the salt is derived, may be insoluble or difficultly soluble in water, and not volatile.

In this case, if both the salt and the base are in solution, decomposition takes place, and the insoluble or difficultly soluble hydroxide, or base, is precipitated. This has already been illustrated.

3. The base from which the salt is derived may be soluble and not volatile.

This is the case, for example, when sodium hydroxide is added to a solution of potassium nitrate. Here sodium nitrate, potassium nitrate, sodium hydroxide, and potassium hydroxide may all be present in the solution, and investigation has shown that all are present and that the quantity of each depends upon the masses of the substances brought together, and upon their affinities.

4. The fourth case is that in which a soluble hydroxide forms an insoluble salt with the acid of a soluble salt, leaving a soluble hydroxide in solution.

This is illustrated by the action of calcium hydroxide on a solution of sodium carbonate, when insoluble calcium carbonate is thrown down, and sodium hydroxide remains in solution, as represented in the equation

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

Some basic hydroxides, which are precipitated by soluble hydroxides, have a weak acid character, and, after they are precipitated, they redissolve in an excess of the soluble

hydroxide. This is true, for example, of the hydroxides of aluminium, chromium, and lead. The salt-like compounds thus formed are generally quite unstable. The precipitation and subsequent solution of the hydroxides of the three metals named take place thus:

$$AlCl_3 + 3NaOH = Al(OH)_3 + 3NaCl;$$
$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O;$$
$$CrCl_3 + 3NaOH = Cr(OH)_3 + 3NaCl;$$
$$Cr(OH)_3 + 3NaOH = Cr(ONa)_3 + 3H_2O;$$
$$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3;$$
$$Pb(OH)_2 + 2NaOH = Pb(ONa)_2 + 2H_2O.$$

In some cases when a soluble hydroxide is added to a salt, an oxide is precipitated instead of the hydroxide. This is analogous to the formation of an anhydride of an acid instead of the acid itself, as when carbonates, sulphites, and nitrites are decomposed.

When a silver salt is treated with a soluble hydroxide, silver oxide is at once precipitated. The same is true of mercury salts:

$$2AgNO_3 + 2KOH = Ag_2O + H_2O + 2KNO_3;$$
$$HgCl_2 + 2NaOH = HgO + H_2O + 2NaCl.$$

It is probable that the first product is the hydroxide, and that this breaks down into the oxide and water:

$$2AgNO_3 + 2KOH = 2AgOH + 2KNO_3;$$
$$2AgOH = Ag_2O + H_2O;$$
$$HgCl_2 + 2NaOH = Hg(OH)_2 + 2NaCl;$$
$$Hg(OH)_2 = HgO + H_2O.$$

Some hydroxides are converted into the oxides by simply boiling the liquids in which they are suspended. Thus, when a salt of copper is treated with a soluble hydroxide, copper hydroxide is first precipitated; but if the solution in which it is suspended is boiled, it is soon changed to the oxide:

$$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2;$$
$$Cu(OH)_2 = CuO + H_2O.$$

The hydroxides corresponding to some of the higher oxides of the metals, as those of chromium and manganese, are acids.

The hydroxides of most of the metals are decomposed by heat into water and the corresponding oxides. Those of the alkali metals, as potassium and sodium, are, however, not decomposed by heat.

**Sulphides.**—Many sulphides are found in nature as, for example, iron pyrites, $FeS_2$; lead sulphide, or galenite, PbS; copper pyrites, $FeCuS_2$; etc. They are made in the laboratory by heating metals with sulphur; by treating solutions of salts with hydrogen sulphide; by treating solutions of salts with soluble sulphides; and by reducing sulphates. Attention has been called to the fact that the sulphides are analogous in composition to the oxides, and that they are to be regarded as salts of hydrogen sulphide formed by substituting metals for the hydrogen of the acid.

The formation of sulphides by the direct combination of sulphur with the metals is shown in the formation of lead sulphide and cuprous sulphide:

$$Pb + S = PbS;$$
$$2Cu + S = Cu_2S.$$

The formation of sulphides by the action of hydrogen sulphide upon solutions of salts was discussed at some length under Hydrogen Sulphide (which see). The extensive use made of this reaction in chemical analysis was also referred to.

The action of soluble sulphides or solutions of salts is in general the same as that of hydrogen sulphide, but in some cases, in which the former will not act, the latter will. Thus, hydrogen sulphide will not precipitate iron sulphide from a solution of an iron salt, because iron sulphide is easily acted upon by dilute acids. When, for example, hydrogen sulphide is passed into a solution of ferrous chloride, it naturally tends to form the sulphide FeS:

$$FeCl_2 + H_2S \rightleftarrows FeS + 2HCl.$$

But, as the action is reversible and hydrogen sulphide is a gas it is evident that equilibrium would occur and no precipitate of ferrous sulphide could form.

If, however, a soluble sulphide, as sodium or ammonium sulphide, is added to a solution of an iron salt, iron sulphide is precipitated, as in this case no free acid is formed. Thus, when ferrous chloride and ammonium sulphide are brought together the reaction takes place as represented in the equation

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl.$$

In ammonium chloride the ferrous sulphide is not soluble.

The formation of a sulphide by reduction of a sulphate is illustrated by the formation of barium sulphide by heating a mixture of barium sulphate and charcoal:

$$BaSO_4 + 4C = BaS + 4CO.$$

The sulphides of the alkali metals are soluble in water. Those of the other metals are insoluble. It should be remarked, however, that the sulphides of aluminium and chromium, though they can be made in absence of water, are instantly hydrolyzed by water, thus:

$$Al_2S_3 + 3H_2O = 2Al(OH)_3 + 3H_2S.$$

Hence, a solution of an alkali sulphide precipitates aluminium and chromium hydroxides from solutions of their salts:

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 6NH_4Cl + 3H_2S.$$

Barium sulphide is decomposed by water, and probably magnesium sulphide also.

The sulphides are stable when heated without access of air; but if heated in the air they are converted into oxides of the metals and sulphur dioxide, or, in some cases, they take up oxygen and are converted into sulphates. The conversion of sulphides into oxides and sulphur dioxide

by heating them in contact with the air has been repeatedly referred to. The process is carried on on the large scale in the preparation of iron ores for reduction, and is called *roasting*. The conversion of a sulphide into a sulphate by heating is a simple process of oxidation. Copper sulphide is converted into the sulphate when heated for some time in the air:

$$CuS + 4O = CuSO_4.$$

This is the reverse of the reaction mentioned by which a sulphate is converted into a sulphide by reduction.

Some sulphides, as those of sodium, potassium, and ammonium, take up sulphur in much the same way that they take up oxygen, and form the polysulphides. The two reactions appear to be analogous:

$$K_2S + 4O = K_2SO_4;$$
$$K_2S + 4S = K_2SS_4, \text{ or } K_2S_5.$$

**Hydrosulphides.**—The hydrosulphides bear the same relation to the sulphides that the hydroxides bear to the oxides. They are not, however, as numerous nor as easily obtained as the hydroxides.

The only hydrosulphides known are derived from the members of the potassium and calcium groups, and these are soluble. They are formed by saturating solutions of the corresponding hydroxides with hydrogen sulphide. Potassium hydrosulphide is formed thus:

$$KOH + H_2S = KSH + H_2O.$$

Ammonium hydrosulphide is formed thus:

$$NH_4OH + H_2S = NH_4SH + H_2O.$$

It also appears probable that whenever a sulphide dissolves in water it is converted into a hydrosulphide and a hydroxide. Thus it seems to be true that potassium sulphide is converted into the hydrosulphide and hydroxide:

$$K_2S + H_2O = KSH + KOH.$$

**Sulpho-salts.**—The relation of the sulpho-salts to the sulphides is like that of the ordinary oxygen salts to the oxides, and that of the chloro-salts, or double chlorides, to the chlorides. They are formed by dissolving the sulphides of certain metals, particularly tin, arsenic, and antimony, in the sulphides of the members of the potassium group:

$$As_2S_3 + 3K_2S = 2K_3AsS_3;$$
$$As_2S_5 + 3K_2S = 2K_3AsS_4;$$
$$SnS_2 + K_2S = K_2SnS_3, \text{ etc.}$$

These sulpho-salts are decomposed by the ordinary acids, the insoluble sulphides being precipitated thus:

$$2K_3AsS_3 + 6HCl = As_2S_3 + 6KCl + 3H_2S;$$
$$2K_3AsS_4 + 6HCl = As_2S_5 + 6KCl + 3H_2S.$$

**General Remarks regarding Binary Compounds.**—Of the binary compounds, most of the oxides, sulphides, halides, antimonides, arsenides, carbides, and silicides are fairly stable substances when exposed to air and moisture. Some of these substances, however, are hydrolyzed by water, yielding generally hydroxides, or, in the case of the halides, basic salts. Examples: calcium oxide, aluminium sulphide, bismuth chloride.

All hydrides and nitrides of the metals, and the oxides, carbides, borides, and silicides of the alkali and alkaline earth metals are completely hydrolyzed by water, yielding hydroxides.

Moissan has made a study of these unstable binary compounds. His work with the electric furnace shows that these substances are generally formed at high temperatures, and are stable under conditions where nearly all the ternary compounds break down. Hence, if at sufficiently high temperature a metal in excess is heated with oxygen and silicon no silicate will be formed but a mixture of oxide and silicide. Heated with oxygen and hydrogen no hydroxide is formed but a mixture of oxide and hydride. Heated with nitrogen and oxygen no nitrate is formed but a mixture of nitride and oxide.

When hydrides are hydrolyzed, hydroxide and hydrogen are formed:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

When nitrides are hydrolyzed they yield hydroxides and ammonia: $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$.

When carbides are hydrolyzed they yield hydroxides and hydrocarbons: $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. The hydrocarbons in contact with heated oxygen yield carbon dioxide and water: $C_2H_2 + 5O = 2CO_2 + H_2O$. Carbon dioxide in contact with bases yields carbonates: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$.

When silicates are hydrolyzed they yield hydroxides and hydrides of silicon:

$$Ca_2Si + 4H_2O = 2Ca(OH)_2 + SiH_4.$$

Silicon hydride, $SiH_4$, is unstable and in contact with heated oxygen burns to silicic acid:

$$SiH_4 + 2O_2 = SiO_3H_2 + H_2O.$$

Silicic acid acts on hydroxides forming silicates:

$$SiO_3H_2 + Ca(OH)_2 = SiO_3Ca + 2H_2O.$$

When sulphides are hydrolyzed they yield hydroxides and hydrogen sulphide:

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

Hydrogen sulphide in contact with heated oxygen ultimately forms sulphuric acid:

$$H_2S + 2O_2 = H_2SO_4.$$

When borides are hydrolyzed, hydroxides and boron hydride are formed:

$$Ca_3B_2 + 6H_2O = 3Ca(OH)_2 + 2BH_3.$$

Boron hydride burns in heated oxygen forming boric acid:

$$2BH_3 + 3O_2 = 2B(OH)_3.$$

Moissan points out the significance of these reactions as bearing on the former condition of the earth and the present condition of the sun and stars. To say the least it is highly probable that the crust of the earth, in its former conditions at temperatures above the dissociation point of water, was made up of elements and of binary compounds. As the earth cooled to temperatures at whieh the oxygen and hydrogen could unite to form water the hydrolysis of some of these binary compounds, and the action of acids upon others, would by the reactions shown above form the silicates, carbonates, sulphates, etc., which are the principal constituents of the crust of the earth at the present time.

When we bear in mind the great heat set free by the formation of water from its elements, and by the decomposition of binary compounds by hydrolysis, it is evident that the cooling of the earth's crust must have been slow, and it must have been accompanied by violent reactions.

Moissan also points out that the present condition of the sun and stars, and some of the phenomena occurring, such as the enormous jets of hydrogen projected beyond the sun's atmosphere, and the sudden blazing up of cooling stars are in harmony with these conceptions.

**Nitrates.**—The nitrates are formed by dissolving the metals in nitric acid, and by treating oxides, hydroxides, carbonates, and some other easily decomposed salts with nitric acid. The action of nitric acid upon metals was discussed under the head of Nitric Acid (which see). It was pointed out that the acid gives up a part of its oxygen to the metal and forms different oxides, according to the conditions. Thus, when the acid acts upon copper the main product of the reduction is nitric oxide, but by changing the concentration of the acid a considerable quantity of nitrous oxide is formed. When zinc is dissolved in nitric acid a part of the acid is reduced to ammonia.

The nitrates are soluble in water, and all are decomposed by heat. Some of them when heated lose only a

third of their oxygen and are reduced to nitrites. This is true of potassium nitrate, the decomposition of which is represented by the equation

$$KNO_3 = KNO_2 + O.$$

Most of the nitrates, however, are decomposed further, forming oxides. This has been shown in the case of lead nitrate, which when heated is converted into lead oxide, while nitrogen peroxide and oxygen are given off:

$$Pb(NO_3)_2 = PbO + 2NO_2 + O.$$

If the oxide of the metal is decomposed by heat, as in the case of mercury, of course the product will be the metal.

**Chlorates.**—These salts, except potassium chlorate, are not commonly met with. Potassium chlorate is manufactured in large quantity, and the other chlorates are generally made from it. The chlorates are soluble in water, and are decomposed by heat more easily than the nitrates are. They are first converted into perchlorates, and these are further decomposed by higher heat into chlorides and oxygen.

The *hypochlorites* are formed by treating some of the metallic hydroxides in dilute solution with chlorine. This has been illustrated in the formation of "bleaching powder," which contains calcium hypochlorite or a compound closely related to it. The hypochlorites, like the chlorates, are decomposed by heat.

**Sulphates.**—The general relations of the sulphates to sulphuric acid were treated of under Sulphuric Acid (which see). Some of these salts occur in nature in large quantity, as those of calcium and barium. The former is known as *gypsum*, the latter as *barytes* or *heavy spar*. Sulphates are made by treating metals, metallic hydroxides or oxides, carbonates, etc., with sulphuric acid; and by treating a solution containing a metal whose sulphate is insoluble, with sulphuric acid or a soluble sulphate.

Zinc and iron give hydrogen and a sulphate when treated with sulphuric acid:

$$Zn + H_2SO_4 = ZnSO_4 + H_2;$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

This kind of action takes place whenever a metal is dissolved in sulphuric acid at the ordinary temperature. If, however, the temperature is raised the displaced hydrogen acts upon some of the sulphuric acid, or the metal extracts some of the oxygen of the acid, reducing it partly to sulphurous acid, when sulphur dioxide is given off. This happens in the case of copper, as has been pointed out. It may be represented either by these equations:

$$Cu + H_2SO_4 = CuSO_4 + H_2;$$
$$H_2SO_4 + 2H = SO_2 + 2H_2O;$$

or by these:

$$Cu + H_2SO_4 = CuO + SO_2 + H_2;$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

The action of sulphuric acid on metallic hydroxides has been fully described.

Most sulphates are soluble in water. The sulphates of barium, strontium, and lead are insoluble in water, and the sulphate of calcium is difficultly soluble. Therefore, if sulphuric acid or a soluble sulphate is added to a solution containing one of the metals, barium, strontium, or lead, a precipitate is formed. A precipitate is also formed when a concentrated solution of a calcium salt is treated in the same way.

When heated with charcoal in the reducing flame of the blowpipe, sulphates are reduced to sulphides:

$$K_2SO_4 + 4C = K_2S + 4CO, \text{ or}$$
$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

*Sulphites* are made from sodium or potassium sulphite which are made by treating sodium or potassium hydroxide in solution with sulphur dioxide:

$$2NaOH + SO_2 = Na_2SO_3 + H_2O.$$

All sulphites are decomposed by the common acids, sulphur dioxide being given off:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

The sulphites are changed to sulphates by oxidation. Thus sodium sulphite is changed to the sulphate when its solution is allowed to stand in contact with the air:

$$Na_2SO_3 + O = Na_2SO_4.$$

The sulphites, like the sulphates, are reduced to sulphides.

**Carbonates.**—Many carbonates are found in nature, some of them in great abundance and widely distributed. The principal one is calcium carbonate. They are made by passing carbon dioxide into solutions of hydroxides, and by adding soluble carbonates to solutions of salts containing metals whose carbonates are insoluble.

The formation of carbonates by the action of carbon dioxide on a solution of a hydroxide is illustrated in the case of potassium hydroxide:

$$2KOH + CO_2 = K_2CO_3 + H_2O.$$

The formation of calcium carbonate takes place in the same way, but the carbonate formed is insoluble:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

If in either case the action is continued, the normal carbonate first formed is converted into acid carbonate:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3;$$
$$CaCO_3 + CO_2 + H_2O = \left.\begin{matrix} Ca \\ H_2 \end{matrix}\right\} (CO_3)_2.$$

All normal carbonates except those of the members of the potassium family are insoluble, and are decomposed by heat into carbon dioxide and the oxide of the metal. The decomposition of calcium carbonate into lime and carbon dioxide is an example:

$$CaCO_3 = CaO + CO_2.$$

When a soluble carbonate is added to a solution of a calcium, barium, or strontium salt, the corresponding insoluble carbonates are precipitated. When a magnesium salt is treated with a soluble carbonate, however, a basic carbonate is precipitated.

**Phosphates.**—Calcium phosphate is very abundant in nature, and a few other phosphates are also found. The methods used for making phosphates are the same as those used in making salts in general.

The normal phosphates of all the metals except the members of the potassium family are insoluble in water. The normal phosphates, as a rule, are not changed by heat. The secondary phosphates, such as secondary sodium phosphates, $HNa_2PO_4$, lose water when heated, and yield pyrophosphates:

$$2HNa_2PO_4 = \underset{\text{Sodium pyrophosphate.}}{Na_2P_2O_7} + H_2O.$$

Those phosphates in which only one-third of the hydrogen is replaced by metal—as, for example, primary sodium phosphate, $H_2NaPO_4$—lose water when heated, and yield metaphosphates:

$$H_2NaPO_4 = \underset{\text{Sodium metaphosphate.}}{NaPO_3} + H_2O.$$

Neither the pyrophosphates nor the metaphosphates are changed by heat.

**Silicates.**—The silicates are very widely distributed in nature. Those which are most abundant are the *feldspars* and their decomposition-products. The principal feldspar is a complex silicate of aluminium and potassium, of the formula $KAlSi_3O_8$, derived from the polysilicic acid $H_4Si_3O_8$, which is formed from three molecules of normal silicic acid by the loss of four molecules of water:

$$3Si(OH)_4 = H_4Si_3O_8 + 4H_2O.$$

Silicates can be made by heating together, at a high tem-

perature, silicon dioxide, in the form of sand, and basic oxides or carbonates:

$$CaO + SiO_2 = CaSiO_3;$$
$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

Only the silicates of the members of the potassium group are soluble in water. When these are treated in solution with dilute acids, they are decomposed, as has been explained under Silicic Acid (which see).

Some silicates, which are insoluble in water, are decomposed by the ordinary acids, such as sulphuric and hydrochloric acids, the silicic acid separating as a difficultly soluble substance, which, if dried on the water-bath, becomes insoluble.

Many silicates, which are not acted upon by strong acids, are decomposed by fusion with sodium or potassium carbonate, when the silicate of potassium or sodium and the oxide of the metal contained in the silicate are formed. Silicates which are not decomposed in either of the ways mentioned yield to hydrofluoric acid. The action consists in the formation of the gas, silicon tetrafluoride, $SiF_4$, and the fluorides of the metals present. Thus, the reaction in the case of feldspar takes place in accordance with the equation,

$$KAlSi_3O_8 + 16HF = KF + AlF_3 + 3SiF_4 + 8H_2O.$$

The silicon fluoride is given off as a gas, and the fluorides formed are soluble in water. Hence, hydrofluoric acid is said to dissolve the silicates.

## EXPERIMENTS.

### Chlorides, Bromides, and Iodides.

Experiment 206.—Dissolve a small crystal of silver nitrate in pure water. Add to a small quantity of this solution in a test-tube a few drops of dilute hydrochloric acid. The white substance thus precipitated is silver chloride, AgCl. To another small portion of the solution add a few drops of a dilute solution of common salt, or sodium chloride, NaCl. The white substance produced in this case is also silver chloride. Add ammonia to each tube. If sufficient is

added the precipitates will dissolve. On adding enough hydrochloric acid to these solutions to combine with all the ammonia the silver chloride is again thrown down. On standing exposed to the light both precipitates change color, becoming finally dark violet. The reactions involved in the above experiments are these. In the first place, when hydrochloric acid is added to silver nitrate this reaction takes place:

$$\overset{+}{\mathrm{Ag}},\overset{-}{\mathrm{NO_3}} + \overset{+}{\mathrm{H}},\overset{-}{\mathrm{Cl}} = \mathrm{AgCl} + \overset{+}{\mathrm{H}},\overset{-}{\mathrm{NO_3}}.$$

When sodium chloride is added this reaction takes place:

$$\overset{+}{\mathrm{Ag}},\overset{-}{\mathrm{NO_3}} + \overset{+}{\mathrm{Na}},\overset{-}{\mathrm{Cl}} = \mathrm{AgCl} + \overset{+}{\mathrm{Na}},\overset{-}{\mathrm{NO_3}}.$$

In the first reaction the ions of nitric acid are formed; in the second, the sodium and silver exchange places. In addition to the insoluble silver chloride, there are formed at the same time the ions of the soluble salt, sodium nitrate. On adding ammonia the silver chloride forms with it a compound which is soluble in water; and on adding an acid, the ammonia combines with it, leaving the silver chloride uncombined and therefore insoluble.

Extensive use is made of insoluble compounds for the purpose of detecting substances in analysis. The only insoluble chlorides are those of silver, lead, and mercury.* If, therefore, on adding hydrochloric acid or a soluble chloride to a solution, a precipitate is formed, the conclusion is justified that one or more of the three metals—silver, lead, or mercury—is present. By taking account of the differences in the properties of these chlorides it is not difficult to decide of which of them a precipitate consists.

## Hydroxides.

Experiment 207.—To some pieces of freshly-burnt lime add enough cold water to cover it. The action which takes place is represented by the equation

$$\mathrm{CaO} + \mathrm{H_2O} = \mathrm{Ca(OH)_2}.$$

The process is known as slaking.

Experiment 208.—To a small quantity of a dilute solution of magnesium sulphate add a dilute solution of caustic soda. The white precipitate is magnesium hydroxide. [Would you expect this precipitate to be soluble in sulphuric acid? in hydrochloric acid? in nitric acid?] The answers follow from these considerations: When acids act upon hydroxides, salts are formed; magnesium sulphate is soluble, as is seen by the fact that we started with a solution of this salt; the only insoluble chlorides are those of silver, lead, and mercury; all nitrates are soluble.

* There are two chlorides of mercury. Only one of them, mercurous chloride, $\mathrm{HgCl}$, is insoluble.

When a solution of an iron salt is treated with sodium hydroxide a precipitate of iron hydroxide is formed:

$$FeCl_3 + 3NaOH = FeO_3H_3 + 3NaCl.$$

EXPERIMENT 209.—To a dilute solution of ferric chloride add caustic soda. The reddish precipitate formed is ferric hydroxide. [From the general statements made above, would you expect this precipitate to be soluble in hydrochloric acid? in nitric acid? Try each. Is it soluble in sulphuric acid?]

EXPERIMENT 210—Add to a solution of an aluminium salt sodium hydroxide. After a precipitate is formed continue to add the sodium hydroxide. Perform similar experiments with a chromium and with a lead salt. Boil each of the solutions obtained. Treat a solution of copper sulphate with sodium hydroxide in the cold. Heat.

## SULPHATES.

EXPERIMENT 211.—Make a dilute solution of barium chloride, of lead nitrate, of strontium nitrate. To a small quantity of each in a test-tube add a little sulphuric acid. [What remains in solution?] Make a somewhat concentrated solution of calcium chloride. To this add sulphuric acid. [What is in solution?] Add more water, and see whether the precipitate will dissolve. The formulas of the salts used in the experiments are barium chloride, $BaCl_2$; lead nitrate, $Pb(NO_3)_2$; strontium nitrate, $Sr(NO_3)_2$. [Write the equations expressing the reactions.] If to the solutions of the salts a soluble sulphate is added instead of sulphuric acid, the same insoluble sulphates will be formed. The sulphates of iron, copper, sodium, and potassium are among the soluble sulphates. Make dilute solutions of small quantities of each of these, and add them successively to the solutions of barium chloride, lead nitrate, and strontium nitrate. The formula of iron sulphate is $FeSO_4$; of copper sulphate, $CuSO_4$; of sodium sulphate, $Na_2SO_4$; and of potassium sulphate, $K_2SO_4$. Write the equations representing the reactions which take place in the above experiments. It need hardly be explained that the action consists in an exchange of places on the part of the metals. Thus, when the soluble salt, iron sulphate, $FeSO_4$, is brought together with the soluble salt, barium chloride, $BaCl_2$, the insoluble salt barium sulphate, $BaSO_4$, and the soluble salt, ferrous chloride, $FeCl_2$, are formed:

$$FeSO_4 + BaCl_2 = FeCl_2 + BaSO_4.$$

## REDUCTION OF SULPHATES TO SULPHIDES.

EXPERIMENT 212.—Mix and moisten a little sodium sulphate and finely-powdered charcoal. Heat the mixture for some time in the reducing flame. After cooling scrape off the salt, dissolve it in a

few cubic centimeters of water, and filter through a small filter. If the change to the sulphide has taken place, sodium sulphide, $Na_2S$, is in solution. A solution of a sulphide when added to a solution containing copper gives a black precipitate of copper sulphide. Try this; also try the action on the solution of the salt of copper of some of the sulphate from which the sulphide was made.

## Carbonates.

Experiment 213.—The formation of carbonates by the addition of soluble carbonates to solutions of salts of metals whose carbonates are insoluble, is illustrated by the following experiments: Make solutions of copper sulphate, iron sulphate, lead nitrate, silver nitrate, calcium chloride, barium chloride. Add to each a little of a solution of a soluble carbonate, as sodium carbonate, potassium carbonate, ammonium carbonate. Note the result in each case. Filter off all the precipitates and prove that they are carbonates. This may be done by treating them with dilute acids, which decompose them, causing an evolution of carbon dioxide, which can be detected by passing a little of it into lime-water. In some of the cases mentioned the insoluble salts formed are basic carbonates, as, for example, those of copper and magnesium. The salts of silver, calcium, and barium are the normal carbonates $Ag_2CO_3$, $BaCO_3$, and $CaCO_3$.

## CHAPTER XXIV.

### ELEMENTS OF FAMILY I, GROUP A : THE ALKALI METALS:—LITHIUM.—SODIUM.—POTASSIUM.—RUBIDIUM.—CAESIUM.—AMMONIUM.

**General.**—The elements of this group which are most abundant in nature are sodium and potassium. While lithium occurs in considerable quantity, the two remaining elements, rubidium and cæsium, have been found in only very small quantities. They are all strongly basic, their hydroxides being the strongest bases known. They form well-characterized salts with all acids, and as a rule their salts are very stable. In all their compounds they act as univalent elements, except in their peroxides. The general formulas of some of the principal compounds are as follows:

$$MCl,\ M_2O,\ M_2S,\ M(OH),\ MNO_3,\ M_2SO_4,\ \text{etc.}$$

The valence of the members of the group towards other elements is, in general, constant.

The relations between the atomic weights are interesting. That of sodium, 23.05, is very nearly half the sum of those of lithium, 7.03, and potassium, 39.15. We have

$$\frac{7.03 + 39.15}{2} = 23.09.$$

So, also, that of rubidium, 85.5, is approximately half the sum of those of potassium, 39.15, and cæsium, 132.9.

$$\frac{39.15 + 132.9}{2} = 86.03.$$

The specific gravity of these elements increases with

the atomic weight; and their melting-points become lower as the atomic weights become higher.

| | At. Wt. | Sp. Grav. | M. P. |
|---|---|---|---|
| Lithium..... | 7.03 | 0.594 | 180° |
| Sodium ..... | 23.05 | 0.972 | 95.6° |
| Potassium..... | 39.15 | 0.865 | 62.5° |
| Rubidium ..... | 85.5 | 1.52 | 38.5° |
| Cæsium.... .... | 132.9 | ? | 26.5° |

The regularity is complete in the case of the melting-points, but in respect to the specific gravities sodium is an exception to the rule. As sodium and potassium and their compounds are much more commonly met with than the other members of the group, these will form the chief subject of this chapter.

## Potassium, K (At. Wt. 39.15).

**Occurrence.**—Potassium is a constituent of many minerals, particularly of feldspar, the common variety of which, as has already been explained, is a complex silicate of aluminium and potassium. It is found also in combination with chlorine as sylvite, and with chlorine and magnesium as carnallite particularly in the great Stassfurt deposits; with sulphuric acid and aluminium, as alum; with nitric acid, as saltpetre or potassium nitrate; and in other forms. The natural decomposition of minerals containing potassium gives rise to the presence of this metal in various forms of combination everywhere in the soil. It is taken up by the plants; and, when vegetable material is burned, the potassium remains behind, chiefly as potassium carbonate. When wood-ash is treated with water the potassium carbonate is dissolved, and it can be obtained in an impure state by evaporating the solution. The substance thus obtained is called *potash*. In the juice of the grape there is contained a salt of potassium, mono-potassium tartrate, which is deposited in large quantity from wine. This is commonly called "crude tartar."

**Preparation.**—Potassium was first prepared by Davy in the year 1807, by the action of a powerful electric current on potassium hydroxide. It was then for many years prepared by heating to a high temperature a mixture of potassium carbonate and carbon, obtained by heating in a closed vessel ordinary mono-potassium tartrate deposited from wine:

$$K_2CO_3 + 2C = 2K + 3CO.$$

The metal is now prepared by electrolysis of potassium hydroxide or potassium chloride.

**Properties.**—Potassium is a light substance, which floats on water. Its freshly cut surface has a bright metallic lustre, almost white; it acts energetically upon water, causing the evolution of hydrogen, which, together with some of the potassium, burns, while potassium hydroxide is formed at the same time. This reaction has been studied in connection with hydrogen. In consequence of its action upon water, potassium cannot be kept in the air. It is kept under some oil, as petroleum, upon which it does not act. In an atmosphere upon which it does not act, as, for example, hydrogen, it can be distilled. Its vapor is green. Its specific gravity is 0.865; its melting-point 62.5°; its boiling-point about 670°. It combines with chlorine and bromine with great energy, and has the power to extract chlorine from its compounds. It can, therefore, be used for the purpose of isolating some elements, as for example, magnesium and aluminium, whose oxygen compounds cannot be reduced by the ordinary methods. As, however, sodium is generally used for this purpose instead of potassium, on account of its lower price, the action will be dealt with more at length under Sodium. Although the metal is converted into vapor, no reliable determination of the specific gravity of the vapor has been made, for the reason that the vessels which have been used for the purpose have always been acted upon, and the results thus vitiated.

**Potassium Hydride,** KH.—This compound is formed

by heating potassium in an atmosphere of hydrogen at about 360°. It forms a mass of white needles. It is easily decomposed.

**Potassium** { **Fluoride,** KF; **Chloride,** KCl; **Bromide,** KBr; **Iodide,** KI —Of these salts the only one that occurs in nature in quantity is the chloride. This is found in the great salt deposits at Stassfurt, Germany, and in some other localities in the form of the mineral *sylvite*, which is more or less impure potassium chloride. It is also found in the form of a compound containing magnesium, potassium, and chlorine, of the formula $MgCl_2.KCl + 6H_2O$, or $KMgCl_3 + 6H_2O$, known as *carnallite*.

The other salts of the group are made by the general methods for making salts, that is, by neutralizing the acids with the hydroxide or carbonate of potassium. It is, however, easier to make the iodide by other methods, and as there is a large demand for this salt for use in medicine and in the art of photography, several methods have been devised for its preparation. Of these, only one need be described. This consists in treating iron filings under water with iodine. Both the iron and iodine dissolve, forming ferrous iodide, $FeI_2$. If to the solution of this compound half as much iodine is added as has already been used in its preparation, ferroso-ferric iodide, $Fe_3I_8$, is formed and remains in solution. By adding a solution of potassium carbonate to this, reaction takes place as represented in the equation :

$$Fe_3I_8 + 4K_2CO_3 + 4H_2O = 8\ KI + Fe_3(OH)_8 + 4CO_2.$$

The hydroxide of iron is insoluble, and can be removed by filtration.

The fact that the specific gravity of hydrofluoric acid at a low temperature corresponds to the formula $H_2F_2$ makes it not improbable that potassium fluoride has the

formula $K_2F_2$. This appears still more probable from the fact that there is an acid potassium fluoride of the formula $KHF_2$, or KF + HF. Similar acid salts have not been obtained from the other acids of the group.

**Properties.**—All these salts are soluble, and crystallize well in cubes. The fluoride is the most easily soluble in water. If deposited from a water solution at the ordinary temperature the crystals have the composition, $KF + 2H_2O$, and are deliquescent. The iodide is soluble in 0.7 part of water at the ordinary temperature, and is also soluble in alcohol (40 parts). The bromide requires about $1\frac{1}{2}$ parts of water for solution at the ordinary temperature, and is but slightly soluble in alcohol. The chloride is soluble in 3 parts of water at the ordinary temperature, and is insoluble in alcohol. All are decomposed by sulphuric acid.

**Applications.**—Potassium chloride is extensively used for the purpose of making other potassium salts, as, for example, the nitrate and carbonate; the bromide is used in medicine; the iodide is used in medicine and in photography.

**Potassium Hydroxide,** KOH.—This well-known substance, commonly called caustic potash, is prepared by treating potassium carbonate in solution with calcium hydroxide in a silver or iron vessel. The reaction is based upon the fact that calcium carbonate is insoluble, and that potassium carbonate and calcium hydroxide are soluble:

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$

Potassium hydroxide is also prepared on the large scale by the action of the electric current on a solution of potassium chloride:

$$2KCl + 2H_2O = 2KOH + H_2 + Cl_2.$$

**Stassfurt Potash Industry.**—Practically all potassium hydroxide is now made from Stassfurt carnallite electrolytically. Indeed most of the potassium salts are made

from these deposits. The average yearly production of crude Stassfurt salts is shown in the following table:

| | | |
|---|---|---|
| Carnallite, $MgCl_3K$ | 1,816,733 | tons. |
| Kainite, $MgSO_4.KCl$ and Schönite, $K_2Mg(SO_4)_2$ | 1,450,020 | " |
| Sylvite, $KCl$ | 191,448 | " |
| Kieserite, $MgSO_2$ | 1,763 | " |

Nearly all the carnallite and kieserite are used for technical purposes.

**Properties of Potassium Hydroxide.**—It is a white brittle substance. In contact with the air it deliquesces, and absorbs carbon dioxide, being completely transformed into potassium carbonate. It is the strongest of the bases. It decomposes the salts of most other bases in solution in water.

Animal substances as, for example, the skin, are disintegrated by the hydroxide. It has a caustic action.

Instead of potassium hydroxide the corresponding sodium compound is used wherever this is possible, as the latter is cheaper. The chief application of the potassium compound outside of the laboratory is for making soft-soap. For this purpose fats are boiled with a solution of potassium hydroxide or carbonate.

**Potassium Oxide,** $K_2O$, is made by reducing saltpetre by metallic potassium: $2KNO_3 + 10K = 6K_2O + N_2$. It is a very unstable, white substance that absorbs oxygen at ordinary temperature with avidity. It is also formed by melting potassium hydroxide and metallic potassium together:

$$2K + 2KOH = 2K_2O + H_2.$$

With water it forms the hydroxide, with a marked evolution of heat:

$$K_2O + H_2O = 2KOH.$$

Potassium also forms other oxides of which the *peroxide* of the formula $KO_2$ is the best studied. This peroxide is an orange-yellow solid and is the final product of the combustion of potassium in the air or in oxygen. It gives up its oxygen very readily to substances which are capable of oxidation, acting so energetically upon some as to cause evolution of light.

**Potassium Hydrosulphide,** KSH, is analogous to potassium hydroxide. Just as the latter is made by the action of potassium on water, so the former can be made by the action of potassium on hydrogen sulphide:

$$K_2 + 2H_2S = 2KSH + H_2.$$

It is, however, obtained most readily by the action of hydrogen sulphide on a solution of potassium hydroxide:

$$KOH + H_2S = KSH + H_2O.$$

**Potassium Nitrate,** $KNO_3$.—This salt is commonly called *saltpetre.* Its occurrence in nature has already been referred to under Nitric Acid (which see). When refuse animal matter is left to undergo decomposition in the presence of bases, nitrates are always the end-products. They are consequently found very widely distributed in the soil. In the East Indies the potassium nitrate formed in the neighborhood of dwellings and stables is collected, and sent into the market. The process of nitrification was formerly carried on artificially on the large scale in the so-called "saltpetre plantations." In these, refuse animal matter was mixed with earthy material, wood ashes, etc., and piled up. These piles were moistened with the liquid products from stables. After the action had continued for two or three years the outer crust was taken off, and extracted with water. The solution thus obtained contained, besides potassium nitrate, calcium and magnesium nitrates. It was treated with a water-extract of wood ashes or with potassium carbonate, by which the calcium and magnesium were thrown down as carbonates. Practically all the saltpetre in the market is made from Chili saltpetre, or sodium nitrate, by treating it with potassium chloride, advantage being taken of the fact that sodium chloride is less soluble in hot water than potassium nitrate. Sodium nitrate and potassium chloride are dissolved in water in the proportion of their molecular weights, and the solution heated. When the solution is sufficiently concentrated, sodium chloride is deposited:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

This being removed, potassium nitrate crystallizes from the mother-liquors.

Potassium nitrate crystallizes in long rhombic prisms of a salty taste. Under some circumstances it crystallizes in rhombohedrons. When dissolved in water it causes a lowering of the temperature. At ordinary temperatures 100 parts of water dissolve from 20 to 30 parts of the salt; at 100°, 100 parts dissolve 247 parts.

**Applications.**—Potassium nitrate is used as an oxidizing agent in the laboratory, and in the manufacture of fireworks. Its chief use, however, is in the manufacture of gunpowder.

**Gunpowder.**—The value of gunpowder is due to the fact that it *explodes* readily, the explosion being a chemical change accompanied by a sudden evolution of gases. It is a mixture of saltpetre, charcoal, and sulphur. When heated, the saltpetre gives off oxygen and nitrogen; the oxygen combines with the charcoal, forming carbon dioxide and carbon monoxide; and the sulphur combines with the potassium, forming potassium sulphide. When a mixture of saltpetre and charcoal is burned, the reaction which takes place is this:

$$4KNO_3 + 5C = 3CO_2 + 2N_2 + 2K_2CO_3.$$

By adding the necessary quantity of sulphur the carbon dioxide, which would otherwise remain in combination with the potassium as potassium carbonate, is given off, and potassium sulphide formed:

$$2KNO_3 + 3C + S = 3CO_2 + N_2 + K_2S.$$

For this reaction the constituents should be mixed in the proportions:

| | |
|---|---|
| Saltpetre | 74.83 |
| Charcoal | 13.31 |
| Sulphur | 11.86 |
| | 100.00 |

This is approximately the composition of all powder.

When gunpowder explodes, the gases formed occupy about 280 times the volume occupied by the powder itself.

The use of gunpowder is decreasing rapidly. For guns and cannon it is practically entirely replaced by *smokeless powder* (which see), and for mining and blasting by gun-cotton, dynamite, and similar explosives.

**Potassium Nitrite,** $KNO_2$, is formed by heating the nitrate to a sufficiently high temperature. The reduction is, however, much facilitated by adding to the nitrate some easily oxidized metal, as lead or iron. When the gases formed by the action of arsenic trioxide on nitric acid are passed into potassium hydroxide, both the nitrite and nitrate are formed, and they can be separated by crystallization.

**Potassium Chlorate,** $KClO_3$.—The character of the reaction by which potassium chlorate is formed when chlorine acts upon a solution of potassium hydroxide has already been discussed (see p. 155). In the manufacture of the chlorate it is found advantageous to make calcium chlorate, and then to treat this with potassium chloride, when, at the proper concentration, potassium chlorate crystallizes out for the reason that it is less soluble than the salts which are brought together. The process in brief consists in passing chlorine into a solution of calcium hydroxide in which an excess of hydroxide is held in suspension. The first action results in the formation of calcium hypochlorite. When the solution of this salt is boiled it is decomposed, yielding the chlorate and chloride:

$$3Ca(OCl)_2 = Ca(O_3Cl)_2 + 2CaCl_2.$$

On now treating the solution with potassium chloride the following reaction takes place:

$$Ca(O_3Cl)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

Potassium chlorate crystallizes in lustrous crystals of the monoclinic system. Its taste is somewhat like that of saltpetre. It melts at a comparatively low temperature (334°), and at 352° begins to decompose, with evolution

of oxygen. At ordinary temperatures 100 parts of water dissolve 6 parts of the salt, and at the boiling temperature 60 parts. In consequence of the ease with which it gives up its oxygen, the chlorate is an excellent oxidizing agent, and it is constantly used in this capacity in the laboratory. Its oxidizing action is well illustrated by grinding a *very little* of it in a mortar with a little sulphur,* when an explosion takes place. With phosphorus the action is exceedingly violent.

The chief uses of potassium chlorate are in the preparation of oxygen, and in the manufacture of matches and fireworks. The tips of Swedish safety matches are made of potassium chlorate and antimony sulphide. The surface upon which they are rubbed to ignite them contains red phosphorus. The chlorate is frequently used in medicine, particularly as a gargle for sore throat.

**Potassium Perchlorate,** $KClO_4$, is formed in the first stage of the decomposition of the chlorate by heat, as was explained under Oxygen (which see). It is prepared best by heating the chlorate in an open vessel until, after having been liquid, it begins to get solid again.

**Potassium Cyanide,** KCN.—Under Cyanogen it was stated that when nitrogen is passed over a highly-heated mixture of carbon and potassium carbonate, potassium cyanide is formed; and that carbon containing nitrogen compounds, as animal charcoal, when ignited with potassium carbonate, reduces the carbonate, forming potassium, in presence of which the carbon and nitrogen combine, forming the cyanide. The simplest way to make the cyanide is by heating potassium ferrocyanide, $K_4Fe(CN)_6$, with potassium:

$$K_4Fe(CN)_6 + 2K = 6KCN + Fe.$$

It is made technically by conducting ammonia over a mixture of potassium carbonate and carbon at high temperature:

$$2NH_3 + K_2CO_3 + C = 2KCN + 3H_2O.$$

* Great care should be taken with all experiments with potassium chlorate. See description of experiments

Potassium cyanide is extremely easily soluble in water, and is deliquescent in moist air. When boiled with water it is decomposed, forming potassium formate and ammonia:

$$KCN + 2H_2O = KCO_3H + NH_3.$$

It combines readily with oxygen when in the molten condition, as shown in its action upon lead oxide (see Exp. 200). In consequence of this power to combine with oxygen to form the cyanate, it is a valuable reducing agent, and is often used in the laboratory in this capacity.

It is used in great quantities in the cyanide process for the extraction of gold from its ores (see Gold), in gold, silver and nickel plating, and in photography as a solvent for silver salts.

Potassium cyanide combines with the cyanides of the metallic elements, forming the so-called double cyanides of which potassium ferrocyanide, $K_4Fe(CN)_6$, is a good example.

**Potassium Sulphocyanate,** KCNS.—Just as potassium cyanide takes up oxygen to form the cyanate, it also takes up sulphur to form the sulphocyanate:

$$KCN + S = KCNS.$$

It is easily prepared by adding sulphur to molten potassium cyanide, or by heating a mixture of dehydrated potassium ferrocyanide, potassium carbonate, and sulphur. It crystallizes particularly well out of its solution in alcohol. It is deliquescent, and when dissolved in water it causes a very considerable lowering of the temperature. Thus, when 500 grams of the salt is mixed with 400 grams of water at the ordinary temperature, the temperature sinks to about $-20°$. Unlike the cyanate, it is not decomposed by water.

**Potassium Sulphate,** $K_2SO_4$.—This salt occurs in combination with others in nature, particularly in the minerals which contain the constituents of potassium sulphate and magnesium sulphate, schönite, $K_2Mg(SO_4)_2 + 3H_2O$, and

leonite, $K_2Mg(SO_4)_2 + 2H_2O$. These occur in Stassfurt and in Kalusz. Potassium sulphate is used in medicine, and in the preparation of ordinary alum and of potassium carbonate.

Potassium sulphate is made technically at Stassfurt, chiefly for use as fertilizer, by adding to a solution of schönite or leonite potassium chloride: $K_2Mg(SO_4)_2 + 2KCl = MgCl_2 + 2K_2SO_4$. As magnesium chloride is much more soluble than potassium sulphate the latter crystallizes out. It is also made similarly from kainite, $MgSO_4KCl + 3H_2O$, by adding potassium chloride.

**Primary, or Acid, Potassium Sulphate,** $KHSO_4$.—This salt is obtained as a secondary product in the preparation of nitric acid by the action of sulphuric acid upon saltpetre. It occurs in nature in the Grotto del Solfo, near Naples; and is made by treating the neutral salt with concentrated sulphuric acid. When heated above its melting-point it gives off water, and is transformed into the disulphate, thus:

$$2KHSO_4 = K_2S_2O_7 + H_2O.$$

When the disulphate is heated in contact with basic oxides it breaks down, forming sulphates. The decomposition is that represented in the equation

$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

The nascent sulphur trioxide thus set free acts with great energy upon the oxides which are present. Hence acid potassium sulphate is a valuable agent for the purpose of decomposing some mineral substances which do not readily yield to the ordinary reagents.

**Sulphites.**—When sulphur dioxide is passed into a solution of potassium carbonate until carbon dioxide ceases to escape, *potassium sulphite*, $K_2SO_3$, is formed. If the gas is passed to saturation the product is the primary or *acid sulphite*, $KHSO_3$.

**Carbonates.**—The normal salt, $K_2CO_3$, is the chief constituent of wood-ashes. When these are extracted with

water the carbonate passes into solution and the salt thus obtained can be purified in a number of ways. The impure salt is known as *potash*. Formerly all the potassium carbonate made was obtained from wood-ashes, but at present not more than half of the supply comes from this source. The other sources are the residues from the manufacture of beet-sugar, potassium sulphate and chloride, and wool-fat. The preparation of the carbonate from the sulphate and chloride is accomplished by the same method as that used in the preparation of sodium carbonate from the chloride. The methods used for this purpose will be treated of under the head of Sodium Carbonate (which see). The salt crystallizes from very concentrated solutions in water. It is deliquescent, and dissolves in water with an evolution of heat, and the solution has a strong alkaline reaction.

The explanation of the alkaline reaction of potassium carbonate in terms of the theory of electrolytic dissociation is very interesting and has already been given (see p. 177).

**Acid Potassium Carbonate,** $HKCO_3$, is formed by passing carbon dioxide over the normal salt, or into the concentrated aqueous solution of the latter. It is much less soluble in water than the normal salt. The dry salt gives off carbon dioxide and water easily when heated, and is converted into the normal salt:

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O.$$

The same decomposition takes place when the water solution is heated, and even on evaporation at the ordinary temperature.

**Phosphates.**—Three phosphates of potassium are known: (1) *Tertiary, or normal potassium phosphate*, $K_3PO_4$; (2) *secondary, or di-potassium phosphate*, $K_2HPO_4$; and (3) *primary, or mono-potassium phosphate*, $KH_2PO_4$. There is nothing particularly characteristic about these salts, except the decompositions which the primary and secondary salts undergo when heated. These decompositions have already been referred to (see p. 824).

**Potassium Silicate,** $K_2SiO_3$.—A compound of the definite composition represented by the formula here given has not been prepared. A solution of potassium silicate in water is prepared by dissolving sand or amorphous silicon dioxide in potassium carbonate or hydroxide. It is prepared on the large scale by melting together quartz powder and purified potash. It is known as *water glass*, for the reason that its solution dries in the air, forming a glass-like looking mass. To distinguish it from the water glass made with sodium carbonate or hydroxide it is called *potash water glass*.

RUBIDIUM, Rb (At. Wt. 85.5).
CÆSIUM, Cs (At. Wt. 132.9).

Both these elements are widely distributed, but only in relatively small quantities. They generally occur in company with potassium, which they resemble closely. They were discovered by means of the spectroscope by Bunsen and Kirchhoff. The characteristic spectrum of rubidium consists of two dark red lines, and this is the origin of the name rubidium (from *rubidus*, dark red). Cæsium was found in the Dürkheim mineral water, and was recognized by two characteristic blue lines, and the name cæsium was given to it on this account (from *cæsius*, sky-blue). Rubidium is found in different varieties of mica, known as lepidolite. Carnallite also contains 0.025 per cent rubidium so that about 400,000 kilograms of rubidium yearly finds its way to the fields in the fertilizers from Stassfurt!

The mineral *pollux*, which is essentially a silicate of cæsium and aluminium, contains cæsium as one of the chief constituents.

It is a remarkable fact that the elements rubidium and cæsium which are so much like potassium accompany it so generally in nature. Similar facts were noted in the group consisting of chlorine, bromine, and iodine, and that of sulphur, selenium, and tellurium. It will be remembered that chlorine is frequently accompanied by bromine and iodine; and sulphur by selenium and tel-

lurium; but that chlorine and sulphur are present in much larger quantities than the elements which accompany them. Further, the relations between the atomic weights of the members of each group are approximately the same.

Rubidium is prepared by the same method as that used in the preparation of potassium.

It is silver-white with a yellowish tint. It melts at 38.5°. It can be converted into vapor which has a blue color. It takes fire in the air at the ordinary temperature. Its action upon water is the same as that of potassium, and its salts are very similar to those of potassium.

Cæsium has been prepared by the electrolysis of molten cæsium cyanide. It melts at 26.5°.

The salts of cæsium are much like those of rubidium and potassium.

## Sodium, Na (At. Wt. 23.05).

**Occurrence.**—Sodium occurs very widely distributed and in large quantities in nature, principally as sodium chloride. It is found in a number of silicates, and is a constituent of plants, especially of those which grow in the neighborhood of the seashore and in the sea. Just as the ashes of inland plants are rich in potassium carbonate, so the ashes of sea-plants and those which grow near the sea are rich in sodium carbonate. It is found everywhere in the soil, but generally in small quantities. Its presence in the soil is due to the decomposition of minerals containing it, such as soda feldspar, or albite. It occurs also as sodium nitrate or Chili saltpetre, and in large quantity in Greenland in the form of *cryolite*, which is a double fluoride of aluminium and sodium, of the formula NaAlF., or $AlF_3 3NaF$.

**Preparation.**—Sodium is generally prepared by the electrolysis of fused sodium hydroxide, the sodium going to the cathode and the hydroxyl to the anode where it decomposes into water and hydrogen. The water thus set free attacks the sodium, regenerating hydroxide so that

the practical yield is only about 40 per cent of the theoretical.

**Properties.**—The properties of sodium are very similar to those of potassium. It is light, floating on water; it has a bright metallic lustre; and at the ordinary temperature it is soft like wax. It decomposes water, but not as readily as potassium does. Its specific gravity is 0.9735; its melting-point 97°, its boiling-point 742°. Its vapor is colorless when seen in thin layers, while thick layers appear purple. When melted and allowed to cool it takes the crystallized form. In the air it is changed to the carbonate by the water vapor and carbon dioxide.

**Applications.**—It is used in obtaining gold from its ores, as sodium cyanide (which see) and as sodium amalgam, further for making sodium peroxide, and for technical organic synthesis. It is used in the laboratory for the purpose of isolating some elements whose oxides cannot easily be reduced, as, for example, aluminium, magnesium, and silicon, which are prepared by treating their chlorides with sodium. Silicon, however, is more readily prepared by treating potassium fluosilicate, $K_2SiF_6$, with sodium. The element is also used, in combination with mercury as sodium amalgam, a substance which affords a ready means of making nascent hydrogen. It also finds constant application in the laboratory for a variety of purposes.

**Sodium Hydride,** NaH, is formed in the same way as the corresponding compound of potassium, and is in every way similar to it.

**Sodium Chloride,** NaCl.—This is the substance which is generally known simply as *salt*, or *common salt*. It occurs very widely distributed, and in immense quantities, in the earth. Among the most important deposits are those at Wieliczka in Galicia, at Stassfurt and Reichenhall in Germany, at Cheshire in England, in New York and Michigan in the United States of America, in Africa, and in Asia. As it is easily soluble in water, many springs and streams, as well as lakes and the ocean, contain it. Sea-water contains 2.7 per cent. In some places sodium

chloride is taken out of mines in solid form. Frequently, however, water is allowed to flow into cavities in the earth, and to remain for some time in contact with the salt. The solution thus formed is afterward drawn or pumped out of the mine and evaporated. It is generally allowed to run slowly down walls made of twigs, so that a large surface of the liquid is exposed to the air. The concentrated solution thus obtained is then evaporated to crystallization by the aid of heat.

In hot countries salt is obtained by the evaporation of sea-water, the heat of the sun being used for the purpose. Large shallow cavities are made in the earth, and into these the water flows at high-tide, or it is pumped up into them if they are too high. The process is continued for some months, and then the mother-liquor is drawn off, and the accumulated salt collected and subjected to proper methods of purification.

The salt obtained by the above methods is not pure. It always contains sodium sulphate, together with magnesium and calcium chlorides. The chlorides of magnesium and calcium, being deliquescent cause it to become moist in the air. Pure salt is not deliquescent.

Sodium chloride crystallizes in colorless, transparent cubes. Some of that which occurs in nature has a blue color. When deposited from an evaporating solution it takes the form of small cubes arranged in groups of the shape of hollow pyramids, known as the hopper-shaped deposits. When deposited, the crystals enclose water, not as water of crystallization, and this is given off when the crystals are heated, the action being accompanied by a crackling sound. This is known as *decrepitation*.

Sodium chloride melts at 815°, and is volatile at a red heat. In hot water it is but little more soluble than in cold. At 100° 100 parts of water dissolve 39 parts, and at ordinary temperatures 36 parts.

Sodium chloride is the starting-point in the preparation of all sodium compounds, as well as of chlorine and hydrochloric acid. Salt is necessary to the life of man and many other animals. The rôle played by it in the

animal economy is not understood, but it is found generally distributed throughout the body in small quantity.

The great salt-producing countries in the order of production are the United States, Great Britain, Russia, Germany, France, and India. The production, in tons, of these countries for 1904 was:

| United States. | Gt. Britain. | Russia (1902). |
|---|---|---|
| 3,084,000. | 2,118,000. | 2,036,000. |
| **Germany.** | **France.** | **India.** |
| 1,875,000. | 1,292,000. | 1,237,000. |

The total production for 1904 was 14,728,000 tons. Michigan and New York each produces over a third of the total production of the United States.

The *fluoride*, *bromide*, *iodide* of sodium are like the corresponding potassium salts and need not be described.

**Sodium Hydroxide,** NaOH.—This compound resembles potassium hydroxide in most respects. Being cheaper it is used more extensively. It is prepared in the same way, by treating sodium carbonate in solution with calcium hydroxide, when insoluble calcium carbonate and soluble sodium hydroxide are formed:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

It is now prepared chiefly by the electrolysis of sodium chloride, either by the use of a mercury cathode (see Chlorine), when the hydroxide is obtained in solution, or by the Acker process in use at Niagara Falls. In this interesting and successful process the temperature is above 400° and the cathode is molten lead. The sodium dissolves in the molten lead which flows off as the solution becomes concentrated, fresh lead flowing in to replace it. By directing a jet of steam on the sodium-lead alloy the reaction, $2Na + 2H_2O = 2NaOH + H_2$, occurs forming pure *molten* sodium hydroxide which is run into moulds while the lead flows again to form the cathode. The chlorine is obtained at the anode in this process as well as in the others. *Chemically pure sodium hydroxide* is generally made by the action of sodium on pure water.

Sodium hydroxide is commonly called *caustic soda.* It is extensively used for the purpose of making soap from fats.

**Oxides.**—Sodium forms two oxides, the monoxide, $Na_2O$, and the peroxide, NaO. In this respect a difference is noticed between sodium and potassium; the latter forming the compounds $K_2O$ and $KO_2$.

**Sodium Peroxide,** NaO, has acquired importance in the arts as a bleaching-agent. It is prepared by heating sodium in a current of dry air at a temperature of 300°. When heated to a high temperature it gives off oxygen. Water decomposes it, forming sodium hydroxide, and setting oxygen free. The substance called "oxone" (see p. 34) is chiefly sodium peroxide. To facilitate its decomposition by water it is mixed with some other substance that serves as a catalyser (see p. 78).

**Sodium Sulphantimonate,** $Na_3SbS_4$, also known as Schlippe's salt, is a particularly beautiful example of the salts of sulpho-acids. It is made, as its composition indicates, by dissolving antimony pentasulphide in a solution of sodium sulphide:

$$Sb_2S_5 + 3Na_2S = 2Na_3SbS_4.$$

**Sodium Nitrate,** $NaNO_3$.—This compound occurs in large quantity in southern Peru on the border of Chili, and is known as Chili saltpetre. The natural salt contains some sodium chloride, sulphate, and iodate. Sodium nitrate is similar to potassium nitrate, but it cannot be used in place of the more expensive potassium salt in the manufacture of the finer grades of gunpowder, as it becomes moist in the air, and does not decompose quickly enough. It is used extensively in the manufacture of nitric acid, and also for the purpose of preparing ordinary saltpetre. The iodine contained in Chili saltpetre is now extracted on the large scale, and this forms an important source of iodine. The chief use of sodium nitrate is as a fertilizer (see Nitric Acid).

**Sodium Sulphate,** $Na_2SO_4$.—This salt was first made by Glauber, as it is now made, by the action of sulphuric acid

on sodium chloride. It is commonly called Glauber's salt. It occurs in a number of natural waters, as in that of Friedrichshall and Carlsbad. It occurs, further, mixed with gypsum and other salts forming mountain chains in Spain and in the Caucasus. It is made in very large quantities in connection with the manufacture of soda, the first reaction in this process being that of sodium chloride upon sulphuric acid. It is also formed in the manufacture of nitric acid by the action of sulphuric acid on Chili saltpetre, and at Stassfurt by the action of sodium chloride on kieserite, $MgSO_4 + H_2O$, by crystallization:

$$MgSO_4 + 2NaCl = Na_2SO_4 + MgCl_2.$$

It crystallizes in large, colorless, monoclinic prisms, which contain ten molecules of water. These crystals are formed, however, only in case the temperature of the solution is below 20° at the time they are deposited. The salt is most easily soluble in water at 33°; above this point the solubility decreases. If deposited from its solution at temperatures above 33° it is anhydrous.

Sodium sulphate easily forms supersaturated solutions which crystallize rapidly, if a small crystal of the salt is thrown into them, and if cooled down to — 8°. This phenomenon is frequently presented by salts, but it is shown in a particularly striking way by this one.

When exposed to the air the salt loses its water of crystallization and crumbles to a white powder. This is the process already described as *efflorescence* (see p. 107).

Sodium sulphate is used as a purgative in medicine, and in the laboratory for the production of cold artificially. A good freezing mixture is made by bringing it together with concentrated hydrochloric acid. Sodium chloride is formed and the water of crystallization of the sulphate takes the liquid form. This change from the solid to the liquid form is accompanied by a marked absorption of heat. Ice can be made in this way without difficulty. The chief uses of the sulphate are in the manufacture of sodium carbonate and of glass, as will be explained farther on.

**Sodium Thiosulphate,** $Na_2S_2O_3 + 5H_2O$.—This is the salt which is commonly called *hyposulphite of soda.* It is made on the large scale by treating caustic soda with sulphur, and conducting sulphur dioxide into the solution. It is also made by boiling a solution of sodium sulphite and adding sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Its chief application is as "anti-chlorine" or absorbent for excess of chlorine in bleaching, and in photography, in which art it is used for the purpose of dissolving the excess of silver salt on the plate which has been exposed to the light, and on which a picture has been developed. The action consists in the formation of salts in which both sodium and silver are contained. These are soluble in water.

**Sodium Carbonate,** $Na_2CO_3$.—This salt, commonly called *soda,* is one of the most important of manufactured chemical compounds. The mere mention of the fact that it is essential to the manufacture of glass and soap will serve to give some conception of its importance. It is found in the ashes of sea-plants, as potassium carbonate is found in the ashes of inland plants. Formerly it was made entirely from plant-ashes, but we are no longer dependent upon this source for our supply of the salt, as two methods have been devised for preparing it from sodium chloride, with which nature provides us in such abundance. As these methods are of great importance, and are, further, very interesting applications of chemical principles, they will be described below.

**Properties.**—Anhydrous sodium carbonate which is formed by heating the crystallized salt is a powder. It melts to a clear liquid when heated to a sufficiently high temperature. It dissolves very readily in water with evolution of heat. The action is, however, not as marked as in the case of potassium carbonate. When the salt is deposited from a water solution it has the composition $Na_2CO_3 + 10H_2O$. This salt, it will be observed, contains the same number of molecules of water of crystallization

as sodium sulphate. Like this, too, it effloresces when exposed to the air. When heated it melts in its water of crystallization, and the salt $Na_2CO_3 + H_2O$, or $(HO)_2C(ONa)_2$, separates. This, however, loses water when heated higher, and is converted into the anhydrous salt. The conduct of the carbonate towards water at different temperatures is suggestive of that of the sulphate. Its maximum solubility is at temperatures between 33° and 70°. Above the latter point the solubility decreases. The crystals of sodium carbonate containing ten molecules of water of crystallization belong to the monoclinic system.

**Applications.**—Sodium carbonate is used in immense quantities in the manufacture of glass, and in the preparation of caustic soda, which is used in the manufacture of soap.

**The Le Blanc Process for the Manufacture of Sodium Carbonate.**—In the manufacture of soda the problem to be solved is the conversion of sodium chloride into sodium carbonate. The first method devised for this purpose is that of Le Blanc. During the French Revolution the supply of potash was cut off from France. This led the government to offer a prize for a practical method for manufacturing soda from common salt. The method proposed by Le Blanc at that time, and which until recently has been used almost exclusively, involves three reactions:

(1) The sodium chloride is converted into sodium sulphate by treating it with sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

(2) The sodium sulphate thus obtained is heated with charcoal, which reduces it to sodium sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

(3) The sodium sulphide is heated with calcium carbonate, when sodium carbonate and calcium sulphide are formed:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The conversion of the sulphate into the carbonate is, therefore, expressed by the equation

$$Na_2SO_4 + 2C + CaCO_3 = Na_2CO_3 + CaS + 2CO_2.$$

Calcium sulphide is insoluble in water containing lime, so that by treating the resulting mass with water the sodium carbonate is separated from the sulphide.

In practice the sodium sulphate is mixed with coal and calcium carbonate, and the mixture heated in furnaces. The coal reduces the sulphate to sulphide, which then acts upon the calcium carbonate as above represented. The product of the action is known as *crude soda* or *black ash.* It contains, as its chief constituents, sodium carbonate and calcium sulphide, together with some calcium oxide, and a number of other substances in small quantities. In order to purify this product, it is broken to pieces, and treated with water; and the solution thus obtained evaporated, when the salt of the composition $Na_2CO_3 + 2H_2O$ is deposited. This is dipped out, and heated, when it loses all its water. The product is the *calcined purified soda* of commerce. This always contains some sulphate and chloride together with a small quantity of sulphite.

When dissolved in water and allowed to crystallize, the salt is deposited in large crystals which contain water in the proportion represented by the formula $Na_2CO_3 + 10H_2O$. This is the so-called *crystallized soda.*

As, in the manufacture of soda by the Le Blanc process, the sulphur remains in combination as calcium sulphide, a process, known as the Chance process, has been devised for its recovery. This consists in passing carbon dioxide into the waste, thus liberating hydrogen sulphide; passing this into another portion of the waste, thus converting the calcium sulphide into the hydrosulphide; and then treating this with carbon dioxide, when a gas rich in hydrogen sulphide is given off:

$$CO_2 + CaH_2S_2 + H_2O = CaCO_3 + 2H_2S.$$

By regulating the supply of air the gas is burned either to sulphur dioxide or to sulphur.

**Ammonia Process for the Manufacture of Soda.**—Another process now in extensive use for the manufacture of soda is the so-called ammonia process, or the *Solvay process*. This depends upon the fact that mono-sodium carbonate, $HNaCO_3$, is comparatively difficultly soluble in water. If, therefore, mono-ammonium carbonate, or acid ammonium carbonate, $HNH_4CO_3$, is added to a solution of common salt, acid sodium carbonate, $HNaCO_3$, crystallizes out, and ammonium chloride remains in the solution:

$$NaCl + HNH_4CO_3 = HNaCO_3 + NH_4Cl.$$

When the acid carbonate thus obtained is heated, it gives off carbon dioxide, and is converted into the normal salt thus:

$$2HNaCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide given off is passed into ammonia, and thus again obtained in the form of acid ammonium carbonate:

$$NH_3 + H_2O + CO_2 = HNH_4CO_3.$$

The ammonium chloride obtained in the first reaction is treated with lime or magnesia, MgO, and the ammonia set free. This ammonia is used again in the preparation of acid ammonium carbonate. The object of using magnesia is to get magnesium chloride, which, when evaporated to dryness and heated, yields magnesia and hydrochloric acid:

$$MgCl_2 + H_2O = MgO + 2HCl.$$

A large proportion of the soda supply of the world is now furnished by the Solvay process.

**Mono-Sodium Carbonate, Primary Sodium Carbonate,** $HNaCO_3$.—This salt is commonly called "bi-carbonate of soda." It is easily prepared by passing carbon dioxide over the ordinary carbonate dissolved in its water of crystallization:

$$Na_2CO_3 + CO_2 + H_2O = 2HNaCO_3.$$

When heated it gives up carbon dioxide and water, and is converted into the normal salt. As was stated in connection with the ammonia-soda process, primary sodium carbonate is much more difficultly soluble in water than the normal salt. At ordinary temperatures 100 parts of water dissolve about 10 parts of the salt.

It is used in medicine, in the preparation of "soda water" and other effervescing drinks, and is a constituent of *baking powders*.

**Phosphates.**—There are three phosphates of sodium just as there are three phosphates of potassium. The point of chief interest presented by them is that the secondary salt, $HNa_2PO_4$, is the one most easily obtained, and is the substance commonly known as sodium phosphate. When a solution of this salt is treated with an excess of sodium hydroxide, and the solution evaporated, *normal* or *tertiary sodium phosphate* crystallizes out. This has the composition $Na_3PO_4 + 12H_2O$. The solution of the latter salt has an alkaline reaction, and when exposed to the air it absorbs carbon dioxide, and is converted into the secondary salt:

$$2Na_3PO_4 + CO_2 + H_2O = 2HNa_2PO_4 + Na_2CO_3.$$

*Secondary sodium phosphate*, $HNa_2PO_4 + 12H_2O$, is easily made by adding sodium carbonate to a solution of phosphoric acid until an alkaline reaction is reached. It is also prepared on the large scale from bone-ash. It forms monoclinic prisms which effloresce in the air.

**Sodium Borate.**—Normal boric acid, as we have seen, has the composition $B(OH)_3$, and there are a number of borates derived from this acid. The salt which boric acid most readily forms with sodium hydroxide or sodium carbonate, however, is that derived from *tetraboric acid*, $H_2B_4O_7$, which is derived from normal boric acid by elimination of water. (See p. 344.) This salt is *borax*, which in crystallized form has the composition represented by the formula $Na_2B_4O_7 + 10H_2O$.

*Borax* occurs in nature in several lakes in Asia and in Clear Lake, Nevada, in the United States. When heated,

borax puffs up, and at red heat it melts, forming a transparent, colorless liquid. The dehydrated salt is known as *anhydrous* or *calcined borax*. In the molten condition, borax has the power to combine with metallic oxides, and, as many of the double borates thus formed are colored, the salt is used in blowpipe work for the purpose of detecting certain metals. Its power to dissolve metallic oxides makes it useful in the process of soldering, as it is necessary to have bright, untarnished metallic surfaces in order that the solder shall adhere firmly. The action of molten borax upon metallic oxides is similar to that which takes place when sodium hydroxide acts upon a solution of borax. Borates of the metals are formed together with sodium borate, or double borates in which part of the hydrogen is replaced by sodium and part by other metals.

The salts of boric acid and their occurrence is shown in the following table of the world's production for 1902:

| | |
|---|---|
| United States, Calcium borate | 18148 tons. |
| Bolivia, " " | 14437 " |
| Peru, " " | 4156 " |
| Italy, Boric acid | 2763 " |
| Germany, Boracite (Magnesium borate) | 196 " |
| | 39700 " |

In 1906 the United States alone produced 58,173 tons calcium borate. All the crude material is worked up into borax or boric acid in refineries.

Borax is chiefly used instead of soap as a cleansing agent. It is also extensively used in the manufacture of porcelain and in glass-painting. It is an antiseptic, preventing the decomposition of some organic substances.

**Sodium Silicate,** $Na_2SiO_3$.—Sodium silicate is formed by dissolving silicon dioxide in sodium hydroxide, and can be obtained in crystallized form. It is prepared on the large scale by melting together quartz sand and sodium carbonate in the proper proportions, and by melting together sodium sulphate, quartz sand, and charcoal powder. This substance is commonly known as *water-glass*. It is

soluble in water, and, when its solution dries, it leaves a transparent coating on the surface on which it is placed. It is extensively used in the manufacture of artificial stone.

**Sodium Cyanide** is made on the large scale by the action of ammonia on metallic sodium and carbon. It is used for the same purposes as potassium cyanide.

## Lithium, Li (At. Wt. 7.03).

Lithium occurs in nature in relatively small quantity, chiefly in the minerals lepidolite, petalite, and spodumene, and in many mineral waters. It is also found in the ashes of a number of plants. It is prepared by the electrolysis of the chloride in the molten condition. The metal is silver-white, melts at 186° and is characterized by its low specific gravity, 0.59. It acts vigorously upon water, but, if the water is at the ordinary temperature, the hydrogen given off does not take fire. In the air it conducts itself much like sodium.

## Ammonium Salts.

Attention has already been called to the marked similarity of the salts of potassium and sodium to those formed by the action of ammonia on the acids, and known as ammonium salts. The most important of these salts will be briefly treated of in this connection. A characteristic property of ammonium salts which distinguishes them from the salts of all the metals is their volatility. When sublimed, they all undergo either partial or complete decomposition.

The simplest kind of decomposition which they undergo is dissociation into ammonia and the acid. This is illustrated in the case of ammonium chloride, which, when heated to a sufficiently high temperature, is dissociated into ammonia and hydrochloric acid. This is an example of true dissociation. The amount of decomposition is constant for any given temperature and pressure.

An ammonium salt of a polybasic acid containing some

metal gives off ammonia and leaves an acid salt, which generally undergoes further decomposition. Thus, sodium-ammonium sulphate, $NaNH_4SO_4$, first gives off ammonia and forms mono-sodium sulphate:

$$SO_4\begin{cases}Na\\NH_4\end{cases} = SO_4\begin{cases}Na\\H\end{cases} + NH_3.$$

The acid salt thus formed then undergoes further change and the pyrosulphate is formed:

$$2SO_4\begin{cases}Na\\H\end{cases} = Na_2S_2O_7 + H_2O.$$

Another example of this kind of decomposition of ammonium salts is that afforded by sodium-ammonium phosphate, $HNaNH_4PO_4$. When heated, this gives off ammonia and then water, the final product being sodium metaphosphate:

$$PO\begin{cases}ONa\\ONH_4\\OH\end{cases} = PO\begin{cases}ONa\\OH\\OH\end{cases} + NH_3;$$

$$PO\begin{cases}ONa\\OH\\OH\end{cases} = PO_3Na + H_2O.$$

Some ammonium salts undergo deeper-seated decompositions, and do not give ammonia as one of the products. This is true especially of such salts as readily give off oxygen. In such cases the ammonia is oxidized, so that the hydrogen forms water. This is illustrated in the decomposition of ammonium nitrate and nitrite:

$$NH_4NO_3 = N_2O + 2H_2O; \text{ and}$$
$$NH_4NO_2 = N_2 + 2H_2O.$$

Further, all ammonium salts are decomposed with evolution of ammonia when treated with basic hydroxides. This has been illustrated in the preparation of ammonia from ammonium chloride by treatment with calcium hydroxide:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

The ammonium salts are made by neutralizing acids with ammonia.

**Ammonium Chloride,** $NH_4Cl$.—This salt is commonly called *sal ammoniac*. At present its principal source is the so-called ammoniacal liquor of the gas-works. This liquid contains a considerable quantity of ammonium carbonate, and, when it is treated with lime, ammonia is given off. This is passed into hydrochloric acid, and the solution of ammonium chloride thus formed evaporated to crystallization. The salt has a sharp, salty taste, and is easily soluble in water. When heated, it is converted into vapor without melting and with very slight decomposition; and when the vapor comes in contact with a cold surface, it condenses in crystalline form. This process of vaporizing and condensing a solid is called *sublimation*. Some of the ammonium chloride met with in the market has been sublimed. The salt is used in the preparation of ammonia, in medicine, and for other purposes. When it is dissolved in water, a considerable lowering of temperature is caused.

**Ammonium Sulphide,** $(NH_4)_2S$.—This compound is extensively used in chemical analysis for the purpose of precipitating those sulphides which are soluble in dilute hydrochloric acid (see p. 230). In the usual method of analyzing a mixture of substances, the first step consists in adding hydrochloric acid to the solution. This precipitates silver, lead, and, under certain conditions, mercury. The precipitate having been filtered off, hydrogen sulphide is passed through the filtrate, when those metals are precipitated whose sulphides are insoluble in dilute hydrochloric acid. The precipitate is filtered off, and ammonium sulphide added to the filtrate, when the metals whose sulphides are soluble in dilute hydrochloric acid are thrown down. Among these are iron, cobalt, nickel, manganese, etc. Any other soluble sulphide might be used; but the advantage of ammonium sulphide is that it is volatile, and hence, by evaporating the solution and heating, it can be got rid of after it has served its purpose. Another use to which it is put in analysis is for

the purpose of dissolving the sulphides of tin, arsenic, and antimony, which are precipitated by hydrogen sulphide, and thus separating these from the other sulphides of the group. This solution depends upon the power of the sulphides to form salts of sulpho-acids.

Ammonium sulphide is made by passing hydrogen sulphide into an aqueous solution of ammonia. If the gas is passed until the solution is saturated, the product is the hydrosulphide:

$$NH_3 + H_2S = NH_4HS.$$

If only half this quantity of the gas is passed, the product is the sulphide:

$$2NH_3 + H_2S = (NH_4)_2S.$$

The simplest way to make the sulphide, however, is to divide a quantity of a solution of ammonia into two equal parts; saturate one half, thus forming the hydrosulphide; and add the other half, when this reaction takes place:

$$HNH_4S + NH_3 = (NH_4)_2S.$$

The product is a colorless liquid of a disagreeable odor. It soon changes color, becoming yellow, and after a time a yellow deposit is formed in the vessel in which it is contained. This change of color is due to the action of the oxygen of the air. Some of the sulphide is decomposed into ammonia, water, and sulphur, thus:

$$(NH_4)_2S + O = 2NH_3 + H_2O + S.$$

The sulphur set free in this way combines with the undecomposed ammonium sulphide, forming the compounds $(NH_4)_2S_2$, $(NH_4)_2S_3$, $(NH_4)_2S_4$, and $(NH_4)_2S_5$. When as much sulphur has been set free as is required to form the pentasulphide, further decomposition by the oxygen of the air causes a deposit of sulphur. Therefore, in bottles containing ammonium sulphide which are allowed to stand for a long time a deposit of sulphur is always found. A solution containing the polysulphides is called

*yellow ammonium sulphide.* It is this which is used for the purpose of dissolving the sulphides of arsenic, antimony, and tin in analytical operations.

As stated above, a solution of *ammonium hydrosulphide*, $HNH_4S$, is made by passing hydrogen sulphide into a solution of ammonia until no more is taken up.

**Ammonium Sulphate,** $(NH_4)_2SO_4$, is technically the most important of ammonium salts. It is the substance from which other ammonium compounds are generally made, and as a fertilizer it is used in rapidly increasing quantities. It is chiefly made from the ammonia of coking ovens, and by distilling sea-weed with steam. The yearly production is over 500,000 tons.

**Ammonium Nitrate,** $NH_4NO_3$, is obtained in crystals, which are easily soluble in water. It is of use chiefly in the preparation of nitrous oxide. When heated suddenly to a high temperature it is decomposed rapidly into nitrogen, water, and nitric oxide:

$$2NH_4NO_3 = N_2 + 2NO + 4H_2O.$$

This decomposition may take place in the preparation of nitrous oxide if in the last stages of the operation the heat is raised too high, and explosions may be caused in this way. When dissolved in water a marked lowering of temperature takes place.

**Sodium-Ammonium Phosphate,** $HNaNH_4PO_4$.—This salt is known as *microcosmic salt*, and is much used in the laboratory in blowpipe work. It is contained in guano and in decomposed urine. It is easily made by mixing solutions of di-sodium phosphate and ammonium chloride, and allowing to crystallize. In crystallized form it contains four molecules of water, $HNaNH_4PO_4 + 4H_2O$. The changes which the anhydrous salt undergoes when heated were described on page 487. When the crystallized salt is heated, the water of crystallization is first given off. The value of the salt in blowpipe work depends upon the fact that at high temperatures the metaphosphate combines with metallic oxides, forming

mixed phosphates, the reactions being like those which metaphosphoric acid undergoes with water:

$$2HPO_3 + H_2O = H_4P_2O_7;$$
$$HPO_3 + H_2O = H_3PO_4;$$
$$2NaPO_3 + M_2O = Na_2M_2P_2O_7;$$
$$NaPO_3 + M_2O = NaM_2PO_4.$$

Many of these double phosphates and pyrophosphates are colored, and furnish a means of detecting some of the metals.

**Reactions of the Members of the Sodium Group which are of Value in Chemical Analysis.**—The chief difficulty experienced in chemical analysis is in distinguishing between similar elements. Sodium and potassium, for example, conduct themselves so much alike in so many respects that we might subject them to the influence of a number of reagents without being able to tell which one we are working with. For purposes of analysis, therefore, it is necessary to take advantage of differences between the elements, and the more striking the differences the better. Those reactions which give rise to the formation of insoluble compounds or precipitates are most frequently used in analysis. Very few salts of the members of the sodium group are insoluble, and the difficulty of distinguishing between these elements is increased by this fact. In ordinary analyses the elements of this group which are of most importance are potassium and sodium, the other elements of the group being but rarely met with. Ammonium compounds are easily distinguished from those of potassium and sodium by the fact that, when treated with caustic soda or potash, they give off ammonia, which is recognized by its characteristic odor. The chief reactions which are of value in distinguishing between potassium and sodium are the following:

*Chlorplatinic Acid*, $H_2PtCl_6$, forms difficultly soluble salts with potassium and ammonium chlorides. These are the *chlorplatinates*, $K_2PtCl_6$ and $(NH_4)_2PtCl_6$. The corresponding salt of sodium is easily soluble.

*Sodium Cobalti-nitrite*, $Na_2Co(NO_2)_6$, forms yellow precipitates with solutions of potassium and ammonium salts; these are the cobalti-nitrites of potassium and ammonium. They are much less soluble than the chlor-platinates.

*Perchloric Acid*, $HClO_4$, forms difficultly soluble *potassium perchlorate*, $KClO_4$, when added to solutions of potassium salts.

*Fluosilicic Acid*, $H_2SiF_6$, forms difficultly soluble salts with potassium and sodium, $K_2SiF_6$ and $Na_2SiF_6$, but not with ammonium.

*Tartaric Acid*, $H_2(C_4H_4O_6)$, forms a difficultly soluble potassium salt of the formula $KH(C_4H_4O_6)$. The corresponding salt of sodium is easily soluble. The formation of mono-potassium tartrate takes place as represented in the equation

$$KCl + H_2(C_4H_4O_6) = KH(C_4H_4O_6) + HCl.$$

Normal or neutral potassium tartrate is soluble in water, so that, if the difficultly soluble acid tartrate is filtered off, and potassium carbonate added to it, it dissolves in consequence of the formation of the neutral salt, which takes place as represented in the equation

$$2KH(C_4H_4O_6) + K_2CO_3 = 2K_2(C_4H_4O_6) + CO_2 + H_2O.$$

If to the solution of the neutral salt, hydrochloric acid is added, the acid salt is again formed and precipitated:

$$K_2(C_4H_4O_6) + HCl = KH(C_4H_4O_6) + KCl.$$

*Di-sodium Pyro-antimonate*, $Na_2H_2Sb_2O_7$, is insoluble in cold water, and is formed when a solution of the corresponding potassium salt is added to a solution of a sodium salt.

**Flame Reactions and the Spectroscope.**—When a clean piece of platinum wire is held for some time in the flame of the Bunsen burner, it then imparts no color to the flame. If now a small piece of sodium carbonate or any other salt of sodium is put on it, it colors the flame in-

tensely yellow. All sodium compounds have this color, and hence the chemist makes use of this fact for the purpose of detecting the presence of sodium. Similarly, potassium compounds color the flame violet; lithium compounds color the flame red; rubidium and cæsium produce colors similar to that of the potassium flame. While it is an easy matter to recognize potassium alone, or any one of the other metals alone, it is difficult to do so when they are together in the same compound. For example, when sodium and potassium are together, the intense yellow caused by the sodium completely masks the more delicate violet caused by the potassium, so that the latter cannot be seen by the unaided eye. In this particular case the difficulty can be overcome by letting the light from the flame pass through a blue glass, or through a thin vessel of glass containing a solution of indigo. The yellow light is thus cut off, while the violet light passes through and can be recognized. A more general method for detecting the constituents of light is by means of a prism of glass. Lights of different colors, which are produced by ether waves of different lengths, are turned out of their course to different extents when passed through a prism, as is seen when white sunlight is passed through a prism. A narrow beam of white light passing in emerges as a band of various colors, called its *spectrum*. It is thus seen that white light is made up of lights of different colors; or, to speak in the language of physics, that motion of the light-ether which produces upon the eye the sensation of white light is made up of a number of motions, each of which alone produces upon the eye the sensation of a color. Similarly, the composition of any light can be determined. Every light has its characteristic spectrum. The light given off from any solid heated to a white heat gives a *continuous spectrum*, like that of the sunlight. An incandescent gaseous substance, on the other hand, gives a spectrum made up of separate bands of color, or a *band spectrum*. The light produced by burning sodium, or by introducing a sodium compound in a colorless flame, gives a spectrum consisting of a narrow yellow band. The

spectrum of the potassium flame consists essentially of two bands, one red and one violet. Further, these bands always occupy definite positions relatively to one another, so that, in looking through a prism at the light caused by potassium and sodium, the yellow band of sodium is seen in its position, and the two potassium bands in their proper positions. There is therefore no difficulty in detecting these elements when present in the same substance or in the presence of other elements which give characteristic spectra.

The light emitted by hydrogen shows a bright green line, a bright red line, and a line in the violet. No other substance shows lines in the same positions. If sunlight is allowed to pass through a prism dark lines appear in the exact positions of the colored hydrogen lines. These dark lines are due to the hydrogen in the atmosphere of the sun. The law of Bunsen and Kirchoff is that a gas absorbs the same wave lengths that it emits. White light from the sun's heated nucleus passing through the hydrogen atmosphere has those wave lengths absorbed which hydrogen emits. Hence the dark lines in the spectrum. Such spectra are called *absorption spectra*. Our knowledge of the presence of terrestrial elements in the sun, stars and nebulæ is due to observations of this kind. The sun and stars are incandescent bodies surrounded by a gaseous atmosphere and yield absorption spectra. The nebulæ are incandescent gases and yield band spectra.

The instrument used for the purpose of observing the spectra of different lights is called the *spectroscope*.* It consists essentially of a prism and two small telescopes. Through one of the telescopes the light to be examined is allowed to pass so as to strike the prism properly. The light emerges from the other side of the prism, and is observed through the other telescope, which is provided with lenses for the purpose of magnifying the spectrum. By

* For an account of the spectroscope and its uses, the student should consult some work on physics. The principles involved in its construction and application are physical principles, and cannot properly be taken up in detail in a text-book of chemistry.

means of a third telescope, an image of a scale is thrown upon the face of the prism from which the spectrum emerges, and is reflected thence into the observing-tube, together with the spectrum, so that the position of the bands can be accurately determined. By means of the spectroscope, it is possible to detect the minutest quantities of some elements, and, since it was devised, several new elements have been discovered through its aid; as, for example, cæsium, rubidium, thallium, indium, gallium, and some of the rare gases in the atmosphere.

## EXPERIMENTS.

### Potassium Salts.

Experiment 214.—In preparing potassium iodide from iodine and potassium hydroxide, proceed as follows: To 30 grams iodine use 15 grams hydroxide. Dissolve the latter in 100 cc. water. Add half this solution to the iodine in a porcelain evaporating-dish. Now slowly add the rest of the liquid until the color disappears. Concentrate the liquid to a syrupy consistence, add 1 gram finely-powdered charcoal, mix, and evaporate to dryness. Heat the residue to redness in an iron vessel. After cooling extract with water.

Experiment 215.—Potassium iodide can also be prepared by the following method: Bring together in a capsule 200 grams water, 10 grams iron filings, and 40 grams iodine; mix, and heat gently. When the solution has become green, decant, filter, and wash. Now heat the liquid nearly to boiling, and gradually add a solution of 35 grams potassium carbonate in 100 grams water. Filter, wash, and evaporate.

Experiment 216.—Dissolve 50 grams potassium carbonate in 500 to 600 cc. water. Heat to boiling in an iron or a silver vessel, and gradually add the slaked lime obtained from 25 to 30 grams of good quicklime. During the operation the mass should be stirred with an iron spatula. After the solution is cool, draw it off by means of a siphon into a bottle. This may be used in experiments in which caustic potash is required.

Experiment 217.—Mix together 15 grams potassium nitrate and 2.5 grams powdered charcoal. Set fire to the mass.

Experiment 218.—Treat a quantity of wood-ashes with water. Filter, and examine by means of red litmus paper. Evaporate to dryness. What evidence have you that the residue contains potassium carbonate?

## Sodium Salts.

Experiment 219.—Make a supersaturated solution of sodium sulphate by heating an excess of the salt with water at 33°. Filter the solution into small flasks and cork them. Let them cool down to the ordinary temperature. On removing the corks and shaking the vessels, the salt will suddenly crystallize out.

Experiment 220.—Make a saturated solution of common salt in ordinary ammonia-water (about 50 cc.). Pass carbon dioxide into this solution until no more is absorbed. Filter off the precipitate, and dry it by spreading it upon layers of filter-paper. Heat some of the salt when dry, and determine whether the gas given off is carbon dioxide or not. When gas is no longer given off by heating, let the tube cool and examine the residue. [Is it a carbonate?]

Experiment 221.—Make ammonium sulphide thus: Divide a given quantity of a solution of ammonia into two equal parts. Saturate one-half by passing hydrogen sulphide through it, and then add the other half.

*

# CHAPTER XXV.

## ELEMENTS OF FAMILY II, GROUP A: GLUCINUM.—MAGNESIUM.—CALCIUM.—STRONTIUM.—BARIUM [ERBIUM].

**General.**—The elements of this group fall into two subgroups. Calcium, strontium, and barium are strikingly alike. They also have some properties in common with the members of the potassium family, and at the same time are related in some degree to the metals of Family III, Group A, which are known as the earth metals. Therefore, calcium, barium, and strontium are generally called the metals of the *alkaline earths*. Glucinum and magnesium resemble the metals of the alkaline earths in some ways, but they also resemble the members of Group B, of the same family, which includes zinc and cadmium. On comparing the group with the elements presented in the last chapter, some analogous facts are noticed. Arranging the five elements of the potassium group in the order of their atomic weights, and the elements of Family II, Group A in the same way, we have this table:

| | | | | |
|---|---|---|---|---|
| Li | Na | K | Rb | Cs |
| 7.03 | 23.05 | 39.15 | 85.5 | 132.9 |
| Gl | Mg | Ca | Sr | Ba |
| 9.1 | 24.36 | 40.1 | 87.6 | 137.4 |

As regards the analogies between the elements in each group, the last three members of each group resemble one another more closely than they resemble the first two members of the group, while the first two members in each group also resemble each other closely. The natural

grouping according to the properties is into the sub-groups:

| *a* | | *b* |
|---|---|---|
| Lithium,<br>Sodium, | and | Potassium,<br>Rubidium,<br>Cæsium. |
| Glucinum,<br>Magnesium, | and | Calcium,<br>Strontium,<br>Barium. |

The relations between the atomic weights of the elements of Family II, Group A, are similar to those of the elements of Family I, Group A. That of magnesium, 24.36, is nearly half the sum of those of glucinum, 9.1, and calcium, 40.1. We have

$$\frac{9.1 + 40.1}{2} = 24.6.$$

So, also, that of strontium, 87.6, is approximately half the sum of those of calcium, 40.1, and barium, 137.4.

$$\frac{40.1 + 137.4}{2} = 88.75.$$

In the calcium group the specific gravities increase in the order of the atomic weights:

| | At. Wt. | Sp. Gr. |
|---|---|---|
| Calcium | 40.1 | 1.57 |
| Strontium | 87.6 | 2.5 |
| Barium | 137.4 | 3.75 |

All the elements of the group are bivalent. The general formulas of the principal compounds are as follows:

$MCl_2$, $M(OH)_2$, $M(NO_3)_2$, $MSO_4$, $M_3(PO_4)_2$, $MSiO_3$, etc.

The chlorides, hydroxides, and nitrates are soluble in water. The sulphates decrease in solubility as the atomic weights increase. Glucinum sulphate, $GlSO_4$, is soluble in its own weight of water; magnesium sulphate, $MgSO_4$, is soluble in about three times its weight of water; calcium

sulphate, $CaSO_4$, dissolves in 400 parts; strontium sulphate, $SrSO_4$, in about 8000 parts; and barium sulphate, $BaSO_4$, in about 400,000 parts of water. Barium sulphate, as will be seen, is practically insoluble in water. The normal carbonates of all except glucinum are insoluble in water. The solubility of the hydroxides increases as the atomic weight increases. Glucinum hydroxide is insoluble; magnesium hydroxide is but slightly soluble. One hundred parts of water at the ordinary temperature dissolve 0.1368 part of calcium hydroxide, 2 parts of strontium hydroxide, and 3 5 parts of barium hydroxide. The solubility of strontium and barium hydroxides is, however, much increased at higher temperatures.

## *CALCIUM SUB-GROUP.*

This sub-group, as has been stated, consists of the three similar elements, calcium, strontium, and barium. Of these calcium occurs most abundantly in nature. Barium and strontium frequently accompany each other, and both are found in some localities in company with calcium. They are much less abundant in nature than calcium.

### Calcium, Ca (At. Wt. 40.1).

**Occurrence.**—Calcium is found in nature in enormous quantities, chiefly in the form of the carbonate, $CaCO_3$, as limestone, marble, and chalk. It also occurs in the form of the sulphate, $CaSO_4$, as gypsum; of the phosphate, $Ca_3(PO_4)_2$, as phosphorite; of the fluoride, $CaF_2$, as fluor spar. It is found in solution in most natural waters either as the carbonate or sulphate; and in the organs of plants and animals. Bones contain a large proportion of calcium phosphate; egg-shells and coral contain calcium carbonate.

**Preparation.**—Calcium is made: (1) By heating together anhydrous calcium iodide and metallic sodium; (2) commercially, by the electrolysis of calcium chloride.

**Properties.**—Calcium is silver-white, hard, and tough It melts at 800°. It is one of the most active elements

known, and combines with all the other elements except argon. It combines with hydrogen to form the hydride $CaH_2$, and burns brilliantly in the air, forming compounds with both oxygen and nitrogen. It decomposes water easily and becomes incandescent if in the form of powder.

**Calcium Chloride,** $CaCl_2$.—This salt is found in nature in combination with other chlorides, particularly in the mineral tachydrite, which occurs in the salt deposits at Stassfurt, and has the composition represented by the formula $CaCl_2.MgCl_2 + 12H_2O$. It is also found in solution in sea-water. It is obtained as a by-product in the preparation of ammonia from ammonium chloride and lime; in the preparation of potassium chlorate from calcium chlorate and potassium chloride (see p. 468); and in the ammonia-soda process. It is made by dissolving calcium carbonate in hydrochloric acid, as in the preparation of carbon dioxide. From very concentrated solutions it crystallizes with six molecules of water, $CaCl_2 + 6H_2O$. When these crystals are exposed to the air they soon deliquesce. When a solution of calcium chloride is evaporated, and care is taken to keep the temperature below 200°, it solidifies, forming a porous mass which has the composition represented by the formula $CaCl_2 + 2H_2O$. This is much used in laboratories as a drying agent, as it absorbs water with great ease. If it is heated above 200° it loses all its water, and the dehydrated chloride melts, forming fused calcium chloride. This is also much used on account of its drying power. Gases are passed through tubes filled with granulated calcium chloride for the purpose of drying them, and the salt is also placed in vessels in which it is necessary that the air should be dry, as in balance-cases, desiccators, etc.

Calcium chloride forms crystallized compounds with ammonia and with alcohol, as well as with water. It is obvious from this that calcium chloride cannot be used for the purpose of drying ammonia gas. When the compounds with ammonia and with alcohol are heated they

break down, yielding ammonia and alcohol respectively, as the compound with water gives up the latter.

**Calcium Fluoride,** $CaF_2$.—This compound occurs in large quantities in nature as the mineral fluor spar. It occurs beautifully crystallized in cubes, and is insoluble in water. It is the source of fluorine compounds in general, and is used in metallurgical operations for the reason that it melts readily and does not act upon other substances easily. It therefore serves as a liquid medium in which reactions take place at high temperatures. A substance that acts in this way and is used for this purpose is called a *flux*. The name fluor spar has its origin in this use of the substance.

**Calcium Oxide,** CaO.—This important compound is commonly called *lime*, or, to distinguish it from the hydroxide or *slaked lime*, it is called *quick-lime*. It is made in large quantity by heating calcium carbonate in appropriately constructed furnaces, known as lime-kilns. Pure lime is made by decomposing some pure form of calcium carbonate, as marble or calc-spar.

Lime is a white, amorphous, infusible substance. When heated in the flame of the compound blowpipe it gives an intense light, as any other infusible substance would do under the same circumstances. When exposed to the air it attracts moisture and carbon dioxide, and is converted into the carbonate. It must therefore be protected from the air. Lime which has been converted into the carbonate by exposure to the air is said to be *air-slaked*.

**Calcium Hydroxide,** $Ca(OH)_2$.—When calcium oxide or quick-lime is treated with water it becomes hot and crumbles to a fine powder. The substance formed in this operation is somewhat soluble in water, the solution being known as *lime-water*. The chemical change that takes place when lime is treated with water has been explained. It consists in the formation of a compound of the formula $Ca(OH)_2$, known as slaked lime; and the operation is known as *slaking*. The action is of the same kind as that with which we have so frequently had to deal in the transformation of oxides into the correspond-

ing hydroxides. Thus when potassium oxide is treated with water it is changed to the hydroxide, with a marked evolution of heat, the reaction being represented in this way:

$$K_2O + H_2O = 2KOH.$$

So, too, when sulphur trioxide is brought in contact with water it appears to form the hydroxide, normal sulphuric acid:

$$SO_3 + 3H_2O = S(OH)_6.$$

The action in the case of calcium oxide is represented in a similar way:

$$CaO + H_2O = Ca(OH)_2.$$

The hydroxide is a fine white powder. At red heat it loses water and is reconverted into the oxide:

$$Ca(OH)_2 = CaO + H_2O.$$

When lime water is exposed to the air it becomes covered with a crust of calcium carbonate, and finally all the calcium is precipitated as calcium carbonate. A solution of calcium hydroxide affords a convenient means of detecting the presence of carbon dioxide, as has been shown in dealing with this gas. The solution has an alkaline reaction, and acts in many respects like solutions of the hydroxides of potassium and sodium.

**Applications.**—Lime is extensively used in the arts, generally in the form of the hydroxide. As we have seen, it is used in the preparation of ammonia and the caustic alkalies, potassium and sodium hydroxides; and of bleaching-powder and potassium chlorate. It is further used in large quantity for the purpose of removing the hair from hides in the process of tanning; in decomposing fats for the purpose of making stearin (stearic acid) for candles; for purifying gas; and especially in the preparation of mortar.

**Bleaching-powder.**—The preparation of bleaching-powder was referred to under Chlorine (which see). The

main reaction involved is that represented by the equation

$$2Ca(OH)_2 + 4Cl = \underbrace{Ca(ClO)_2 + CaCl_2}_{\text{Bleaching-powder.}} + 2H_2O.$$

The compound is often called "chloride of lime" and simply "bleach." Assuming that the reaction takes place in the same way that chlorine acts on caustic potash, the product is a mixture of calcium hypochlorite, $Ca(ClO)_2$, and calcium chloride, for it is held that the reaction with potassium hydroxide takes place as represented in this equation:

$$2KOH + 2Cl = KClO + KCl + H_2O.$$

An objection to the view that calcium chloride is present as such in bleaching-powder is found in the fact that the substance is not deliquescent, as it should be if calcium chloride were present. This has led to the suggestion that bleaching-powder in the dry form is not a mixture of two compounds, as represented above, but that it is rather one compound of the formula $Ca\begin{cases} Cl \\ OCl \end{cases}$ or $CaOCl_2$. The evidence appears to be rather in favor of the view that bleaching-powder in the dry form is a single compound of the constitution represented by the last formula given. When treated with water, however, it conducts itself like a mixture of the hypochlorite and chloride. This is entirely in accordance with the theory of electrolytic dissociation, as the ions would be the same in both cases:

$$CaCl_2 = \overset{++}{Ca} + 2\bar{Cl};$$

$$Ca(OCl)_2 = \overset{++}{Ca} + 2\bar{O}Cl.$$

$$2Ca\begin{cases} Cl \\ OCl \end{cases} = 2\overset{++}{Ca} + 2\bar{O}Cl + 2\bar{Cl}.$$

Bleaching-powder is a white substance of the odor of hypochlorous acid. It is soluble in about twenty parts of water, though the commercial product always leaves a slight residue, mainly of calcium hydroxide. When treated with an acid it gives up all its chlorine. Thus,

with hydrochloric acid the reaction takes place as represented in these equations:

$$Ca(ClO)_2 + 2HCl = CaCl_2 + 2HClO;$$
$$2HCl + 2HClO = 2H_2O + 2Cl_2.$$

With sulphuric acid the action also probably takes place in two stages. The acid acts upon the hypochlorite, setting hypochlorous acid free; and upon the chloride, setting hydrochloric acid free. The hydrochloric and hypochlorous acids then react with each other as represented above:

$$Ca(ClO)_2 + H_2SO_4 = CaSO_4 + 2HClO;$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl;$$
$$2HCl + 2HClO = 2H_2O + 2Cl_2.$$

When exposed to the action of carbon dioxide hypochlorous acid is liberated. Hence, when it is allowed to lie in the air this decomposition takes place slowly. The hypochlorous acid acts further upon the calcium chloride, liberating chlorine:

$$CaCl_2 + 2HOCl + CO_2 = CaCO_3 + H_2O + 2Cl_2.$$

It may be, however, that the action takes place between carbon dioxide and the compound $CaOCl_2$, thus:

$$CaOCl_2 + CO_2 = CaCO_3 + Cl_2.$$

It any case, the fact remains that carbon dioxide sets the chlorine free from bleaching-powder.

A solution of bleaching-powder alone bleaches very slowly. If, however, something is added which has the power to decompose it, bleaching takes place, the action being due to the presence of hypochlorous acid and chlorine. As is clear from what was said above, the passage of carbon dioxide through the solution or the addition of an acid would cause it to bleach. So, too, certain salts produce a similar effect. The explanation of this is the instability of the hypochlorites formed by the salts added. When a concentrated solution

of bleaching-powder is heated it gives off oxygen, and the salt is converted into the chloride. In dilute solution, however, the hypochlorite is converted into chlorate and chloride:

$$3Ca(ClO)_2 = Ca(ClO_3)_2 + 2CaCl_2.$$

This fact is taken advantage of, as has been shown, for the purpose of making calcium chlorate, and from this potassium chlorate (see p. 468). In contact with certain oxides, as copper oxide, ferric oxide, and with hydroxides, as cobalt and nickel hydroxides, a solution of bleaching-powder readily gives up oxygen when heated.

**Applications.**—The chief application of bleaching-powder is, as its name implies, for bleaching. It is also used as a disinfectant, and as an antiseptic.

**Calcium Carbonate,** $CaCO_3$.—This salt occurs in immense quantities in nature in the well-known forms limestone, calc-spar, marble, and chalk. The variety of calc-spar found in Iceland, and known as Iceland spar, is particularly pure calcium carbonate. It crystallizes in a number of different forms, the most common being rhombohedrons, as seen in ordinary calc-spar. A second variety of crystallized calcium carbonate is *aragonite.* This is found in nature crystallized in rhombic prisms, and in forms derived from this. When heated, aragonite falls to pieces, the particles being small crystals of the form characteristic of calc-spar. This is a case of dimorphism similar to that presented by sulphur, which, it will be remembered, crystallizes in two forms, the rhombic and monoclinic, the latter of which passes into the former spontaneously. These forms are produced artificially very readily. When calcium carbonate is precipitated from a solution of a calcium salt by adding a soluble carbonate at ordinary temperatures the precipitate is made up of microscopic crystals which have the same form as calc-spar. If, however, the solution from which the carbonate is precipitated is hot, the salt consists of microscopic crystals of the form of aragonite.

The most abundant form of calcium carbonate is lime-

stone, of which many great mountain-ranges are largely made up. This is a compact form of the compound, that has a gray color, and frequently consists of minute crystals. It is always more or less impure, containing clay and other substances. Limestone mixed with a considerable proportion of clay is called *marl*. Many natural waters contain calcium carbonate in solution—probably in the form of the acid carbonate. When such a water evaporates the carbonate is again deposited. It happens in some places that a water charged with the carbonate works its way slowly through the earth and drops from the top of a cave. Under these circumstances there is a gradual deposit of the salt which remains suspended. Such hanging formations of the carbonate are known as *stalactites*. At the same time that part of the liquid which falls to the bottom of the cave forms a projecting mass below the stalactite. Such projecting masses are called *stalagmites*. The formation of stalactites takes place in much the same way as that of icicles.

Much of the calcium carbonate found in nature has its origin in the remains of animals, and fossils are very abundant in it. *Chalk* consists almost exclusively of the shells of microscopic animals.

When carbon dioxide is passed into a solution of calcium hydroxide, the carbonate is precipitated; and, if the current of gas is continued long enough, the carbonate is redissolved. It appears, therefore, that calcium carbonate is soluble in water that contains carbonic acid. It is probable that the cause of this is to be found in the formation of an acid carbonate. Natural waters which come in contact with limestone gradually take up more or less of the carbonate, with the aid of the carbon dioxide of the air, and when such a water is boiled, the carbonate is precipitated. A water containing calcium carbonate in solution is called a *hard water;* and as this kind of hardness is easily removed by boiling, it is called *temporary hardness* in order to distinguish it from a kind which is not removed by boiling, and is therefore called *permanent hardness*. Temporary hardness is also removed by adding

lime to the water, when normal carbonate is formed, which is at once precipitated.

The decomposition of calcium carbonate by heat, leading to the formation of lime, or calcium oxide, and carbon dioxide, has been treated of on p. 454.

**Applications.**—Calcium carbonate is used, in the arts, for a great many purposes, as in the manufacture of glass; as a flux (see p. 501) in many important metallurgical operations, as in the reduction of iron from its ores; in the preparation of lime for mortar; etc. As is well known, further, marble and some of the varieties of limestone are extensively used in building; and large quantities of chalk are also used.

**Calcium Sulphate,** $CaSO_4$.—This compound is very abundant in nature. The principal natural variety is *gypsum*, which occurs in crystals containing two molecules of water, $CaSO_4 + 2H_2O$. This is perhaps derived directly from the normal acid $S(OH)_6$, having the constitution represented by the formula $(HO)_2S{<}^{O}_{O}{>}Ca$. The salt of the formula $CaSO_4$ also occurs in nature, and is called *anhydrite*. A granular form of gypsum is called *alabaster*. Calcium sulphate is difficultly soluble in hot and cold water, but its solubility is markedly increased by the presence of certain other salts; as, for example, sodium chloride. It is comparatively easily soluble in hydrochloric acid and in nitric acid. When heated to 100°, or a little above, it loses nearly all its water and forms a powder known as *plaster of Paris*, which has the power of taking up water and forming a solid substance. This process of solidification is known as "setting." Plaster of Paris is very largely used in making casts, on account of its power to harden after having been made into a paste with water. The hardening is a chemical process, and is caused by the combination of water with the salt to form the crystallized variety:

$$CaSO_4 + 2H_2O = (HO)_2S{<}^{O}_{O}{>}Ca.$$

When heated to 200°, and above, all the water is given off from gypsum, and the product then combines with water only very slowly, and is of no value for making casts. In general, the higher the temperature to which the gypsum is heated, the greater the difficulty with which the product combines with water.

Many natural waters contain gypsum in solution. Such waters act in some respects like those which contain calcium carbonate. With soap, for example, they form insoluble compounds. They are called hard waters. This kind of hardness is not removed by boiling, and it is therefore called *permanent hardness*. Magnesium sulphate acts in the same way, producing permanent hardness.

When calcium sulphate is treated with a solution of a soluble carbonate, it is decomposed, forming the carbonate as represented in the equation

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3.$$

This change is effected by allowing the two to stand in contact at the ordinary temperature.

**Applications.**—Besides being used for making casts, calcined gypsum is used in surgery for making plaster-of-Paris bandages, and as a fertilizer. Its action as a fertilizer is believed by some to be due to the fact that it has the power to hold ammonia and ammonium carbonate in combination, and thus to make them available for the plants. It has recently been shown that it in some way facilitates the process of nitrification, and perhaps it is in consequence of this that it facilitates plant-growth.

**Calcium Phosphates.**—There are three phosphates of calcium: (1) The *normal phosphate*, $Ca_3(PO_4)_2$; (2) the *secondary phosphate*, $CaHPO_4$; and (3) the *primary phosphate*, $CaH_4(PO_4)_2$.

(1) *Normal calcium phosphate*, $Ca_3(PO_4)_2$, is derived from phosphoric acid by the substitution of calcium for all the hydrogen. It is found in nature in large quantity as *phosphorite*, and in combination with calcium fluoride or chloride as *apatite*. It is, further, the chief inorganic

constituent of bones, forming 85 per cent of bone-ash, and is contained in the excrement of animals, as in guano, etc. It is found everywhere in the soil, and is taken up by the plants for whose development it is essential. That it is also essential to the life of animals is obvious from the fact that the bones consist so largely of it. The phosphate needed for the building up of bones is taken into the system with the food. From these statements, it is clear that calcium phosphate is of fundamental importance, and that a fertile soil must either contain this salt or something from which it can be formed. Now, when a crop is raised on a given area, a certain amount of the phosphate contained in it is withdrawn. If the plants were allowed to decay where they grow, the phosphate would be returned and the soil would continue fertile; but in cultivated lands this is not the case. The crops are removed, and with them the calcium phosphate contained in them, and the soil therefore becomes exhausted. If the substances removed are used as food, some of the phosphate is found in the excrement of the animals; and, if this excrement is put on the soil, it is again rendered fertile. There are, however, other sources of calcium phosphate, and some of these are utilized extensively in the preparation of artificial fertilizers. The natural form of the phosphate, as that in bone-ash, in phosphorite, and in guano, is mainly the normal or neutral phosphate. This is insoluble in water, and is therefore taken up by the plants with difficulty. To make it quickly available, it must be converted into a soluble phosphate. This is done by treating it with sulphuric acid in order to bring about the reaction represented in this equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

The primary phosphate thus formed is soluble in water, and is of great value as a fertilizer. The mixture of the soluble phosphate and of calcium sulphate is known as "superphosphate of lime." The sulphate, as we have seen, is also of value as a fertilizer. The value of superphosphates depends chiefly upon the amount of soluble

phosphate contained in them; and in dealing with them it is customary to state how much "soluble" and how much "insoluble phosphoric acid" they contain. When a superphosphate is allowed to stand for a time, some of the soluble primary phosphate is converted into insoluble phosphates by contact with basic hydroxides and water. This is known as the process of "reversion," and that part of the phosphoric acid which is contained in the insoluble phosphate is spoken of as "reverted phosphoric acid."

Normal calcium phosphate, as has been stated, is insoluble in water, and is formed when a soluble normal phosphate is added to a solution of a calcium salt. It is also formed when di-sodium phosphate and ammonia are added to a solution of a calcium salt, thus:

$$2HNa_2PO_4 + 3CaCl_2 + 2NH_3 = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl.$$

Normal or tertiary calcium phosphate is soluble in hydrochloric acid and in nitric acid, in consequence of the formation of calcium chloride, or nitrate, and the primary phosphate. If ammonia is added to this solution, the tertiary phosphate is again precipitated, as represented below:

$$Ca_3(PO_4)_2 + 4HCl = 2CaCl_2 + H_4Ca(PO_4)_2;$$
$$2CaCl_2 + H_4Ca(PO_4)_2 + 4NH_3 = Ca_3(PO_4)_2 + 4NH_4Cl.$$

(2) *Secondary calcium phosphate*, $CaHPO_4$, is formed, as above described, when a solution of a calcium salt is treated with secondary sodium phosphate.

(3) *Primary calcium phosphate*, $H_4Ca(PO_4)_2$, is commonly called the acid phosphate of calcium. It is formed when ordinary insoluble calcium phosphate is treated with concentrated sulphuric acid, and is contained in the so-called superphosphates. It is also formed by treating the neutral phosphate with phosphoric acid and with hydrochloric acid. When treated with but little water, it is converted into the secondary salt and free acid:

$$H_4Ca(PO_4)_2 = HCaPO_4 + H_3PO_4.$$

**Production of Phosphate Rock for Fertilizers.**—In the year 1905 the United States produced 1,978,345 tons, Algeria 334,784, Tunis 521,731, France 476,720, Belgium 193,304, and other countries for which the statistics are not yet available had produced smaller quantities.

**Fertilizers.**—The most important constituents of all plant foods are nitrogen, phosphoric acid, potassium salts and lime. Nitrogen is obtained by the use of animal manure; in commercial fertilizers Chili saltpetre, ammonium sulphate, guano, and the nitrogenous by-products from the packing houses and the menhaden oil industry are the chief sources, to which must now be added calcium nitrate from the Birkelund-Eyde process (p. 292), and calcium cyanamide from the Frank process (p. 515).

Phosphoric acid is applied as ground bone and as superphosphate which is made from phosphate rock and from the phosphatic slag of the Thomas-Gilchrist basic steel process (which see).

Lime occurs in the phosphates, and gypsum and slaked lime are also used.

Potassium is applied as sulphate derived from the Stassfurt deposits.

It should be noted that ammonia, calcium, and potassium are not applied as chlorides, chlorine-ion being apparently injurious to land plants.

**Action of Acid and Basic Fertilizers on Soils.**—Fertilizers having an acid reaction with litmus render the soil porous, giving ready access of air and water to the plant roots. Fertilizers having a basic reaction with litmus have the opposite effect. Hence, independently of the *food* constituents, an acid fertilizer is better for a dense clay soil, and a basic fertilizer is better for a porous sandy soil.

**Calcium Silicate,** $CaSiO_3$, occurs in nature as the mineral wollastonite, and, in combination with other silicates, in a large number of minerals, as garnet, mica, the zeolites, etc. It is formed when a solution of sodium sili-

cate is added to a solution of calcium chloride, and when a mixture of calcium carbonate and quartz is heated to a high temperature.

**Glass.**—Ordinary glass is a silicate of calcium and sodium made by melting together sand (silicon dioxide, $SiO_2$) with lime and sodium carbonate or soda. Instead of calcium carbonate, lead oxide may be used; and instead of sodium carbonate, potassium carbonate. The properties of the glass are dependent upon the materials used in its manufacture.

**Theory of Glass.**—Fused silicon dioxide when cooled forms an amorphous vitreous mass which is the simplest glass (see Quartz Glass). The glass formation occurs at much lower temperature when metallic oxides are dissolved in the fused silicon dioxide. The metallic oxides in practical use are those of sodium, potassium, calcium, barium, lead, and zinc. Within certain limits metal oxides may be dissolved to any extent, and glass results. The maximum limit for the metallic oxide is the formation of salts of normal silicic acid, $SiO_4H_4$, for example, $SiO_4CaNa_2$. The limit of silicon dioxide is more elastic as glass generally contains salts of polysilicic acids.

Hot glass is plastic, like amorphous supercooled sulphur; cold glass is brittle, yet it retains some plasticity. If a piece of glass is scratched with a diamond and continued pressure is applied, welding takes place and the scratch disappears. Glass like amorphous sulphur is considered a supercooled solid solution, rather than a definite chemical compound.

*Ordinary window glass* is a sodium-calcium glass. The purer the calcium carbonate and silica, the better the quality of the glass. This glass is comparatively easily acted upon by other substances, and is therefore not adapted to the preparation of vessels which are to be used to hold acids and other chemically active substances. It answers, however, very well for windows. The difference between ordinary window glass and plate glass is essentially that the former is blown and then cut into pieces,

while the latter, when in the molten condition, is run into moulds and there allowed to solidify.

*Bohemian glass* is made with potassium carbonate. If pure carbonate is used, as well as pure calcium carbonate and silica, a very beautiful glass is the result. It is characterized by great hardness, by its difficult fusibility, and by its resistance to the action of chemical substances. It is particularly well adapted to the manufacture of vessels and tubes for use in chemical laboratories.

*Jena glass* is used for chemical apparatus. It contains boric acid. Barium silicate and zinc silicate are also used in making glass which resists the action of acids and alkalies.

*Flint-glass* is made by melting together lead oxide, potassium carbonate, and silicon dioxide. It is characterized by its power to refract light, its high specific gravity, its low melting-point, and the ease with which it is acted upon by reagents. Owing to its high refractive power, it is largely used in the manufacture of lenses for optical instruments.

*Strass* is a variety of lead-glass that is particularly rich in lead. Its refracting power is so great that it is used in the manufacture of artificial gems.

Colors are given to glass by putting in the fused mass small quantities of various substances. Thus, a cobalt compound makes glass blue; copper or chromium makes it green; one of the oxides of copper makes it red; uranium gives it a yellow color; etc. The most common variety of glass is that used in the manufacture of ordinary bottles. It is generally green to black, and sometimes brown. In its manufacture, impure materials are used, chiefly ordinary sand, limestone, sodium sulphate, common salt, clay, etc.

When glass is suddenly cooled, it is very brittle and breaks into small pieces when scratched or slightly broken in any way. This is shown by the so-called Prince Rupert's drops, which are made by dropping glass, in the molten condition, into water. When the end of such a drop is broken off, the entire mass is completely shattered

into minute pieces. It is clear from this that, in the manufacture of glass objects, care must be taken not to cool them suddenly. In fact they are cooled very slowly, the process being known as *annealing*. For this purpose they are placed in furnaces the temperature of which is but little below that of fusion, and they are kept there for some time, the heat being gradually lowered. If red-hot glass is introduced into heated oil or paraffin, and allowed to cool very slowly, it is found to be extremely hard and elastic. The glass of De la Bastie is made in this way. Vessels made of it can be thrown about upon hard objects without breaking, but sometimes a slight scratch will cause the glass to fly into pieces as the Rupert's drops do.

**Mortar.**—Mortar is made of slaked lime and sand. When this mixture is exposed to the air, calcium carbonate is slowly formed and the mass becomes extremely hard. The water contained in the mortar soon passes off, but nevertheless freshly plastered rooms remain moist for a considerable time. This is due to the fact that a reaction takes place between the carbon dioxide and calcium hydroxide by which calcium carbonate and water are formed,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$

and it is the water thus liberated that keeps the air moist. The complete conversion of the lime into carbonate requires a long time, because the carbonate which is formed on the surface protects, to some extent, the lime in the interior.

It is generally regarded as unwholesome to live in rooms with freshly plastered walls, because the air is constantly kept moist in consequence of the reaction above mentioned. It is, however, difficult to see why the presence of a little extra moisture in the air should be unwholesome; and, if there is any danger from freshly plastered walls, it seems probable that the cause must be sought for elsewhere. It is possible that the constant presence of moisture in the pores of the wall interferes with the important

process of diffusion, and that therefore when the room is closed this natural method of ventilation cannot come into play.

When limestones which contain magnesium carbonate and aluminium silicate in considerable quantities are heated for the preparation of lime, the product does not act with water as calcium oxide does, and this lime is not adapted to the preparation of ordinary mortar. On the other hand, it gradually becomes solid, in contact with water, combining with the water to form hydrated aluminium calcium silicates. Such substances are known as natural *cements*, or *hydraulic cements*.

**Portland Cement.**—Far more important than the natural cement is the artificial or Portland cement, which is made by heating together lime and aluminium silicate, and powdering the fused product. It has been found recently that blast-furnace slags fused with lime and sand in suitable proportions forms an equally good cement.

**Concrete.**—When broken rock and cement are mixed, and the mass allowed to harden, a material as durable as the best stone results. This is called concrete. It has been used for a long time for building under water, and is now coming into general use as house-building material. The manufacture of cement is increasing rapidly, chiefly to supply the demand for concrete. In the year 1904, 3,000,000 tons of cement was produced in the United States, 2,500,000 in Germany, 2,500,000 in England and 2,240,000 in other countries, giving a total of 10,240,000 tons.

**Calcium Cyanamide** is made by Frank's process by conducting nitrogen (obtained from liquid air) over heated calcium carbide in an electric furnace:

$$CaC_2 + 2N = CNNCa + C.$$

The substance is the calcium salt of cyanamide, $CNNH_2$. It is used as a fertilizer. In contact with the soil its nitrogen passes into the forms of ammonia and nitrates.

**Calcium Sulphide,** CaS, is formed by heating calcium

sulphate with charcoal. It is converted by water into the hydrosulphide and the hydroxide:

$$2CaS + 2H_2O = Ca(SH)_2 + Ca(OH)_2.$$

The hydrosulphide is easily soluble in water, while the hydroxide is difficultly soluble. If the water is saturated with the hydroxide, it does not act upon the sulphide. The sulphide is phosphorescent. After having been exposed to sunlight, it continues to give light for some time afterward. This and the similar compound, barium sulphide, are now used in the preparation of luminous objects, such as match-boxes, clock-faces, plates for house-numbers, etc.

**Calcium Nitride,** $Ca_3N_2$, a bronze-colored mass, is formed by heating calcium in nitrogen. It is decomposed by water, with the formation of calcium hydroxide and ammonia.

**Calcium Carbide,** $C_2Ca$, is formed by heating lime and carbon together in an electric furnace, when the reaction represented by the following equation takes place:

$$CaO + 3C = CaC_2 + CO.$$

It is manufactured on the large scale, the form of carbon used being coke. The carbide forms a crystalline mass. That of average quality has a reddish color. That of bad quality has a grayish or black color. When pure it is transparent and white. When treated with water it yields acetylene, $C_2H_2$ (which see).

*Calcium borates* occur in nature as colemanite, $Ca_2B_6O_{11}$, which is the chief source of boric acid (see Borax), and borocalcite, $CaB_4O_7$.

### Strontium, Sr (At. Wt. 87.6).

**Occurrence and Preparation.**—Strontium occurs in nature in the form of the sulphate, $SrSO_4$, as celestite, and in the form of the carbonate, $SrCO_3$, as strontianite. The latter is found in large quantities in Westphalia. The element is isolated by the action of an electric current on the molten chloride.

**Properties.**—It is similar to calcium. It is oxidized by contact with the air, and decomposes water rapidly with evolution of hydrogen, which does not, however, take fire spontaneously.

**Compounds of Strontium.**—The compounds of strontium are similar to those of calcium. Its *chloride* has not the same power to combine with water that calcium chloride has, though it deliquesces when left in contact with the air. The *oxide* is not easily made by decomposition of the carbonate by heat, as the carbonate is much more stable than that of calcium. It is, however, prepared without difficulty by heating the nitrate. When brought in contact with water, the oxide forms the *hydroxide*, which is analogous to calcium hydroxide. It is more easily soluble in water than the latter. Strontium hydroxide has the singular property of uniting with sugar, forming difficultly soluble crystalline compounds. It is therefore used for extracting the remaining beet sugar from molasses. The compound is decomposed by carbon dioxide into strontium carbonate and sugar. This is the chief use of strontium compounds.

*Strontium nitrate*, $Sr(NO_3)_2$, is made in considerable quantity for the purpose of preparing a mixture which, when burned, gives a red light (red-fire, Bengal-fire). It is easily made by dissolving strontianite or strontium carbonate in nitric acid.

*Strontium sulphate*, $SrSO_4$, occurs in nature in beautiful crystals as the mineral celestite. It is formed when a soluble sulphate is added to a solution of a strontium salt. Its solubility lies between that of calcium sulphate and that of barium sulphate.

## Barium, Ba (At. Wt. 137.4).

**Occurrence and Preparation.**—Barium occurs in nature in the same forms of combination as strontium, viz., as the carbonate, $BaCO_3$, in witherite; and as the sulphate, $BaSO_4$, in barite or heavy spar. It is prepared by electrolysis of the molten chloride.

**Properties.**—It closely resembles calcium and strontium, being a white metal, melting at 850°, which is oxidized by contact with the air, and readily decomposes water at the ordinary temperature.

**Barium Chloride,** $BaCl_2 + 2H_2O$, is prepared by dissolving barium carbonate in hydrochloric acid. It dissolves easily in water, but not as easily as the chlorides of strontium and calcium. The order of solubility, beginning with the most soluble, is, calcium, strontium, barium—the same as in the case of the sulphates.

**Barium Hydroxide,** $Ba(OH)_2$, is formed by dissolving barium oxide in water, just as calcium hydroxide is formed by treating calcium oxide with water. In hot water it is much more easily soluble than calcium hydroxide, and it is also more easily soluble in cold water. As such a solution acts in the same general way as lime-water, it is sometimes used in the laboratory for the purpose of detecting carbon dioxide, barium carbonate being insoluble. Like lime-water, it has an alkaline reaction.

**Barium Oxide,** BaO, is made by heating the nitrate, as the carbonate is not easily decomposed by heat. The most interesting property of the oxide is its power to take up oxygen when heated to dark red in the air or in oxygen, when it forms

**Barium Peroxide or Dioxide,** $BaO_2$.—This peroxide is a white powder that looks like the simple oxide. When heated to a temperature a little higher than that required for its formation, it breaks down into barium oxide and oxygen. The formation of the peroxide by heating the oxide in the air, and the decomposition of the peroxide at a higher temperature, make it possible to extract oxygen from the air and to obtain it in the free state. This method of preparing oxygen on the large scale from the air was referred to under Oxygen. Specimens which have been in use for two years are said to be as efficient as at first. When a solution of hydrogen dioxide, $H_2O_2$, is added to a solution of barium hydroxide, a precipitate is formed which has the composition $BaO_2 + 8H_2O$. When filtered and put in a vacuum over sulphuric acid, it loses

all its water and leaves behind pure dioxide. Barium dioxide is a convenient starting point in the preparation of hydrogen peroxide (see Hydrogen Peroxide, p. 125).

It is interesting to compare the action of hydrochloric acid on barium peroxide and on the corresponding compound of manganese. With the latter the reaction takes place as represented in this equation:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2;$$

while with barium peroxide the reaction takes place thus:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

It is probable that in the case of manganese dioxide some intermediate reactions take place which are impossible in the other case (see Manganese Dioxide).

**Barium Sulphide,** BaS, is made by reducing the sulphate by heating with charcoal. It is phosphorescent, like the corresponding calcium compound.

**Barium Sulphate,** $BaSO_4$.—This occurs in nature as barite, or heavy spar, and is precipitated when a soluble sulphate or sulphuric acid is added to a solution of a barium salt. It is insoluble in water. When freshly precipitated, it is easily soluble in concentrated sulphuric acid. It is artificially prepared for use as a pigment and is known as *permanent white.* On account of its insolubility it is much used in chemical analysis for the purpose of detecting and estimating sulphuric acid.

**Barium Carbonate,** $BaCO_3$, occurs in nature as witherite, and is made pure by adding ammonium carbonate and a little ammonia to a solution of barium chloride. The carbonate usually found in the market is made by precipitating a solution of the crude sulphide with sodium carbonate, or by heating together sodium carbonate and natural barium sulphate, or heavy spar. Made in either way it contains alkaline carbonate, from which it is impossible to separate it completely by washing. The carbonate, like the other salts of barium, is poisonous. It has the power to unite, and form insoluble compounds, with metallic oxides of the formula $M_2O_3$, as, for example,

ferric oxide, $Fe_2O_3$, and is used in analytical operations for the purpose of separating iron from other metals, like manganese, which are not precipitated by it.

**Phosphates of Barium.**—The phosphates of barium correspond in general to those of calcium.

**Reactions which are of Special Value in Analysis.**—The sulphates of calcium and strontium are completely converted into the carbonates by contact with a solution of ammonium carbonate in ammonia. The sulphate of barium is not changed in this way. Consequently, if a mixture of the three sulphates is treated with ammonium carbonate, those of calcium and strontium will be converted into carbonates, while that of barium will remain unchanged. By filtering, washing with water, and treating with dilute nitric or hydrochloric acid, the carbonates will be dissolved, while the sulphate will not. If nitric acid is used, the solution may be evaporated to dryness, and treated with a mixture of alcohol and ether. Calcium nitrate will dissolve; strontium nitrate will not.

*Fluosilicic acid* produces a precipitate of barium fluosilicate, $BaSiF_6$, in solutions of barium salts. This is insoluble in a mixture of alcohol and water, and difficultly soluble in water. The corresponding salts of calcium and strontium are soluble.

*Calcium sulphate* in solution produces a precipitate in a solution of a strontium salt or of a barium salt, but not in one of a calcium salt.

*Strontium sulphate* in solution precipitates barium sulphate from a solution of a barium salt, but forms no precipitate in a solution of a strontium salt.

When boiled with a solution of one part of sodium carbonate and three parts of sodium sulphate, the sulphates of strontium and calcium are completely converted into carbonates, while the sulphate of barium remains unchanged.

Barium chloride is insoluble in absolute alcohol; calcium chloride is easily soluble; while strontium chloride dissolves in warm absolute alcohol.

*Ammonium oxalate*, $(NH_4)_2C_2O_4$, produces precipitates

of the oxalates in solutions of calcium, barium, and strontium. Only the calcium salt is insoluble in dilute acetic acid.

*Potassium bichromate*, $K_2Cr_2O_7$, precipitates barium chromate, $BaCrO_4$. The corresponding salt of calcium is soluble in water. Barium chromate is easily soluble in hydrochloric or nitric acid.

All three elements of the group give colored flames which have characteristic spectra. Calcium compounds color the flame reddish yellow; strontium compounds give an intense red; and barium compounds a yellowish-green color. The spectra are more complicated than those of the elements of the potassium group, but each one contains characteristic lines which can easily be recognized.

## *MAGNESIUM SUB-GROUP.*

### Glucinum (Beryllium), Gl (At. Wt. 9.1).

**Occurrence and Preparation.**—The principal form in which the element glucinum occurs in nature is the mineral beryl, which is a silicate of aluminium and glucinum of the formula $Al_2Gl_3(SiO_3)_6$. Emerald has the same composition, but is colored green by the presence of a little chromic oxide. The element can be isolated by decomposing the chloride by heating it with potassium or sodium. It is also called beryllium.

### Magnesium, Mg (At. Wt. 24.36).

**Occurrence.**—Magnesium occurs abundantly in nature, though by no means as abundantly as calcium. Among the widely distributed minerals that contain it are magnesite, which is the carbonate, $MgCO_3$; dolomite, a double carbonate of magnesium and calcium; serpentine, talc, soapstone, meerschaum, hornblende, all of which contain magnesium silicates. Further, it is found in solution in many spring-waters in the form of the sulphate, or, as it is called, Epsom salt. Kainite is a sulphate and chloride of the composition expressed by the formula $K_2SO_4.MgSO_4.MgCl_2 + 6H_2O$; kieserite is magnesium sul-

phate $MgSO_4 + H_2O$; carnallite is a double chloride, $KMgCl_3 + 6H_2O$.

Magnesium compounds are contained in the soil, being formed by the decomposition of various minerals. It is to some extent taken up by the plants, and subsequently into the animal body. It is found in the bones and in the blood in small quantities.

**Preparation.**—The metal is made by the electrolysis of its chloride. In practice carnallite, $MgKCl_3 + 6H_2O$, is used. This is dehydrated and then melted in an iron crucible. A carbon rod brought into the molten mass serves as the anode, while the crucible itself acts as the cathode. The metal magnesium separates at the cathode.

**Properties.**—It is a silver-white metal with a high lustre. In the air it changes only slowly, but it gradually becomes covered with a layer of the hydroxide. At ordinary temperatures magnesium does not decompose water; at 100° it decomposes it slowly. It melts at 633° and boils at about 1100°. When heated above its melting-point in oxygen or in the air, it takes fire and burns with a bright flame, forming the white oxide. The light of the flame is very efficient in producing certain chemical changes, such as those involved in photography when a permanent impression is made by the light upon a sensitive plate. It has also the power to cause hydrogen and chlorine to combine just as the sunlight and the electric light do.

**Applications.**—The principal use to which magnesium is put is for the purpose of producing a bright light, as for photographing in spaces to which the sunlight does not have access, and for signaling (flash light). It is also used to some extent as an ingredient of materials employed in making fireworks. It is used in the laboratory as a reducing agent and as an absorbent for nitrogen.

**Compounds of Magnesium.**—The compounds of magnesium present a general resemblance to those of glucinum. As the element is much more abundant in nature, its compounds have been studied more extensively. Its acid properties are somewhat weaker, and its basic properties stronger, than those of glucinum. Its hydroxide does not

form salts with the hydroxides of potassium and sodium. On the other hand, its chloride is decomposed when its water solution is evaporated to dryness. The hydroxide is very slightly soluble in water, and this solution has a slightly alkaline reaction.

**Magnesium Chloride,** $MgCl_2$.—This salt, as has been stated, occurs in nature. It is easily formed by dissolving magnesium oxide or carbonate in hydrochloric acid. On evaporating at as low a temperature as possible, there finally crystallizes out of the very concentrated solution a salt of the composition $MgCl_2 + 6H_2O$, analogous to crystallized calcium chloride, $CaCl_2 + 6H_2O$, and strontium chloride, $SrCl_2 + 6H_2O$. When this crystallized salt is heated for the purpose of driving off the water, it is completely converted into the oxide:

$$MgCl_2 + H_2O = MgO + 2HCl.$$

This reaction is utilized technically to make hydrochloric acid from carnallite residues.

The chloride is a white, crystalline mass that deliquesces in the air. At a bright red heat it is volatile and it can be distilled in an atmosphere of hydrogen.

**Magnesium Oxide,** MgO.—This compound is commonly called *magnesia*. A fine white variety, known as *magnesia usta*, is made by heating precipitated basic magnesium carbonate. It is a white, loose powder, which is difficultly soluble in water, forming with it the hydroxide, $Mg(OH)_2$, which is also difficultly soluble. Magnesia is used, in medicine, as an application to wounds, and, mixed with a solution of ferric sulphate, as an antidote in cases of poisoning by arsenic. As magnesia is infusible, it is used to protect vessels which are subjected to a high temperature. When mixed with water and allowed to lie in the air, it becomes very hard. Mixtures of magnesia with sand also have this property, and are used as hydraulic cements. It is used, further, in the manufacture of firebricks.

**Magnesium Sulphate,** $MgSO_4$.—The mineral kieserite, which occurs in Stassfurt, has the composition expressed

by the formula $MgSO_4 + H_2O$; or, more probably, this should be written $(HO)_2MgSO_3$, in which it appears as a derivative of the acid $SO(OH)_4$. The salt, $MgSO_4 + 7H_2O$ (or $H_2MgSO_5 + 6H_2O$), also occurs in nature. It is this variety that is generally obtained when a solution of magnesium sulphate is evaporated to crystallization. It crystallizes in large rhombic prisms, or, if rapidly deposited from very concentrated solutions, in small, needle-shaped crystals. At ordinary temperatures, 100 parts of water dissolve 125 parts of the salt. The water solution has a bitter, salty taste. When heated, it readily loses 6 molecules of water, but it requires a temperature of over 200° to drive off the last molecule. This has led to the belief that the salt with one molecule has the constitution above given, being a derivative of the acid $SO(OH)_4$.

**Applications.**—Magnesium sulphate finds extensive application. It is used in medicine as a purgative, and is known as Epsom salt, for the reason that it is contained in the water of Epsom springs; it is used further in the manufacture of sodium sulphate and potassium sulphate, and as a fertilizer in place of gypsum, it having been shown to be advantageous in some cases. Its chief use is for loading cotton fabrics.

**Magnesium Carbonate,** $MgCO_3$.—Magnesium shows a marked tendency to form basic salts with carbonic acid. When a neutral magnesium salt is treated with a soluble carbonate, a basic carbonate is precipitated, the composition of which varies according to the conditions under which it is prepared. The basic carbonate manufactured on the large scale is known as *magnesia alba.* It is this form of the carbonate that is used in the preparation of *magnesia usta.* Normal magnesium carbonate, $MgCO_3$, occurs in nature as magnesite. It crystallizes in the same form as calcium carbonate, or is isomorphous with it. It is insoluble in water, but like calcium carbonate it dissolves in water containing carbon dioxide in solution. From this solution crystals having the composition $MgCO_3 + 3H_2O$ and $MgCO_3 + 5H_2O$ are deposited under the proper conditions.

**Phosphates.**—The conduct of the phosphates of magnesium is very similar to that of the phosphates of calcium. All three are known; and of these only the primary salt is soluble in water. A salt much utilized in analysis is *ammonium-magnesium phosphate*, $Mg(NH_4)PO_4$. This is difficultly soluble in water, and may therefore be used either for the purpose of detecting magnesium or phosphoric acid.

The corresponding salt of arsenic acid, $Mg(NH_4)AsO_4$, is similar to the phosphate, and on account of its insolubility it is also used in chemical analysis.

**Borates.**—A borate of magnesium together with magnesium chloride occurs in nature, and is known as boracite. It has the composition expressed by the formula $2Mg_3B_8O_{15} + MgCl_2$. The borate, $Mg_3B_8O_{15}$, is derived from the acid, $H_6B_8O_{15}$, which is related to normal boric acid, as is shown by the equation

$$8B(OH)_3 = H_6B_8O_{15} + 9H_2O.$$

**Silicates.**—The simplest silicate of magnesium found in nature is olivine, which is represented by the formula $Mg_2SiO_4$. It is the neutral salt of normal silicic acid. Serpentine is derived from the acid, $O<\begin{matrix}Si(OH)_3\\Si(OH)_3\end{matrix}$, and has the composition $Mg_3Si_2O_7 + 2H_2O$.

**Magnesium Silicide,** $Mg_2Si$, is made by heating together magnesium chloride, sodium fluosilicate, sodium chloride, and sodium. Under these circumstances the sodium sets magnesium free from the chloride, and silicon from the fluosilicate. Both unite to form magnesium silicide. When treated with hydrochloric acid it gives silicon hydride, $SiH_4$, and hydrogen:

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

The liberation of hydrogen is due to the presence of an excess of magnesium.

**Magnesium Nitride** is a greenish-yellow powder made by heating magnesium in a current of nitrogen or air. Treated with water ammonia is evolved:

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3.$$

**Reactions of Magnesium Salts which are of Special Value in Chemical Analysis.**—*Soluble hydroxides* (KOH, NaOH, $NH_4OH$) precipitate magnesium hydroxide. If ammonium chloride is present ammonia does not precipitate the hydroxide.

*Di-sodium phosphate* with ammonia and ammonium chloride precipitates ammonium-magnesium phosphate from the solution of a magnesium salt.

*Sodium* and *potassium carbonates* precipitate basic magnesium carbonate.

## Erbium, E (At. Wt. 166).

As regards the position of erbium in the periodic system, a final statement cannot as yet be made. It is even questionable whether it is an element.

## EXPERIMENTS.

### Calcium Salts.

Experiment 222.—Dissolve 10 to 20 grams limestone or marble in common hydrochloric acid. Filter, and evaporate to dryness. Expose a few pieces of the residue to the air.

### Magnesium and its Salts.

Experiment 223.—Make anhydrous magnesium chloride thus: Dissolve 180 grams *magnesia usta* in ordinary hydrochloric acid; shake the solution with an excess of magnesia to remove iron and aluminium; filter; add 400 grams ammonium chloride; evaporate to dryness, keeping the mass constantly stirred. The double salt thus formed must be dried until a small specimen put in a test-tube is found not to give off water when heated. The dry salt is then ignited in a crucible placed in a furnace until ammonium chloride is no longer given off, when the molten mass, which is anhydrous magnesium chloride, is poured out on a stone and, after it is broken up, it is put in a dry bottle provided with a good stopper.

# CHAPTER XXVI.

## ELEMENTS OF FAMILY III, GROUP A: ALUMINIUM.—SCANDIUM.—YTTRIUM.—YTTERBIUM.—SAMARIUM.

**General.**—There is in some respects a resemblance between boron and the principal member of this group; but, as boron acts almost exclusively as an acid-forming element, it was treated of in connection with the elements of Family V, Group B, or the nitrogen group. Attention was, however, called to the fact that the analogy between these elements and boron is but slight. The points of resemblance between boron and the members of Family III, Group A, will be indicated below. The principal member of this group is aluminium. The others are all rare, and some have been but imperfectly studied, owing to serious difficulties in the way of obtaining their compounds in pure condition. They are trivalent in their compounds, the general formulas being such as the following:

$MCl_3$, $M(OH)_3$, $M(NO_3)_3$, $M_2(SO_4)_3$, $M_2(CO_3)_3$, $MPO_4$, etc.

Aluminium oxide is weakly basic, and somewhat acidic, though less so than boron oxide. Aluminium hydroxide has the power to neutralize most acids, and also to form salts with strong bases. Boron oxide, on the other hand, has scarcely any basic properties, though it does form a few extremely stable compounds, in which the boron takes the place of the hydrogen of acids. (See Boron Phosphate, p. 345.)

### Aluminium, Al (At. Wt. 27.1).

**Occurrence.**—Aluminium is an extremely important element in nature and in the arts. It occurs widely dis-

tributed, and abundantly in many different forms of combination. Among them are the feldspars, the micas, cryolite, bauxite. The feldspars are silicates of aluminium and potassium or sodium of the formula $AlMSi_3O_8$. Mica is a general name applied to a large number of minerals which are silicates of aluminium and some other metal, as potassium, lithium, magnesium, etc. The simplest form of mica is that represented by the general formula $KAlSiO_4$, according to which the mineral is a salt of orthosilicic acid, $Si(OH)_4$. Cryolite is a double fluoride of aluminium and sodium, or the sodium salt of fluoaluminic acid, $Na_3AlF_6$. Bauxite is a hydroxide of aluminium in combination with a hydroxide of iron. Aluminium also occurs in the products of decomposition of minerals. One of the most important of these is clay, which is found in all conditions of purity—from the white kaolin to ordinary dark-colored clay. Kaolin is the aluminium salt of orthosilicic acid of the formula $Al_4(SiO_4)_3 + 4H_2O$. Aluminium silicate is found in all soils, but is not taken up by plants, and does not find entrance into the animal body. The name aluminium has its origin in the fact that the salt alum was known at an early date, and the metal was afterwards isolated from it.

**Preparation.**—The preparation of aluminium on the large scale presents a problem of the highest importance. The element has properties that adapt it to many uses to which iron is put, and for many purposes it has advantages over iron. Further, nature furnishes unlimited quantities of the compounds of aluminium, which are distributed everywhere over the earth. While, however, iron, lead, tin, copper, and other metals can be isolated from their natural compounds without serious difficulty, aluminium, which is more abundant than any of them, and in many respects more valuable than any of them, is locked in its compounds so firmly that it is only by electrolytic methods with cheap electric current that it can be isolated at moderate price.

The best method for the preparation of aluminium

consists in the electrolysis of aluminium oxide, in the form of bauxite in a bath of fused cryolite. The oxide is contained in iron crucibles, and carbon rods are introduced into the molten mass. The iron crucible forms one electrode and the carbon rods the other.

In the year 1906, 7,500 tons of aluminium was produced in the United States and in 1905, 5,674. In 1888 the price was $4 a pound; in 1893 it ranged from 65 to 75 cents; in 1907 it was about 50 cents. The lightness of aluminium must be considered in comparing it with other metals; bulk for bulk, aluminium is cheaper than copper and nearly as cheap as zinc.

**Properties.**—The color of aluminium is like that of tin, and it has a high lustre. It is very strong, and yet malleable. Its malleability nearly equals that of gold and silver. It can be beaten to thin leaves (aluminium foil). It is lighter than most metals in common use, its specific gravity being 2.5 to 2.7 according to the condition, while that of iron is 7.8, that of silver 10.57, that of tin 7.3, and that of lead 11.37. It does not change in dry or in moist air; and in the compact form it does not act upon water even at elevated temperatures. It melts at about 660°, which is higher than the melting-point of zinc, and lower than that of silver. Hydrochloric acid dissolves it with ease, forming aluminium chloride. At the ordinary temperatures nitric and sulphuric acids do not act upon it; at higher temperatures, however, action takes place, and the corresponding salts are formed. It dissolves in solutions of the caustic alkalies, forming the so-called aluminates. It reduces many oxides when heated with them to a sufficiently high temperature; and is used in the preparation of boron and silicon. When a mixture of finely divided aluminium and ferric oxide is heated by means of a burning magnesium wire or by means of a cartridge made of magnesium powder and barium peroxide, the aluminium is oxidized at the expense of the ferric oxide, and an extremely high temperature is produced. This is the brightest white heat (about 8000°) and is sufficient to melt the iron and also the aluminic oxide

which are formed. A method of welding has been devised by Goldschmidt which is based upon this reaction.

**Applications.**—The metal is used to a considerable extent in the preparation of ornaments, and of useful articles in which lightness is a matter of importance, as in telescopes, opera-glasses, cooking-utensils, etc. A large part of the aluminium made is employed in casting iron, as an addition of one or two per cent of aluminium gives a dense casting free of bubbles. Aluminium foil is used exclusively now for glass decoration, and ornamental cardboard articles in place of silver foil which blackens with time. An alloy with a small percentage of silver is used for the beams of chemical balances. Aluminium bronze, which is an alloy with copper, is also used quite extensively. It will be again referred to under Copper.

**Aluminium Chloride,** $AlCl_3$.—When aluminium hydroxide is dissolved in hydrochloric acid a solution of aluminium chloride is formed, and from this solution a compound of the formula $AlCl_3 + 6H_2O$ can be obtained in crystallized form. Like calcium and magnesium chlorides, this salt is deliquescent. When heated to drive off the water the salt conducts itself like magnesium chloride, but the decomposition into the oxide and hydrochloric acid takes place more easily than that of magnesium chloride. The reaction is represented by the equation

$$2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl.$$

The dry chloride is prepared by the same method as that used in the preparation of silicon chloride and boron chloride, viz., by passing chlorine over a heated mixture of the oxide and carbon. The chloride, being volatile, sublimes, and is deposited in the cool part of the vessel, when pure, as a white, laminated, crystalline mass. Generally, however, it is more or less colored in consequence of the presence of impurities. When exposed to the air it attracts moisture and gives off hydrochloric acid. It dissolves in water very easily, with a marked evolution of heat, but, from what was said above, it is evident that it cannot be obtained from this solution again by evapora-

tion. It is volatile without change. The specific gravity of its vapor at high temperatures leads to the formula $AlCl_3$.

**Aluminium Hydroxide,** $Al(OH)_3$.—Normal aluminium hydroxide, $Al(OH)_3$, occurs in nature as the mineral hydrargillite It is precipitated from a solution of aluminium chloride by ammonia:

$$AlCl_3 + 3NH_4OH = Al(OH)_3 + 3NH_4Cl.$$

Obtained by precipitation it forms a gelatinous mass, suggestive of starch-paste, and it is on this account extremely difficult to wash it completely free from the substances in the solution. It dries in the air, forming a gummy substance of the composition $Al(OH)_3$. When heated under proper conditions it loses water, and forms the compound $AlO_2H$:

$$Al(OH)_3 = AlO.OH + H_2O.$$

This compound is found in nature as the mineral diaspore. If heated to a higher temperature it is converted into the oxide, $Al_2O_3$:

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

In the conduct of the chloride and of the hydroxide aluminium exhibits a certain resemblance to boron. The acidic character of the latter is, however, more strongly marked than that of the former. Boron chloride is more easily decomposed by water than aluminium chloride, and, as the decomposition takes place at the ordinary temperature, the product is the hydroxide instead of the oxide, as in the case of aluminium. The hydroxide, $B(OH)_3$, readily loses water and forms metaboric acid, which in composition is analogous to diaspore; and at a higher temperature the oxide, $B_2O_3$, is formed.

**Aluminates.**—When sodium or potassium hydroxide is added to a solution of an aluminium salt, aluminium hydroxide is at first precipitated, but an excess of the reagent dissolves the precipitate. This action is due to the acidic character of aluminium hydroxide. It is prob-

able that in solution the action with potassium hydroxide and with sodium hydroxide is represented in the following equations:

$$Al(OH)_3 + 3KOH = Al(OK)_3 + 3H_2O, \text{ and}$$
$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O.$$

On evaporating the solution of the potassium salt, however, the product obtained has the formula AlO.OK, and is plainly the salt of the hydroxide AlO.OH, which may be called meta-aluminic acid, to suggest its analogy to metaboric acid, BO.OH. When aluminium hydroxide and sodium carbonate are melted together, the salt AlO.ONa is formed, as has been shown by determining the amount of carbon dioxide given off when a known weight of the hydroxide is employed. When, however, the solution of the hydroxide in caustic soda is evaporated, the salt $Al(ONa)_3$ is deposited.

These salts are very unstable, though their solutions can be boiled without undergoing decomposition. Carbon dioxide decomposes them at once with precipitation of aluminium hydroxide. Similar salts are formed with calcium and barium. Among them may be mentioned those of the following formulas: $Ca_3(AlO_3)_2$, $Ca(AlO_2)_2$, $Ba_3(AlO_3)_2$, and $Ba(AlO_2)_2$. The calcium salts are insoluble in water, and some of them become hard in contact with water. They are therefore of importance in the manufacture of hydraulic cements. The barium salts are soluble in water.

Many aluminates occur in nature, forming the important group of minerals known as the *spinels*. Of these, spinel itself is the magnesium salt of the hydroxide AlO.OH, and is represented by the formula $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Mg$, or $Mg(AlO_2)_2$. Chrysoberyl is the corresponding glucinum salt $Gl(AlO_2)_2$; and gahnite is the zinc salt $Zn(AlO_2)_2$. These salts are extremely stable, differing markedly in this respect from those above referred to, which are made in the laboratory. They are decomposed by heating them, in finely powdered condition, with primary or acid potassium sulphate, the action of which was described on

p. 471. As will be seen farther on, there are other salts similar in structure to the aluminates which occur in nature. Among these chromic iron, or chromite, which is an iron salt of a hydroxide of chromium of the formula CrO.OH, may be mentioned here. The salt is to be regarded as made up according to the formula $\begin{matrix}CrO.O\\CrO.O\end{matrix}>Fe$, or $Fe(CrO_2)_2$. Further, magnetic oxide of iron or magnetite, $Fe_3O_4$, is regarded as belonging to the same group, and its constitution represented thus: $\begin{matrix}FeO.O\\FeO.O\end{matrix}>Fe$, or $Fe(FeO_2)_2$; and there is also a compound of magnesium, $\begin{matrix}FeO.O\\FeO.O\end{matrix}>Mg$. For the sake of emphasizing these analogies, the formulas of the compounds above mentioned are here presented in tabular form:

| | |
|---|---|
| Potassium aluminate | AlO.OK |
| Sodium aluminate | AlO.ONa |
| Calcium aluminate | $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Ca$ |
| Barium aluminate | $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Ba$ |
| Spinel | $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Mg$ |
| Chrysoberyl | $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Gl$ |
| Gahnite | $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Zn$ |
| Chromite | $\begin{matrix}CrO.O\\CrO.O\end{matrix}>Fe$ |
| Magnetite | $\begin{matrix}FeO.O\\FeO.O\end{matrix}>Fe$ |
| Magnesio-ferrite | $\begin{matrix}FeO.O\\FeO.O\end{matrix}>Mg$ |

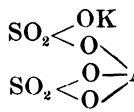
**Aluminium Oxide,** $Al_2O_3$.—As has been stated, the oxide is formed by heating the hydroxide. It is found in nature in the form of ruby, sapphire, and corundum. The natural variety is extremely hard; and granular corundum, which is known as *emery*, is used for polishing. The red color of the ruby is caused by the presence of a

trace of a chromium compound; while the blue color of the sapphire is probably due to the presence of a trace of a cobalt compound. Aluminium oxide is infusible in the hottest furnace fire, but it melts in the flame of the oxy-hydrogen blowpipe, and on cooling it becomes crystalline. In the electric furnace it melts and is vaporized. By mixing it with various easily fusible substances and heating, it is obtained in the form of crystals, and by adding certain metallic oxides these crystals can be colored. In this way artificial rubies and sapphires have been prepared, that have all the properties of the natural ones. When the oxide is moistened with a few drops of a solution of cobaltous nitrate and then ignited, it turns blue. This fact is taken advantage of in chemical analysis for the purpose of detecting aluminium. When the oxide is made by gently igniting the hydroxide, it dissolves in strong acids. If, however, it is heated to a high temperature, acids will not dissolve it. The natural varieties of the oxide, further, are not soluble in acids. By fusion with acid potassium sulphate insoluble aluminium oxide is converted into a soluble compound.

**Aluminium Sulphate,** $Al_2(SO_4)_3$.—This salt is made by dissolving the hydroxide of aluminium in dilute sulphuric acid, and evaporating to crystallization, when a salt of the composition $Al_2(SO_4)_3 + 18H_2O$ is deposited. When heated this salt loses its water of crystallization, and, if the temperature is raised to that of red heat, the anhydrous salt is decomposed with loss of sulphur trioxide and formation of aluminium oxide. This decomposition is, however, not complete. The sulphate is manufactured on the large scale for various purposes, as, for example, for a mordant, for sizing paper, etc.

**Alums.**—When a solution of aluminium sulphate is brought together with a solution of potassium sulphate in the proportion of their molecular weights, a salt crystallizes out which has the composition represented by the formula

$$KAl(SO_4)_2 + 12H_2O, \text{ or } K_2SO_4 + Al_2(SO_4)_3 + 24H_2O.$$

The most rational view held regarding this compound is that it has the constitution  , with perhaps some of the so-called water of the crystallization present in the form of hydroxyl. This salt, which has long been known under the name of *alum*, is the type of a class of similar compounds, all of which are called alums. These may be regarded as derived from the ordinary form by substituting sodium, ammonium, or any other member of the sodium group, besides some other metals, for the potassium. Thus a series of alums is obtained, of which the following are examples:

$$NaAl(SO_4)_2 + 12H_2O;$$
$$LiAl(SO_4)_2 + 12H_2O;$$
$$(NH_4)Al(SO_4)_2 + 12H_2O;$$
$$CsAl(SO_4)_2 + 12H_2O.$$

Again, alums are derived from the ordinary form by substituting for the aluminium some other element that resembles aluminium, as, for example, iron, chromium, and manganese. Such alums are represented by the following formulas:

$$KFe(SO_4)_2 + 12H_2O;$$
$$KCr(SO_4)_2 + 12H_2O;$$
$$KMn(SO_4)_2 + 12H_2O.$$

All the alums have certain properties in common. They are all soluble in water, and all crystallize in the same forms, which are regular octahedrons combined with cubes. If a crystal of one alum is suspended in the solution of any other one it will continue to grow. They are all strictly isomorphous. The principal alums containing aluminium are those of potassium and ammonium, both of which are manufactured on the large scale.

**Potassium Alum, Potassium-Aluminium Sulphate,** $KAl(SO_4)_2 + 12H_2O$.—Ordinary alum is found in nature

in some volcanic regions. The mineral alunite, which is a basic salt of the formula $K(AlO)_3(SO_4)_2 + 3H_2O$, or perhaps $K[Al(OH)_2]_3(SO_4)_2$, occurs in larger quantities. When this salt is heated and treated with water, ordinary alum dissolves, and is easily obtained from the solution. Another source of alum is *alum shale.* This occurs in large quantities in nature, and consists of coal, clay, and iron pyrites. When it is heated in contact with the air the coal burns, as do also the sulphur and pyrites, and sulphuric acid is formed. When allowed to lie for a time in contact with the air the iron pyrites is converted into sulphate and sulphuric acid. The latter acts upon the clay or aluminium silicate, forming aluminium sulphate from which alum can easily be made. It is easier to treat the shale and similar substances with sulphuric acid directly, and this method is now generally employed.

Alum dissolves readily in hot water, 357.5 parts of the crystallized salt dissolving in 100 parts of water at 100°. At 0° only 3.9 parts dissolve, and at the ordinary temperature about 12 parts. It crystallizes beautifully in regular octahedrons, occasionally with cube faces developed on them. Under some circumstances it crystallizes in cubes. When heated, alum melts in its water of crystallization, and if heated to a sufficiently high temperature the water passes off, leaving *burnt alum.*

**Applications.**—Alum is used very extensively in the preparation of pigments, as a mordant,* in the sizing of paper, for clarifying water, etc.

* In dyeing with dyes like indigo or Prussian blue, an insoluble colored precipitate is formed in the fibre of the substance dyed. Hence such dyes form fast colors with any fabric. The majority of the dyes used are soluble in water.

*Substantive dyes* are those which can be removed from their solution by contact with a fabric, combining with the fibre to form colors more or less fast according to the nature of the fibre.

*Adjective dyes* are those which do not combine directly with the fibre but require the use of a mordant. Salts of aluminium and of tin are common mordants. On treating the fabric with the mordant the latter combines with the fibre of the fabrics. On treating the mordanted fabric with the dye, the dye forms a fast color (or insoluble chemical compound) with the mordant.

**Ammonium Alum, Ammonium-Aluminium Sulphate,** $(NH_4)Al(SO_4)_2 + 12H_2O$, is in most respects much like the potassium compound, and can be used in place of it for almost all purposes for which alum is used. It is somewhat more easily soluble than ordinary alum. As it is cheaper than the latter it is largely manufactured instead of it.

**Sodium Alum** is much more soluble in water than either potassium or ammonium alum, and this makes it difficult to prepare it in pure condition. It is therefore not manufactured, although sodium compounds are cheaper than those of either potassium or ammonium.

**Aluminium Silicates.**—It has been stated that aluminium silicate enters into the composition of a number of important minerals. It occurs in enormous quantities in nature. The most important of the minerals containing it are the feldspars, of which ordinary feldspar, $KAlSi_3O_8$, and albite, or sodium feldspar, $NaAlSi_3O_8$, are the most abundant. These again enter into the composition of granite together with quartz and mica, and mica is itself a double silicate of aluminium. As remarked under Silicic Acid (which see), the natural silicates are for the most part salts of polysilicic acids that are derived from orthosilicic acid by loss of water from two or more molecules. Up to the present but little more has been done with the many natural silicates than to determine their percentage composition. It appears probable from what has already been learned regarding their constitution that investigations in this direction will before long yield interesting results. As yet, however, the methods for such investigations are quite unsatisfactory, owing largely to the fact that the compounds are so extremely stable that but few reagents decompose them, and if they are decomposed at all, the products are such that no conclusion can be drawn regarding the constitution. A careful study of the relations in which minerals occur in nature will undoubtedly be of assistance, as this will throw some light upon the conditions under which they were formed.

One of the most common decompositions of minerals,

constantly taking place, and that has taken place to an enormous extent, is that of feldspar. Under the influence of moisture and the carbon dioxide of the air, this substance slowly decomposes, the products being mainly potassium or sodium carbonate, silicic acid, and aluminium silicate. The alkali carbonate, being soluble, is carried away, and finds its way into the soil. The silicate of aluminium is not soluble, but it easily forms emulsions with water, and is therefore carried down the sides of the hills and mountains upon which it is formed into the valleys, and much of it finds its way into streams. Sometimes this carrying away is prevented, and then large beds of comparatively pure clay, known as kaolin, are formed. The clay found in the valleys is always more or less impure and colored.

*Kaolin.*—This is the purest form of aluminium silicate found in nature. It always contains water. Its composition varies, some specimens on analysis giving results which lead to the formula $Al_4(SiO_4)_3 + 4H_2O$, according to which the substance is a salt of normal silicic acid, $Si(OH)_4$. Other specimens have the composition $HAlSiO_4 + H_2O$, or $Si\begin{cases} OH \\ O_2Al + H_2O \end{cases}$. When heated alone kaolin does not melt; but if feldspar is added to it, the whole melts, and forms a translucent mass known as *porcelain*. Other substances besides feldspar may be used for this purpose.

*Clay.*—Clay, as has been stated, is a name given to the impure varieties of aluminium silicate that have been carried down from the place of formation. Among the substances besides aluminium silicate found in clays are calcium carbonate, magnesium carbonate, sand, and hydroxides of iron. The color is largely determined by the amount of the hydroxides of iron present. The better varieties are used in the manufacture of the so-called "stone-ware," gas-retorts, and fire-bricks. The colored varieties are used for making ordinary earthenware and bricks. *Marl* is clay mixed with considerable quantities of calcium carbonate.

*Ultramarine.*—The substance occurring in nature and known as *lapis lazuli* consists of a silicate of sodium and aluminium together with a sulphur compound, probably a polysulphide of sodium. The coloring matter, known as ultramarine, obtained by powdering it was formerly very expensive, but it is now made artificially by the ton, by first heating clay with sodium sulphate and carbon. This yields a green substance, which, when heated with sulphur in a current of air yields the blue ultramarine. It is used as paint, and by laundries as blueing.

*Porcelain.*—It was stated above that when kaolin is heated alone it does not melt, but that when feldspar is added to it, or when that found in nature contains feldspar, as is frequently the case, it melts and forms a compact, translucent mass. Further, when kaolin or any other variety of clay is mixed with water, a plastic substance results, that can be kneaded and worked into any desired form. These facts form the basis of the manufacture of earthenware, porcelain, etc. The ease with which the mass melts depends upon the quantity of feldspar or other flux added to it. If but little is added it melts with difficulty; if much is added it melts easily.

In the manufacture of the finest kinds of porcelain kaolin is used. This is generally mixed with a little feldspar or chalk, gypsum or some other flux, and sand is also added. All these substances must be very finely ground.

The mixture is then worked into the desired forms, and carefully dried. After the objects are dried they are next burned, first at a red heat at which the mass becomes solid, afterwards at a white heat for the purpose of forming a glaze upon the surface. The product after the first burning is that which is familiar as porous earthenware; that formed in the second burning is the porcelain with glaze as it is commonly used.

In order to form the glaze upon the porcelain the porous earthenware first formed is drawn through a vessel containing proper materials in finely powdered condition and suspended in water. The materials used are generally the

same as those used for the porcelain itself, but they are mixed in different proportions, with less kaolin, and more sand and feldspar, so as to make them more easily fusible. After this treatment the objects are again heated to a high temperature.

*Earthenware.*—The ordinary varieties of earthenware are made from clays which are much less pure than kaolin. Ordinary colored clay is used. The objects are formed, and then subjected in general to the same kind of treatment as porcelain. They are glazed in different ways. One method consists in bringing the glazing material on the earthenware before it is burned; another, in putting the objects in the furnace without a glaze, and towards the end of the firing process throwing sodium chloride into the furnace. The salt is thus brought in contact with the ware in the form of vapor. A chemical change takes place, resulting in the formation of a silicate of aluminium and sodium upon the surface. This melts, and forms a glaze.

Bricks are the most common variety of unglazed earthenware. Owing to the presence of other substances besides aluminium silicate, as, for example, calcium carbonate, the material is comparatively easily fusible. The color of bricks is largely due to the presence of oxides of iron.

**Alloys.**—Aluminium forms alloys with magnesium. Those containing 10 to 25 per cent magnesium come into the market under the name of *magnalium*. This has a specific gravity 2 to 2.5, and is therefore lighter than aluminium, but it is much harder. Magnalium containing a considerably higher percentage of aluminium is used in making mirrors, for which it is well adapted on account of its hardness and its power of taking a high polish. Aluminium amalgam is an extremely active substance. It decomposes water energetically.

**Reactions of Aluminium Salts which are of Special Value in Chemical Analysis.**—*Potassium* and *sodium hydroxides* precipitate aluminium hydroxide, which is soluble in an excess of the reagents.

*Ammonia* precipitates the hydroxide, which is only slightly soluble in an excess of the reagent.

*Hydrogen sulphide* and *carbon dioxide* precipitate aluminium hydroxide from a solution of an aluminate; that is, from a solution of aluminium hydroxide in a caustic alkali.

*Ammonium sulphide* and other soluble sulphides precipitate the hydroxide. This is due to the instability of the sulphide of aluminium, or, going farther back, to the weak basic character of the hydroxide. The reaction of ammonium sulphide with aluminium sulphate takes place as represented in the following equation:

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 3(NH_4)_2SO_4 + 3H_2S + 2Al(OH)_3.$$

*Soluble carbonates* precipitate aluminium hydroxide for the same reason that the soluble sulphides do. The reaction between aluminium sulphate and sodium carbonate takes place thus:

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 3Na_2SO_4 + 3CO_2 + 2Al(OH)_3.$$

## Other Members of Family III, Group A.

**Scandium,** Sc (At. Wt. 44.1).—This element was discovered in 1880 in the minerals euxenite and gadolinite. Its compounds are similar to those of aluminium. It forms an oxide of the formula $Sc_2O_3$; a sulphate, $Sc_2(SO_4)_3$; a double sulphate, $KSc(SO_4)_2$; etc. It is of special interest for the reason that its properties were foretold by Mendeléeff several years before it was discovered. The prophecy was based upon the position of the element in the periodic system. When the relations between the atomic weights and properties of the elements were first described in a comprehensive way by Lothar Meyer and Mendeléeff, the latter described the properties of an element then unknown, which he called *ekaboron*. This should have the atomic weight about 44, should form an oxide of the formula $M_2O_3$, etc. It has been shown that the properties of scandium agree very closely with those foretold.

**Yttrium,** Y (At. Wt. 89), like scandium, is found in gadolinite, euxenite, and some other rare minerals.

**Ytterbium,** Yb (At. Wt. 173).—This rare element, like scandium and yttrium, is found in gadolinite and euxenite—most abundantly in the latter. Its compounds in general resemble those of yttrium.

**Samarium,** Sm (At. Wt. 150.3), has been obtained from Samar skite, a North Carolina mineral. It has also been found in small

quantities in some other minerals, as cerite, gadolinite, and orthite. In general it resembles aluminium in its chemical conduct.

The chemistry of *lanthanum* is so intimately connected with that of cerium and didymium, that, although these three elements appear to belong to different families, they will be briefly treated of together.

## EXPERIMENTS.

### Aluminium Chloride.

Experiment 224.—Aluminium chloride is made thus: Mix aluminium oxide with starch-paste; form the mass into small balls the size of ordinary marbles; ignite these in a crucible in a furnace; put them in a porcelain tube; and then pass dry chlorine over them, at the same time heating the tube to redness. The chloride will sublime and be deposited in the front end of the tube or in a receiver if the heat is sufficient. It can be purified by subliming it over heated iron or aluminium.

## CHAPTER XXVII.

### ELEMENTS OF FAMILY I, GROUP B: COPPER.—SILVER.—GOLD.

**General.**—The facts which strike one most forcibly on comparing the elements of this group with those of Group A of the same family are, that they are much less active chemically, and that they furnish a greater variety of compounds. Sodium and potassium and the other members of Group A display the greatest activity, as we have seen. The basic character is most strongly developed in them. Further, in nearly all their compounds they act with the same valence. They are univalent in all their salts. Copper, silver, and gold, however, are not chemically active elements, and the activity grows less with increasing atomic weight. Copper and gold form two series of compounds each, and silver also forms a few compounds in which it appears with a valence greater than one. In the two series of salts formed by copper the element appears to be univalent and bivalent, as in the chlorides CuCl and $CuCl_2$. Gold, however, is univalent and trivalent, while silver is almost exclusively univalent. It must be said that the resemblance between gold and the other members of Group B, Family I, is apparently not as marked as that between mercury and copper and silver.

### Copper, Cu (At. Wt. 63.6).

**General.**—The compounds of copper which are most commonly met with are those in which it acts as a bivalent element. Its principal compounds are *copper oxide*, CuO; the *sulphate*, $CuSO_4$; and the *sulphide*, CuS. In all these the copper is bivalent. But besides these there are such compounds as CuCl and $Cu_2O$, in which the element ap-

pears to be univalent. There are, then, two series of salts, of which the following will serve as examples:

| | |
|---|---|
| CuCl | $CuCl_2$ |
| CuBr | $CuBr_2$ |
| $Cu_2O$ | CuO |

Those compounds which are of the first order, corresponding to the chloride CuCl, are called *cuprous compounds.* Thus, CuCl is *cuprous chloride;* $Cu_2O$, *cuprous oxide*, etc. On the other hand, compounds of the second order are called *cupric compounds.* Thus, $CuCl_2$ is *cupric chloride;* CuO, *cupric oxide;* $CuSO_4$, *cupric sulphate*, etc.

**Forms in which Copper occurs in Nature.**—Copper is a widely distributed element, and it occurs also in large quantities. It occurs in the uncombined condition, or as *native copper*, in large quantity in the United States, in the neighborhood of Lake Superior, in China, Japan, Siberia, and Sweden. The most valuable ores of copper are the oxides, *ruby copper* or cuprous oxide, $Cu_2O$, and cupric oxide, CuO; the carbonates, as malachite, $Cu_2(OH)_2CO_3$; the sulphides, as chalcocite, $Cu_2S$; copper pyrites, $Cu_2S.Fe_2S$; and others.

**Metallurgy of Copper.**—The metallurgy of copper is comparatively complicated, owing to the difficulty of converting the ores of copper into the oxide. In most of the ores used sulphur and iron are contained, as well as smaller quantities of other elements, as arsenic, antimony, lead, etc. The ores are first *roasted* (see p. 448) with the object of converting the sulphides partly into oxides. Under these circumstances the sulphides of iron are more easily converted into the oxides than the sulphides of copper. By adding a material rich in silicic acid, and melting the roasted ore in a blast furnace with charcoal, the oxide of iron is partly reduced, and converted into silicate, which runs off with the slag. In this way a product is obtained that is richer in copper than the roasted ore. This, which is called the *matte*, contains copper sulphide and iron sulphide. The *matte* is again roasted and melted in the same way as the ore, and a further quantity

of iron is removed, while some of the copper is reduced. A reaction which plays an important part in these processes is that which takes place between cuprous oxide and cuprous sulphide, forming metallic copper and sulphur dioxide:

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

Sometimes it is necessary to repeat the roasting and melting with charcoal and sand a number of times, the matte becoming richer in copper at each successive stage.

Bessemer "converters" (which see) are also in use to purify copper. Their use depends on the fact that when air is forced through the molten impure copper in the converter iron is burned to iron oxide and sulphur to sulphur dioxide.

Pure copper is now made by the electrolysis of a solution of copper sulphate, a sheet of pure copper being the cathode and a block of impure copper the anode:

$$\overset{++}{Cu}, \overset{=}{SO_4} = Cu + \overset{=}{SO_4};$$

$$\overset{=}{SO_4} + H_2O = H_2SO_4 + O.$$

The sulphuric acid attacks the anode dissolving copper and thus constantly regenerating the solution of copper sulphate. Impurities in the copper including gold and silver are deposited at the bottom of the tanks. From this deposit,—the "anode mud"—gold and silver are obtained. Electrolytic (or pure) copper conducts electricity twice as well as ordinary copper.

**Properties.**—Copper is a hard metal, of a reddish color and metallic lustre. It does not change in dry air, but in moist air it gradually becomes covered with a green layer of a basic carbonate. It melts at 1084° and boils at 1500°. It is very malleable and tenacious. Hence its use for wire for conducting electric currents. Weight for weight aluminium offers less resistance to the passage of the current than copper, and aluminium is the cheaper metal, but the superior tenacity of copper makes it

cheaper to use copper wires. It decomposes water only at bright-red heat. When heated in the air to a comparatively high temperature it becomes covered with a layer of cupric oxide; at a lower temperature cuprous oxide is formed. Nitric acid dissolves it, copper nitrate, $Cu(NO_3)_2$, being formed, and the oxides of nitrogen being evolved (see p. 298); dilute sulphuric acid does not act upon it unless the air has access to it; concentrated sulphuric acid when heated with it forms cupric sulphate, $CuSO_4$, and sulphur dioxide. Dilute acids in general do not act upon it unless the air has access to it. This fact is of importance in connection with the use of copper vessels in culinary operations. Substances containing vegetable acids can be boiled in bright copper with impunity, for the water-vapor prevents the access of air, but, on cooling, the air is admitted, and then action takes place, causing solution of some of the copper, which is objectionable. Ammonia in contact with copper absorbs oxygen, and the copper dissolves in consequence of the formation of a compound of cupric oxide and ammonia. This fact is sometimes taken advantage of for the preparation of nitrogen, as has already been stated (see p. 263).

**Applications.**—As is well known, copper is used very extensively for a variety of purposes, among which the following may be mentioned: for electrical apparatus, coins, copper vessels, roofs, for covering the bottoms of ships, etc. It is also used for copper plating; and in the preparation of a number of valuable alloys, such as brass, bronze, gun-metal, bell-metal, etc.

The demand for copper has increased enormously within recent years on account of its use for electrical dynamos, cables and wires, and the increasing use of copper salts as germicides. The total production of copper in 1906 was 798,487 tons, of which the United States produced 458,903, Mexico 67,900, Spain 52,528.

**Alloys.**—*Brass* is a mixture or compound of about one part of zinc to two parts of copper; these proportions may, however, be varied between quite wide limits.

There is a variety of brass containing equal parts of zinc and copper, and another containing one part of zinc to five parts of copper. *Pinchbeck* is made by combining two parts of copper and one of brass.

*Bronze* consists of copper, zinc, and tin. The proportion of copper varies from 65 to 84 per cent; that of zinc from 11 to 31.5 per cent; and that of tin from 2.5 to 4 per cent. When exposed to the air bronze becomes covered with a green coating of basic copper carbonate, which protects it from further action. This coating is now often produced artificially by various methods, as by washing the surface with a solution of salts and acids.

*Gun-metal* consists generally of copper and tin in the proportion of 11 parts of tin and 100 parts of copper.

*Bell-metal* contains a larger proportion (from 20 to 25 per cent) of tin than gun-metal.

*Alloys with aluminium* containing aluminium and copper in widely different proportions are made. That with 3 per cent of copper has a whiter color than aluminium, the color being more like that of silver. On the other hand, an alloy of copper with 5 to 10 per cent of aluminium has a color resembling that of gold. This, which is known as aluminium bronze, is very hard and elastic, and is not easily acted upon by chemical reagents. It is now used to a considerable extent in the manufacture of ornamental and useful articles.

*German silver* is an alloy consisting of copper, zinc, and nickel. The proportion of copper varies from 40 to 60 per cent; that of zinc from 19 to 44 per cent; and that of nickel from 6 to 22 per cent.

**Cuprous Chloride,** CuCl, is formed by heating cupric chloride, $CuCl_2$; and by boiling an excess of copper filings with concentrated hydrochloric acid with the addition of a little nitric acid, filtering through asbestos, and pouring into water. It is a white, crystalline compound, difficultly soluble in water. When exposed to the air it turns green in consequence of the formation of a basic chloride. It is volatile at a high temperature, and a de-

determination of the specific gravity of the vapor gave a result corresponding to the formula $Cu_2Cl_2$. It has markedly the power to combine with chlorine, and therefore acts as a reducing agent.

**Cupric Chloride,** $CuCl_2$.—This compound is formed by treating copper or cuprous chloride with chlorine. It is also easily made by dissolving cupric hydroxide, or carbonate, in hydrochloric acid. From its solution in water the chloride crystallizes with two molecules of water, $CuCl_2 + 2H_2O$. The crystals when heated lose their water without suffering further decomposition, except at high heat, when a part of the chlorine is given off, and cuprous chloride is formed. Cupric chloride combines with ammonia, forming a compound of the formula $CuCl_2.6NH_3$ which dissolves in water forming a dark blue solution. When heated it loses four molecules of ammonia, and the compound $CuCl_2.2NH_3$ is left behind.

**Cuprous Hydroxide,** Cu(OH).—The simple compound of the formula here given is not known, but a derivative of this, of the formula $Cu_8O_3(OH)_2$ or $4Cu_2O.H_2O$, is easily made by adding sodium hydroxide to a solution of a cuprous salt. It is readily converted into cuprous oxide by gentle heat.

**Cuprous Oxide,** $Cu_2O$, occurs in nature, and is known as *ruby copper* or *cuprite*. It is easily prepared by treating a solution of glucose, or starch sugar, with copper sulphate and potassium hydroxide. By boiling, the copper is thrown down in the form of cuprous oxide. At first this is yellow, and it is supposed by some that the yellow compound is the hydroxide, but satisfactory evidence of this has not been furnished, The yellow precipitate is soon converted into the red oxide. Cuprous oxide is not changed by prolonged contact with the air. It dissolves in nitric and sulphuric acids, forming cupric salts; and if the acids are dilute, copper is deposited. This will be clear from a consideration of the following equation:

$$Cu_2O + H_2SO_4 = CuSO_4 + H_2O + Cu.$$

**Cupric Hydroxide,** $Cu(OH)_2$, like the hydroxides of most base-forming elements, is precipitated by the addition of a soluble hydroxide to a cupric salt. It is a voluminous, blue precipitate. When allowed to stand in a solution, or when the solution is boiled, the hydroxide loses a part of its hydroxyl, and is converted into a black compound of the formula $Cu(OH)_2 + 2CuO$; and this when dried and heated is converted into the oxide CuO.

**Cupric Oxide,** CuO.—Cupric oxide is found in nature in the neighborhood of Lake Superior in the United States, and is formed by heating copper to redness in contact with the air, or by heating the nitrate. It loses its oxygen very readily when treated with reducing agents, such as hydrogen and carbon. It is used extensively in quantitative analysis for the purpose of estimating the composition of organic compounds, or such as contain carbon and hydrogen. Its use is based upon the fact that when organic compounds are heated with the oxide they are oxidized, the carbon being converted into carbon dioxide and the hydrogen into water. By passing the products of the oxidation through calcium chloride, and a solution of potassium hydroxide, the water is retained in the first, and the carbon dioxide in the second, and the weight of each formed can easily be determined.

**Cupric Sulphate,** $CuSO_4$.—This salt is manufactured on the large scale, and, in the crystallized form, containing five molecules of water, $CuSO_4 + 5H_2O$, is commonly called "blue vitriol" or "blue stone." It is found to some extent in nature, being formed by the action of the oxygen of the air on the sulphide. It is most conveniently made by dissolving metallic copper in concentrated sulphuric acid, or by treating cupric sulphide with sulphuric acid. The action of sulphuric acid on the metal consists essentially in the formation of cupric sulphate, sulphur dioxide, and water, as expressed in the equation

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

The question whether the copper reduces the sulphuric acid directly, or the hydrogen given off from the acid

effects the reduction, is an open one. But there are other products formed besides those mentioned. At first a brown substance of the composition $Cu_2S$ is deposited. As the action proceeds oxysulphides are formed, the final product of a series of changes having the composition $Cu_2OS$, or CuO.CuS, which is black and insoluble in water. Under some conditions a considerable part of the copper is transformed into the oxysulphides by sulphuric acid. Cupric sulphate is obtained in large blue crystals of the triclinic system, which have the composition $CuSO_4 + 5H_2O$. When heated to 100°, four molecules of water are given off, but the last one is not given off until the temperature 200° is reached. This makes it appear probable that the salt has the constitution represented by the formula $CuSO_4(OH)_2$, corresponding in this respect to magnesium sulphate (which see). When heated higher, it loses all its hydroxyl, and the salt, $CuSO_4$, is left in the form of a white powder, which has the power to take up water from the air, becoming blue again. It dissolves in three parts of cold water and one-half part boiling water. Copper sulphate, containing seven molecules of water, $CuSO_4 + 7H_2O$, is obtained when mixed with solutions of the sulphates of iron, zinc, or magnesium, all of which crystallize with seven molecules of water. In this form cupric sulphate is isomorphous with the other sulphates. These salts have in general received the name of vitriols, and the old names "green vitriol," "white vitriol," and "blue vitriol" are still used to some extent, though rarely by chemists. Among the similar salts included under the same general head are the following:

| | |
|---|---|
| Zinc sulphate (white vitriol) . . . . | $ZnSO_4 + 7H_2O$ |
| Magnesium sulphate . . . . . | $MgSO_4 + 7H_2O$ |
| Glucinum sulphate . . . . . | $GlSO_4 + 7H_2O$ |
| Ferrous sulphate (green vitriol) . . . | $FeSO_4 + 7H_2O$ |
| Nickel sulphate . . . . . | $NiSO_4 + 7H_2O$ |
| Cobalt sulphate . . . . . | $CoSO_4 + 7H_2O$ |
| Copper sulphate (blue vitriol) . . . . | $CuSO_4 + 7H_2O$ |
| | $(CuSO_4 + 5H_2O)$ |

**Applications.**—Cupric sulphate is used extensively in the preparation of blue and green pigments, in copper plating by electrolysis, in galvanic batteries, for the purpose of preserving wood, and as a remedy against *phylloxera* (see p. 391), and insects and worms harmful to fruit and vegetables. The use of solutions containing copper sulphate for spraying fruit trees and young vegetables has become so common that enormous quantities of copper sulphate are used for this purpose.

**Cupric Nitrate,** $Cu(NO_3)_2$, is easily formed by dissolving copper in dilute nitric acid. It is easily soluble in water, and is deposited in crystallized form, the crystals containing three or six molecules of water according to the temperature, the salt with six molecules being formed at the lower temperature. Like other copper salts, it has a blue color.

**Cupric Arsenite,** $CuHAsO_3$, is formed as a greenish-yellow precipitate when an ammoniacal solution of arsenious acid is added to a solution of cupric sulphate. It is known as *Scheele's green.* A compound of cupric arsenite and cupric acetate, which is made by treating a basic acetate of copper with arsenious acid, is known as *Paris green* or *Schweinfurt green.*

*Paris green* is used to some extent as a pigment, but chiefly as an insecticide for potatoes, cabbage, and other plants.

**Cupric Carbonates.**—When a soluble carbonate is added to a solution of cupric sulphate a voluminous, greenish precipitate is formed, which has the composition

$Cu(OH)_2 . CuCO_3$, or $\begin{matrix} Cu<OH \\ \quad\quad O \\ Cu<OH \end{matrix}\!\!>CO$. This is plainly a basic

carbonate. The mineral malachite, which has a beautiful green color, has the same composition as the precipitate just mentioned.

**Cuprous Sulphide,** $Cu_2S$.—This compound occurs in

nature, and is known as chalcocite. It is, further, a constituent of copper pyrites, which is a compound of cuprous and ferric sulphides, $Cu_2S.Fe_2S_3$ or $CuFeS_2$. It can be made by heating copper and sulphur together in the right proportions. It has a grayish-black color; does not give up its sulphur, even when heated in hydrogen; and is the more stable of the two sulphides of copper.

**Cupric Sulphide,** CuS.—This is formed as a black precipitate when hydrogen sulphide is passed into a solution of a cupric salt. In water alone cupric sulphide is somewhat soluble. Hence in washing out a precipitate of copper sulphide with water a little of it will pass through in solution. It also easily undergoes oxidation, and, as it forms the sulphate, some is dissolved in this way unless proper precautions are taken. It is slightly soluble in ammonium sulphide, but insoluble in sodium sulphide. The above facts are of importance in the analysis of compounds containing copper, as will readily be seen. When heated, cupric sulphide loses half its sulphur, and is converted into cuprous sulphide.

**Copper Plating.**—The process of copper plating consists in brief in depositing upon an object a layer of copper by putting it in a bath containing some copper salt, and connecting it with one pole of an electric battery. Decomposition of the copper salt takes place, and copper is deposited upon the object. Alkaline solutions of the double cyanides are best adapted to the purpose. The process is extensively used in the preparation of *electrotype* plates. These are prepared either from wood-cuts or from type by making a mould of gutta-percha, covering this with graphite, and immersing the plate thus prepared in the copper-plating bath. The plate thus made is an exact reproduction of the wood-cut or type of which the impression in gutta-percha was taken.

**Reactions which are of Special Value in Chemical Analysis.**—*Potassium* or *sodium hydroxide* forms a blue precipitate which becomes black on standing or when heated. (See Cupric Hydroxide.)

*Ammonia* first forms a greenish precipitate, which is a

basic salt. With cupric sulphate the reaction takes place thus:

$$\begin{matrix} SO_2{<}^{O}_{O}{>}Cu \\ SO_2{<}^{O}_{O}{>}Cu \end{matrix} + 2NH_3 + 2H_2O = \begin{matrix} Cu{<}^{OH}_{O} \\ Cu{<}^{O}_{OH} \end{matrix} > SO_2 + (NH_4)_2SO_4.$$

If the action is carried further, the basic salt dissolves, forming a dark blue solution.

*Potassium* or *sodium carbonate* precipitates the basic carbonate referred to under Cupric Carbonate (which see). The change in color from blue to green which takes place in this precipitate is probably due to a loss of water.

*Potassium ferrocyanide*, $K_4Fe(CN)_6$, forms a reddish-brown precipitate, which is the corresponding copper salt, $Cu_2Fe(CN)_6$. This compound is decomposed by caustic alkalies, forming cupric oxide and the corresponding alkali salt, $Na_4Fe(CN)_6$ or $K_4Fe(CN)_6$.

In the oxidizing flame the bead of borax or microcosmic salt is greenish blue, while when heated in the reducing flame it appears opaque and red. The red color is due to the reduction of the oxide to copper or cuprous oxide.

## Silver, Ag (At. Wt. 107.93).

**General.**—In nearly all the compounds of silver the element is univalent. It, however, forms three oxides of the formulas $Ag_4O$, $Ag_2O$, and $AgO$. The compounds correspond closely in many respects to the cuprous compounds. The same question arises here as in the case of copper as to whether the molecular weights correspond to the simple formulas AgCl, AgBr, $AgNO_3$, etc., or to the doubled formulas $Ag_2Cl_2$, $Ag_2Br_2$, $Ag_2(NO_3)_2$, etc. There is no evidence at present available by which a decision between the two possibilities can be reached. The simpler formulas will therefore be used here.

**Forms in which Silver Occurs in Nature.**—Silver occurs to some extent native, but for the most part in combination, particularly with sulphur, and in company wi h

lead. The principal ore of silver is the sulphide, $Ag_2S$, which occurs in combination with other sulphides, as of lead, copper, arsenic, antimony, etc. The compounds with chlorine, bromine, and iodine are also found, but in smaller quantity than the sulphide. Small quantities of the sulphide are found in almost all varieties of galenite or lead sulphide.

**Metallurgy of Silver.**—Much of the silver in use is obtained from galenite, PbS. This mineral is treated so as to cause the separation of the lead (which see), and the silver is separated from sulphur at the same time. But it is dissolved in a large quantity of lead, and the problem that presents itself to the metallurgist is how to separate the small quantity of silver from the large quantity of lead. This is accomplished by melting the mixture and allowing it to cool until crystals appear. These are almost pure lead. They are dipped out by means of a sieve-like ladle, and the liquid left is again allowed to stand, when another crop of crystals is formed, and this can be removed in the same way as the first. By this means, and by again melting the crystals which have been removed, allowing the liquid to crystallize, and removing the crystals formed, there is finally obtained a product rich in silver, but still containing lead. This is heated in appropriate vessels in contact with the air, when the lead is oxidized, while the silver remains in the metallic state. This is known as *Pattinson's method.* It has been superseded by the

**Zinc Method, or Parkes's Method.**—This consists in treating the molten alloy with zinc, which takes up all the silver, and the alloy of zinc and silver thus formed is removed, and afterwards treated with superheated steam, by which the zinc is oxidized while the silver is left unchanged.

**Amalgamation Process.**—Some ores of silver are treated in another way, known as the *amalgamation process.* The ores are mixed with common salt and roasted, when the silver is obtained in the form of the chloride. This is then reduced to silver by means of iron and water, the

reaction taking place as represented in the following equation:

$$2AgCl + Fe = FeCl_2 + 2Ag.$$

The mixture is next treated with mercury, which forms an amalgam with silver, while the other metals present do not combine with the mercury. The amalgam can be separated from the rest of the mass without much difficulty, and when heated to a sufficiently high temperature the mercury distils over, leaving the silver.

**Purification.**—The silver in the market is not pure, the impurities being gold, platinum, palladium, and a little lead and iron. From all but the last it is separated by dissolving it in concentrated sulphuric acid and diluting the solution of silver sulphate thus formed. The silver is precipitated from the solution by metallic iron, then washed and fused. Another method is exactly like the method of obtaining pure copper. A solution of silver nitrate is electrolyzed, the cathode being a sheet of pure silver, the anode crude silver which wastes away regenerating the solution (see Copper). Both of these methods are used in the mints. Pure silver is technically called "fine silver." (For statistics see Gold.) For chemical purposes silver can be purified by dissolving it in nitric acid, precipitating by means of hydrochloric acid, filtering and thoroughly washing the chloride, and reducing this either by melting it with sodium carbonate, or by pouring a little dilute hydrochloric acid upon it, and bringing a piece of zinc in contact with it. In the former case the reaction is

$$2AgCl + Na_2CO_3 = 2Ag + CO_2 + O + 2NaCl;$$

in the latter it is

$$Zn + 2AgCl = ZnCl_2 + 2\,Ag.$$

**Properties.**—Silver is a white metal with a high lustre, of specific gravity 10.5. It is not acted upon by the air, oxygen, or water. It melts at 962°, lower than copper

or gold. At 2050°, the temperature of the oxyhydrogen blowpipe, it distils, and in the experiments of Stas on the atomic weights of chlorine and silver the metal used was purified in this way. It is very malleable, can be drawn out to very thin wires or beaten to thin foil. It is also very tenacious. It is harder than gold and softer than copper, and its hardness is much increased by the addition of a little copper. It combines very readily with sulphur, forming black silver sulphide, and with chlorine, bromine, and iodine. The blackening of silver coins and other objects carried about the person is caused by the presence of minute quantities of sulphur compounds in the perspiration; and the blackening of spoons by contact with eggs is due to the presence of sulphur in the albumen of the eggs. When pure silver is melted in the air it absorbs about twenty times its volume of oxygen, and this is given off when the metal solidifies, causing in some cases a sputtering of the silver. This phenomenon is observed in the separation of silver from its ores in those processes in which it is necessary to melt the metal. It is known as "spitting."

At the ordinary temperatures silver is converted into the peroxide, AgO, by ozone. When treated with hydrochloric acid the metal becomes covered with a thin layer of the chloride, and no further action takes place, but it is dissolved easily by concentrated sulphuric acid and dilute nitric acid. With the concentrated acids reduction-products are formed as with copper. Silver is readily dissolved by a solution of potassium cyanide, hence, such a solution is used in removing stains caused by silver salts. It is not acted upon by the alkaline hydroxides nor by potassium nitrate in the molten condition, while platinum is. Therefore silver vessels are used when it is desired to melt these substances in the laboratory, or to evaporate their solutions, as in the preparation of the caustic alkalies.

**Allotropic Forms of Silver.**—M. Carey Lea has discovered several curious allotropic forms of silver, the principal of which are briefly described by him as follows:

"*A*. Soluble, deep red in solution, mat lilac, blue, or green while moist, brilliant bluish-green metallic when dry. *B*. Insoluble, derived from *A*, dark reddish-brown while moist, when dry somewhat resembling *A*. *C*. Gold silver, dark brown while wet, when dry exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-colored. Insoluble in water; appears to have no corresponding soluble form."

The form *A* is soluble in water, and the solution thus formed has a deep red color. The different varieties are formed by the action of reducing agents on solutions of silver salts. For example, the red, soluble form is obtained by mixing dilute solutions of ferrous citrate and a silver salt. All the allotropic forms of silver are readily changed to the ordinary form.

Lea further says: "All the forms of allotropic silver are sensitive to light. *A* when exposed to the sunlight soon becomes brown. The bright blue-green variety of *B* is changed into the pure gold-colored variety of *C*. Other forms of *B* turn brown on exposure to light." The red-yellow variety of *C* changes to a bright gold color. "Continued exposure seems to produce little further change so long as the substance is dry. But if the paper on which the silver is placed is kept moist by a wet pad, with three or four days of good sunshine, the change goes on until the silver becomes perfectly white, and is apparently changed to normal silver."

**Silver Plating,** see Gold Plating.

**Alloys of Silver.**—For practical use, as in making coins and silver-ware, an alloy with copper is used, the pure metal being too soft. The alloy usually contains from $7\frac{1}{2}$ to 10 per cent of copper. This alloy is harder than pure silver, and is capable of a higher polish. Silver amalgam is an alloy of silver and mercury, which is readily formed by bringing the two metals together.

**Argentous Chloride,** $Ag_2Cl$ or $Ag_4Cl_3$, is formed by treating argentous salts with hydrochloric acid, and, possibly, to some extent when silver chloride, AgCl, is exposed to the light, though this is doubtful.

**Silver Chloride, Argentic Chloride,** AgCl, is of special importance on account of its use in photography and in chemical analysis. It occurs to some extent in nature in Mexico and in the United States. It is easily formed as a white precipitate by adding hydrochloric acid to a solution of a silver salt, as, for example, the nitrate. In consequence of its insolubility in water it affords a convenient means of detecting silver and chlorine. If allowed to stand in the light it changes color, becoming first violet and finally black. This change in color appears to be due entirely to the reduction of the chloride to the form of metallic silver. Concentrated hydrochloric acid dissolves it somewhat, and from this solution it crystallizes in octahedrons. An aqueous solution of ammonia dissolves it very easily, in consequence of the formation of a compound of the chloride with ammonia analogous to those formed by copper salts. The composition of the compound in the solution is, however, not known.

**Silver Bromide,** AgBr, and **Silver Iodide,** AgI, are similar to the chloride. Both occur in nature, and both are precipitated from solutions of silver salts by adding the corresponding hydrogen acids. The bromide is less easily soluble in ammonia than the chloride, and the iodide is almost insoluble in it. The bromide is formed by treating the chloride at the ordinary temperature with hydrobromic acid; and the iodide is formed from the chloride and from the bromide by treating these with hydriodic acid at ordinary temperatures. At higher temperatures, however, both the bromide and iodide are converted into the chloride by hydrochloric acid. Silver dissolves in concentrated hydriodic acid, and from the solution a salt of the formula $AgI + HI$ or $HAgI_2$ is formed. It seems probable that this is a derivative of the acid $H_2I_2$, from which the double salt KI.AgI is also derived, as indicated in the formula $KAgI_2$. Silver bromide at low temperatures is white, but easily changes to yellow, and by exposure it becomes darker, but not as readily as the chloride. The iodide is yellow, and undergoes change in the light only very slowly. The chloride

and iodide exist in several modifications, which differ from one another in their conduct towards light, and in their solubility.

**Application of the Chloride, Bromide and Iodide of Silver in the Art of Photography.**—The art of photography is based upon the changes which certain compounds, especially salts of silver, undergo when exposed to the light. Silver iodide is best adapted to most purposes. The salt is so changed by the light that when treated with certain compounds, such as ferrous sulphate, pyrogallic acid, etc., called "developers," a deposit of finely divided silver is formed upon the plate in those places affected by the light. A plate of glass or a sheet of properly prepared paper is covered in the dark with a thin layer of a salt of silver. The plate is then exposed in the camera to the action of the light which is reflected from the object to be photographed. According to the intensity of the light given off from the various parts of the object, the change of the silver salt takes place to a greater or less extent, and thus an image of the object is impressed upon the plate. But after the action of the "developer" is complete there is still upon the plate unchanged silver salt, and if this were now exposed to the light it would undergo change and the image would be obliterated. To remove this salt the plate is washed with a solution of sodium thiosulphate, $Na_2S_2O_3$ (hyposulphite), which dissolves the salt in consequence of the formation of a double salt of the formula $2Na_2S_2O_3.Ag_2S_2O_3$, which is readily soluble in water.

**Silver Triazoate,** $AgN_3$.—This is derived from triazoic acid (which see). It is formed by adding a solution of the acid to a solution of a silver salt. It is extremely explosive and should be dealt with very cautiously. Serious accidents have been caused by it. In appearance it resembles silver chloride, but it does not darken when exposed to the light.

**Silver Oxide,** $Ag_2O$.—The principal compound of silver and oxygen is that which has the composition $Ag_2O$, and in which the silver is univalent, as it is in its compounds

with chlorine, bromine, and iodine. It is formed when a soluble hydroxide is added to a solution of a silver salt, and also by the action of concentrated solutions of the caustic alkalies on silver chloride. It is easily decomposed by heat and by reducing agents.

**Other Oxides of Silver.**—Besides the ordinary oxide, silver forms a suboxide, $Ag_4O$, corresponding to the suboxide of copper, $Cu_4O$, and a peroxide of the formula $AgO$ (or $Ag_4O_3$), which is perhaps analogous to cupric oxide.

**Sulphides of Silver.**—As has been stated, silver occurs in nature mostly in combination with sulphur as silver glance, $Ag_2S$, which in many minerals is in combination with other sulphides. Examples of such double sulphides are the minerals stromeyerite, $Cu_2S.Ag_2S$, and pyrargyrite, $3Ag_2S.Sb_2S_3$. Articles coated or inlaid with silver sulphides are popularly called "oxidized silver."

**Silver Nitrate, Argentic Nitrate,** $AgNO_3$.—This salt is formed by dissolving silver, or silver oxide, in nitric acid, evaporating to dryness, and heating until the salt is melted. It crystallizes in colorless, rhombic plates. It is not changed in the light unless it comes in contact with organic substances, when it is reduced and metallic silver deposited. Hence the solution produces black spots on the fingers and clothing. As it melts easily, it is generally cast in small, cylindrical moulds, and is found in the market in the form of thin sticks, and is known as *lunar caustic.* It disintegrates flesh, and is used in surgery as a caustic to remove superfluous growths. Owing to the formation of a dark deposit when the salt is exposed to the light, it is used as a constituent of indelible inks.

**Silver Cyanide,** $AgCN$, is formed as a caseous precipitate when a solution of hydrocyanic acid is added to a solution of silver nitrate. It does not change color in the light, is soluble in ammonia, but not in nitric acid. It readily forms double cyanides with the cyanides of other metals. Of these, the salt with potassium cyanide, $KAg(CN)_2$ or $KCN.AgCN$, may be mentioned.

**Reactions which are of Special Value in Chemical Analysis.**—*Hydrochloric acid* precipitates insoluble silver chloride from solutions of silver salts.

*Soluble hydroxides* precipitate silver oxide, not the hydroxide. Ammonia redissolves the precipitate in consequence of the formation of a compound of the oxide with ammonia of the composition $Ag_2O.2NH_3$. In dry condition this salt is very explosive, and is known as fulminating silver.

*Soluble carbonates* precipitate the carbonate, $Ag_2CO_3$, which has a yellowish-white color.

*Ammonium carbonate* redissolves the precipitate formed by it.

*Sodium phosphate*, $HNa_2PO_4$, gives a precipitate of the normal salt $Ag_3PO_4$, which is yellow.

*Potassium ferrocyanide*, $K_4Fe(CN)_6$, precipitates white silver ferrocyanide, $Ag_4Fe(CN)_6$.

*Potassium ferricyanide*, $K_3Fe(CN)_6$, gives the corresponding silver salt, which is reddish brown.

*Potassium chromate* or *potassium bichromate* (which see) gives a brownish-red precipitate of silver chromate.

## Gold, Au (At. Wt. 197.2).

**General.**—Gold forms two series of compounds, in one of which it is univalent and in the other trivalent. In this respect it differs from the other members of the group. Examples of the compounds belonging to the two series are represented by the following formulas:

| | |
|---|---|
| AuCl | $AuCl_3$ |
| AuBr | $AuBr_3$ |
| $Au_2O$ | $Au_2O_3$ |

Those of the first series are called *aurous compounds*, those of the second series *auric compounds*. The basic character of gold is very weak, so that salts of the ordinary acids, as sulphuric, nitric, carbonic, etc., are not known. On the other hand, its higher oxide, $Au_2O_3$, and hydroxide, $Au(OH)_3$, have acid properties, and form salts similar in

composition to the meta-aluminates $MAlO_2$, and the meta-borates $MBO_2$. These are the *aurates*, of which potassium aurate, $KAuO_2$, is an example. So, also, the chloride combines readily with the chlorides of potassium and sodium, forming the *chlor-aurates*, $KAuCl_4$, and $NaAuCl_4$, which are analogous to the aurates.

**Forms in which Gold occurs in Nature.**— Gold is generally found in nature in the native condition—a fact which is due to the chemical inactivity of the element. That which is found in nature is never pure, but contains silver, and also, in different localities, iron, copper, and other metals. It is also found to some extent in combination with tellurium in the compounds $AuTe_2$ and $(AuAg)_2Te_3$. Native gold is frequently found enclosed in quartz, or more commonly in quartz sand. It is found in various parts of the United States as in California, South Dakota, Alaska, and in Australia, Hungary, Siberia, and Africa.

**Metallurgy of Gold.**—From the chemical point of view the metallurgy of gold is in general very simple. There are two kinds of gold mining—called *placer mining* and *vein mining*. In the former the earth and sand which contain gold are washed with water, which carries away the lighter particles, and leaves the gold mixed with other heavy materials. This mixture is then treated with mercury, which forms an amalgam with the gold, as it does with silver, and when this is placed in a properly constructed retort and heated, the mercury passes over and leaves the gold behind. If silver is present, as is frequently the case, this is separated with the gold. In *vein mining* the gold ores are taken out of veins in the earth, and the gold is separated by grinding the ores and treating them with mercury, as in the last stage of placer mining. *Hydraulic mining* is a modification of ordinary placer mining. It consists in forcing water under pressure against the sides of hills and mountains in which gold occurs loosely mixed with the earth. The earth is thus carried away and the heavier gold is deposited in sluices.

Some ores, especially those which contain tellurium, and also ores like the ores of South Africa and many of the American ores, which contain the gold in very finely divided condition, cannot be satisfactorily treated by the amalgamation process, and a method involving the use of potassium cyanide has been devised for these. In a solution of this salt gold dissolves, and from the solution it is either precipitated by zinc, or obtained by filtering the solution through charcoal which absorbs the gold. This method has come into extensive use of late years.

Another process that is much used in the treatment of ores that do not give up their gold to mercury is known as the *chlorination process.* This consists in treating the finely ground ore with chlorine made from bleaching powder and sulphuric acid, and then precipitating the gold from the solution of the chloride by means of hydrogen sulphide. From the sulphide the metallic gold can be easily obtained.

The gold obtained by any of the above methods is not pure. It can be separated from silver by dissolving it in *aqua regia*, evaporating off the nitric acid, then diluting, and treating with a reducing agent, when metallic gold is precipitated. Thus when ferrous sulphate is used the following reaction takes place:

$$3FeSO_4 + AuCl_3 = Fe_2(SO_4)_3 + FeCl_3 + Au.$$

Another method of separating silver from an alloy with gold consists in treating the metal with nitric acid or with boiling concentrated sulphuric acid, which dissolves the silver and leaves the gold. This process is not satisfactory, however, unless the amount of gold in the alloy is less than 25 per cent. If the proportion of gold is greater than this, the alloy is melted with silver enough to bring the percentage of gold down to that mentioned. This is known as "*quartation.*"

Pure gold is now generally obtained by electrolysis.

**Production of Gold and Silver.**—The figures for the production of gold and silver for the last hundred years are interesting.

*Yearly average production of gold and silver in metric tons* (1000 kilograms).

| Year | Gold | Silver |
|---|---|---|
| 1800–1850 | 24 | 655 |
| 1851–1880 | 188 | 1422 |
| 1881–1890 | 158 | 3125 |
| 1891–1895 | 245 | 4901 |
| 1896–1900 | 387 | 5153 |
| 1901–1905 | 485 | 5197 |

An average of the last few years gives as the value of the gold $350,000,000; of the silver $100,000,000.

Formerly most of the gold and silver was used for coinage. Now both are largely used for other purposes.

*Use of gold for coinage and industrial purposes in tons.*

| Year | Coinage | Industrial purposes |
|---|---|---|
| 1831–1850 | 42 | 19 |
| 1851–1870 | 32 | 32 |
| 1871–1880 | 73 | 41 |
| 1881–1885 | 23 | 70 |

At present it is estimated that 100-120 tons of gold yearly are used for industrial purposes, notably for jewelry, for gold-plated objects, for dentistry, for photography, for stained glass, and for gilding porcelain and glass. Fifteen tons of gold yearly are used for the latter purpose alone.

*Gold production by countries for 1906, in tons.*

Australasia, 124; Africa, 203; United States, 142. Total including other countries, 602. As will be seen, Africa at present leads the world.

**Properties.**—Gold is a yellow metal with a high lustre. It is quite soft, and extremely malleable, so that it is possible to make from it sheets the thickness of which is not more than 0.000002 millimeter. Thin sheets are translucent, and the transmitted light appears green. Its specific gravity is 19.3; its melting-point is 10640°. It

crystallizes in the regular system. Gold combines directly with chlorine, but not with oxygen. The three acids, hydrochloric, nitric, and sulphuric, do not act upon it; but *aqua regia* dissolves it, forming auric chloride, $AuCl_3$, in consequence of the evolution of nascent chlorine. Molten caustic alkalies and their nitrates act upon it and form aurates.

**Colloidal Gold.**—By the action of a strong electric discharge under water, gold is very finely divided and goes into colloidal solution forming a "hydrosol." Many other metals behave similarly.

**Alloys of Gold.**—The principal alloy of gold is that which contains copper. The standard gold coin of the United States contains nine parts of gold to one of copper. The composition of gold used for jewelry is usually stated in terms of carats. Pure gold is 24-carat gold; 20-carat gold contains 20 parts of gold and 4 parts of copper; 18-carat gold contains 18 parts of gold and 6 parts of copper, etc. Copper gives gold a reddish color, and makes it harder and more easily fusible. Gold is also alloyed with silver; and the alloy with mercury, known as gold amalgam, is extensively used in the processes for extracting gold from its ores.

**Chlorides of Gold.**—When gold is dissolved in *aqua regia* it is converted into *auric chloride*, $AuCl_3$; and if this solution is evaporated a part of the chloride is decomposed into *aurous chloride*, AuCl, and chlorine. When gold is treated with dry chlorine it yields a mixture of auric chloride and metallic gold. When treated with a solution of stannous chloride a solution of auric chloride gives a purple-colored precipitate, known as the *purple of Cassius*, which appears to consist of finely divided gold.

**Gold Sulphide,** $Au_2S_3$.—This compound is precipitated together with sulphur from cold solutions of gold salts by means of hydrogen sulphide, and forms a brownish-black mass. It forms soluble compounds with the sulphides of the alkali metals.

When hydrogen sulphide is passed into hot solutions of gold salts aurous sulphide, $Au_2S$, is thrown down as a

steel-gray substance. This is soluble in pure water and is precipitated by hydrochloric acid.

**Gold and Silver Plating** is now almost exclusively done by the electrolytic method, the bath being a solution of gold-potassium cyanide or silver-potassium cyanide, the cathode the object to be plated, the anode a strip of gold or silver respectively.

## EXPERIMENTS.

### Copper and its Salts.

Experiment 225.—Cuprous chloride is made by dissolving copper turnings in hydrochloric acid with the aid of a little nitric acid added from time to time. After solution is effected pour into water, when white cuprous chloride will be precipitated.

### Silver and its Salts.

Experiment 226.—Dissolve a ten or twenty-five cent piece in dilute nitric acid. Dilute the solution to 200 to 300 cc. with hot water.—Add a hot solution of common salt until it ceases to produce a precipitate. Filter off the white silver chloride and wash with hot water. Dry the precipitate in the filter by placing the funnel with the filter and precipitate in an air bath heated to 100°–110°. Remove the precipitate from the filter and put it into a porcelain crucible. Heat gently with a small flame until the chloride is melted; then let it cool. Cut out a piece of sheet zinc large enough to cover the bottom of the crucible, and lay it on the silver chloride. Now add a little water and a few drops of dilute sulphuric acid and let the whole stand for twenty-four hours. The silver chloride will be reduced to silver, and zinc chloride formed:

$$Zn + 2AgCl = ZnCl_2 + 2Ag.$$

Take out the piece of zinc and wash the silver with a little dilute sulphuric acid, and then with water. Dissolve the silver in dilute nitric acid and evaporate to dryness on a water-bath, until all the nitric acid is driven off. Dissolve the residue in water, and put the solution either in a bottle of dark glass or one wrapped in dark paper.

Experiment 227.—To a solution of silver nitrate containing about 5 grams of the salt in 100 cc. of water, add a few drops of mercury, and let it stand. In a few days the silver will be deposited in the form of delicate crystals. The formation is called the "silver tree."

## CHAPTER XXVIII.

### ELEMENTS OF FAMILY II, GROUP B: ZINC.—CADMIUM.—MERCURY.

**General.**—There is a strong resemblance between the first two elements of this group and magnesium, while mercury, in a general way, resembles the first two members of the copper group. Just as gold in the copper group furnishes a greater variety of compounds than the first two members of that group, so mercury furnishes a greater variety of compounds than the other members of the group to which it belongs. Zinc and cadmium, like magnesium, give only one class of compounds, and in these they are bivalent. The general formulas of some of the principal ones are:

$$MCl_2,\ M(OH)_2,\ MO,\ MSO_4,\ MCO_3,\ MS.$$

Mercury, on the other hand, gives two series of compounds, known as the *mercurous* and *mercuric* compounds, which correspond closely to the two series of copper salts. The power to form compounds belonging to both series is more strongly developed in mercury than in copper. Examples of the two classes are represented in the following formulas:

| Mercurous Compounds. | Mercuric Compounds. |
|---|---|
| $HgCl$ | $HgCl_2$ |
| $HgI$ | $HgI_2$ |
| $Hg_2O$ | $HgO$ |
| $HgNO_3$ | $Hg(NO_3)_2$, etc. |

Just as the first member of Group A, Family II, glucinum, shows a somewhat acidic character in its hydroxide, while the other members of that group do not, so also the first member of Group B, Family II, zinc, is acidic,

while the other members of the group are not. Glucinum hydroxide and zinc hydroxide dissolve in caustic alkalies, forming glucinates and zincates; while the hydroxides of all the other members of the two groups of this family are insoluble in caustic alkalies.

## Zinc, Zn (At. Wt. 65.4).

**General.**—Zinc, in almost all its compounds, exhibits a close resemblance to magnesium. It always acts as a bivalent element.

**Forms in which it occurs in Nature.**—Zinc occurs in nature in combination, principally as the carbonate, or smithsonite, $ZnCO_3$; as the sulphide, or sphalerite, $ZnS$; and as the silicate, $Zn_2SiO_4$. Among other compounds of zinc found in nature are gahnite, $Zn(AlO_2)_2$, and franklinite, which contains the compound $Zn(FeO_2)_2$, with magnetite, $Fe(FeO_2)_2$.

**Metallurgy.**—The metallurgy of zinc is much simpler than that of magnesium, for the reason that the ores are easily converted into the oxide by roasting, and the oxide is easily reduced by heating it with charcoal. Owing to the volatility of the metal the vessels in which the reduction is effected must be so constructed as to facilitate the condensation of the vapors. The vessels used are either earthenware muffles or tubes, open at one end and connected with iron receivers. At first the zinc vapor is condensed in the form of a fine dust, as in the case of sulphur. This forms the commercial product called *zinc dust*. It always contains zinc oxide. Afterwards the zinc condenses to the form of a liquid, and this is cast in plates. The zinc thus obtained is not pure, but contains lead and iron, and sometimes arsenic and cadmium. It is called *spelter*. By repeated distillation it can be obtained pure. When distilled under diminished pressure, it is deposited in beautiful lustrous crystals, the forms of which are extremely complicated.

Pure zinc is now made by electrolysis of zinc chloride.

The total production of zinc for 1906 was 775,871 tons of which 224,770 were produced in the United States.

**Properties.**—Zinc has a bluish-white color and a high lustre. The crystals above referred to, which are perfectly pure zinc, have a brilliant lustre, and do not change in the air. At different temperatures zinc has markedly different properties. At ordinary temperatures it is quite brittle; at 100°–150° it can be rolled out in sheets, but above 200° it becomes brittle again. It melts at 419°, and boils at 918°. When heated in the air it takes fire, and burns with a bluish flame, forming zinc oxide. This can be shown by means of the oxyhydrogen blowpipe. In dry air it does not change. Ordinary zinc dissolves in all the common acids, usually with evolution of hydrogen. In the case of nitric acid, however, the hydrogen acts upon the acid, reducing it to ammonia. The purer the zinc the less readily is it acted upon by sulphuric acid, and the pure crystals above referred to are scarcely acted upon at all by this acid. Zinc also dissolves in the caustic alkalies, forming zincates. Pure zinc can be made to act upon sulphuric acid by adding a few drops of platinum chloride.

**Applications.**—Zinc is extensively used as sheet-zinc, in making galvanic batteries, for galvanizing iron, etc. Zinc dust is a very efficient reducing agent, either in alkaline or in acid solution. With caustic alkalies—as, for example, with potassium hydroxide—it gives hydrogen and a zincate:

$$Zn + 2KOH = Zn(OK)_2 + H_2.$$

With sulphuric acid also it gives hydrogen readily. Zinc is used in the preparation of important alloys.

**Primary Cells.**—To produce a current of electricity by chemical action the chemical energy of the substances interacting is transformed into electrical energy. If a strip of zinc is placed in a solution of copper sulphate, this reaction occurs:

$$Zn + \overset{++}{Cu},\overset{=}{SO_4} = Cu + \overset{++}{Zn},\overset{=}{SO_4}.$$

Zinc dissolves and copper is precipitated; the copper ion gives up its electric charge to the zinc. A current of electricity is not

generated because the changes take place in the solution, so that it is not possible to collect and control the electric energy.

In the Daniell cell this is made possible by keeping the solutions separate, but allowing the ions to pass from pole to pole. Fig. 40 shows this cell diagrammatically.

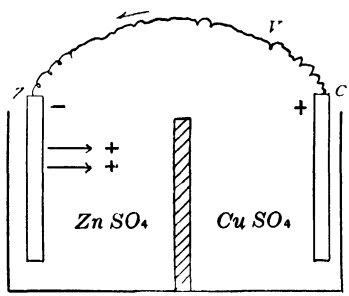



FIG 79.

As represented, the cell is a vessel divided into two parts by a porous clay partition. The vessel on the left of the partition contains a solution of zinc sulphate into which dips a bar of zinc, Z. The space to the right of the partition contains a solution of copper sulphate and a bar of copper dips into this. A wire connects the copper and zinc bars. Metallic copper from the copper sulphate is deposited on C, while simultaneously zinc dissolves from the surface of Z. At the same time a current of electricity passes from C to Z as indicated by the arrow. As the positive zinc ions leave the surface of the pole Z, this becomes negatively charged from the loss of positive ions. As metallic copper is deposited on the surface of the pole C, it becomes positively charged from the discharge of the positive copper ions. The current passes from + to − through the wire, and carried by the zinc ions passes from − to + through the liquids and through the diaphragm or partition.

Similar cells may be made, in which instead of zinc and copper other metals in solutions of their salts are used; and it is always found that one of the metals is reduced from its salt, while the other dissolves and is ionized. Which of the two will be precipitated and which ionized can be ascertained beforehand by dipping a strip of each in a solution of a salt of the other. One of the two metals will precipitate the other from the solution of its salt. The precipitating metal will be the anode in the cell, the metal precipitated the cathode. A given metal may act as precipitating and as precipitated metal; iron, for example, is precipitated by zinc but precipitates copper.

All the metals can be arranged in a series so that each metal precipitates each of the metals following it in the series from their salt-solutions, and is precipitated by each of the preceding metals of the series.

In the cell the *amount of electromotive force* (see pp. 150, 151) produced will vary according to the metals and electrolytes used in the cells, although reactions between equivalent amounts of the metals and electrolytes must by Faraday's law give the same

*amounts of electricity.* If cells of different metals and their salts are used, and the difference in potential measured by an instrument called a voltmeter introduced into the circuit at V, Fig. 79, values can be found for each metal which are given in the table below, which gives the difference in potential in volts for the metals in normal solutions. The signs + and − indicate the nature of the charge of the solution:

| | | | |
|---|---|---|---|
| Magnesium | + 1.24 Volts. | Lead | − 0 10 Volts. |
| Aluminium | + 1.03 " | Copper | − 0.59 " |
| Zinc | + 0 51 " | Mercury | − 1.03 " |
| Cadmium | + 0.16 " | Silver | − 1.06 " |
| Iron | + 0.09 " | | |

It will be seen that a zinc-cadmium cell gives + 0.51 minus + 0 16 = 0 35 volts. While a zinc-copper cell gives + 0 51 minus − 0.59 = 1.10 volts and a zinc-silver cell gives + 0.51 minus − 1.06 = 1.57 volts.

**Alloys.**—Iron covered with a layer of zinc is known as *galvanized iron.* As has been mentioned, zinc is a constituent of *brass.* It combines readily with mercury to form zinc amalgam, and this fact is taken advantage of for the purpose of preserving the zinc plates in galvanic batteries. Zinc plates covered with a layer of the amalgam are acted upon much more slowly than zinc itself. The amalgamation is effected by cleaning the zinc, dipping it in dilute sulphuric acid, and rubbing mercury over the surface with a brush or a piece of cloth.

**Zinc Chloride,** $ZnCl_2$.—This is prepared by treating zinc with chlorine, or by dissolving zinc in hydrochloric acid, evaporating to dryness, and distilling the residue. It is a white, deliquescent mass. From a very concentrated solution in hydrochloric acid it is obtained in crystals of the composition $ZnCl_2 + H_2O$. When the solution is evaporated there is always some decomposition into basic chloride, the hydroxide, and oxide. The basic chloride is formed thus:

$$Zn<\begin{matrix}Cl\\Cl\end{matrix} + HHO = Zn<\begin{matrix}OH\\Cl\end{matrix} + HCl;$$

the hydroxide thus:

$$Zn<\begin{matrix}OH\\Cl\end{matrix} + HHO = Zn<\begin{matrix}OH\\OH\end{matrix} + HCl;$$

and by higher heating the hydroxide yields the oxide and water:

$$Zn<\begin{matrix}OH\\OH\end{matrix} = ZnO + H_2O.$$

The chloride combines readily with water, and is used in the laboratory, as sulphuric acid and phosphorus pentoxide are, for the purpose of extracting the elements of water from compounds. It has a caustic action, and is used in surgery on this account. Further, it acts as a disinfectant, and its solution is used for the purpose of preserving wood, particularly railroad ties, from decay.

The chloride readily forms double chlorides like those formed by magnesium chloride. That formed with ammonium chloride, $(NH_4)_2ZnCl_4$, is made by mixing a solution of zinc in hydrochloric acid with a solution of ammonium chloride. This is used in soldering, as it cleans the surface of the metal, in consequence of the action of the zinc chloride on the oxides.

**Zinc Hydroxide,** $Zn(OH)_2$, is precipitated as a white amorphous powder when a soluble hydroxide is added to a solution of a zinc salt. It is redissolved by an excess of the reagent, and the zincate thus formed is decomposed on boiling, the hydroxide being reprecipitated.

**Zinc Oxide,** ZnO, is formed in very finely divided condition by burning zinc in the air. The product is known as *Flores zinci*, and is sometimes called philosopher's wool. It is prepared on the large scale by burning zinc and by heating the basic carbonate, which is formed by adding sodium carbonate to a solution of zinc sulphate. It is a white powder, that turns yellow when heated. It is chiefly used as a constituent of paint under the name of *zinc white.*

**Zinc Sulphide,** ZnS.—This compound occurs in nature, and is known as zinc blende. The mineral always contains a sulphide of iron, and also a small quantity of cadmium sulphide. When hydrogen sulphide is passed into a solution of a zinc salt only a part of the zinc is thrown down as the sulphide, if the salt used is one of a strong

acid, like sulphuric, nitric, or hydrochloric acid. The reason of this is that the sulphide is soluble in these acids, even when they are quite dilute. In the reaction the acid is set free and ionized, and although some sulphide is thrown down, the action soon stops:

$$\overset{++}{Zn},\ \overset{--}{SO_4} + \overset{+}{H},\overset{+}{H},\ \overset{--}{S} = ZnS + \overset{+}{H},\overset{+}{H},\ \overset{--}{SO_4}.$$

If the acetate of zinc is used the precipitation is complete, because dilute acetic acid does not dissolve zinc sulphide, or because acetic acid is only slightly dissociated, and therefore the disturbing hydrogen ions are not present. If sodium or potassium acetate is added to a solution of a neutral salt of zinc, hydrogen sulphide precipitates all the zinc, for the reason that the ions of the strong acid that are first formed react with the acetate and form the ions of the corresponding salt and also acetic acid, which exists in the solution largely in undissociated condition. Thus the hydrogen ions are eliminated, and the zinc sulphide is not dissolved:

$$\overset{++}{Zn},\ \overset{--}{SO_4} + \overset{+}{H},\overset{+}{H},\overset{--}{S} = ZnS + \overset{+}{H},\overset{+}{H},\ \overset{--}{SO_4}.$$

$$2\ \overset{+}{Na},\ \overset{-}{C_2H_3O} + \overset{+}{H},\overset{+}{H},\ \overset{--}{SO_4} = 2C_2H_4O_2 + \overset{+}{Na},\overset{+}{Na},\overset{--}{SO_4}.$$

The sulphide is, further, completely precipitated by soluble sulphides, as potassium and ammonium sulphides. Obtained by precipitation, zinc sulphide is a white amorphous substance.

**Zinc Sulphate,** $ZnSO_4$.—This salt is readily formed by oxidation of the sulphide, and is hence found in nature accompanying the sulphide. It is manufactured by carefully roasting zinc blende, and extracting with water. It crystallizes from the solution in water in large rhombic prisms of the composition $ZnSO_4 + 7H_2O$. Like magnesium sulphate, it easily loses six molecules of water, but the last one is removed with difficulty. It appears, therefore, that the constitution of the salt should be expressed by the formula $(HO)_2ZnSO_3$. Zinc sulphate, as has been stated (see p. 550), is commonly called white

vitriol. It is easily reduced when heated with charcoal. The salt is used extensively in the preparation of cotton prints and in medicine.

**Zinc Carbonate,** $ZnCO_3$, occurs in nature as smithsonite.

**Reactions which are of Special Value in Chemical Analysis.**—The principal reactions which are made use of for the purpose of separating zinc from other elements are those with hydrogen sulphide and ammonium sulphide; with potassium and sodium hydroxide; with potassium and sodium carbonates; and with ammonium carbonate. Another reaction used for analytical purposes is that which takes place when zinc salts are heated on charcoal before the blowpipe, moistened with cobalt nitrate, and ignited. Under these circumstances a green mass known as Rinmann's green is formed, which is probably a zincate of cobalt, $Zn<\begin{matrix}O\\O\end{matrix}>Co$.

### Cadmium, Cd (At. Wt. 112.4).

**General.**—The compounds of cadmium are similar to those of zinc and magnesium. The element occurs in nature in much smaller quantity than either of these, often in company with zinc, and its compounds are not as frequently met with. It is always bivalent. A mineral known as greenockite is cadmium sulphide, CdS.

**Preparation and Properties.**—Cadmium is obtained principally from different varieties of zinc blende, and separates with the zinc. It melts at 321° and boils at 778°. Being more volatile than zinc, it passes over first when the mixture is distilled. From this first distillate, which contains the oxides of zinc and cadmium, the metals are reduced by heating with charcoal. It has a color like that of tin, and is harder than tin. According to the specific gravity of its vapor, its molecule is identical with its atom, for the molecular weight is approximately 112.

*Cadmium chloride*, $CdCl_2$, like zinc chloride, is volatile; the *sulphate* crystallizes well, but is not analogous in com-

position to the sulphates of magnesium and zinc, as the composition of the crystallized salt is represented by the formula $3CdSO_4 + 8H_2O$; the *normal carbonate*, $CdCO_3$, is precipitated by soluble carbonates.

**Cadmium Sulphide,** CdS, is a beautiful yellow substance, that is thrown down from a solution of a cadmium salt by hydrogen sulphide. It does not dissolve in dilute acids, and is therefore completely precipitated by hydrogen sulphide. It is soluble in concentrated solutions of potassium iodide, bromide, and chloride. It is used as a constituent of yellow paints.

**Analytical Reactions.**– Cadmium, as has just been stated, is precipitated by hydrogen sulphide. It is thrown down together with the other elements of the hydrogen sulphide group (see p. 230). As the sulphide is not soluble in ammonium sulphide, it is easily separated from those of arsenic, antimony, and tin by treating with this reagent, when it is left undissolved in company with the sulphides of mercury, lead, bismuth, and copper. The double salt of cuprous cyanide and potassium cyanide is not decomposed by hydrogen sulphide, whereas the corresponding salt of cadmium is decomposed by it, and the yellow sulphide is precipitated.

The hydroxide of cadmium differs from that of zinc in not having acid properties. It does not dissolve in the caustic alkalies, though it does dissolve in ammonium hydroxide.

## Mercury, Hg (At. Wt. 200).

**General.**—As already stated, mercury yields two series of compounds, known as mercurous and mercuric compounds, which are analogous to the two series of copper compounds. While, however, copper forms with the oxygen acids salts belonging to the cupric series, as $CuSO_4$, $Cu(NO_3)_2$, etc., mercury forms salts belonging to both series. There is, for example, a *mercurous nitrate*, $HgNO_3$, and a *mercuric nitrate*, $Hg(NO_3)_2$; a *mercurous sulphate*, $Hg_2SO_4$, and a *mercuric sulphate*, $HgSO_4$, etc.

Mercurous compounds are readily converted into mercuric compounds by the action of oxidizing agents, and mercuric are converted into mercurous compounds by the action of reducing agents. The reactions will be treated of under the individual compounds. The question as to the correct formula of the mercurous salts is in the same condition as that in regard to the formula of cuprous salts, with this difference: the molecular weight of mercurous chloride leads to the formula HgCl, but it has been shown that when the chloride is heated some mercury is set free, and this has led to the suggestion that the molecule corresponds to the formula $Hg_2Cl_2$, and that the compound breaks down into mercury and mercuric chloride when heated. It is, however, quite possible that the compound has the simpler formula, and that under the influence of heat it is partly decomposed, as represented in the equation

$$2HgCl = HgCl_2 + Hg.$$

The fact that mercury is set free is, therefore, by no means satisfactory evidence that the formula of mercurous chloride is $Hg_2Cl_2$, and in the present state of the problem it is justifiable to write the formula HgCl.

**Forms in which Mercury occurs in Nature.**—Mercury occurs native to some extent, but principally in the form of the sulphide, HgS, which is known as cinnabar. This is sometimes found crystallized, but generally amorphous. The chief localities are Idria, Almaden in Spain, and New Almaden in California.

**Metallurgy of Mercury.**—In order to obtain mercury from the sulphide this is roasted in vessels so constructed as to condense and collect the vapor of mercury given off. In the roasting process the sulphur is oxidized to sulphur dioxide, which of course escapes. In some places the ore is mixed with limestone and distilled from clay or iron retorts, when the mercury passes over. Crude mercury is redistilled in order to purify it. It is also purified by treating it with dilute nitric acid or with a solution of ferric chloride.

**Production.**—The total production of mercury in 1905

was 3,110 tons of which the United States produced 1036 and Spain 1020.

**Properties.**—Mercury is a silver-white metal of a high lustre. At ordinary temperatures it is liquid, though at — 39.5° it becomes solid. Its specific gravity is 13.5959. It does not change in the air at ordinary temperatures. It boils at 357.25°, and is converted into a colorless vapor, the specific gravity of which leads to the conclusion that, as in the case of cadmium, the molecule and atom are identical, or that the molecule consists of only one atom. It is insoluble in hydrochloric acid and in cold sulphuric acid; but dissolves in hot concentrated sulphuric acid, and is easily soluble in nitric acid. The vapor of mercury is very poisonous.

**Applications.**—Mercury is extensively used in the manufacture of thermometers, barometers, etc.; as tin-amalgam for mirrors; and in the processes by which gold and silver are obtained from their ores.

**Amalgams.**—The alloys formed by mercury with other metals are called amalgams. These compounds are generally obtained without difficulty by bringing mercury in contact with other metals. Among the amalgams which are of chief interest are those of sodium, ammonium, silver, and gold. *Sodium amalgam* is made by bringing mercury and sodium together. Crystallized amalgams containing the constituents in the proportions represented in the formulas $Hg_6Na$ and $HgNa_3$ have been obtained. Generally speaking, sodium amalgam is easily decomposed by water, the mercury separating in the free state and the sodium acting upon the water, forming hydrogen and sodium hydroxide. It is much used in the laboratory as a convenient means of producing hydrogen in alkaline solutions. It serves as an excellent reducing agent in some cases. *Ammonium amalgam* has already been referred to under the head of Ammonium (which see). It is a curious substance, that is formed when an electric current acts upon a solution of ammonia containing some mercury which is connected with the negative pole, and also very easily by pouring a solution of ammonium

chloride upon sodium amalgam. In the latter case sodium chloride and ammonium amalgam are formed. Apparently the reaction takes place according to the following equation:

$$NH_4Cl + NaHg = NaCl + NH_4Hg.$$

The product is extremely voluminous, and swells up during the reaction, so that it occupies many times the volume occupied by the sodium amalgam. It has a metallic lustre, resembling in general the other amalgams. It is very unstable at the ordinary temperature, breaking down into mercury, hydrogen, and ammonia. At a low temperature, however, it has been obtained in crystallized form. The metallic lustre and general outward appearance of the compound suggests that whatever is in combination with mercury in it has probably metallic properties, and this affords some confirmation of the ammonium theory, according to which the presence of the complex, $NH_4$, in the salts formed by ammonia is assumed. *Silver amalgam* and *gold amalgam* vary in composition according to the method of preparation, and when heated are comparatively easily decomposed.

**Mercurous Chloride,** HgCl, is commonly called calomel. Like cuprous chloride, CuCl, and argentic chloride, AgCl, it is insoluble in water. It is formed most readily by reducing mercuric chloride. The reduction can be accomplished by means of sulphurous acid, when the following reaction takes place:

$$2HgCl_2 + 2H_2O + SO_2 = 2HgCl + H_2SO_4 + 2HCl.$$

It is also formed by heating together mercuric chloride and mercury, and by subliming a mixture of mercuric sulphate, sodium chloride, and mercury. This method is the one mostly used in the manufacture of calomel. The product obtained by sublimation is crystalline; the precipitated substance forms a loose powder. As was stated above, the specific gravity of the vapor corresponds to

that required for the formula HgCl. When acted upon for some time by light it is partly decomposed into mercury and mercuric chloride. This is a fact of great importance, inasmuch as calomel is much used in medicine, and mercuric chloride is an active poison. Bottles in which calomel is kept should be carefully protected from the action of the light.

Just as mercuric chloride is converted into mercurous chloride by reducing agents, so the latter is converted into the former by oxidizing agents. When, for example, mercurous chloride is treated with nitric acid it is converted into mercuric chloride and mercuric nitrate.

**Mercuric Chloride,** or **Corrosive Sublimate,** $HgCl_2$, is made by subliming a mixture of sodium chloride and mercuric sulphate,

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4,$$

and by dissolving mercury in *aqua regia*, evaporating to dryness, and subliming the residue. It is a white, transparent, crystalline mass; it is soluble in water, and can be obtained in crystalline form from the solution. It is more easily soluble in alcohol and ether than in water, and is extracted from a water solution by shaking with ether. It is quite volatile, and the specific gravity of its vapor corresponds to that required for the formula $HgCl_2$. It is easily reduced to mercurous chloride by contact with organic substances, and by reducing agents in general. The action of sulphur dioxide has already been treated of as furnishing a method for the preparation of mercurous chloride. Stannous chloride abstracts chlorine from it and forms mercurous chloride and metallic mercury, while the stannous chloride is converted into stannic chloride:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4;$$
$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

Mercuric chloride is an active poison, and has been used extensively in this capacity. It has a very marked influence upon the lower organisms, which play such an im-

portant part in producing disease and the decay of organic substances, and is used as a disinfectant. Wood impregnated with a solution of it is partly protected from decay. In surgery it is used for the purpose of preventing contamination of wounds by the hands and instruments of the surgeon, it being customary now for the surgeon to wash his hands and instruments in a dilute solution of the chloride before performing an operation.

**Mercurous Iodide,** HgI, can be made by treating mercury with iodine; or by treating mercuric iodide with mercury; and more easily by adding potassium iodide to a solution of a mercurous salt, when it is thrown down as a greenish-yellow powder. It is unstable, and breaks down, yielding mercury and mercuric iodide. When treated with potassium iodide it suffers the same decomposition, the iodide which is formed combining with the potassium iodide, while mercury is deposited. Mercurous iodide is used in medicine. As it is more easily decomposed than mercurous chloride, and mercuric iodide is poisonous, care should be taken in its use.

**Mercuric Iodide,** $HgI_2$, is made by direct combination of mercury and iodine, and by the action of potassium iodide upon a solution of a mercuric salt, when it is precipitated as a beautiful, scarlet-red powder. Though insoluble in water, it is soluble in alcohol and ether. It dissolves, further, in a solution of potassium iodide in consequence of the formation of a double iodide, or iodomercurate. When heated to about 150° the color changes from red to yellow, and after cooling the yellow substance changes to red. Sometimes it can be kept in the condition in which it has a yellow color for some time after it has cooled down, and then if touched at one point the change to the red substance takes place rapidly through the entire mass. Both the red and the yellow modifications are crystallized, but in different forms. The red crystals are tetragonal; the yellow ones are rhombic or monoclinic. From what has been said, the monoclinic structure is evidently an unstable one for this compound. It is possible that the difference between the two forms is

due to a difference in the complexity of the molecules; perhaps the larger molecules of the red iodide are decomposed by heat into the smaller molecules of the yellow iodide. When the iodide is first precipitated from a solution of mercuric chloride by potassium iodide it is yellow, but it rapidly turns red.

**Mercuric Oxide,** HgO, like the iodide, presents itself in two colors—the red and the yellow. When mercury is heated for a long time at a temperature near the boiling-point so that the air has access to it, it is converted into the red oxide. When a solution of a mercuric salt is treated with caustic soda or caustic potash the yellow oxide is precipitated. When heated, the red oxide becomes darker, and finally nearly black, and on cooling the red color reappears. The yellow oxide also becomes darker on heating. Exposed to the light, the red oxide loses some of its oxygen, and mercury is deposited. When heated to a sufficiently high temperature both varieties give up all their oxygen, as was seen in the case of the red oxide in the preparation of oxygen. It will be remembered that *oxygen was discovered by heating this compound.* The student will at this stage better appreciate the importance of this discovery than when it was first mentioned. It will now be seen that a large number of the chemical phenomena with which we have to deal involve the action of oxygen.

**Mercuric Sulphide,** HgS, is the principal compound of mercury found in nature. This natural variety, which is known as cinnabar, is a red crystallized compound. When prepared by treating a solution of a mercuric salt with hydrogen sulphide it is an amorphous, black powder. This black powder can, however, be converted into the red crystallized variety by sublimation, and by allowing it to stand in contact with a solution of the sulphide of an alkali metal. The sulphide, whether amorphous or crystallized, is acted upon with difficulty by acids. Dilute nitric acid, which easily dissolves the sulphides of those metals that resemble mercury, leaves it unacted upon, and advantage is taken of this fact for the purpose of

separating it from the sulphides of lead, bismuth, copper, and cadmium in qualitative analysis. It is dissolved by concentrated nitric acid and by *aqua regia*. The substance used in medicine under the name *Ethiops martialis* is an intimate mixture of amorphous sulphide and sulphur Like the oxide, cinnabar turns dark when heated, and it slowly undergoes the same change when exposed to the light, in consequence of a slight decomposition into mercury and sulphur. When that which has not been heated to too high a temperature is cooled down again, it acquires its original red color. If it has been heated to the temperature of sublimation, the black color of that which does not sublime is permanent. Cinnabar is used as a pigment.

**Mercuric Cyanide,** $Hg(CN)_2$, is formed by dissolving mercuric oxide in an aqueous solution of hydrocyanic acid. It is soluble in water, and crystallizes well in quadratic prisms. When heated it is decomposed into cyanogen and mercury, and this affords the most convenient method of making cyanogen.

*Fulminating mercury* is an explosive compound much used in the manufacture of gun-caps. It is made by dissolving mercury in nitric acid and adding alcohol. Its explosion consists in a sudden breaking down into nitrogen, carbon dioxide, and mercury. The composition of the compound is represented by the formula $C_2N_2O_2Hg$.

**Mercurous Nitrate,** $HgNO_3$, is made by treating nitric acid with an excess of mercury. It is easily decomposed, forming difficultly soluble basic salts, some of which are of complicated composition. The simplest is that which has the composition $HgOH.HgNO_3$.

**Mercuric Nitrate,** $Hg(NO_3)_2$, is formed by treating mercuric oxide with an excess of nitric acid and evaporating, when the salt can be obtained in crystals. It is easily decomposed by water, with formation of a basic salt that is insoluble in water.

**Compounds formed by Salts of Mercury with Ammonia.**—When mercuric chloride is treated with ammonia a white precipitate is formed, the composition of which is

represented by the formula $HgClNH_2$. The formation takes place according to the equation

$$HgCl_2 + 2NH_3 = HgClNH_2 + NH_4Cl.$$

The compound is known as *white precipitate*, or *infusible white precipitate*. By adding a solution of mercuric chloride to a boiling solution of ammonium chloride containing ammonia, a compound having the composition $Hg(NH_3Cl)_2$ separates out on cooling. This is called *mercuric diammonium chloride*, or *fusible white precipitate*. Mercurous compounds corresponding to both the above-mentioned derivatives of mercuric chloride are known. The first, or *mercurous chloramide*, $Hg_2NH_2Cl$, is the black substance formed when mercurous chloride is treated with ammonia:

$$2HgCl + 2NH_3 = Hg_2NH_2Cl + NH_4Cl.$$

The second, or *mercurous ammonium chloride*, $HgNH_3Cl$, is formed by treating calomel with ammonia gas.

Similar compounds are obtained from the other salts of mercury. In a solution of mercurous nitrate ammonia forms a black precipitate, known in pharmacy as *Mercurius solubilis Hahnemanni*.

**Reactions which are of Special Value in Chemical Analysis.**—Among the most characteristic reactions of *mercurous* compounds are the following:

*Sodium* or *potassium hydroxide* gives a black precipitate of mercurous oxide.

*Ammonia* gives a black precipitate which is a compound of mercurous oxide and ammonia.

*Hydrochloric acid* and *soluble chlorides* form mercurous chloride, and the precipitate turns black when treated with ammonia.

The reactions with stannous chloride, potassium iodide, hydrogen sulphide, and ammonium sulphide have been explained.

The principal reactions of the *mercuric* salts are the following:

*Sodium* or *potassium hydroxide* produces a yellow precipitate of mercuric oxide.

The reactions with hydrogen sulphide, stannous chloride, and potassium iodide have been described above.

## ELEMENTS OF FAMILY III, GROUP B: GALLIUM.—INDIUM.—THALLIUM.

**General.**—All the elements of this group are rare. Gallium forms compounds which in composition are analogous to those of aluminium, in which it is trivalent, as in the compounds $GaCl_3$, $Ga_2O_3$, $Ga(NO_3)_3$, $Ga_2(SO_4)_3$, etc. On the other hand, it also forms compounds in which it is bivalent, as in the chloride $GaCl_2$ and the oxide GaO Indium also forms compounds in which the element is trivalent, and a few in which it is bivalent. Thallium, like gold, is trivalent and univalent in its compounds.

**Gallium,** Ga (At. Wt. 70).—This element is found in some varieties of zinc blende, and was discovered in that which occurs at Pierrefitte, in France. It is a hard, bluish-white metal, melting at 30.1°. It owes its name to the Latin name of France, Gallia. Like scandium, it is of special interest for the reason that its properties were foretold by Mendeléeff some years before it was discovered, and it was described by him under the name of eka-aluminium, as scandium was described under the name of eka-boron.

**Indium,** In (At. Wt. 115).—Indium was discovered in a variety of zinc blende found at Freiberg, in Germany. The discovery was made by means of the spectroscope, and as the spectrum of the element contains two very characteristic blue lines it was called indium. It is a silver-white, soft, and tenacious metal. It melts at 155°. It has since been found in other varieties of zinc blende, but always in small quantity.

**Thallium,** Tl (At. Wt. 204.1).—This element was discovered in the flue-dust of a sulphuric-acid factory in the Harz mountains, by the aid of the spectroscope. As it colors the flame a beautiful green, it was called thallium, from the Greek θαλλος, signifying a green branch. It is a very soft, white metal that is oxidized quickly in moist air. It melts at 302° It has since been found in a number of varieties of iron pyrites and copper pyrites.

## EXPERIMENTS.

### Zinc and its Salts.

**Experiment 228.**—Heat a small piece of zinc on charcoal in the oxidizing flame of the blowpipe. The white fumes of zinc oxide (philosopher's wool) will be seen, and the charcoal will be covered

with a film which is yellow while hot, but becomes white on cooling.

EXPERIMENT 229.—Dissolve some zinc dust in a solution of sodium hydroxide, and see whether hydrogen is given off.

## MERCURY AND ITS SALTS.

EXPERIMENT 230.—Make a solution of mercurous nitrate by treating at the ordinary temperature an excess of mercury with nitric acid, that is not too concentrated; and with this solution study the conduct of mercurous salts.

EXPERIMENT 231.—Heat some of the solution of mercurous nitrate to boiling, then add a few drops of concentrated nitric acid, and boil again. With the solution thus obtained study the conduct of mercuric salts.

# CHAPTER XXIX.

## ELEMENTS OF FAMILY IV, GROUP B: GERMANIUM.—TIN.—LEAD.

**General.**—Of the elements of this group germanium is extremely rare. It was discovered by Winkler in 1885. Tin and lead, on the other hand, have long been known, and are extensively used. All form two series of compounds, in one of which they are bivalent and in the other quadrivalent. The general formulas of some of the principal compounds of the first series are as follows:

$$MCl_2,\ MO,\ M(OH)_2,\ M(NO_3)_2,\ MSO_4,\ MCO_3,\ \text{etc.}$$

The general formulas of some of the principal compounds of the other series are as follows:

$$MCl_4,\ MO_2,\ M(OH)_4,\ MO(OH)_2,\ \text{etc.}$$

These elements have already been referred to at the close of Chapter XXI (see p. 407), and attention was there called to the resemblance between them and carbon and silicon. In this connection it will be well to repeat what was there said. Of the three elements of the group, germanium and tin are more acidic in character than lead. They combine with chlorine in two proportions, forming the chlorides $GeCl_2$, $SnCl_2$, $PbCl_2$, $GeCl_4$, $SnCl_4$, $PbCl_4$. With oxygen they combine to form the compounds $GeO_2$, $SnO_2$, and $PbO_2$. Stannic oxide, $SnO_2$, and lead peroxide, $PbO_2$, form salts with bases, and these have the composition represented by the general formulas $M_2SnO_3$ and $M_2PbO_3$, and are therefore analogous to the silicates, carbonates, and titanates. On the other hand, further, salts are known which are derived from the oxide PbO. These have the general formula $M_2PbO_2$, and are to be regarded as salts of an acid $Pb(OH)_2$. These salts

are not stable, and are not easily obtained. In most of its compounds lead plays the part of a base-forming element. Notwithstanding the marked analogy between some of the compounds of tin and those of the members of the silicon group, it appears, on the whole, advisable to treat of this element in company with lead, which it also resembles in many respects. The analogy of germanium and tin with carbon and silicon is shown in the boiling points and specific gravities of their chlorine compounds:

| | $CCl_4$ | $SiCl_4$ | $GeCl_4$ | $SnCl_4$ | $CHCl_3$ | $SiHCl_3$ | $GeHCl_3$. |
|---|---|---|---|---|---|---|---|
| B Pt | 77° | 58° | 86° | 114° | 61° | 33° | 72° |
| Sp. Gr. | 1.6 | 1.5 | 1.9 | 2.2 | 1.33 | 1.65 | —— |

## Germanium, Ge (At. Wt. 72.5).

Germanium is the third element the properties of which were foretold by Mendeléeff by the aid of the periodic law. As it occurs in the silicon group he called it *eka-silicon*. It was discovered in a silver ore occurring at Freiberg, Germany. It is a gray-white substance with metallic lustre. It melts at about 900°. The name has, of course, reference to the country in which it was discovered. It acts mostly as a base-forming element, being perhaps more like tin than any other one metal. It forms the two chlorides $GeCl_2$ and $GeCl_4$, and the corresponding fluorides $GeF_2$ and $GeF_4$; but preferably it forms those compounds in which the element is quadrivalent The fluoride forms double salts resembling the fluosilicates, as, for example, *potassium fluogermanate*, $K_2GeF_6$.

## Tin, Sn (At. Wt. 119).

**General.**—The compounds of tin with which we generally have to deal belong, with the exception of stannous chloride, to the series in which the metal is quadrivalent, and in this series it acts as an acid-forming element. The chloride, $SnCl_4$, corresponds to the chlorides of carbon and silicon, $CCl_4$ and $SiCl_4$. Unlike these elements, however, it does not form a compound with hydrogen.

**Occurrence.**—Tin occurs almost exclusively as tin-stone or cassiterite in nature. This is the dioxide, $SnO_2$, corresponding to carbon dioxide, $CO_2$; silicon dioxide, $SiO_2$; titanium dioxide, $TiO_2$; etc. It also occurs in small

quantities in company with gold as metallic tin, and in a variety of pyrites of the formula $Cu_4SnS_4 + FeSnS_4$, known as stannite.

**Metallurgy.**—The ores are roasted for the purpose of getting rid of the sulphur and arsenic, and the oxide is then heated with coal in a furnace. After the reduction is complete the tin is drawn off and cast in bars. This tin is impure, and when again slowly melted, that which first melts is purer. By letting it run off as soon as it melts, the alloy which melts at a higher temperature remains behind, and the tin is thus rendered much purer. The commercial variety of tin known as *Banca tin* is the purest. It receives its name from Banca, in the East Indies, where it is made. *Block-tin*, made in England, is also comparatively pure.

**Production.**—In 1906, 108,500 tons of tin were produced, mostly in the Malay States.

**Properties.**—Tin is a white metal, which in general appearance resembles silver. It is soft and malleable, and can be hammered out into very thin sheets, forming the well-known tin-foil. Its specific gravity is 7.3. At 200° it is brittle, and at 232° it melts. It boils at about 1600°. At ordinary temperatures it remains unchanged in the air. It dissolves in hydrochloric acid, forming stannous chloride, $SnCl_2$; in sulphuric acid, forming stannous sulphate, $SnSO_4$, sulphur dioxide being evolved at the same time. Ordinary concentrated nitric acid oxidizes it, the product being a compound of tin, oxygen, and hydrogen, known as *metastannic acid*, which is a white powder insoluble in nitric acid and in water. It is dissolved by a hot solution of potassium hydroxide which forms potassium stannate, $K_2SnO_3$.

Below 20° ordinary tin passes slowly over into a gray modification which is brittle and has a lower specific gravity (5.8) than ordinary tin. The formation of this gray tin explains the crumbling of tin roofs and tin organ pipes in very cold countries. This crumbling is known as the *tin pest.*

**Applications.**—It is used in making alloys, of which

bronze (see p. 547), soft solder, and britannia metal are the most important. It is used also for protecting other metals, as in the tinware vessels in such common use, which are made of iron covered with a layer of tin. Copper vessels are also frequently covered with tin.

**Alloys.**—Bronze has already been treated of under Copper. It consists of copper and tin, and sometimes a little zinc. *Soft solder* is made of equal parts of tin and lead, or of two parts of tin and one of lead. *Britannia metal* is composed of nine parts of tin and one of antimony with a little copper. *Tin amalgam* is made by bringing tin and mercury together, and is used in the silvering of mirrors Alloys of tin and antimony are much used for machine bearings. Those in common use contain not only these two elements, but also copper and lead.

**Stannous Chloride,** $SnCl_2$, is formed by dissolving tin in hydrochloric acid. If the solution is concentrated enough the compound crystallizes out. The crystals have the composition $SnCl_2 + 2H_2O$. This is the commercial product known as *tin salt.* It is easily soluble in water, but if the solution is dilute it becomes turbid in consequence of the formation of the insoluble basic salt, $2Sn<^{OH}_{Cl} + H_2O$:

$$2SnCl_2 + 3H_2O = 2Sn<^{OH}_{Cl} + H_2O + 2HCl.$$

This same decomposition takes place when the solution is allowed to stand in contact with the air. Under these circumstances a part of the stannous chloride is converted into stannic chloride by oxidation:

$$3SnCl_2 + H_2O + O = SnCl_4 + 2Sn(OH)Cl.$$

When the crystals are heated they melt at about 40°, and if heated higher they undergo partial decomposition, forming the oxide and hydrochloric acid:

$$SnCl_2 + H_2O = SnO + 2HCl.$$

Stannous chloride has a marked tendency to combine with chlorine and to pass over into stannic chloride

This power has already been shown in its action upon mercuric chloride and upon mercurous chloride. It reduces the former, first to mercurous chloride, and it then abstracts the chlorine from this, leaving metallic mercury:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4;$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4.$$

Stannous chloride is a good mordant. (See p. 536.)

**Stannic Chloride,** $SnCl_4$, formed by treating tin with chlorine, is a colorless liquid which boils at 114°, and the specific gravity of its vapor is that required by a compound of the formula $SnCl_4$. In the air it gives off fumes in consequence of the action of moisture. It has long been known by the name *spiritus fumans Libavii.* It combines with water, forming a number of crystallized hydrates. When its solution in water is boiled stannic acid is precipitated:

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$

Stannic chloride is used as a mordant. (See p. 536.) With other chlorides it forms the *chlorostannates* of the general formula $M_2SnCl_6$ or $SnCl_4.2MCl$, of which the ammonium salt, $(NH_4)_2SnCl_6$, or *pink salt*, is the best known. This is manufactured for use in making cotton-prints.

**Stannic Hydroxide,** $Sn(OH)_4$, is perhaps formed when a solution of stannic chloride in water is boiled. The precipitate obtained has, however, the composition $H_2SnO_3$, and this is known as *stannic acid.* Stannic acid is precipitated also by treating a solution of a stannate with just enough acid to effect decomposition. The decomposition with hydrochloric acid takes place as represented in the equation

$$Na_2SnO_3 + 2HCl = 2NaCl + H_2SnO_3.$$

The compound thus obtained is insoluble in water, but is easily soluble in hydrochloric, nitric, and sulphuric acids, and in the caustic alkalies. With the alkalies it forms stannates, as *sodium stannate*, $Na_2SnO_3$, and *potassium*

*stannate*, $K_2SnO_3$. The former is made on the large scale, and is known as *preparing-salt.*

*Metastannic Acid.*—When tin is treated with concentrated nitric acid it is converted into a white powder which is insoluble in water and in acids, but nevertheless seems to be a hydroxide of tin of the same composition as stannic acid. This is known as *metastannic acid.* With alkalies it forms salts which in properties and composition are entirely different from the stannates. They are known as the *metastannates.* Two sodium salts are known, which differ in composition. One of these has the composition $Na_2Sn_5O_{11}$, the other is $Na_2Sn_9O_{19}$. They are probably derived from acids analogous to the polysilicic acids, which may be called *polystannic acids.* The question as to the composition of metastannic acid is an open one.

**Stannic Oxide,** $SnO_2$, as has been stated, is the principal form in which tin occurs in nature. The mineral is known as cassiterite or tin-stone. It is found at Cornwall, England; on the East Indian islands Banca and Biliton; and in Malacca. It crystallizes in the tetragonal system, and is generally colored from brown to black. It is formed as a white powder by burning tin in the air, and by heating the different varieties of stannic hydroxide. It is infusible, and is not acted upon by concentrated hydrochloric or nitric acid. Concentrated sulphuric acid, however, converts it into a gelatinous liquid from which stannic oxide is precipitated by water.

**Stannous Sulphide,** SnS, which is formed when hydrogen sulphide is passed into a solution of stannous chloride, is a brownish-black powder. When treated with the soluble sulphides and sulphur, or with a soluble polysulphide, it dissolves, forming a sulphostannate as represented in these equations:

$$SnS + (NH_4)_2S + S = (NH_4)_2SnS_3;$$
$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

**Stannic Sulphide,** $SnS_2$.—This compound is obtained in crystallized form by heating together tin-filings, sulphur,

and dry ammonium chloride; and in amorphous form by treating a solution of stannic chloride with hydrogen sulphide. In the former case it is a golden-yellow crystalline substance; in the latter a yellow powder. The crystalline variety is known as *mosaic gold.* When heated to a high temperature it is converted into stannous sulphide. The precipitated variety is easily dissolved by concentrated hydrochloric acid, and converted into metastannic acid by concentrated nitric acid. The crystallized variety is not soluble in hydrochloric acid, and is affected but slightly by nitric acid. The crystallized variety, or mosaic gold, is used as a pigment, particularly for bronzing. Stannic sulphide dissolves easily in the soluble sulphides, forming *sulphostannates:*

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3;$$
$$SnS_2 + K_2S \quad = K_2SnS_3.$$

**Reactions which are of Special Value in Chemical Analysis.**—The reactions with hydrogen sulphide, and the conduct of the precipitated sulphides when treated with ammonium sulphide or polysulphide, are of chief importance for analytical purposes when tin is present.

The reducing action of stannous compounds serves to distinguish them from stannic compounds.

The *carbonates of the alkali metals* precipitate the hydroxides, and these do not dissolve in an excess of the carbonate. Metallic *zinc* precipitates the tin from a solution of a tin compound as a spongy mass. If the precipitation is carried on in a platinum vessel, the platinum is not colored by it. By this means it can be distinguished from antimony, which is reduced under the same circumstances, but is deposited as a black coating upon the platinum.

## Lead, Pb (At. Wt. 206.9).

**General.**—The basic properties of lead are stronger, and its acidic properties weaker, than those of tin. Its principal compounds are those in which it acts as a base-forming element. The compounds in which it is quadrivalent,

such as $PbO_2$, are comparatively unstable, and when treated with acids they readily pass over into the compounds of the series in which the lead is bivalent. Thus lead peroxide itself readily gives up oxygen when treated with acids, and yields salts of bivalent lead.

**Forms in which Lead occurs in Nature.**—Lead occurs in nature as the sulphide, PbS, which is known as galenite or galena. Other natural compounds of the metal are the carbonate, $PbCO_3$, known as cerussite; the phosphate, $Pb_3(PO_4)_2$; the chromate, $PbCrO_4$, or crocoisite; and the molybdate, $PbMoO_4$, or wulfenite.

**Metallurgy.**—Most of the lead in the market is obtained from the sulphide, and as the natural sulphide generally contains silver both metals have to be considered in the treatment of the ore. Under the head of Silver (which see) reference was made to the methods by which this metal is separated from the lead after both have been separated from their compounds. Here it will only be necessary to show how the metals are extracted together from the ore. This is accomplished in one of two ways:

(1) By heating the sulphide with iron, when the latter combines with the sulphur, forming iron sulphide, while the lead is set free.

(2) By roasting the sulphide until it is partly converted into lead oxide and lead sulphate, and then heating the mixture without access of air, when two reactions take place, which are represented in these equations:

$$PbS + 2PbO = 3Pb + SO_2;$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

The lead is thus set free, and the sulphur is driven off as sulphur dioxide.

**Production.**—The production of lead has doubled within the last fifteen years. In 1906 it was 921,679 tons of which the United States produced 341,379.

**Properties.**—Lead is a bluish-gray metal, with a high lustre. It is very soft, and not very strong; melts at 325°, and has the specific gravity 11.37. It boils at about 1470°. When heated in contact with the air it becomes

covered with a layer of oxide, as can be seen in a vessel containing the molten metal. Pure water acts upon lead when air containing carbon dioxide has access to it, and some of the lead dissolves. Water charged with carbon dioxide under pressure dissolves lead to some extent. If the water contains calcium carbonate, it acts only very slightly upon the metal. Further, water that contains organic matter in a state of decomposition dissolves lead with comparative ease. Nitric acid dissolves lead readily; as, however, lead nitrate is insoluble in nitric acid, it is necessary to use comparatively dilute acid. Concentrated sulphuric acid dissolves lead to some extent, and therefore a little lead sulphate is sometimes contained in commercial sulphuric acid. When such a solution is diluted with water the sulphate is precipitated. Hence when some specimens of the commercial acid are diluted with water they become turbid, and after standing for a time they become clear, as the lead sulphate settles. Hydrochloric acid acts only slightly upon lead. Acetic acid dissolves the metal very readily. It is precipitated in metallic form from a solution of one of its salts by metallic zinc. The formation is sometimes very beautiful, especially if the zinc is suspended in the solution. It is called the "lead tree," or *Arbor Saturni*. The action consists in a substitution of zinc for the lead. After the action is complete all the lead is deposited as metallic lead, and the zinc has entered into its place, forming a salt which remains in solution. Thus, if lead nitrate is used, zinc nitrate is in the solution.

**Applications.**—Lead is extensively used for making sulphuric-acid chambers, evaporating-pans for alum and sulphuric acid, shot, water-pipes, and for making various alloys. The use of lead water-pipes is important from the sanitary point of view, as is evident from the statements above made concerning the action of water upon the metal. Ordinary drinking-water acts under most circumstances only very slightly upon lead, and not enough is dissolved to be dangerous to those using the water. Nevertheless, circumstances may at

any time arise which will increase the solvent power of the water, and thus cause serious results; and it would undoubtedly be better if the use of such pipes could be entirely avoided in cases in which the water is to be used for drinking purposes. *Babbitt's metal*, which is used for machine bearings, contains copper, antimony, tin, and lead. Much lead is now used in making storage batteries.

**Lead Chloride,** $PbCl_2$, is formed when hydrochloric acid or a soluble chloride is added to a cold solution of a lead salt, and appears as a white precipitate. It is soluble in hot water, and forms long, needle-shaped crystals. It is soluble in concentrated hydrochloric acid. It occurs in nature in small quantity, as cotunnite.

**Lead Tetrachloride,** $PbCl_4$, is a liquid that forms a crystalline mass at $-15°$. It is decomposed into the dichloride and chlorine at the ordinary temperature. At 105° this takes place with explosion. It is formed by passing chlorine into concentrated hydrochloric acid containing lead chloride. After saturation, ammonium chloride is added, when the double salt, $PbCl_4.2NH_4Cl$, separates in yellow crystals. Ice-cold concentrated sulphuric acid decomposes it into ammonium sulphate, hydrochloric acid, and lead tetrachloride, which collects as a yellow oil below the sulphuric acid.

**Lead Iodide,** $PbI_2$, is a yellow substance that crystallizes from water in beautiful lustrous laminæ. It is precipitated when potassium iodide is added to a solution of a lead salt.

**Oxides of Lead.**—Lead forms five distinct compounds with oxygen, the formulas and names of which are as follows: *lead suboxide*, $Pb_2O$; *lead oxide*, PbO; *lead sesquioxide*, $Pb_2O_3$; *minium*, $Pb_3O_4$; and *lead peroxide*, $PbO_2$.

**Lead Suboxide,** $Pb_2O$.—This compound is formed when lead is exposed to the air.

**Lead Oxide,** PbO.—This is formed by heating lead nitrate, and is then left behind in the form of a yellow powder. If heated to fusion it solidifies, forming a yellowish or reddish mass known as *litharge*. This is formed in large quantity in the process of separating silver

from lead. With the strongest bases it forms salts similar to those formed by zinc. This is seen in the solubility of the hydroxide in sodium and potassium hydroxide, which is due to the formation of compounds known as plumbites:

$$Pb(OH)_2 + 2KOH = Pb(OK)_2 + 2H_2O.$$

Heated with silicon dioxide it forms a silicate which is easily fusible. Lead oxide is used extensively in the manufacture of flint glass for optical purposes, as was described under Glass (which see). It also finds application in glass painting and porcelain painting, and is used in the manufacture of lead salts, particularly "sugar of lead," which is an acetate.

**Lead Peroxide,** $PbO_2$, is formed by treating *minium* or *red lead* with dilute nitric acid. Minium has the composition $Pb_3O_4$. When treated with nitric acid, a part dissolves as lead nitrate, and lead peroxide remains behind, as represented in the equation

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

The peroxide is formed in general by the action of oxidizing agents upon the lower oxides of lead. One of the most convenient methods of making it consists in treating lead acetate with a filtered solution of bleaching-powder. It is a dark-brown powder, insoluble in water. When ignited it loses half of its oxygen, and it gives up its oxygen readily to other substances. Towards hydrochloric acid it acts like manganese dioxide, giving lead chloride and chlorine according to the equation

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

It appears probable that the tetrachloride is first formed, and that this then breaks down into the dichloride and chlorine. When the peroxide is treated in the cold with hydrochloric acid it dissolves, and when this solution is heated it gives off chlorine. Further, when it is treated with caustic alkalies lead peroxide is thrown down.

Lead peroxide dissolves in concentrated caustic potash and forms a salt of the formula $K_2PbO_3$, or $PbO<\begin{matrix}OK\\OK'\end{matrix}$ analogous to potassium stannate, $K_2SnO_3$, silicate, $K_2SiO_3$, carbonate, $K_2CO_3$, etc. Other salts derived from the acid $H_2PbO_3$ are known, and are called *plumbates*.

**Storage Battery.**—An efficient galvanic battery can be made by putting two lead plates in dilute sulphuric acid, one of the plates being covered with a layer of lead peroxide. The sulphuric acid acts upon the lead, converting it into lead sulphate, which forms a solid layer upon the plate. On the other hand, the acid acts upon the lead peroxide, reducing the lead to the bivalent condition and forming with it lead sulphate. As long as the chemical action can take place, that is to say, as long as there is lead peroxide present, the battery continues to act. When it ceases to act it can be restored to the active condition by passing an electric current through it in the opposite direction. Under these conditions the lead sulphate on one plate is reduced to metallic lead, and that on the other is oxidized to lead peroxide. These facts are taken advantage of in the preparation of the well-known storage batteries.

**Red Lead, Minium.**—When lead oxide is gently heated in the air it takes up oxygen, and is converted into the red compound known as minium or red lead. The commercial article of this name varies in composition, but approximates to that represented by the formula $Pb_3O_4$, and, if the oxide is slowly heated, the amount of oxygen taken up is that required to form a compound of the above formula. Red lead varies in color from red to yellowish, according to the method of preparation. When heated it becomes dark, but the red color appears again on cooling. When heated to a high temperature it loses oxygen and yields lead oxide:

$$Pb_3O_4 = 3PbO + O.$$

When treated with dilute nitric acid lead nitrate is formed, and lead peroxide is left undissolved. Red lead

is used as a pigment, and sometimes in place of litharge when an oxide of lead is needed, as in the manufacture of glass, as a flux in the manufacture of porcelain, etc.

**Lead Sulphide,** PbS.—This is the principal compound from which lead is obtained. The natural variety is called galena or galenite. It is formed as a black precipitate, when hydrogen sulphide is passed into a solution of a lead salt. If the solution contains a large amount of hydrochloric acid, a red precipitate, $PbS.PbCl_2$, may be formed. When heated in the air the sulphur passes off as sulphur dioxide, and the lead is converted into oxide. Concentrated hydrochloric acid dissolves it. Concentrated nitric acid converts it into the sulphate.

**Lead Nitrate,** $Pb(NO_3)_2$.—The nitrate is easily made by dissolving lead, lead oxide, or carbonate in nitric acid. The salt crystallizes well, and is easily soluble in water. It is difficultly soluble in dilute nitric acid, and insoluble in concentrated nitric acid, resembling in this respect barium nitrate. It is decomposed by heat, giving nitrogen peroxide, $NO_2$, and lead oxide.

**Lead Carbonate,** $PbCO_3$.—The carbonate occurs in nature as cerussite, crystallized in forms which are the same as those of barium carbonate, and of that variety of calcium carbonate known as aragonite. It can be obtained by adding lead nitrate to a solution of ammonium carbonate, but, when solutions of lead salts are treated with the secondary carbonates of the alkali metals, precipitates of basic carbonates are always obtained. When an excess of sodium carbonate is added to a solution of lead nitrate, the precipitate has the composition $3PbO.2CO_2 + H_2O$. The salts usually obtained are more complicated than this, but the relations between them and lead oxide and carbonic acid are of the same kind. Basic lead carbonate is prepared and used extensively, under the name of *white lead*, as a pigment. It is manufactured by different methods. The principal ones are the following:

(1) *The Dutch Method.*—This consists in exposing sheets of lead wound in spirals to the action of vinegar, air, and carbon dioxide from decaying organic matter.

The spirals of sheet lead are placed in earthenware vessels, on the bottom of which, but not in contact with the lead, the vinegar is placed. The vessels thus arranged are placed in beds of horse-manure. In consequence of decomposition, which is set up in the manure, carbon dioxide is given off slowly, and enough heat is generated to start the action upon the lead. The chemical changes involved in the process are, mainly, the formation of a basic acetate of lead, and the subsequent decomposition of this by carbon dioxide, forming a basic carbonate, and leaving the acetic acid free to act upon a further quantity of lead.

(2) *The French Method.*—In this method a solution of basic lead acetate is prepared by treating a solution of the neutral salt with lead oxide. This is then decomposed by passing carbon dioxide into it, when a basic carbonate is thrown down. The carbon dioxide is generally made by burning coke.

(3) *The English Method.*—This is a modification of the Dutch method, and differs from it chiefly in the substitution of spent tan in a state of fermentation for manure, and the use of dilute acetic acid in place of vinegar. There is less risk of discoloration in consequence of the formation of hydrogen sulphide, but the fermentation takes place more slowly.

An objection to white-lead paint is that it turns dark under the influence of hydrogen sulphide. It also turns yellow in consequence of the action of some substance contained in the oil with which the lead carbonate is mixed when used as a paint.

**Lead Sulphate,** $PbSO_4$, occurs to some extent in nature. It is formed by adding sulphuric acid or a soluble sulphate to a solution of a lead salt, and by oxidation of lead sulphide. Like barium sulphate, it is practically insoluble in water. As stated above, it is somewhat soluble in concentrated sulphuric acid, and it is therefore always found in the concentrated acid of commerce. Nitric acid and hydrochloric acid dissolve it in considerable quantity. It dissolves further quite readily in solutions of some am-

monium salts, as in ammonium tartrate and acetate. When heated to redness it is partly decomposed with loss of sulphur trioxide.

**Reactions which are of Special Value in Chemical Analysis.**—The reactions of lead salts with the soluble hydroxides, with sulphuric acid, hydrochloric acid, hydrogen sulphide, soluble carbonates, potassium chromate and dichromate, are the ones which are principally used in analysis. All these have been treated of in this chapter, with the exception of those with potassium chromate and bichromate, which will be taken up in the chapter on Chromium (which see). In anticipation it may be said that the reactions are based upon the fact that lead chromate, $PbCrO_4$, like barium chromate, is insoluble in water.

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The elements of Family V, Group A, are vanadium, columbium, didymium, and tantalum. As they are closely related to the members of Group B, of the same family, they were treated of at the end of Chapter XVII in connection with the members of the phosphorus group. Among them the one that is least known is didymium. This in turn is more or less closely related to two other elements of nearly the same atomic weight which occur in Families III and IV. These are lanthanum and cerium. A few words in regard to these three rare elements will suffice for the present.

### Lanthanum, Cerium, Didymium.

These three elements occur together in several rare minerals of Norway, as cerite, gadolinite, and allanite. Cerite is a silicate of the three metals, and its composition is represented by the formula $\left.\begin{matrix}Ce_4\\La_4\\Di_4\end{matrix}\right\}(SiO_4)_3 + 3H_2O$. It is probably a mixture of three isomorphous silicates. The principal constituent is cerium silicate, $Ce_4(SiO_4)_3$. The complete separation of the constituents of the mineral is a very difficult operation.

**Lanthanum,** La (At. Wt. 138.9), forms an oxide of the formula $La_2O_3$, analogous to that of aluminium. Its chloride also is analogous to that of aluminium, and has the composition $LaCl_3$; and in all its salts it acts as a trivalent element.

**Cerium,** Ce (At. Wt. 140.25), forms two series of compounds, in one of which it is trivalent, resembling lanthanum and the other

members of the aluminium group; while in the other series it is quadrivalent, resembling silicon and the other members of the silicon group.

**Didymium**, Di, has already been referred to on p. 342 in connection with the members of Family V, Group A, which it resembles in some respects. In most of its compounds it is, however, trivalent, forming compounds, of some of which the following are the formulas:

$$DiCl_3,\ Di_2O_3,\ Di(NO_3)_3,\ Di_2(SO_4)_3,\ Di_2(CO_3)_3,\ \text{etc.}$$

**Praseodymium**, Pr, **and Neodymium**, Nd.—While the name didymium is still given above, and this substance dealt with as though it were an element, as it was at first held to be, it has been shown by Auer von Welsbach to consist of two very similar elements to which he has given the names *praseodymium* and *neodymium*. When the double nitrate of ammonium and didymium is repeatedly recrystallized it is separated into two salts, one of which is green, and the other rose-colored. When the nitrate or oxalate of one of these new elements is ignited it forms a black oxide, while the nitrate or oxalate of the other gives a pinkish oxide. The element that gives green salts is called praseodymium, and the other is called neodymium. The atomic weight of neodymium is 143.6; that of praseodymium 140.5.

## EXPERIMENTS.

### Tin and its Compounds.

Experiment 232.—Dissolve tin in hydrochloric acid and let the the product crystallize.

Experiment 233.—Pass dry chlorine over granulated tin contained in a retort connected with a receiver, using the arrangement illustrated in Fig. 61, page 349. Redistil the product. Treat some of the liquid with water, and boil.

### Lead and its Compounds.

Experiment 234.—Make specimens of lead chloride and lead iodide, and crystallize them from water.

Experiment 235.—Make lead sesquioxide by bringing together lead acetate and sodium hydroxide, and treating the solution with a solution of sodium hypochlorite.

Experiment 236.—Treat some red lead with dilute nitric acid. Filter, wash, and treat the substance left on the filter with hydrochloric acid.

## CHAPTER XXX.

### ELEMENTS OF FAMILY VI, GROUP A: CHROMIUM.—MOLYBDENUM.—TUNGSTEN.—URANIUM.

**General.**—At the end of Chapter XIV, in connection with the elements of the sulphur group, the four elements which form the subject of this chapter were briefly referred to, for the reason that in some respects they resemble sulphur. As was there stated, this resemblance "is seen mainly in the formation of acids of the formulas $H_2CrO_4$, $H_2MoO_4$, $H_2WO_4$, and $H_2UO_4$; and the oxides $CrO_3$, $MoO_3$, $WO_3$, and $UO_3$." Further, it was stated that "when the acids of chromium, molybdenum, tungsten, and uranium lose oxygen, they form compounds that have little or no acid character. The lower oxides of chromium form salts with acids, and these bear a general resemblance to the salts of aluminium, iron, and manganese. The chromates lose their oxygen quite readily when acids are present with which the chromium can enter into combination as a base-forming element." "Molybdenum and tungsten do not form salts of this character: indeed they seem to be practically devoid of the power to form bases. Uranium, on the other hand, forms some curious salts."

The member of the group, whose compounds are most commonly met with in the laboratory and in the arts, is chromium, and this will receive principal attention here.

### CHROMIUM, Cr (At. Wt. 52.1).

**General.**—This element forms three series of compounds, in which it appears to be respectively bivalent, trivalent, and sexivalent. Of these the members of the series in which it is trivalent are most stable under ordinary circumstances. Some of the principal members of the

first series, or the *chromous compounds*, are represented by the formulas

$$CrCl_2,\ Cr(OH)_2,\ CrSO_4,\ CrCO_3.$$

Of the second series, or the *chromic compounds*, some of the principal members are

$$CrCl_3,\ Cr_2O_3,\ Cr_2(SO_4)_3,\ Cr(NO_3)_3,\ KCr(SO_4)_2 + 12H_2O.$$

And, finally, the members of the third series are derived from the oxide $CrO_3$, and they are for the most part salts of the acid of the formula $H_2CrO_4$, known as *chromic acid*, or of an acid of the formula $H_2Cr_2O_7$, known as *bichromic acid*, which is closely related to chromic acid.

When exposed to the air the chromous compounds are converted into chromic compounds, and they are in general readily converted into chromic compounds by the action of oxidizing agents, as cuprous and mercurous compounds are converted into cupric and mercuric compounds. If the oxidation takes place in acid solution the limit is reached when a chromic salt is formed. If, however, the action takes place in the presence of a strong base the limit is reached in the formation of a chromate. Thus, suppose chromous oxide to be treated with an oxidizing agent in the presence of sulphuric acid, the final product will be chromic sulphate, as represented in the following equations:

$$CrO + H_2SO_4 = CrSO_4 + H_2O;$$
$$2CrSO_4 + H_2SO_4 + O = Cr_2(SO_4)_3 + H_2O.$$

On the other hand, if the oxidation takes place in the presence of caustic potash the final product is potassium chromate, as shown in the following equation:

$$CrO + 2KOH + O_2 = K_2CrO_4 + H_2O.$$

When a chromate is treated with an acid in the presence of a reducing agent, it forms a salt of the chromic series.

**Forms in which Chromium occurs in Nature.**—The principal form in which chromium occurs in nature is the mineral chromite, also known as chromic iron and chrome

iron ore. This has the composition $FeCr_2O_4$, and, as will be pointed out below, it is probably analogous to the spinels (see p. 532), being an iron salt of the acid CrO.OH, which may be called metachromous acid. This view is represented by the formula $\begin{matrix}CrO.O\\CrO.O\end{matrix}>Fe$. It occurs also in the mineral crocoisite, which is lead chromate, $PbCrO_4$. The name chromium is derived from the Greek χρῶμα, meaning color; and the element is so called because most of its compounds are colored.

When chromic oxide is heated with carbon in an electric furnace a mixture of carbides of chromium is formed. By heating this with lime in an electric furnace calcium carbide and chromium are formed. It is most conveniently obtained by igniting a compact mixture of chromic oxide and aluminium shavings by means of a Goldschmidt cartridge consisting of powdered aluminium and barium peroxide.

**Properties.**—Chromium has a bright metallic lustre and is capable of high polish. It is very hard, and difficultly fusible, its melting-point being above that of platinum. It burns brilliantly in oxygen, though it is not changed by exposure to the air at ordinary temperatures. It is dissolved by hydrochloric acid. Nitric acid does not attack it. When treated with salts of potassium which easily give up their oxygen, as the chlorate and nitrate, it is converted into potassium chromate.

**Ferro-chromium** is an alloy of chromium and iron containing 60 per cent chromium which is made from chrome iron ore in the electric furnace. It is used in making chrome steel.

**Chromic Chloride,** $CrCl_3$.—This compound is made in solution by dissolving chromic hydroxide, $Cr(OH)_3$, in hydrochloric acid. The solution has a dark-green color. When evaporated, crystals of the composition $CrCl_3 + 6H_2O$ are deposited. If these are heated in the air they undergo decomposition just as aluminium chloride does, and the product left behind is chromic oxide:

$$2CrCl_3 + 3H_2O = Cr_2O_3 + 6HCl.$$

If, however, the crystallized chloride is heated in an atmosphere of chlorine or hydrochloric acid, the water is given off, and the anhydrous chloride, which has a beautiful reddish-violet color, is formed. This dissolves in water and forms a green solution. But if the dry chloride thus obtained is sublimed, it is deposited in lustrous laminæ of the same color; and this variety is insoluble in water and acids, and is only slowly acted upon by boiling alkalies. This insoluble, crystallized variety of the chloride is obtained also by passing a current of chlorine over a heated mixture of carbon and chromic oxide. The insoluble chloride is rendered soluble by adding a little chromous chloride to it.

**Chromic Hydroxide,** $Cr(OH)_3$.—When ammonia is added to a solution of a chromic salt, a light-blue, voluminous precipitate, which has the composition $Cr(OH)_3 + 2H_2O$, is formed. When this is filtered off and dried in a vacuum the water is given off and the hydroxide is left behind. This is readily converted by heat into a compound of the formula CrO.OH, and finally into chromic oxide, $Cr_2O_3$. The green precipitates formed in solutions of chromic salts by sodium and potassium hydroxides always contain some of the alkali metal in combination.

Chromic hydroxide, like aluminium hydroxide, dissolves in the soluble hydroxides, and forms salts known as chromites, which are derived from the acid CrO.OH. Thus with potassium hydroxide the action takes place as represented in the equation

$$Cr(OH)_3 + KOH = CrO.OK + 2H_2O.$$

When a solution containing potassium or sodium chromite is boiled the salt is decomposed and chromic hydroxide precipitated, though the precipitate thus formed always contains some of the alkali metal in combination. It will be noticed that in this respect aluminium and chromium conduct themselves differently towards the alkaline hydroxides.

It has already been stated that chromite, $(CrO.O)_2Fe$,

is regarded as an iron salt of the same order as the potassium salt referred to.

**Chromic Oxide,** $Cr_2O_3$, is formed by igniting the hydroxides, and is most readily prepared by heating ammonium bichromate, or by passing ammonia over heated chromic trioxide. It can be obtained in crystals. As ordinarily obtained it is a green powder, which after ignition is almost insoluble in acids. It is, however, rendered soluble by heating it with fusing acid potassium sulphate. The oxide colors glass green, and is used in painting porcelain.

**Chromic Sulphate,** $Cr_2(SO_4)_3$, is made by dissolving the hydroxide in concentrated sulphuric acid when it is deposited in purple crystals of the composition $Cr_2(SO_4)_3 + 15H_2O$. If the solution of this salt is boiled, the solution becomes green, and crystals cannot be obtained from it. But by standing for some time the green solution becomes reddish purple again, and yields the crystallized salt. Other salts of chromium act in the same way. They exist in two varieties, one of which is violet, while the other is green. The violet salts are converted into the green salts by boiling, and the green salts are converted into the violet by standing.

**Chrome-Alums.**—Chromic sulphate, like aluminium sulphate, combines with other sulphates, such as potassium, sodium, and ammonium sulphates, and forms well-crystallized salts, which are closely analogous to ordinary alum. They all contain twelve molecules of water, as represented in the formulas below:

| | |
|---|---|
| Chrome-Alum . . . . . | $KCr(SO_4)_2 + 12H_2O$ |
| Sodium Chrome-Alum. . . . | $NaCr(SO_4)_2 + 12H_2O$ |
| Ammonium Chrome-Alum . . | $(NH_4)Cr(SO_4)_2 + 12H_2O$ |

The potassium compound which is commonly called chrome-alum is made by adding a reducing agent, such as alcohol or sulphur dioxide, to a solution of potassium bichromate containing sulphuric acid. If the solution is heated it turns green, and crystals cannot be obtained

from it. But on standing for a considerable time its color changes, and violet crystals of the alum are deposited. This change can be hastened by putting some crystals of the violet salt in the concentrated green solution. Potassium bichromate finds application in dyeing and tanning.

**Chromic Acid and the Chromates.**—It has been stated that when chromium compounds belonging to the chromous and chromic series are oxidized in the presence of bases they are converted into chromates. These salts are derived from an acid of the formula $H_2CrO_4$, which is unknown, as it breaks down spontaneously into chromium trioxide, $CrO_3$, and water, when it is set free from its salts, just as carbonic and sulphurous acids break down respectively into carbon dioxide and water, and sulphur dioxide and water. The starting-point for the preparation of the chromates and the compounds related to them is chromic iron. This is ground fine, intimately mixed with a mixture of caustic potash and lime, and then heated in shallow furnaces in contact with the air. Under these circumstances oxidation is effected by the oxygen of the air. The iron is converted into ferric oxide, and the chromium gives, with the calcium and potassium, the corresponding chromates, $CaCrO_4$ and $K_2CrO_4$. When the mass is treated with water these salts dissolve, and ferric oxide remains undissolved. By treating the solution with potassium sulphate the calcium salt is converted into the potassium salt, and thus all the chromium appears in the form of potassium chromate. The changes referred to are represented in the following equations:

$$2(CrO_2)_2Fe + 8KOH + 7O = 4K_2CrO_4 + Fe_2O_3 + 4H_2O;$$
$$2(CrO_2)_2Fe + 4CaO + 7O = 4CaCrO_4 + Fe_2O_3;$$
$$CaCrO_4 + K_2SO_4 = K_2CrO_4 + CaSO_4.$$

As potassium chromate is easily soluble in water, and therefore difficult to purify, it is converted into the bichromate, which is less soluble and crystallizes well. The

change is easily effected by adding the necessary quantity of a dilute acid. If nitric acid is used the reaction is represented by the following equation:

$$2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$$

The salt thus obtained is manufactured on the large scale and is the starting-point for the preparation of other chromium compounds.

**Potassium Chromate,** $K_2CrO_4$, formed as above described, is a light-yellow crystallized substance easily soluble in water. It is isomorphous with potassium sulphate. Acids convert it into the bichromate, as just stated.

**Potassium Bichromate,** $K_2Cr_2O_7$.—This salt forms large, triclinic, red plates. It is soluble in ten parts of water at the ordinary temperature, and is much more soluble in hot water. When heated it at first melts without undergoing decomposition; at white heat, however, it is decomposed, yielding the chromate, chromic oxide, and oxygen:

$$2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + 3O.$$

It undergoes a similar change, but much more readily, when heated with concentrated sulphuric acid. In this case, however, the chromic oxide forms chromic sulphate with the acid, and this forms chrome-alum with the potassium sulphate:

$$K_2Cr_2O_7 + 4H_2SO_4 = 2KCr(SO_4)_2 + 4H_2O + 3O.$$

All the oxygen in the chromate in excess of that required to form the alum and water is given off. This also is the character of the action towards reducing agents in general.

Concentrated hydrochloric acid is oxidized by the bichromate, and chlorine is evolved:

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 6Cl.$$

Here two atoms of chlorine are required to form potassium chloride with the potassium, and six to form chromic chloride with the chromium; and the eight hydrogen

atoms in combination with this chlorine combine with four atoms of oxygen of the bichromate, leaving three more to oxidize hydrochloric acid. Consequently one molecule of the bichromate sets free six atoms of chlorine:

$$3O + 6HCl = 3H_2O + 6Cl.$$

When the bichromate in solution is treated with potassium hydroxide, its color changes to yellow, in consequence of the formation of the chromate, the action taking place as represented in this equation:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Potassium bichromate finds extensive use in the arts and in the laboratory as an oxidizing agent. With gelatin it forms a mixture sensitive to light, which turns it dark, and makes it insoluble. This fact is made the basis of a number of photogravure or photographic reproduction processes. The bichromate is used, further, in dyeing.

**Chromium Trioxide,** $CrO_3$, crystallizes out on cooling when either the chromate or the bichromate is treated in concentrated solution with concentrated sulphuric acid. It is a beautiful, red substance, which crystallizes in needles. When dissolved in water it forms a solution from which, by neutralization, the chromates can be obtained. It is an extremely active oxidizing agent, destroying most organic substances when brought in contact with them.

**Relations between the Chromates and Bichromates.**— The fact that chromium trioxide with water gives chromic acid, which is a dibasic acid, whose salts in general resemble those of sulphuric acid, leads to the belief that the structure of chromic acid should be represented by a formula similar to that of sulphuric acid, thus:

$$O_2S(OH)_2 \qquad O_2Cr(OH)_2.$$

Just as sulphuric acid by loss of water is converted into disulphuric acid or pyrosulphuric acid, so chromic acid is converted into bichromic acid, and in all probability the

relation between the chromates and bichromates is the same as that between the sulphates and disulphates, as represented by the equations

$$\begin{matrix} SO_2{<}^{OH}_{OH} \\ SO_2{<}^{OH}_{OH} \end{matrix} = \begin{matrix} SO_2{<}^{OH}_{O} \\ SO_2{<}_{OH} \end{matrix} + H_2O;$$

$$\begin{matrix} CrO_2{<}^{OH}_{OH} \\ CrO_2{<}^{OH}_{OH} \end{matrix} = \begin{matrix} CrO_2{<}^{OH}_{O} \\ CrO_2{<}_{OH} \end{matrix} + H_2O.$$

But, as has been stated, neither chromic acid nor bichromic acid is known, as they break down into chromium trioxide and water when set free from their salts. The conversion of potassium chromate into the bichromate by treatment with an acid is represented as shown below;

$$\begin{matrix} CrO_2{<}^{OK}_{OK} \\ CrO_2{<}^{OK}_{OK} \end{matrix} + \begin{matrix} HNO_3 \\ HNO_3 \end{matrix} = \begin{matrix} CrO_2{<}^{OK}_{OH} \\ CrO_2{<}^{OH}_{OK} \end{matrix} + 2KNO_3;$$

$$\begin{matrix} CrO_2{<}^{OK}_{OH} \\ CrO_2{<}^{OH}_{OK} \end{matrix} = \begin{matrix} CrO_2{<}^{OK}_{O} \\ CrO_2{<}_{OK} \end{matrix} + H_2O.$$

**Sodium Chromate,** $Na_2CrO_4$, and **Sodium Bichromate,** $Na_2Cr_2O_2$, are made in the same way as the potassium compounds. They are both deliquescent as ordinarily made. It has, however, recently been shown that a sodium bichromate which is not deliquescent can be made; and at present it is largely manufactured instead of the somewhat more expensive potassium salt.

**Barium Chromate,** $BaCrO_4$, like the sulphate, is insoluble in water, and is precipitated when a solution of a barium salt is brought together with a soluble chromate or bichromate. It is soluble in hydrochloric acid and nitric acid, but not in acetic acid. The strontium salt is

somewhat soluble in water, and easily in hydrochloric, nitric, and acetic acids.

**Lead Chromate,** $PbCrO_4$, occurs in nature, and is formed as a beautiful, yellow precipitate when a solution of a lead salt is treated with a solution of a chromate or bichromate. It is used as a pigment under the name *chrome yellow.*

**Reactions which are of Special Value in Chemical Analysis.**—The reactions of chromic salts with the *alkaline hydroxides* have been explained. With the *soluble carbonates* they give precipitates which consist mainly of the hydroxide, though carbonic acid is to some extent in combination in them. These precipitates are soluble in a large excess of the carbonate.

The solution of chromic oxide in an alkali is green, but by oxidizing agents it is turned yellow in consequence of the formation of a chromate.

*Hydrogen sulphide* does not precipitate chromium from its salts. *Ammonium sulphide* precipitates chromium hydroxide, the reaction being the same as in the case of aluminium (which see).

*Chromates* give with barium and lead salts yellow precipitates (see Barium Chromate and Lead Chromate).

When heated with sulphuric acid, the chromates are decomposed, with evolution of oxygen. The action of hydrochloric acid upon the chromates was explained above. With borax or microcosmic salt chromium compounds form green beads, both in the oxidizing and reducing flames.

## Molybdenum, Mo (At. Wt. 96).

**General.**—Molybdenum is of interest on account of the variety of its compounds. It forms four compounds with chlorine, the formulas of which appear to be $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$. With oxygen also it forms four compounds, but, while the first three are analogous to the first three chlorine compounds just mentioned, the last differs from the last chlorine compound. In it the element is sexivalent. The formulas of the oxygen compounds are MoO, $Mo_2O_3$, $MoO_2$, and $MoO_3$.

**Occurrence and Preparation.**—Molybdenum occurs in nature prin-

cipally as molybdenite, which is the sulphide $MoS_2$, and as wulfenite, which is lead molybdate, $PbMoO_4$. It occurs also, but in smaller quantity, as molybdenum trioxide, $MoO_3$. It is obtained in free condition by heating the oxides or chlorides in a current of hydrogen.

**Molybdic Acid and the Molybdates.**—Molybdenum trioxide, $MoO_3$, combines readily with bases, forming salts which in composition are analogous to the chromates. When ammonium molybdate is treated with moderately dilute nitric acid free molybdic acid crystallizes out. This has the composition represented by the formula $H_2MoO_4 + H_2O$.

**Lead Molybdate,** $PbMoO_4$, occurs in nature, and is known as wulfenite. It can be obtained artificially by melting together sodium molybdate, lead chloride, and sodium chloride; or by treating a solution of sodium molybdate with a solution of lead nitrate. If the reagents are pure the artificially prepared salt is white, while the natural variety is always yellow or red.

**Phospho-molybdic Acid.**—Among the best known and most frequently met with compounds of molybdic acid with acids is that which it forms with phosphoric acid, known as *phospho-molybdic acid.* When a solution of ammonium molybdate in an excess of nitric acid is added in excess to a solution of phosphoric acid or a phosphate, a yellow precipitate is formed. This is *ammonium phospho-molybdate,* which, when dried, has the composition represented by the formula $12MoO_3(NH_4)_3PO_4$. This is insoluble in water and in dilute acids, and also in a nitric acid solution of ammonium molybdate. On account of the properties mentioned, this salt furnishes a valuable means of detecting phosphoric acid and of precipitating it from its solutions. When the salt is treated with *aqua regia* it is decomposed, and from the solution formed a compound of the composition $H_3PO_4.11MoO_3 + 12H_2O$ crystallizes out.

## Tungsten, W (At. Wt. 184).

**General.**—Like molybdenum, tungsten forms a large variety of compounds. With chlorine it forms four, of which the formulas are $WCl_2$, $WCl_4$, $WCl_5$, and $WCl_6$. With oxygen, however, it forms but two compounds, and these are represented by the formulas $WO_2$ and $WO_3$. The trioxide forms salts with bases which are analogous to the molybdates.

**Occurrence and Preparation.**—Tungsten occurs in nature as tungstates. The principal one is the iron salt, which always, however, contains some manganese. This is known as wolframite, and has the composition represented by the formula $FeWO_4$. Calcium tungstate, $CaWO_4$, or scheelite, and lead tungstate, $PbWO_4$, or stolzite, are also found in nature, but in smaller quantity than wolframite.

**Properties.**—Tungsten forms lustrous, steel-colored laminæ, or a black powder. It is very hard and difficultly fusible, and has the specfic gravity 19.129. It is not changed by contact with the air at ordinary temperatures. At higher temperatures it combines with oxygen and forms the trioxide, $WO_3$. Nitric acid and *aqua regia* convert it into the trioxide, It is used in the manufacture of steel, as the addition of from 8 to 9 per cent of it makes steel extremely hard.

**Tungstic Acid and the Tungstates.**—When the required quantities of tungsten trioxide and potassium carbonate are brought together in solution, or are melted together, potassium tungstate, $K_2WO_4$, is formed. If a solution of this salt is treated with a strong acid at the ordinary temperature, a white precipitate of the composition $H_2WO_4 + H_2O$ is formed. This is tungstic acid, analogous to crystallized molybdic acid. If the solutions are hot the precipitate has the composition $H_2WO_4$.

## Uranium, U (At. Wt. 238.5).

**General.**—Uranium has stronger basic properties than either molybdenum or tungsten; and it differs from chromium in the fact that the trioxide forms salts with acids. These salts are the uranyl salts which are derived from the hydroxide, $UO_2(OH)_2$ or $H_2UO_4$. The corresponding compounds of chromium, molybdenum, and tungsten are acids. Uranium also forms salts in which it acts as a quadrivalent element, as $U(SO_4)_2$. While the hydroxide, $UO_2(OH)_2$, forms salts with acids, it also forms salts with the strongest bases. These are analogous in composition to the bichromates, and have the general formula $M_2U_2O_7$. With chlorine, uranium forms the compounds $UCl_3$, $UCl_4$, and $UCl_5$; and with oxygen the following: $UO_2$, $U_3O_8$, $UO_3$, and $UO_4$.

**Occurrence and Preparation.**—Uranium occurs in nature chiefly in the form of the mineral known as pitchblende or uraninite, which consists of the oxide, $U_3O_8$, mixed with a number of other substances. When this is finely powdered and treated with concentrated nitric acid, uranyl nitrate, $UO_2(NO_3)_2$, is obtained, and, by igniting this at not too high a temperature, the trioxide, $UO_3$, is left behind. In order to isolate the metal, the oxide, $U_3O_8$, is heated with charcoal in the electric furnace.

**Properties.**—Uranium has the color of nickel and the specific gravity 18.4.

**Oxides.**—The oxide of uranium which is formed as the last product of the action of oxygen on uranium or the other oxides when these are heated in the air is that which has the composition $U_3O_8$, which is also the composition of the natural variety. When this is treated with nitric acid, however, it is converted into uranyl nitrate, $UO_2(NO_3)_2$, which is a derivative of the *trioxide*, $UO_3$; and when the nitrate is ignited, the trioxide is left behind. By reduction with hydrogen the trioxide is converted into the *dioxide*, $UO_2$; and when either the dioxide or the trioxide is heated in the air, the product obtained is the oxide $U_3O_8$.

**Uranous Salts.**—In the uranous salts, uranium acts as a quadrivalent element, replacing four atoms of hydrogen, as, for example, in the sulphate, which has the composition $U(SO_4)_2$. But few salts of this order are known.

**Uranyl Salts.**—As already explained, the uranyl salts are derivatives of the hydroxide $UO_2{<}^{OH}_{OH}$, and are formed by the action of acids, as represented in the equations below:

$$UO_2{<}^{OH}_{OH} + {}^{HO}_{HO}{>}SO_2 = UO_2{<}^{O}_{O}{>}SO_2 + 2H_2O;$$

$$UO_2{<}^{OH}_{OH} + {}^{HO.NO_2}_{HO.NO_2} = UO_2{<}^{O.NO_2}_{O.NO_2} + 2H_2O.$$

They are derived from the acids by substituting uranyl, $UO_2$, which is bivalent, for the hydrogen.—*Uranyl nitrate*, $UO_2(NO_3)_2$, is easily obtained, as above described, and crystallizes well in lemon-yellow prisms.—*Uranyl sulphate*, $UO_2(SO_4)$, is formed by treating the nitrate with sulphuric acid.

**Uranates.**—When a uranyl salt is treated with a soluble hydroxide a precipitate is formed. This is a salt of an acid, $H_2U_2O_7$, which may be called *diuranic acid*, as in composition it is analogous to bichromic and disulphuric acids.

*Sodium diuranate*, $Na_2U_2O_7$, is a fine yellow powder, which is manufactured and sold under the name *uranium yellow*, being used as a pigment for coloring glass, etc.—*Ammonium diuranate*, $(NH_4)_2U_2O_7$, is also manufactured on the large scale. When it is treated with a solution of ammonium carbonate it dissolves, and from the solution a salt of the composition $UO_2(CO_3) + 2(NH_4)_2CO_3$ crystallizes out. The solubility of ammonium diuranate in ammonium carbonate is utilized in analysis.

Many uranium salts exhibit in solution a beautiful fluorescence.

**Radium,** Rd (At. Wt. 225).—Uranium and thorium emit rays that have the power to pass through black paper and sheets of some metals, and then produce changes in a photographic plate like those produced by the direct action of light. These rays also have the power to convert the air into a partial conductor of electricity. Substances that act in this way are said to be *radioactive*. M. and Mme. Curie have discovered in pitch-blende an element, *radium*, which is more than a million times as radioactive as uranium. A small fraction of a gram of radium chloride was obtained from a ton of the residues of pitch-blende after the uranium had been extracted.

It has been shown that there is a relation between the amount of uranium in a uranium ore and the amount of radium in the ore; and it has been suggested that radium and the other radioactive elements, polonium and actinium, are formed from uranium by the decomposition of this element.

Several different kinds of rays are given off from radium, and these can be easily recognized by the peculiar effects produced by them. Some of the rays render phosphorescent substances luminous and to a lesser degree produce the same effect in glass, paper, and many common materials. They rapidly discolor glass and convert yellow phosphorus into the red variety. A minute quantity of radium bromide covered with thin mica and laid for a few minutes on the skin produces a painful burn which slowly develops and may take months to heal.

In addition to the different kinds of radiation, radium is constantly giving out heat in relatively large quantity. One gram of pure radium evolves about one hundred gram-calories of heat.

Further, when a salt of radium is heated to a high temperature it gives off something called an *emanation*. This can be condensed by passing it into a tube surrounded by liquid air. It is unstable and yields *helium* as one of its products of decomposition.

It appears probable that there are other elements of the same general character as radium. Two of these, also found in pitch-blende, have been called *polonium* and *actinium*.

## EXPERIMENTS.

### Chromic Acid and the Chromates.

Experiment 237.—Powder some chromic iron very fine. Add 3 grams to a molten mixture of 3 grams each of potassium carbonate, potassium hydroxide, and potassium nitrate, heated in a porcelain crucible. After cooling treat the mass with water. Potassium chromate is in the solution.

Experiment 238.—To the solution of potassium chromate obtained in the last experiment add nitric acid to decompose the unacted-upon potassium carbonate, and give the solution an acid reaction. The color will change from yellow to red. The red color indicates the presence of the bichromate.

Experiment 239.—Treat a solution of 10 to 20 grams potassium bichromate with potassium hydroxide until the color becomes pure yellow, and evaporate to crystallization.

Experiment 240.—Make a solution of potassium bichromate saturated at the ordinary temperature. Pour into this 1½ times its volume of ordinary concentrated sulphuric acid. After the liquid cools, and the chromium trioxide separates, filter with the aid of a filter-pump through glass wool.

Experiment 241.—To a solution of potassium bichromate add some hydrochloric acid and a little alcohol. On boiling, the alcohol is oxidized, and the solution now contains chromic chloride.

## CHAPTER XXXI.

### ELEMENTS OF FAMILY VII, GROUP A: MANGANESE (Mn, At. Wt. 55).

**General.**—At the close of Chapter XII which treats of the elements of Family VII, Group B, or the chlorine group, reference was made to manganese, and attention was called to the fact that in some respects it resembles chlorine. The resemblance is seen in the formation of an oxide, $Mn_2O_7$, and an acid, $HMnO_4$, analogous to perchloric acid. On the other hand, in most of its compounds it plays the part of a base-forming element, and in this capacity it forms two series of compounds, known as *manganous* and *manganic* compounds. In the former the element appears to be bivalent, and in the latter trivalent. The formulas of some of the principal manganous compounds are:

$MnCl_2$, $Mn(OH)_2$, $MnO$, $Mn(NO_3)_2$, $MnSO_4$, $MnCO_3$, etc.

The formulas of some of the principal manganic compounds are:

$$Mn(OH)_3,\ Mn_2O_3,\ MnO(OH),\ Mn_2(SO_4)_3,$$
$$KMn(SO_4)_2 + 12H_2O,\ \text{etc.}$$

These two series of compounds are analogous in composition to the chromous and chromic compounds, but while the chromic compounds are more stable than the chromous compounds, the manganous compounds are more stable than the manganic compounds. By contact with the air, the manganous are not as a rule converted into the manganic compounds.

Corresponding to chromic acid, there is a *manganic acid*, $H_2MnO_4$; and, further, there is the *permanganic acid* already mentioned, of the formula $HMnO_4$. An analogous

compound of chromium, perchromic acid, $HCrO_4$, is believed to be formed when hydrogen peroxide is added to an aqueous solution of chromic acid, but this is by no means certain. Manganic acid and its salts are very unstable, and are readily converted into permanganic acid and the permanganates. On the other hand, perchromic acid, if it exists at all, is spontaneously decomposed, yielding ordinary chromic acid. To sum up, then, both chromium and manganese form four classes of compounds. But, while chromium under ordinary circumstances preferably forms chromic salts and salts of chromic acid, manganese preferably forms manganous salts and salts of permanganic acid.

Manganese forms a number of oxides corresponding to the formulas MnO, $Mn_2O_3$, $Mn_3O_4$, $MnO_2$, and $Mn_2O_7$.

**Forms in which Manganese occurs in Nature.**—The principal natural compound of manganese is the black oxide or pyrolusite, $MnO_2$. Besides this, however, there are several manganese compounds found in nature, the principal ones being braunite, $Mn_2O_4$, hausmannite, $Mn_3O_4$, manganite, $Mn_2O_2(OH)$, and rhodocroisite, which is the carbonate, $MnCO_3$.

**Preparation and Properties.**—The metal is isolated from its oxides by heating them to a high temperature with charcoal in the electric furnace, but better by igniting a mixture of the oxide, $Mn_3O_4$, and aluminium according to the method of Goldschmidt. It looks like cast iron, is brittle and hard, and has the specific gravity 8. It easily becomes oxidized in the air, decomposes warm water, and dissolves readily in dilute acids. It is used as a constituent of some useful alloys, and imparts certain desirable properties to iron, as will be pointed out when that metal is taken up.

**Production.**—Over a million tons of manganese ores were mined in 1905, of which 427,000 tons were obtained in Russia; 254,000 in India; and 234,000 in Brazil.

**Manganous Chloride, $MnCl_2$.**—This chloride is obtained in solution by dissolving any one of the oxides or hydroxides or the carbonate of manganese in hydrochloric acid

with the aid of gentle heat. Its formation in the preparation of chlorine from manganese dioxide and hydrochloric acid was referred to under Chlorine (which see).

When manganic hydroxide, $Mn(OH)_3$, is treated in the cold with hydrochloric acid, a deep brown-colored solution is formed, which is believed to contain the *trichloride*, $MnCl_3$. On standing, however, this solution gives off chlorine slowly, and when heated it gives it off rapidly, and the color changes to pink when only manganous chloride is left in the solution.

Phenomena similar to those just mentioned are observed when manganese dioxide is treated with hydrochloric acid in the cold, and it is believed that the *tetrachloride*, $MnCl_4$, is contained in the solution.

While the *tetrafluoride* itself has not been isolated, a solution is obtained by treating manganese dioxide with concentrated hydrofluoric acid which with potassium fluoride gives a salt of the formula $MnF_4.2KF$ or $K_2MnF_6$.

**General Remarks concerning the Oxides.**—The series of oxides of manganese strongly suggests that of the oxides of lead. Manganese, however, forms one oxide, the heptoxide, $Mn_2O_7$, of which there is no analogue among the compounds of lead. Placing the formulas of the oxides of the two metals side by side, we have the following table:

| | | | | |
|---|---|---|---|---|
| PbO | MnO | $Pb_3O_4$ | $Mn_3O_4$ | $Mn_2O_7$. |
| $Pb_2O_3$ | $Mn_2O_3$ | $PbO_2$ | $MnO_2$ | |

Just as lead oxide when heated is converted into red lead, $Pb_3O_4$, so the other oxides of manganese are converted into the oxide, $Mn_3O_4$, when heated. This has already been seen in the preparation of oxygen by heating the dioxide. In the same way, the oxide, $Mn_2O_3$, loses enough oxygen, and the lowest oxide, MnO, takes up enough to form the same product:

$$3Mn_2O_3 = 2Mn_3O_4 + O;$$
$$3MnO + O = Mn_3O_4.$$

When treated with energetic oxidizing agents in the presence of the alkalies, all the oxides are converted into manganates. On the other hand, if a manganate is reduced in the presence of an acid the tendency to form manganous compounds shows itself, and all oxygen present in excess of that required to form the manganous salt is given off.

**Manganous Hydroxide,** $Mn(OH)_2$, is formed as a white precipitate when a soluble hydroxide is added to a solution of a manganous salt. Suspended in the alkali, or in contact with air, it absorbs oxygen, and is converted into hydroxides corresponding to the higher oxides.

**Manganous-manganic Oxide,** $Mn_3O_4$, occurs in nature as the mineral hausmannite. It is formed by igniting the other oxides in contact with the air. When heated with dilute nitric acid it acts like the corresponding oxide of lead, giving manganous nitrate, and leaving manganese dioxide:

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

It breaks down in the same way with dilute sulphuric acid.

**Manganic Oxide,** $Mn_2O_3$, occurs in nature as the mineral braunite, and it can be made from the other oxides by igniting them in oxygen. A hydroxide related to this, and having the composition MnO.OH, analogous to the compounds of aluminium and chromium of the formulas AlO.OH and CrO.OH, is found in nature, and is known as manganite. The hydroxide, $Mn(OH)_3$, is formed when manganous hydroxide, $Mn(OH)_2$, is exposed in a solution of ammonia in contact with the air, and forms a brownish-black powder.

**Manganese Dioxide,** $MnO_2$.—This important compound occurs in nature in considerable quantity, and is known as pyrolusite or the black oxide of manganese. It is obtained artificially by gently igniting manganous nitrate. A hydroxide derived from the dioxide is obtained by treating a manganous salt in alkaline solution with a soluble hypochlorite or chlorine or bromine. The chief

application of the dioxide is in the preparation of chlorine. It is also used for making oxygen and for the purpose of decolorizing glass. In the last process a small quantity is added to the molten glass. This alone would give the glass an amethyst color. Without it the glass would be green. One color counteracts the other, and the glass appears colorless.

**Weldon's Process for the Regeneration of Manganese Dioxide in the Preparation of Chlorine.**—Under the head of Chlorine (which see), Weldon's process was referred to; but as a satisfactory explanation of the working of the process could not be given without dealing with some rather complicated compounds of manganese, a fuller account was postponed until these compounds should be taken up. The object in view is to utilize the waste liquors from the chlorine factories. When manganese dioxide is treated with hydrochloric acid manganous chloride and chlorine are formed, according to the equation

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The manganous chloride was of no special value until it was shown that by a comparatively simple method it can be converted into a compound which with hydrochloric acid gives chlorine. When it is treated in solution with lime the corresponding hydroxide is precipitated:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2;$$

and when this hydroxide mixed with lime is allowed to stand exposed to the air oxidation takes place, and a compound $CaMnO_3$ or $CaMn_2O_5$ is formed:

$$Mn(OH)_2 + Ca(OH)_2 + O = CaMnO_3 + 2H_2O;$$
$$2Mn(OH)_2 + Ca(OH)_2 + 2O = CaMn_2O_5 + 3H_2O.$$

These compounds give chlorine when treated with hydrochloric acid. They may indeed be regarded as consisting of lime and manganese dioxide, $CaO.MnO_2$ and

$CaO.2MnO_2$, and the action of hydrochloric acid as taking place thus:

$$CaO.MnO_2 + 6HCl = CaCl_2 + MnCl_2 + 3H_2O + Cl_2;$$
$$CaO.2MnO_2 + 10HCl = CaCl_2 + 2MnCl_2 + 5H_2O + 2Cl_2.$$

In practice the waste liquor is mixed with calcium carbonate in order to neutralize the acid. After settling, lime enough is added to precipitate the manganese as hydroxide, and to form with this a mixture in molecular proportions. Into this mixture steam and air are passed, when the oxidation referred to takes place, and calcium manganite is formed.

**Sulphides.**—When a solution of a manganous salt is treated with ammonium sulphide, a flesh-colored precipitate, which is thought to be the hydrosulphide, is formed. When this is exposed to the air it turns dark in consequence of oxidation; and if allowed to stand in the liquid, if this is concentrated, it turns green and becomes crystalline. The product thus formed is manganous sulphide, MnS. This occurs in nature as alabandite. A disulphide, $MnS_2$, corresponding to the dioxide is also found in nature, and is known as hauerite.

**Manganous Sulphate,** $MnSO_4$, is formed by heating the oxides of manganese with concentrated sulphuric acid. If higher oxides than manganous oxide are used, oxygen is given off:

$$MnO + H_2SO_4 = MnSO_4 + H_2O;$$
$$Mn_2O_3 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O;$$
$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

It crystallizes at low temperatures with seven molecules of water, and at ordinary temperatures with five, in this respect resembling cupric sulphate (which see). The salt of the formula $MnSO_4 + 7H_2O$ forms bright-red, monoclinic prisms; while that of the formula $MnSO_4 + 5H_2O$ forms pink, triclinic crystals. Between 20° and 30° it forms monoclinic prisms with four molecules of water.

**Manganic Sulphate,** $Mn_2(SO_4)_3$, is formed when the oxide $Mn_3O_4$, or the finely divided, precipitated dioxide,

$MnO_2$, is treated with sulphuric acid at not too high a temperature. It forms a dark-green amorphous powder, which is easily decomposed by heat and by water. With the sulphates of the alkali metals it forms salts analogous to the alums, as $KMn(SO_4)_2 + 12H_2O$ and $NH_4Mn(SO_4)_2 + 12H_2O$, in which manganese takes the place of aluminium.

**Manganic Acid and the Manganates.**—When an oxide of manganese is treated with an energetic oxidizing agent in the presence of a strong base it is converted into a manganate, just as the oxides of chromium are converted into chromates, and the compounds of sulphur into sulphates. These three classes of compounds are analogous as far as the composition is concerned, as shown by the formulas

| $M_2MnO_4$ | $M_2CrO_4$ | $M_2SO_4$ |
|---|---|---|
| Manganate | Chromate | Sulphate. |

The manganates are, however, quite unstable except in alkaline solution, and when they decompose they form the permanganates.—*Potassium manganate*, $K_2MnO_4$, is formed by fusing manganese dioxide with potassium hydroxide, when, if the air is not in contact with the mass, the reaction takes place as represented in the equation

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O.$$

It is also made by fusing the dioxide with potassium hydroxide and potassium chlorate, when this reaction takes place:

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O.$$

When the mass obtained in either way is treated with water a dark-green solution of the manganate is formed, and by allowing this to evaporate at the ordinary temperature in a partial vacuum, or in an atmosphere free of oxygen, the salt is obtained in small crystals, which are almost black. When a solution of a manganate is treated with an acid, the manganic acid is at once decomposed into permanganic acid and manganese dioxide:

$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O.$$

The change of a manganate to a permanganate is effected simply by passing carbon dioxide into the solution, or by boiling or allowing the solution to stand in the air. The change by means of carbon dioxide is represented by the equation

$$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + MnO_2 + 2KMnO_4.$$

With water the change takes place thus:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

The potassium hydroxide and the manganese dioxide react upon each other to form a manganite of more or less complicated composition. While the manganates are decomposed by acids, forming permanganates, the latter are decomposed by alkalies, forming manganates. Thus when a solution of potassium permanganate is boiled with potassium hydroxide the color changes to green, owing to the formation of the manganate:

$$2KOH + 2KMnO_4 = 2K_2MnO_4 + H_2O + O.$$

This change takes place readily in the presence of substances that have the power to take up oxygen; but if such substances are present the reduction goes further, forming finally a manganite which is a derivative of the hydroxide, $MnO(OH)_2$.

**Permanganic Acid and the Permanganates.**—The simplest method of obtaining the permanganates is by decomposition of the manganates, as described in the last paragraph.

**Potassium Permanganate,** $KMnO_4$, is manufactured on the large scale by oxidizing manganese dioxide in the presence of a base. This first yields the manganate, $K_2MnO_4$. Sometimes the oxidation is effected by the oxygen of the air; sometimes by the action of an oxidizing agent, as potassium chlorate or nitrate. The fundamental reaction in each case is that represented by the equation

$$MnO_2 + 2KOH + O = K_2MnO_4 + H_2O.$$

As will be observed, it is a reaction of the same kind as that involved in the conversion of a sulphite into a sulphate. Probably the first action of the hydroxide upon the dioxide consists in the formation of the manganite, $K_2MnO_3$, and this is then oxidized to the manganate. When the solution of the manganate is treated with sulphuric acid the permanganate is formed as explained above. The salt is easily soluble in water, and is deposited from its solution in crystals, isomorphous with potassium perchlorate, which appear nearly black, with a greenish lustre. Its solution in water has a purple or reddish-purple color, according to the concentration. Very concentrated solutions appear almost black. The salt is used extensively in the laboratory and in the arts as an oxidizing agent. Its action will be readily understood from what has already been said in regard to the conduct of manganese towards acids and towards alkalies. When the permanganate undergoes decomposition in the presence of an acid the manganese forms a manganous salt, and all the oxygen present in excess of that needed for this purpose is given off. Thus the decomposition with sulphuric acid takes place as represented in the equation

$$2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + 5O.$$

Therefore, when potassium permanganate is used as an oxidizing agent in acid solution, two molecules of the salt $KMnO_4$ give five atoms of oxygen. On the other hand, when the action takes place in alkaline solution the action reaches its limit in a manganite, which, for purposes of calculation, may be regarded as having the composition $K_2MnO_3$. The first change is from the permanganate to the manganate as represented in the equation

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O,$$

and then each molecule of the manganate loses another atom of oxygen,

$$K_2MnO_4 = K_2MnO_3 + O.$$

Therefore, when the permanganate is used as an oxidizing agent in alkaline solution, two molecules of the salt yield three atoms of oxygen.

The permanganates and manganates are valuable disinfecting agents, and the sodium salts are extensively used for this purpose, under the name of *Condy's liquid.*

When a solution of barium permanganate is treated with sulphuric acid, free permanganic acid is obtained in solution. It is more readily obtained by the action of an electric current on a solution of potassium permanganate. If the negative electrode is placed in a porous cup filled with water, and this cup in a solution of potassium permanganate into which is inserted the positive electrode, the alkali accumulates in the porous cup and can be removed, and a solution of the acid remains in the outer vessel. The acid is unstable. When dry potassium permanganate is added to concentrated sulphuric acid, oily drops separate and collect upon the bottom of the vessel. These are *manganese heptoxide*, $Mn_2O_7$, which is formed thus:

$$2KMnO_4 + H_2SO_4 = K_2SO_4 + Mn_2O_7 + H_2O.$$

The compound bears to permanganic acid the relation of an anhydride:

$$2HMnO_4 = Mn_2O_7 + H_2O.$$

It is very explosive.

**Reactions which are of Special Value in Chemical Analysis.**—The conduct of manganous salts towards *soluble hydroxides* has been described. The hydroxide is soluble in ammonia and ammonium salts, but this solution turns brown when exposed to the air and the manganese is gradually precipitated as the hydroxide $Mn(OH)_3$.

*Soluble carbonates* precipitate manganous carbonate.

The conduct towards *ammonium sulphide* has been described. When *oxidizing agents* like *hypochlorites*, *chlorine* or *bromine* act upon manganous salts in solution in presence of soluble hydroxides, hydroxides correspond-

ing to the dioxide $MnO_2$, such as $Mn(OH)_4$, $MnO(OH)_2$, are precipitated. Instead of the above-mentioned oxidizing agents, *potassium permanganate* may be used.

The action of potassium permanganate and manganate as oxidizing agents when used in alkaline and in acid solutions has been described above.

Manganese is easily detected by heating the substance under examination with *nitric acid* and *lead peroxide*, when permanganic acid will be formed if manganese is present, and its formation will be shown by the purple color of the solution.

With *microcosmic salt* and *borax* manganese gives an amethyst-colored bead in the oxidizing flame, which becomes colorless in the reducing flame.

## EXPERIMENTS.

### Manganese and its Compounds.

Experiment 242.—Make and crystallize some manganous chloride by treating manganese dioxide with hydrochloric acid. Also make some manganous sulphate by heating manganese dioxide with sulphuric acid. Use these solutions for the purpose of studying the conduct of manganous salts.

Experiment 243.—In a small porcelain crucible heat together 5 grams manganese dioxide, 5 grams solid potassium hydroxide, and 2½ grams potassium chlorate. When the mass has turned green, dissolve the contents in water, and neutralize most of the free alkali in the solution. Or pass carbon dioxide through the solution without boiling.

## CHAPTER XXXII.

### ELEMENTS OF FAMILY VIII, SUB-GROUP A: IRON.—COBALT.—NICKEL.

**General.**—The three elements which form this group are in many respects very similar, and their atomic weights differ but little from one another. That of iron (55.9) is nearly the same as that of manganese (55), while cobalt and nickel have nearly the same atomic weight. There is much in iron that suggests manganese. It forms two series of compounds, the *ferrous* and *ferric* compounds, which are analogous to the *manganous* and *manganic* compounds. In the first series iron appears to be bivalent, as shown in the formulas

$$FeCl_2,\ Fe(OH)_2,\ FeO,\ FeS,\ FeSO_4,\ FeCO_3,\ \text{etc.}$$

In the second series it appears to be trivalent, as indicated in the formulas

$$FeCl_3,\ Fe(OH)_3,\ Fe_2O_3,\ Fe(NO_3)_3,\ Fe_2(SO_4)_3,\ \text{etc.}$$

Like chromium and manganese it also forms an acid known as *ferric acid*, $H_2FeO_4$, which in composition is analogous to chromic and manganic acids. The soluble salts of this acid are, however, unstable, and on decomposing yield ferric hydroxide. Oxidizing agents readily convert ferrous compounds into ferric compounds, and reducing agents reconvert the latter into the former. When exposed to the air most ferrous compounds are oxidized to ferric compounds. The ferrous compounds in which iron is bivalent are similar to the compounds of the zinc group. The ferric compounds, however, in which the iron is trivalent, are similar to the aluminium compounds; and in ferric acid it exhibits a resemblance to chromium. Cobalt and nickel resemble iron in respect to

their power to form two series of compounds corresponding to the ferrous and ferric compounds. Both elements preferably form compounds of the lower series, examples of which are represented by the formulas

$CoCl_2$, $Co(OH)_2$, $CoO$, $Co(NO_3)_2$, $CoSO_4$, etc.
$NiCl_2$, $Ni(OH)_2$, $NiO$, $Ni(NO_3)_2$, $NiSO_4$, etc.

Cobalt forms a few compounds corresponding to the ferric series; and nickel forms a hydroxide of the formula $Ni(OH)_3$. While the power of cobalt to form compounds in which it is trivalent is much weaker than that of iron, it is stronger than that of nickel, the latter being almost exclusively bivalent.

## Iron, Fe (At. Wt. 55.9).

**Introductory.**—The importance of this metal to mankind can hardly be overestimated, and for many centuries it has played a commanding part in the industries. It requires little thought to convince one that without it the earth would be quite a different place from what it now is. In the earliest periods of history metals were but little used, as but few of them are furnished ready for use by nature. Stones were therefore first used, and these were shaped into a variety of implements, many of which still exist, and furnish evidence of the Stone Age. After a time copper and tin were used in the form of an alloy or bronze, as copper is found in nature in the free condition. During this period, known as the Bronze Age, stone implements gave way to those made of bronze. Afterwards men learned to extract iron from its ores, and the Iron Age was introduced; and this has continued up to the present, as nothing has since been found that can advantageously take the place of iron.

**Forms in which Iron occurs in Nature.**—Iron occurs in small quantity native in meteorites, in the basalts of Bohemia and Greenland, and in some gabbros. The iron meteorites always contain nickel, and frequently small quantities of other elements, as manganese and carbon. Compounds of iron occur in enormous quantities, and

widely distributed in the earth. Among the more important are the following-named: hematite, $Fe_2O_3$; magnetite, $Fe_3O_4$; brown iron ore, $Fe_4O_3(OH)_6$; siderite, or the carbonate, $FeCO_3$; pyrite, $FeS_2$; pyrrhotite, $Fe_7S_8$. It is also contained in many silicates in small quantity, and in consequence of the disintegration of the constituents of rocks it is found in the soil, and in many natural waters. In the vegetable kingdom it is always found in chlorophyll, and in the animal kingdom always in the blood. The compounds which are chiefly used for the purpose of making iron, or the iron ores, are magnetite, $Fe_3O_4$; hematite, $Fe_2O_3$; brown iron ore, $Fe_4O_3(OH)_6$; and spathic iron, or siderite, $FeCO_3$.

**Metallurgy.**—The ores of iron, after they are broken up, are first roasted, in order to drive off water from the hydroxides; to decompose carbonates; to oxidize sulphides; and, as far as possible, to convert the oxides into ferric oxide, $Fe_2O_3$, which is the most easily reduced oxide of iron. After the ores are prepared in this way they are reduced by heating them with carbon and fluxes in the blast-furnaces, when the iron collects in the molten condition under the so-called slag at the bottom of the furnace.

Blast-furnaces differ somewhat in construction, but the essential parts are represented in Fig. 80. The inner walls of the furnace are made of fire-bricks, and these are surrounded by ordinary bricks or stonework. The furnaces vary in height from 25 to 80 or 90 feet. Those having a height of 90 feet seem to have the greatest efficiency. The ore with coke and limestone is carried to the top of the furnace by a hoist *AA*. It is there brought into the hopper *B*. By lowering the bell *C* the mixture of substances is emptied into a second hopper *D*. When the bell *E* is lowered the materials drop into the furnace. The use of the two bells and two hoppers makes it possible to prevent the escape of large volumes of gas when the materials are introduced into the furnace. Air heated to 600° or 800° is now blown into the furnace through tubes *F* called *tuyères*. The coke burns, the charge melts, the

ore is reduced, and gases pass to the upper part of the furnace which contain over 20 per cent of carbon monoxide by volume. These gases escape through a large pipe *J* just below the charging hoppers.

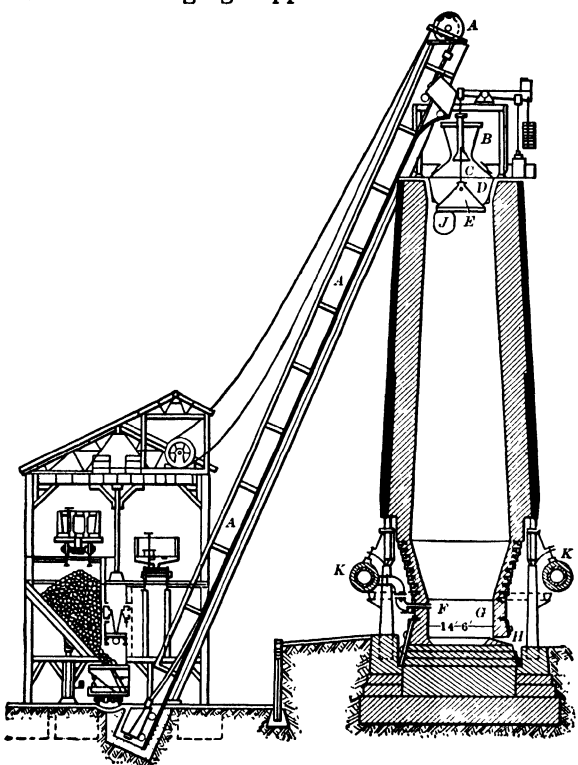



Fig. 80.

The reduction of the ores is accomplished by placing in the furnace alternating layers of coke or charcoal, and the ores mixed with proper fluxes. The nature of the flux depends upon the ore. If this contains silicon dioxide or clay, lime is added; while, if it contains considerable lime, minerals rich in silicic acid are used, such as feldspar, clay-slate, etc. The object of the flux is to form a slag in which the reduced iron collects, and by which it is pro-

tected from oxidation. When the fire is once started in a blast-furnace the operation of reduction is continuous until the furnace is burned out. Alternate layers of ore and flux and carbon are added, and, as the reduced iron collects below, it is from time to time drawn off and allowed to solidify in moulds of sand. The reduction is largely accomplished by carbon monoxide. In the lower part of the furnace the fuel burns to carbon dioxide, but this comes in contact with hot carbon, and is then reduced to the monoxide. The hot monoxide in contact with the oxides of iron reduces these to spongy metallic iron in the upper part of the furnace:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

As the temperature is too low for the spongy iron to melt, it sinks gradually to the hotter part of the furnace and absorbs carbon with which it combines forming the pig iron. This fuses at a much lower temperature than pure iron. At the same time the molten iron and coke reduce some of the silicon dioxide to silicon which also combines with the iron. A large proportion of the carbon monoxide escapes oxidation, and this is carried from the top of the furnace to the bottom by properly arranged pipes, and is then utilized as fuel to heat the air blast.

**Varieties of Iron.**—The iron obtained as above described is known as *pig iron* or *cast iron*. It is quite impure, containing carbon, phosphorus, sulphur, silicon, etc. If, when drawn from the furnace, the iron is cooled rapidly, nearly all the carbon contained in it remains in chemical combination, and the iron has a silver-white color. This product is known as *white cast iron*. If the iron cools slowly, most of the carbon separates as graphite, and this being distributed through the mass gives it a gray color. This product is known as *gray cast iron*. If the ore contains considerable manganese, this is reduced with the iron, and iron made from such ores and containing manganese has the power to take up more carbon than ordinary iron. This product, containing from 3.5 to 6 per cent combined carbon, is known as *spiegel iron*.

Pig iron usually contains 3 to 4 per cent carbon, 0.1 to 5 per cent silicon, and may contain up to 3 per cent phosphorus.

All varieties of cast iron are brittle and easily fusible. The gray iron is rich in silicon, fuses at a lower temperature than the white, and is not as brittle; it is therefore well adapted to making castings. When cast iron is treated with hydrochloric acid the carbon that is present in combined form is given off in combination with hydrogen as hydrocarbons, some of which have a disagreeable odor. This is, of course, the cause of the bad odor noticed in dissolving ordinary cast iron in acids. The uncombined or graphitic carbon, on the other hand, remains undissolved. Owing to its brittleness, cast iron cannot be welded. When the carbon, silicon, and phosphorus are removed the iron becomes tough and malleable, and its melting-point is much raised. The product thus obtained is known as *wrought iron.*

*Puddling.*—Wrought iron is obtained from cast iron by the puddling process. The puddling furnace has a flat, oval hearth and low, arched roof. The sides of the hearth are lined with a layer of iron ore (oxide). Coal is burned on a grate and the flame passes into the furnace at one end and out at the other, thus coming in contact with the roof and the charge of iron. By contact with the flame, and by the heat radiated from the roof, the cast iron melts. The carbon and silicon are removed from the molten cast iron, partly by the oxygen in the air or flame, but principally by the oxygen in the iron ore, which is itself thus reduced to wrought iron in spongy condition. The temperature of the puddling furnace is not high enough to melt the wrought iron; it is scraped into lumps which are lifted from the furnace dripping with slag, and hammered and rolled to make the iron dense and expel the slag. The crude bars are reheated, and again hammered and rolled. The product of the puddling furnace is never perfectly homogeneous. It is impossible to get rid of the last traces of slag. Hence the great improvement in the character of the product when the Bessemer and Siemens-

Martin processes were introduced. The essential feature of both of these processes is that the temperature is high enough to give a *molten* product, the difference in gravity being enough entirely to separate molten slag from molten iron. The puddling process could only treat 400–650 pounds of pig iron at one heating. It is now largely superseded by the other processes.

Wrought iron contains less than 0.6 per cent of carbon, and, as the percentage of carbon decreases, the malleability increases and the melting-point rises. The melting-point of good wrought iron is about 1600°. Small quantities of sulphur, phosphorus, silicon, and manganese exert a very marked influence upon its properties. The process of welding consists in heating two pieces of iron until they become pasty (about 600°), putting some borax upon one of them, laying them together, and hammering, when, as is well known, they adhere firmly together. The object of the borax is to keep the surfaces bright, which it does by uniting with the oxide and forming an easily fusible borate.

*Bessemer Process.*—Molten cast iron is poured into a large vessel called the converter. The charge in a converter is from 10 to 20 tons. This is converted into wrought iron in 20 minutes. The carbon and silicon are entirely oxidized and removed by means of a blast of air forced through the metal from below. No fuel is used, as the heat generated by the oxidation of carbon, sulphur, and silicon is sufficient for the purpose. The converter contains molten wrought iron after the oxidation. By addition of spiegel iron or of ferro-manganese, ferro-chrome, ferro-nickel, ferro-silicon, ferro-tungsten, or any desired alloy of iron in molten condition and of known weight, a product containing any desired percentage of carbon, and of the metals mentioned, is obtained. The molten metal is poured into moulds, each ingot thus obtained being of the size to roll while still hot into a rail or other desired object.

*Thomas-Gilchrist Process.*—Iron which contains more than a very small percentage of phosphorus is not adapted

to the manufacture of Bessemer steel in the ordinary way; but it has been found that, if the converters are lined with lime and magnesia, such iron may be used. Under these circumstances the phosphorus is oxidized, and forms calcium and magnesium phosphates, which are of value as fertilizers (see Calcium Phosphate). This process is known as the Thomas-Gilchrist or the basic-lining process.

**Open-hearth or Siemens-Martin Furnace.**—This is a furnace in which "generator gas" (see Fuel Gases) is used as fuel, the gas being previously heated by the Siemens regenerative process. This process consists in having two chambers filled throughout with loosely piled firebrick. While the hot waste furnace gases heat one of these chambers the colder generator gas is passing through the other abstracting its heat; when the first chamber is very hot the waste gases are diverted to the second chamber, and the colder gas is heated in the first, and passes thence to the furnace. The heating power of this heated gas is, of course, much greater than that of cold gas or of solid fuel. In fact, the temperature of the Siemens-Martin, furnace is so high that "wrought iron" can be obtained in it in the molten condition. Three processes are carried on in this furnace.

*a.* Into a bath of molten pig iron scrap wrought iron is thrown which dissolves. This action is continued until the percentage of carbon is reduced as far as desired. Sulphur and silicon reduce iron oxide to iron forming a slag of sulphates and silicates.

*b.* As in the puddling process, carbon is removed from the molten cast iron by iron oxide ore with which the furnace may be lined.

*c.* Processes *a* and *b* are combined. The quality of the open-hearth product is better than that of the Bessemer product. In the Bessemer process there is a loss of iron amounting to 10–15 per cent of the pig iron used. There is no loss in the open hearth process. The charge is from 5 to 20 tons. It requires much more time than the Bessemer process. The Thomas-Gilchrist basic linings are

also used in the Siemens-Martin furnace, and the process is then called the "basic open-hearth process." As the product is primarily molten wrought iron, additions of molten spiegel iron, ferro-chrome, etc., may be made, as described for the Bessemer process.

*Steel and Wrought Iron.*—These terms are confusing. The product of the puddling furnace is called wrought iron; while those formed in the Bessemer process and in the Siemens-Martin furnace are technically called *steel* irrespective of composition. Bessemer steel often contains less than 0.6 per cent of carbon, and Siemens-Martin steel may be the purest form of wrought iron, containing less carbon and silicon than the product of the puddling furnace.

*Tempering.*—When steel is heated and cooled suddenly, it is rendered extremely hard and brittle; and when hardened steel is carefully heated, and allowed to cool slowly, it becomes very elastic. This process is called tempering.

The studies of Osmond on the nature of iron and steel explain many phenomena hitherto not understood. Osmond has shown by chemical and microscopic work that iron exists in three allotropic forms. $\alpha$-Iron is stable below 765°; it is soft, ductile, magnetic, and does not hold iron carbide in solid solution. This is "wrought iron." $\beta$-Iron is stable above 765°; it is non-magnetic, and cannot hold iron carbide in solid solution. $\gamma$-Iron is stable above 890°; it is non-magnetic; iron carbide dissolves in it.

If a solution of carbon in molten iron containing the proportion of carbon suitable for steel, in other words molten steel, is suddenly chilled, the cold mass (which is a solid solution of iron carbide—$Fe_3C$, cementite—in $\gamma$-iron) is hard steel. If the molten steel is cooled slowly a product results which is a mechanical mixture of $\alpha$-iron, cementite, and sometimes graphite. The large excess of $\alpha$-iron makes the product soft. This is soft steel. If the soft steel is heated to temperatures above 890° and suddenly chilled it is changed to hard steel. Moderate

reheating and cooling (tempering) gives products of varying hardness, as desired.

Osmond also explains the effect of slow and rapid cooling of cast iron. Supposing 5 to 6 per cent of carbon to be present, slow cooling would cause graphite to separate, and gray cast iron to form. Rapid cooling yields a product which is mainly cementite and is the white cast iron.

These facts also help to explain the process of "annealing" and the process of making cement steel. The object of the "annealing" process is to render small castings less brittle. If the casting is small, the iron cools suddenly; hence the casting is white and brittle; it is chiefly cementite. The annealing process consists in packing the castings in iron oxide and heating them for 48 hours. Two reactions take place—a chemical reaction, the removal of the carbon from the surface of the casting by the action of the iron oxide, and a physical reaction, the change of the brittle, white cast iron to the less brittle, gray cast iron by the slow cooling. The castings become gray with soft surface. "Cement steel" is made by heating bars of wrought iron packed in powdered charcoal. Carbon combines with the wrought iron to form steel, and the slow cooling yields a soft steel.

**Properties of Iron.**—Pure iron is almost unknown. Of the commercial varieties, it follows from what has been said that wrought iron is the purest. That which is used for piano-strings is the purest iron obtainable in the market; it contains only about 0.3 per cent of impurities. Pure iron can be made in the laboratory by igniting the oxide or oxalate in a current of hydrogen, and by reducing ferrous chloride in hydrogen. In larger quantity it can be prepared by melting the purest wrought iron in a lime crucible by means of the oxyhydrogen flame. The impurities are taken up by the crucible, and a regulus of the pure metal is left behind. That made by reduction of the oxide or oxalate is, of course, in finely divided condition. If in its preparation the temperature is kept as low as possible, the product takes fire when brought in contact with the air; while if the temperature is high,

the product has not this power. Iron is white, and is one of the hardest metals. Its melting-point is higher than that of wrought iron. Pure iron is attracted by the magnet. In contact with a magnet, or when placed in a coil through which an electric current is passing, it becomes a magnet; but the purer it is the sooner it loses the magnetic power when removed from the magnet or the coil. Steel, however, retains its magnetism. When heated to a sufficiently high temperature iron burns, and forms the oxide, $Fe_3O_4$. This takes place much more easily in oxygen than in the air. In dry air iron does not undergo change, but in moist air it *rusts*, or it becomes covered with a layer of oxide and hydroxide, which is formed by the action of the air, carbon dioxide, and water. Water that contains salts in solution facilitates the rusting. Various methods are adopted to protect iron from this change, most of which are, however, purely mechanical. A method which promises valuable results is that invented by Barff. This consists in introducing the iron into water vapor at a temperature of 650°, when it becomes covered with a firmly adhering layer of oxide.

Iron dissolves in acids with evolution of hydrogen, and generally with formation of ferrous salts:

$$Fe + 2HCl = FeCl_2 + H_2;$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

When cold nitric acid is used, ferrous nitrate and ammonium nitrate are the products; if the acid is warmed, ferric nitrate and oxides of nitrogen are formed. When an iron wire that has been carefully polished is introduced for an instant into red fuming nitric acid it can afterward be put into ordinary nitric acid without undergoing change. It is said to be in the *passive state*; and the commonly accepted explanation of the phenomenon is that the wire is covered with a thin layer of oxide. As, however, the passive condition is lost by contact with an ordinary wire, the explanation does not appear to be adequate.

**Ferrous Chloride,** $FeCl_2$.—This is a colorless mass, which deliquesces in the air, is volatile at a high temperature, and determinations of the specific gravity of its vapor made at very high temperatures have shown that its molecule under these conditions should be represented by the formula $FeCl_2$. At lower temperatures the molecule appears to be more complex.

A solution of ferrous chloride made by dissolving iron in hydrochloric acid is used in medicine under the name *Liquor Ferri chlorati.* It contains 10 per cent iron.

**Ferric Chloride,** $FeCl_3$.—Ferrous chloride is readily converted into ferric chloride by oxidation. The simplest way to make a solution of the ferric compound is to dissolve iron in hydrochloric acid and pass chlorine into it to complete saturation. Anhydrous ferric chloride is obtained by heating iron wire in dry chlorine. It forms black, lustrous, crystalline laminæ; is volatile at a lower temperature than the ferrous compound; and the specific gravity of the vapor is that required by a compound whose molecule is represented by the formula $FeCl_3$. When treated with nascent hydrogen, ferric chloride is converted into ferrous chloride:

$$FeCl_3 + H = FeCl_2 + HCl.$$

A solution of ferric chloride is used in medicine under the name *Liquor Ferri sesquichlorati.*

**Cyanides.**—The compounds which iron forms with cyanogen are of special interest. The simple compounds, ferrous cyanide, $Fe(CN)_2$, and ferric cyanide, $Fe(CN)_3$, corresponding to the above-mentioned chlorides, are not known, but double compounds of these with other cyanides are well known, and some of them are manufactured on the large scale. When a solution of potassium cyanide acts upon metallic iron or the oxides of iron, a solution is formed from which the salt known as *potassium ferrocyanide* or *yellow prussiate of potash* crystallizes. This has the composition $K_4Fe(CN)_6 + 3H_2O$, and may be regarded as made up of a molecule of ferrous cyanide and four molecules of potassium cyanide, as represented

in the formula $Fe(CN)_2.4KCN + 3H_2O$. When this salt is treated with chlorine it is converted into *potassium ferricyanide* or *red prussiate of potash*, $K_3Fe(CN)_6$, which is to be regarded as consisting of ferric cyanide and potassium cyanide, as shown in the formula $Fe(CN)_3.3KCN$. The transformation is represented thus:

$$K_4Fe(CN)_6 + Cl = K_3Fe(CN)_6 + KCl.$$

From these two a number of other cyanogen compounds are obtained. When treated in concentrated solution with concentrated hydrochloric acid they yield the free acids, and by treating them with solutions of different metallic salts corresponding salts of these acids are obtained. Among the most important of these derivatives are the following:

| | |
|---|---|
| Ferrohydrocyanic acid, $H_4Fe(CN)_6$ | Ferrihydrocyanic acid, $H_3Fe(CN)_6$ |
| Potassium ferrocyanide, $K_4Fe(CN)_6$ | Potassium ferricyanide, $K_3Fe(CN)_6$ |
| Sodium ferrocyanide, $Na_4Fe(CN)_6$ | Sodium ferricyanide, $Na_3Fe(CN)_6$ |
| Barium ferrocyanide, $Ba_2Fe(CN)_6$ | |
| Ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$ | Ferrous ferricyanide, $Fe_3[Fe(CN)_6]_2$ |
| Ferri-potassium ferrocyanide, $KFeFe(CN)_6$ | |

**Potassium Ferrocyanide,** $K_4Fe(CN)_6 + 3H_2O$.—As stated above, this salt can be made by treating iron or the oxides of iron with a solution of potassium cyanide. On the large scale it is manufactured by melting crude potash or potassium carbonate, and gradually adding a mixture of iron filings or turnings, and refuse animal matter, as claws, horns, hoofs, hair, etc. Or the potash is melted with the animal substances and potassium cyanide thus formed, and this treated in solution with ferrous carbonate, when the ferrocyanide is formed. It forms large, yellow pyramids belonging to the tetragonal system. At the ordinary temperature it dissolves in three to four parts of water, and more easily in hot water. It gives up its water of crystallization very easily. When

heated it is decomposed, forming potassium cyanide, nitrogen, and a compound of iron and carbon:

$$K_4Fe(CN)_6 = 4KCN + N_2 + FeC_2.$$

**Ferrohydrocyanic Acid,** $H_4Fe(CN)_6$, formed as above described, is a white crystalline substance, easily soluble in water and alcohol. The ferric salt is the substance commonly called *insoluble Prussian blue.* The relation of the salt to the acid is shown by the formulas

| $H_4Fe(CN)_6$ | $Fe_4[Fe(CN)_6]_3$ |
|---|---|
| Ferrohydrocyanic acid | Ferric ferrocyanide, or Prussian blue |

**Ferric Ferrocyanide, or Prussian Blue,** $Fe_4[Fe(CN)_6]_3$. —This compound is readily formed by adding a solution of a ferric salt to a solution of potassium ferrocyanide, and appears as a dark-blue precipitate:

$$3K_4Fe(CN)_6 + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12KCl.$$

**Potassium Ferricyanide,** $K_3Fe(CN)_6$.—This is formed by treating the ferrocyanide, either dry or in solution, with chlorine. It forms large, dark-red, monoclinic prisms. It dissolves in about three times its weight of water at the ordinary temperature, and is more easily soluble in hot water.

**Ferrihydrocyanic Acid,** $H_3Fe(CN)_6$, is a crystallized substance.

**Ferrous Ferricyanide,** $Fe_3[Fe(CN)_6]_2$, is commonly called Turnbull's blue. It is formed by adding potassium ferricyanide to a solution of ferrous sulphate, or any ferrous salt:

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4.$$

**Ferrous Hydroxide,** $Fe(OH)_2$, is formed when a soluble hydroxide is added to a solution of a ferrous salt. It is a white precipitate, but it is usually obtained as a greenish mass, as it is very easily oxidized by the oxygen of the air and that contained in the solutions. When allowed to stand in contact with the air it turns dirty green, and finally brown, being converted into ferric hydroxide.

When heated in the air it loses water, and takes up oxygen, forming ferric oxide.

**Ferric Hydroxide,** $Fe(OH)_3$.—This compound is formed most readily by adding ammonia to a solution of a ferric salt, when it appears as a voluminous, brownish-red precipitate. When filtered, washed, and dried, its composition is not changed. If heated to 100°, or if the solution is boiled for some time, it loses water, and forms compounds of the formulas FeO.OH, $Fe_2O(OH)_4$, etc. The latter is derived from the normal hydroxide as represented in the equation

$$2Fe(OH)_3 = Fe_2O(OH)_4 + H_2O.$$

The mineral pyrosiderite is the hydroxide FeO.OH. Brown iron ore is $Fe_4O_3(OH)_2$; and bog iron ore is $Fe_2O(OH)_4$. All these are derivatives of the normal hydroxide. The normal hydroxide differs from aluminium hydroxide in the fact that it has no acid properties. Therefore, if the two hydroxides are heated together with a caustic alkali only the aluminium hydroxide dissolves. The compound FeO.OH, corresponding to AlO.OH and CrO.OH, yields salts under some circumstances. Thus a calcium salt, $\begin{matrix}FeO.O\\FeO.O\end{matrix}\!>\!Ca$, is formed by heating together ferric oxide and lime to a high temperature. In composition this is plainly analogous to the spinels. Magnetic oxide of iron or magnetite is believed to be the corresponding ferrous salt, $\begin{matrix}FeO.O\\FeO.O\end{matrix}\!>\!Fe$. Franklinite also is a salt of the same order, containing zinc. It is essentially a zinc salt, of the formula $\begin{matrix}FeO.O\\FeO.O\end{matrix}\!>\!Zn$, but some of the zinc is replaced by iron and manganese.

**Ferrous-ferric Oxide,** $Fe_3O_4$.—As stated above, this compound is believed to be analogous to the spinels, and is represented as the ferrous salt of the hydroxide FeO.OH, as shown in the formula $(FeO.O)_2Fe$. It is found in nature as the mineral magnetite, and loadstone, that occurs in Sweden, Norway, and elsewhere. It is, further, formed

when iron is burned in oxygen, and when water is passed over red-hot iron. Some of the magnetite that occurs in nature has the power to attract iron, or is magnetic.

**Soluble** or **Colloidal Ferric Hydroxide** is formed when a solution of ferric chloride or ferric acetate is treated with ferric hydroxide, and the solution thus formed dialyzed (see p. 404). The ferric salts pass through the membrane, and the ferric hydroxide remains in solution in water, forming a deep-red liquid. It is used in medicine. Small quantities of salts cause the precipitation of ferric hydroxide from the solution.

**Ferric Oxide,** $Fe_2O_3$, is found in nature, and is known as hematite or specular iron ore, forming one of the most valuable ores of iron. It can be made in the laboratory by igniting the hydroxide. As hematite, it is a black, crystallized substance with a high lustre. Otherwise it has a red or a reddish-brown color. The oxide found in nature and that which has been strongly ignited are very difficultly soluble in acids. When ferrous sulphate is heated to a high temperature there is left a residue of ferric oxide known as *rouge*, which is used as a red pigment and as a polishing powder. A specially fine variety of rouge for polishing is manufactured by heating ferrous oxalate, $FeC_2O_4$, in contact with the air.

**Ferrous Sulphide,** FeS, is formed by direct union of iron and sulphur when the two are heated together. It is manufactured by heating iron filings and sulphur together in a crucible. The pure compound is yellow and crystalline. When heated in contact with the air it is oxidized to ferrous sulphate, if the temperature is not too high. At a higher temperature the products are sulphur dioxide and ferric oxide. When a solution of a ferrous salt is treated with ammonium sulphide, ferrous sulphide is precipitated as a black powder. When a ferric salt is treated with ammonium sulphide it is reduced to the ferrous condition, and then ferrous sulphide is precipitated:

$$Fe_2(SO_4)_3 + (NH_4)_2S = 2FeSO_4 + (NH_4)_2SO_4 + S;$$
$$2FeSO_4 + 2(NH_4)_2S = 2FeS + 2(NH_4)_2SO_4.$$

The sulphide thus obtained is readily oxidized in the air, and forms the sulphate. The compact variety is used in making hydrogen sulphide (which see).

**Ferrous Carbonate,** $FeCO_3$.—This salt occurs in nature as spathic iron or siderite. It crystallizes in forms similar to those of calc spar or calcium carbonate, $CaCO_3$. Like this, further, it dissolves in water which contains carbon dioxide, and is therefore contained in natural waters which come in contact with it. When a solution of a ferrous salt is treated with a soluble carbonate a white precipitate is formed, which is ferrous carbonate; but in contact with the air this is rapidly oxidized and decomposed, leaving ferric hydroxide, which with carbonic acid does not form a salt. In this respect ferric hydroxide acts like aluminic and chromic hydroxides, and therefore when a soluble carbonate is added to a solution of a ferric salt the hydroxide and not ferric carbonate is thrown down.

**Ferrous Sulphate,** $FeSO_4$.—This important compound is manufactured on the large scale by the spontaneous oxidation of pyrite in contact with the air, and by dissolving iron in sulphuric acid. It is frequently called "green vitriol" (see p. 550), and more commonly "copperas." Under ordinary conditions it crystallizes in transparent, green, monoclinic crystals with 7 molecules of water, just as zinc sulphate, magnesium sulphate, etc., do; and when heated, 6 of these are given off readily, while the last is given off with difficulty—a fact which makes it appear probable that the salt is a derivative of tetrahydroxyl-sulphuric acid, as represented in the formula

$$OS\begin{cases}(OH)_2\\O\\O>Fe\end{cases}.$$ While it ordinarily crystallizes in monoclinic crystals, it takes the rhombic form if its supersaturated solution is touched with a crystal of zinc sulphate. It also crystallizes in the triclinic system with 5 molecules of water, like cupric sulphate, if a crystal of the latter salt is placed in its concentrated solution.

**Ferric Sulphate,** $Fe_2(SO_4)_3$.—This salt is formed by oxidation of ferrous sulphate. It is also formed by dissolving ferric oxide or hydroxide in sulphuric acid.

*Ferrous Phosphate,* $Fe_3(PO_4)_2$, occurs in nature crystallized with 8 molecules of water as the mineral vivianite. Both this salt and ferric phosphate, $FePO_4$, are insoluble and are formed when solutions of ferrous and ferric salts are treated with sodium phosphate.

**Iron Disulphide,** $FeS_2$, is not analogous to any oxygen compound of iron. In it the metal appears to be quadrivalent. The disulphide occurs very widely distributed and in large quantities in nature as the mineral iron pyrites or pyrite, which crystallizes in the regular system, and as marcasite, which crystallizes in the rhombic system. It can be made artificially, and if crystallized it appears in the form of pyrite. Its conduct under the influence of heat has been repeatedly referred to in connection with the roasting of iron and other ores. As pyrite it has a golden yellow color, and it has frequently been taken for gold by those not familiar with it. The name "fool's gold," by which it is sometimes popularly known, is a reminder of this fact.

*Arsenopyrite,* FeAsS, also called arsenical pyrites, occurs in nature, and is a valuable source of the element arsenic; for when it is heated it gives off arsenic, and ferrous sulphide is left behind (see p. 328).

**Reactions which are of Special Value in Chemical Analysis.**—*Ferrous Compounds.*—The reactions of ferrous compounds with the *soluble hydroxides* and *carbonates*, *ammonium sulphide*, *potassium ferricyanide* and with *oxidizing agents* have been explained above. With ammonium salts ferrous chloride forms double salts, which are soluble; therefore, if ammonium chloride is added to a solution of the salt ammonia does not precipitate the hydroxide. Further, ammonia does not completely precipitate the hydroxide from a solution of a ferrous salt, as an ammonium salt is formed. By standing in the air, however, these solutions containing the double salts are oxidized and ferric hydroxide is precipitated. The reac-

tions with potassium cyanide will be understood from what has been said concerning the compounds of ferrohydrocyanic and ferrihydrocyanic acids.

*Ferric Compounds.*—The reactions of ferric compounds with the *soluble hydroxides* and *carbonates*, *ammonium sulphide*, *potassium ferrocyanide*, and *potassium ferricyanide* have been explained above. When *hydrogen sulphide* is passed through a solution of a ferric salt, reduction to the corresponding ferrous salt takes place, and sulphur separates, which gives the solution a milky appearance:

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S;$$
$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

When a neutral solution of a ferric salt is treated with *suspended barium carbonate* the iron is precipitated as the hydroxide.

When a neutral solution of a ferric salt is treated with *potassium* or *sodium acetate* it turns dark red, in consequence of the formation of ferric acetate which remains in solution. When the solution is boiled the acetate breaks down into acetic acid and a basic acetate of iron, which is precipitated. When the basic acetate is filtered off, washed, and heated it is changed to ferric hydroxide:

$$FeCl_3 + 2NaC_2H_3O_2 + H_2O = (HO)Fe(C_2H_3O_2)_2 + 2NaCl + HCl;$$
$$(HO)Fe(C_2H_3O_2)_2 + 2H_2O = Fe(OH)_3 + 2C_2H_4O_2.$$

When *potassium sulphocyanate*, KCNS, is added to a solution of a ferric salt a blood-red color is produced. This occurs even in extremely dilute solutions of ferric salts.

The borax bead is colored bottle-green in the reducing flame, and brown-red to yellowish red in the oxidizing flame, when treated with compounds of iron.

## Cobalt, Co (At. Wt. 59).

**General.**—As stated in the remarks introductory to the iron group, cobalt, like nickel, preferably forms compounds which are analogous to ferrous compounds. It

however, forms a few which are analogous to ferric compounds, its power in this direction being greater than that of nickel. Its salts form a great variety of compounds with ammonia, and these have been extensively studied.

**Occurrence and Preparation.**—Cobalt occurs in nature, almost always in company with nickel. The principal minerals containing it are smaltite, $CoAs_2$, and cobaltite, $CoS_2.CoAs_2$. In each of these iron, and generally some nickel, take the place of a part of the cobalt.

**Properties.**—Cobalt has a silver-white color, with a slight cast of red. It is harder than iron, and melts at a somewhat lower temperature; is tenacious; and has the specific gravity 8 8. It melts at about 1520°. It dissolves in nitric acid.

**Cobaltous Chloride,** $CoCl_2$, is formed by heating cobalt in chlorine gas, and in solution by treating cobalt carbonate with hydrochloric acid. From the solution it crystallizes in dark-red prisms of the composition $CoCl_2+6H_2O$. The anhydrous salt is blue. When the blue salt is treated with water it turns red, and when the red salt is heated it turns blue. This difference in color between the anhydrous and the hydrated salts is characteristic of cobalt salts. If marks are made on paper with a dilute solution of one of the salts the color is not perceptible. If, however, the paper is held before a fire, the salt loses water and turns blue, and as the blue is more intense than the red, it is visible. When the salt becomes moist again it becomes invisible. This is the basis of the preparation of the so-called *sympathetic inks*.

**Cobaltous Hydroxide,** $Co(OH)_2$, is formed as a red precipitate when a soluble hydroxide is added to a cobaltous salt, and the blue precipitate, which is first formed and is a basic salt, is allowed to stand. It is oxidized by contact with the air, forming cobaltic hydroxide, which breaks down into *cobaltic oxide*, $Co_2O_3$.

**Cobaltic Hydroxide,** $Co(OH)_3$, is formed when calcium hypochlorite is added to a solution of a cobaltous salt. It is a black powder. When heated it is converted into black *cobaltic oxide*, $Co_2O_3$.

**Cobalt Sulphide,** CoS, is the black precipitate formed by adding ammonium sulphide to a cobaltous salt. It is not soluble in dilute acids, and differs from ferrous sulphide in this respect. Other sulphides of cobalt are those of the formulas $Co_9S_4$ and $CoS_2$. The former is found in nature, and is known as linnæite. The latter occurs in combination with other sulphides, and with arsenides; as in cobaltite, $CoS_2.CoAs_2$.

**Cyanides.**—Cobaltous cyanide is an insoluble dirty-red compound formed when potassium cyanide is added to a solution of a cobalt salt. It dissolves in an excess of potassium cyanide, forming a double cyanide. $K_4Co(CN)_6$, which is analogous to potassium ferrocyanide. When this solution is boiled the cyanide is oxidized, forming a compound analogous to potassium ferricyanide, thus:

$$2K_4Co(CN)_6 + H_2O + O = 2K_3Co(CN)_6 + 2KOH.$$

This acts like the corresponding iron compound. The cobalt is not precipitated from it by ammonium sulphide or sodium hydroxide. This conduct towards potassium cyanide distinguishes cobalt from nickel salts.

*Smalt.*—The beautiful pigment known by this name is essentially a cobalt glass in which cobalt takes the place of calcium. It is made by heating compounds of cobalt with quartz and potassium carbonate. The glass thus formed is powdered very finely and used as a pigment. It does not change color in the sunlight, and is not affected by acids nor by alkalies.

## Nickel, Ni (At. Wt. 58.7).

**General.**—Nickel differs from cobalt in respect to the difficulty with which it forms nickelic compounds or those in which it is trivalent. Nevertheless it does form an oxide of the composition $Ni_2O_3$, and the corresponding hydroxide, $Ni(OH)_3$. In all other compounds it is bivalent, the compounds being analogous to ferrous compounds.

**Occurrence and Preparation.**—Nickel occurs native in

meteorites. The principal minerals containing it are the arsenide, NiAs, known as niccolite, and the sulpharsenide, NiSAs or $NiS_2.NiAs_2$, known as gersdorffite.

**Properties.**—Nickel is a white metal with a slight cast of yellow. It is very hard, and capable of a high polish. The metal in its ordinary condition is brittle, but after treatment with a little magnesium it becomes very malleable. Its specific gravity is 8.8. and it melts at 1484°. It is not changed in the air; it dissolves slowly in hydrochloric and sulphuric acids, and readily in nitric acid. Like iron, it is magnetic.

**Alloys.**—Alloys of nickel are extensively used. *Argentan* or *German silver* consists of copper, zinc, and nickel. Various nickel alloys are used for making coins. The 5-cent pieces in the United States are made of an alloy consisting of 25 per cent nickel and 75 per cent copper. In Switzerland, and Belgium also, nickel coins are used.

**Other Applications of Nickel.**—Besides as a constituent of important alloys, nickel is extensively used at present in nickel plating. Iron objects are covered with a thin layer of the metal for the purpose of protecting them from rusting. Much nickel is used in making nickel steel. The plating is carried out in the same way as silver plating and copper plating are—by means of electrolysis—a bath of nickel-ammonium sulphate being used.

**Nickelous Hydroxide,** $Ni(OH)_2$, is formed when a nickel salt is treated with a soluble hydroxide, and is a green insoluble substance. When heated it is converted into the green *oxide*, NiO.

**Nickelic Hydroxide,** $Ni(OH)_3$, is precipitated as a black powder when a solution of a nickel salt is treated with sodium hypochlorite.

**Cyanides.**—When potassium cyanide is added to a solution of a nickel salt, nickel cyanide, $Ni(CN)_2$, is precipitated as a greenish-white substance. With an excess of potassium cyanide this forms the salt, $Ni(CN)_2.2KCN$, which, owing to the fact that nickelous salts are not converted into nickelic salts by oxidation, does not undergo change when boiled with potassium cyanide. When

hydrochloric acid is added to a solution of the double cyanide, nickelous cyanide is precipitated. If boiled with precipitated mercuric oxide the double cyanide is decomposed and nickel oxide is thrown down.

**Nickel Carbonyl,** $Ni(CO)_4$.—This interesting compound is formed when finely divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400°, is allowed to cool in a slow current of carbon monoxide. A gas is formed which can easily be condensed, its boiling-point being 43°. At −25° it solidifies, forming needle-shaped crystals. When the gas is passed through a heated tube pure nickel is deposited. Advantage of this fact is taken for the purpose of preparing pure nickel on the large scale. Cobalt does not form a compound of this kind.

**Reactions of Cobalt and Nickel which are of Special Value in Chemical Analysis.**—The reactions with the *soluble hydroxides* have been explained. With *ammonium sulphide* both give black sulphides, which are not easily dissolved by dilute hydrochloric acid. From solutions of the acetates *hydrogen sulphide* precipitates the sulphides Nickel sulphide is slightly soluble in ammonium sulphide, and the solution has a brownish-yellow color.

The action of the hypochlorites upon solutions of nickel and cobalt salts has been explained above. The reactions with potassium cyanide have also been explained. These furnish a good method for separating the two metals.

When a solution of *potassium nitrite* is added to a solution of a cobalt salt containing free acetic acid or nitric acid, a precipitate of cobaltic potassium nitrite is formed. This is a compound of cobaltic nitrite, $Co(NO_2)_3$, and potassium nitrite, of the composition $Co(NO_2)_3.3KNO_2$. The formation involves oxidation of the cobaltous salt, and this is effected by some of the nitrogen trioxide which is set free. Thus with the chloride the action may be represented as follows:

$$CoCl_2 + 7KNO_2 + 2C_2H_4O_2 =$$
$$2KCl + Co(NO_2)_3.3KNO_2 + 2KC_2H_3O_2 + H_2O + NO.$$

Nickel does not form a similar compound of a nickelic salt, but does form a double nitrite, containing the nickelous salt $Ni(NO_2)_2.4KNO_2$.

Cobalt compounds color the bead of microcosmic salt blue both in the reducing and oxidizing flame. Nickel colors it reddish brown in the oxidizing flame when hot, and pale yellow when cold. In the reducing flame it is gray.

## EXPERIMENTS.

### Iron and its Compounds.

Experiment 244.—Make ferric chloride by heating the purest iron wire in a current of chlorine. Also make a solution by dissolving iron in hydrochloric acid, and oxidizing the solution with nitric acid. For this purpose heat to boiling some of the solution in hydrochloric acid and then add a few drops of concentrated nitric acid. Repeat this two or three times Test for ferric chloride by means of sodium hydroxide

Experiment 245.—Make ferrous sulphate by dissolving iron in dilute sulphuric acid, and evaporating to crystallization. Dissolve equivalent quantities of ferrous sulphate and ammonium sulphate, and evaporate to crystallization.

Experiment 246.—Dissolve ferric hydroxide in sulphuric acid, and evaporate to dryness.

## CHAPTER XXXIII.

### ELEMENTS OF FAMILY VIII, SUB-GROUP B: RUTHENIUM.—RHODIUM.—PALLADIUM.

### ELEMENTS OF FAMILY VIII, SUB-GROUP C: OSMIUM.—IRIDIUM.—PLATINUM.

**General.**—Comparing the members of the three sub-groups of Family VIII with reference to their atomic weights and specific gravities, we have the following remarkable table:

| Fe | Co | Ni |
|---|---|---|
| At. Wt. 55.9 | At. Wt. 59 | At. Wt. 58.7 |
| Sp. Gr. 7.8 | Sp. Gr. 8.5 | Sp. Gr. 8.8 |
| **Ru** | **Rh** | **Pd** |
| At. Wt. 101.7 | At. Wt. 103 | At. Wt. 106.5 |
| Sp. Gr. 12.26 | Sp. Gr. 12.1 | Sp. Gr. 11.5 |
| **Os** | **Ir** | **Pt** |
| At. Wt. 191 | At. Wt. 193 | At. Wt. 194.8 |
| Sp. Gr. 22.48 | Sp. Gr. 22.42 | Sp. Gr. 21.50 |

It will be observed that the atomic weights and specific gravities of the members of each sub-group are approximately the same. But just as there is a gradual change in the chemical conduct from iron to nickel in the iron group, so a similar gradation of properties is observed in the other two groups. As far as the variety of compounds which they form is concerned, ruthenium and osmium are more like iron than they are like rhodium and iridium. Further, rhodium and iridium resemble each other as regards the variety of their compounds more closely than they resemble palladium and platinum, and a similar resemblance is noticed between palladium and platinum. A full discussion of these relationships would lead too far.

## The Platinum Metals.

The six elements of Sub-Groups B and C, Family VIII, are generally grouped together and spoken of as the platinum metals. They occur together in nature, and almost always in alloys, into the composition of which all enter. The chief constituent is platinum, which is present to the extent of 50 to 80 per cent, and over. The alloys occur in only a few localities, in the Ural Mountains, in California, Colombia, Borneo, and a few other places, and form small pieces which are mixed with sand and earth. They generally contain also gold, iron, and copper. Palladium occurs, further, in a gold ore which is found in Brazil.

**Metallurgy.**—The process for obtaining the metals from the ores is based mainly upon the following facts: (1) Gold is soluble in dilute *aqua regia*, while platinum requires concentrated *aqua regia;* (2) platinic chloride, $PtCl_4$, and iridium chloride, $IrCl_4$, form, with ammonium chloride, difficultly soluble compounds of the formulas $(NH_4)_2PtCl_6$ ($PtCl_4.2NH_4Cl$) and $(NH_4)_2IrCl_6$ ($IrCl_4.2NH_4Cl$) When these compounds are ignited, they are completely decomposed, and the metals are left behind. When, therefore, platinum-ore has been freed as far as possible from sand and earth, it is first treated with dilute *aqua regia*, which removes the gold, and then with concentrated *aqua regia*, which dissolves the platinum together with a little iridium, leaving an alloy of iridium and osmium.

When the solution thus obtained is treated with ammonium chloride, both metals are precipitated ; and when the precipitate is ignited, both metals are left behind in the form of a spongy mass. This consists, however, almost wholly of platinum, the amount of iridium being very small.

## Ruthenium, Ru (At. Wt. 101.7).

**Preparation.**—Ruthenium is obtained from the residue which is left undissolved when platinum-ore is treated with concentrated nitro-hydrochloric acid.

**Properties.**—When heated in oxygen it burns and forms the oxide,

$RuO_2$. It is insoluble in the strong acids, and even in nitro-hydrochloric acid it is almost insoluble. Owing to its power to form salts of ruthenious acid, it is dissolved when heated with potassium hydroxide and an oxidizing agent, such as saltpetre or potassium chlorate, and afterwards treated with water.

## Osmium, Os (At. Wt. 191).

**Preparation.**—As stated above, this element is left undissolved in the form of an alloy with iridium when platinum ore is treated with concentrated nitro-hydrochloric acid. In order to separate it from the iridium, advantage is taken of the fact that it forms a volatile peroxide, $OsO_4$, similar to that formed by ruthenium while iridium does not.

**Properties.**—The metal does not melt at the highest temperatures reached artificially. It has the highest specific gravity of all known substances, is easily oxidized when in finely divided condition; and is converted either by the oxygen of the air or by nitric acid into osmium peroxide, $OsO_4$. The oxides as well as the metal form the *peroxide*, $OsO_4$, when heated in the air. This is also formed by treating a heated mixture of sodium chloride and the alloy of osmium and iridium with chlorine and water vapor. It is commonly called *osmic acid*, though its acid properties are very weak. Like ruthenium peroxide it is volatile. It sublimes in colorless, lustrous needles, and boils without decomposition at a temperature a little above 100°. It has an intense odor similar to that of chlorine, and its vapor attacks the eyes and respiratory organs somewhat as chlorine does. It dissolves slowly in water, and reducing agents precipitate the metal from the solution. A solution of osmic acid is used in microscopic work. When injected into the tissues, the parts are hardened and colored.

## Rhodium, Rh (At. Wt. 103).

Rhodium has no acid properties, and does not form a peroxide corresponding to those of ruthenium and osmium. It is a silver-white ductile metal which melts at about 1700°. On the other hand, its oxide, $Rh_2O_3$, is basic. The chloride $RhCl_3$ is readily formed. It is doubtful whether the di- or tetrachloride has been made.

## Iridium, Ir (At. Wt. 193).

**Preparation.**—The extraction of iridium with platinum and with osmium from platinum-ore was referred to above. In order to separate it from platinum, advantage is taken of the fact that it forms a trichloride, $IrCl_3$, which with ammonium chloride gives an easily soluble double chloride.

**Properties.**—Iridium has a grayish-white color, and resembles polished steel. Its specific gravity is nearly the same as that of osmium, being 22.42. It is harder and more brittle than platinum; melts at a higher temperature, about 2200°; and unless it is finely divided it is not dissolved by nitro-hydrochloric acid. When heated with potassium hydroxide and saltpetre it is converted into the oxide.

## Palladium, Pd (At. Wt. 106.5).

**Preparation.**—The chief source of palladium is a Brazilian gold-ore. From this ore the metal can be obtained by various methods, one of which consists in melting it together with silver and then treating it with nitric acid, when silver and palladium dissolve, and the gold remains undissolved. The silver is precipitated as chloride and the palladium as the cyanide, and when the latter is ignited it is decomposed, leaving palladium.

**Properties.**—Palladium resembles iridium and platinum in appearance. It melts at about 1550°. Its specific gravity is only about half as great as that of platinum, being 11.5. It is more easily fusible than platinum, and dissolves in nitric acid and in hot concentrated sulphuric acid. The property of palladium which has perhaps attracted most attention is its power to absorb hydrogen, and form

**Palladium-Hydrogen.**—The formation of this compound was referred to under Hydrogen (which see). The combination takes place even at the ordinary temperature, but best at 100°. If the metal is brought into hydrogen at this temperature, it absorbs more than 900 times its volume, forming an alloy of the composition $Pd_2H$. This alloy has a greater volume and lower specific gravity than the palladium from which it is formed. At 130° it begins to decompose under the atmospheric pressure, but continued heating at a red heat is necessary to decompose it completely. If allowed to lie in contact with the air the hydrogen is oxidized to water. Palladium-hydrogen acts as a strong reducing agent, the hydrogen given off by it being apparently in the nascent or atomic condition.

## Platinum, Pt (At. Wt. 194.8).

**Preparation.**—A general idea of the method of procedure in extracting platinum from its ores was given on p. 653. Thus prepared, however, it always contains iridium, and for some purposes for which platinum is used this is objectionable. In order to purify the metal advantage is taken of the fact that iridium chloride can be converted into a trichloride, which with ammonium chloride forms an easily soluble double salt. The metal as obtained by igniting ammonium chlorplatinate forms a gray

spongy mass known as *spongy platinum*. When a solution of platinous chloride is boiled with potassium hydroxide, and alcohol gradually added, the salt is reduced, and the platinum is precipitated as an extremely fine powder, known as *platinum black*. When spongy platinum and platinum black are heated to fusion by the oxyhydrogen flame they are converted into the compact variety.

**Properties.**—Platinum is a grayish-white metal resembling polished steel; it can be drawn out into very fine wire; it melts above 1700° in the flame of the oxyhydrogen blowpipe, and it is volatile above its melting-point; its specific gravity is 21.5. At white heat it can be welded. It is not dissolved by nitric acid, hydrochloric acid, or sulphuric acid, but it dissolves in nitro-hydrochloric acid, forming the acid, $H_2PtCl_6$. Fusing alkalies, and particularly a mixture of caustic potash and saltpetre, act upon it; but the alkaline carbonates do not. In contact with red-hot charcoal and silicon dioxide a compound of silicon and platinum is formed. Finely divided platinum has to a remarkable extent the power of condensing gases upon its surface It absorbs, for example, 200 times its own volume of oxygen, and other gases in a similar way. The oxygen thus absorbed is in the active condition, and if oxidizable substances are brought in contact with it they are easily oxidized. Thus when a current of hydrogen is allowed to flow against a piece of spongy platinum it takes fire, owing to the presence of the condensed oxygen in the pores of the platinum. Similarly, when sulphur dioxide and oxygen are allowed to flow together over spongy platinum, or even the compact metal, the two gases unite to form sulphur trioxide.

**Applications of Platinum.**—The metal is of great value to the chemist on account of its power to resist high temperatures and the action of most chemical substances. It is used in the laboratory in the form of wire, foil, crucibles, evaporating-dishes, tubes, etc., etc. From what was said above it cannot be used with alkalies and saltpetre, nor with nitro-hydrochloric acid. Platinum vessels, further, should not be placed upon red-hot charcoal.

Metallic salts which are easily reduced, such as those of antimony and bismuth, should not be heated in platinum vessels, as the reduced elements, like silicon, form alloys with the platinum, and these, as a rule, are easily fusible. In the concentration of sulphuric acid on the large scale platinum stills are used. The price of platinum is not as high as that of gold, but much higher than that of silver.

**Alloys of Platinum.**—The only alloy of platinum that is of any special importance is that which it forms with iridium. A small percentage of iridium diminishes the malleability of platinum very markedly, and makes it brittle; it, however, increases its resistance to the action of reagents. An alloy of 90 per cent platinum and 10 per cent iridium has been adopted by the French Government as the best material from which to make normal meter bars. This alloy is very hard, as elastic as steel, more difficultly fusible than platinum, entirely unchangeable in the air, and is capable of a high polish.

**Chlorides.**—Like palladium, platinum forms two chlorides, *platinous chloride*, $PtCl_2$, and *platinic chloride*, $PtCl_4$. Platinous chloride is formed by passing chlorine over platinum sponge heated to 240° to 250°. Platinic chloride is formed by heating chlorplatinic acid, $H_2PtCl_6$, in a current of chlorine to 360°. Platinic chloride is easily soluble in water.

**Chlorplatinic Acid,** $H_2PtCl_6$, is formed by direct union of platinic chloride with hydrochloric acid, and by dissolving platinum in *aqua regia* and evaporating the solution. It crystallizes with 6 molecules of water, and forms a series of salts called the *chlorplatinates*, to which reference has already been made. Those most commonly met with in the laboratory are the potassium salt, $K_2PtCl_6$, or $PtCl_4.2KCl$, and the ammonium salt, $(NH_4)_2PtCl_6$, or $PtCl_4.2NH_4Cl$, both of which are difficultly soluble in water, and are therefore precipitated when chlorplatinic acid (platinic chloride) is added to solutions containing potassium or ammonium chloride. The sodium salt is easily soluble in water. Chlorplatinic acid appears to be analogous to fluosilicic acid, $H_2SiF_6$.

**Sulphides.**—There are two sulphides of platinum which are analogous to the two oxides, PtO and $PtO_2$. These are *platinous sulphide*, PtS, and *platinic sulphide*, $PtS_2$. They are black insoluble compounds, that are precipitated when hydrogen sulphide or soluble sulphides are added to solutions of platinous and platinic chlorides.

## EXPERIMENT.

### Platinum.

Experiment 247.—Prepare a solution of chlorplatinic acid as follows: Heat platinum in a flask with concentrated nitric acid, adding from time to time a few drops of hydrochloric acid. After the metal is dissolved evaporate to dryness on a water-bath. Dissolve in water and filter.

### Chemical Analysis.

At the end of each chapter treating of the metallic or base-forming elements there is given a list of such reactions as are of special value for analytical purposes, together with such explanatory statements as seem called for. The student who is engaged in analytical work will generally find these explanations sufficient to enable him to keep his ideas clear in regard to the reactions with which he is dealing, provided, at the same time, he carefully studies the chapter to which the explanations form an appendix. As an introduction to analytical work, a general study of chemical reactions is necessary, and the fuller this is the better. There are many small books in existence in which good directions are given for work of this kind. The student is, however, advised to supplement the book he may be using by such experiments as may suggest themselves on reading the corresponding chapters in this book. The directions there found will generally be quite sufficient for the purpose, and it is therefore not considered necessary to give more specific directions in this place. In general, the more the student occupies himself in the laboratory with chemical substances the more rapidly will his chemical ideas grow. But it is necessary that he should avoid working by "rule of thumb," and for this purpose constant reference to some larger text-book in which the relations between the substances and the reactions he is dealing with are discussed in a broad way is of the highest importance.

## CHAPTER XXXIV.

### SOME FAMILIAR COMPOUNDS OF CARBON.

**Organic Chemistry.**—When the compounds that are obtained from plants and animals were first studied, they were supposed to be entirely different from the compounds obtained from the inorganic, or mineral, constituents of the earth. The former were called *organic compounds* because they were obtained from organized things; while the latter were called *inorganic compounds*. Organic compounds were the subject of *Organic Chemistry*, and inorganic compounds formed the subject of *Inorganic Chemistry*. These names are still in use, though they have lost their original meaning. Organic Chemistry now means only the *Chemistry of the Compounds of Carbon*.

**Occurrence of the Compounds of Carbon.**—The compound of carbon that occurs most widely distributed in nature is carbon dioxide. This, as has been pointed out, is the starting-point of all life on the globe. All living things are formed from it either directly or indirectly. Attention has been called to the fact that starch and cellulose are the principal compounds found in plants, and that fats, albumin, and fibrin are the most common substances found in animals.

**Formation of Hydrocarbons.**—Certain natural processes which are not thoroughly understood have given rise to the formation of a complex mixture of organic compounds, principally hydrocarbons, in *petroleum*.

**Distillation of Coal.**—The destructive distillation of coal for the purpose of making illuminating-gas, and the formation of *coal tar* have already been referred to. Coal-tar is one of the most important sources of compounds of

carbon. The hydrocarbons benzene, $C_6H_6$, toluene, $C_7H_8$, xylene, $C_8H_{10}$, naphthalene, $C_{10}H_8$, anthracene, $C_{14}H_{10}$, etc., are obtained from this source.

**Distillation of Wood.**—Wood is heated in closed vessels mostly for the purpose of making charcoal, as already explained. Among the products obtained from this source are *wood-spirit*, or *methyl alcohol*, and *pyroligneous acid*, or *acetic acid*. Large quantities of acetic acid are prepared in this way.

**Distillation of Bones.**—In order to make bone-black, bones are subjected to destructive distillation. The oil which passes over is collected and known as *bone-oil*. This is the source of a large number of compounds that are of special interest on account of their connection with the valuable alkaloids quinine, morphine, etc.

**Fermentation.**—A number of the most important compounds of carbon are formed by a process known as *fermentation*. This is a general term meaning any process in which a chemical change is effected by means of minute animal or vegetable organisms. The best-known example of fermentation is that of sugar, which gives rise to the formation of ordinary *alcohol*.

**Classes of Compounds of Carbon.**—The chief classes of these compounds are the *hydrocarbons*, the *alcohols*, the *aldehydes*, the *acids*, the *ethers*, and the *ethereal salts*. First, a few of the best-known examples of each of these classes will be taken up, and afterwards some other familiar compounds which do not belong to any one of these classes.

### HYDROCARBONS.

**Compounds of Carbon and Hydrogen.**—It is not an easy matter to effect combination between carbon and hydrogen in the laboratory except in a few simple cases. In nature processes are in operation which give rise to the formation of a large number of compounds containing these elements; and, further, in the manufacture of illuminating-gas from coal the conditions are such as to cause the combination of carbon and hydrogen, several interesting compounds

being thus formed. There are no other two elements that combine with each other in as many different proportions as carbon and hydrogen. The compounds thus formed are known as *hydrocarbons*. The number of hydrocarbons known is large, being somewhere near two hundred. Fortunately, investigation has shown that quite simple relations exist between these compounds; and hence, though the number is large, the study is not as difficult as it at first appears.

**Petroleum** is an oily liquid found in many places in the earth in large quantity, particularly in Pennsylvania and the Caucasus. In the earth it contains both gases and liquids. When it is brought into the air, the pressure being removed, the gases are given off. There are several gaseous hydrocarbons given off, and a large number of liquids left behind.

**Refining of Petroleum.**—The vapors from petroleum when mixed with air are explosive, and the thicker liquids clog the lamps and wicks. Therefore these must be removed before the oil is fit for household use. This is done by (1) distilling, (2) washing with sulphuric acid, (3) washing with alkali, and (4) washing with water. The product thus prepared is called *kerosene*.

In refining petroleum a number of products are obtained which cannot be used in lamps. Those which are lighter than kerosene, that is to say those which boil at a lower temperature, are known as *gasoline*, *naphtha*, *benzine*, etc. From the heavier portions, or those which boil at higher temperatures than kerosene, *lubricating oils* and *paraffin* are made. Each of these substances is a mixture of several chemical compounds.

**Hydrocarbons contained in Petroleum.**—The simplest hydrocarbon contained in petroleum is methane, or marsh-gas, $CH_4$; the next has the composition $C_2H_6$, the next $C_3H_8$, etc. It will be seen that these compounds bear a simple relation to one another, as far as composition is concerned. They are the first members of a series the names and symbols of the first eight members of which are given below:

$CH_4$, Methane, or Marsh-gas;
$C_2H_6$, Ethane;
$C_3H_8$, Propane;
$C_4H_{10}$, Butane;
$C_5H_{12}$, Pentane;
$C_6H_{14}$, Hexane;
$C_7H_{16}$, Heptane;
$C_8H_{18}$, Octane.

**Homology.**—The first member of the series differs from the second by $CH_2$; there is also this same difference between any two consecutive members of the series. This relation is known as *homology*, and such a series is known as an *homologous series*. Carbon is distinguished from all other elements by its power to form homologous series.

**The Ethylene Series of Hydrocarbons.**—Besides the series above mentioned, which is known as the *marsh-gas series*, there are other homologous series of hydrocarbons. There is one beginning with ethylene, $C_2H_4$, examples of which are

Ethylene, $C_2H_4$;
Propylene, $C_3H_6$;
Butylene, $C_4H_8$.

**The Acetylene Series.**—There is a series beginning with acetylene, examples of which are

Acetylene, $C_2H_2$;
Allylene, $C_3H_4$.

**The Benzene Series.**—Another series begins with benzene, $C_6H_6$. Some of the members of this series are

Benzene, $C_6H_6$;
Toluene, $C_7H_8$;
Xylene, $C_8H_{10}$.

**Marsh-gas, Methane, Fire-damp,** $CH_4$.—Marsh-gas is found in nature in petroleum, and is given off when the oil is taken out of the earth, and the pressure is removed. It is formed, as the name implies, in marshes, as the

product of a reducing process. Vegetable matter is composed of carbon, hydrogen, and oxygen. When it undergoes decomposition in the air in a free supply of oxygen, the final products formed are carbon dioxide and water. When the decomposition takes place without access of oxygen, under water for example, marsh-gas, which is a reduction-product, is formed. The gas can be made in the laboratory by treating aluminium carbide, $C_3Al_4$, with water:

$$C_3Al_4 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

It can also be made by passing a mixture of hydrogen sulphide and the vapor of carbon bisulphide over heated copper.

Marsh-gas is met with in coal mines, and is known to the miners as *fire-damp*, "damp" being the general name applied to a gas, and the name fire-damp meaning a gas that burns. To prepare it in the laboratory, it is most convenient to heat a mixture of sodium acetate and quicklime. The change that takes place will be readily understood by regarding it as a simple decomposition of acetic acid. Acetic acid has the formula $C_2H_4O_2$. When heated alone, it boils and does not suffer decomposition. If it is converted into a salt, and heated in the presence of a base, it breaks down into marsh-gas and carbon dioxide:

$$C_2H_4O_2 = CH_4 + CO_2.$$

The carbon dioxide remains behind in the form of a carbonate.

Marsh-gas is a colorless, transparent, tasteless, inodorous gas. It is slightly soluble in water. It burns, forming carbon dioxide and water. When mixed with air, the mixture explodes if a flame or spark comes in contact with it. This is one of the causes of the explosions which so frequently occur in coal mines. To prevent these explosions a special lamp was invented by Sir Humphry Davy, which is known as *Davy's safety lamp* (p. 383).

**Substitution-products of the Hydrocarbons.**—Marsh-gas

and other hydrocarbons undergo change when treated with chlorine and bromine. The change consists in the substitution of one or more atoms of chlorine or of bromine for the same number of atoms of hydrogen. In the case of marsh-gas and chlorine the possible changes are represented as below:

$$CH_4 + Cl_2 = CH_3Cl + HCl;$$
$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl;$$
$$CH_2Cl_2 + Cl_2 = CHCl_3 + HCl;$$
$$CHCl_3 + Cl_2 = CCl_4 + HCl.$$

All the products represented are known.

**Chloroform,** $CHCl_3$.—Chloroform can be made as above indicated, but it is made on the large scale by treating alcohol (which see) or acetone (which see) with bleaching-powder. It is a heavy liquid with an ethereal odor and a somewhat sweet taste. It is one of the most valuable anæsthetics, though there is a little danger attending its use.

**Iodoform,** $CHI_3$.—This compound, like chloroform, is a substitution-product of marsh-gas. It is made by bringing together alcohol, an alkali, and iodine. It is a solid substance, soluble in alcohol and ether, but insoluble in water. It crystallizes in six-sided, yellow plates. It is extensively used as a dressing for wounds in surgery.

**Ethylene, Olefiant Gas,** $C_2H_4$.—This hydrocarbon is formed by heating a mixture of ordinary alcohol and concentrated sulphuric acid. The reaction is represented thus:

$$\underset{\text{Alcohol.}}{C_2H_6O} = H_2O + \underset{\text{Ethylene.}}{C_2H_4}.$$

Ethylene is a colorless gas, that can be condensed to a liquid. It burns with a luminous flame. With oxygen it forms an explosive mixture.

**Acetylene,** $C_2H_2$.—Acetylene is formed when a current of hydrogen is passed between carbon poles, that are incandescent in consequence of the passage of a powerful electric current. In this case carbon and hydrogen combine directly. It is formed also when the flame of an

ordinary laboratory gas-burner (Bunsen burner) "strikes back," or burns at the base without a free supply of air. It is now made on the large scale by treating calcium carbide, $CaC_2$, with water:

$$CaC_2 + H_2O = C_2H_2 + CaO.$$

Its odor is unpleasant. It burns with a luminous, smoky flame. With proper burners it burns without smoking, and it is much used for purposes of illumination.

ALCOHOLS.

**Methyl Alcohol, Wood-spirit,** $CH_4O$.—This is formed in the distillation of wood together with other products. It has, when pure, a pleasant odor and taste, and acts upon the animal system very much as ordinary alcohol does. It, however, produces very injurious effects when taken internally. Blindness and even death may result. It burns without giving light or smoke, and can therefore be used in lamps for heating-purposes as ordinary alcohol is. It is used in the manufacture of varnishes.

**Ethyl Alcohol, Spirits of Wine,** $C_2H_6O$.—This well-known substance is formed by the fermentation of grape-sugar or glucose.

**What Change takes Place in the Sugar?**—If the solution in a flask in which sugar has been allowed to ferment is examined carefully it will be found to contain alcohol and no sugar. Grape-sugar has the composition expressed by the formula $C_6H_{12}O_6$. By fermentation it is decomposed, forming alcohol, $C_2H_6O$, and carbon dioxide, $CO_2$, thus:

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

**What Causes the Change?**—It has been found that this change of grape-sugar is caused by small organized bodies that grow in the solution. These bodies are contained in ordinary yeast.

**Germs in the Air.**—When fruit-juices containing sugar are exposed to the air they undergo fermentation

without the addition of yeast. This is due to the fact that the germs or seeds of the bodies which cause fermentation are everywhere floating in the air. Hence when a liquid in which these seeds can grow is exposed to the air, the bodies are formed and fermentation takes place.

**Different Kinds of Fermentation.**—The fermentation which yields alcohol is only one of many kinds. Among the others are; (1) *lactic-acid fermentation*, which takes place in the souring of milk; and (2) *acetic-acid fermentation*, which causes the transformation of alcohol into acetic acid. The latter ferment is contained in "mother of vinegar."

**Distillation of Fermented Liquids.**—In order to get the alcohol from liquids that have undergone fermentation they must be distilled. For this purpose very efficient stills have been devised, which give nearly pure alcohol. Usually alcohol contains impurities known as *fusel oil.*

**Properties of Alcohol.**—Pure ethyl alcohol has a peculiar, pleasant odor. It remains liquid at very low temperatures, but has been converted into a solid at a temperature of $-130.5°$. It burns with a flame which does not deposit soot, and was hence formerly much used in laboratories for heating purposes, and is still used where gas cannot be obtained. Its effects upon the human system are well known. It intoxicates when taken in dilute form, while in large doses it is poisonous. It lowers the temperature of the body when taken internally, although it causes a sensation of warmth.

**Uses of Alcohol.**—Alcohol is the principal solvent for organic substances. It is hence extensively used in the arts, as in the manufacture of varnishes, perfumes, and tinctures of drugs. Most beverages in use owe their intoxicating power to the presence of alcohol. The milder forms of beer contain from 2 to 3 per cent; light wines about 8 per cent; while whiskey, brandy, etc., sometimes contain as much as 60 to 75 per cent.

**Denatured Alcohol** is ordinary alcohol to which something has been added to make it unfit for use as a bever-

age. Manufacturers and others are permitted to use this alcohol without the payment of tax.

**Glycerin,** $C_3H_8O_3$.—Glycerin is an alcohol that occurs very widely distributed as a constituent of fats. The relation it bears to the fats will be explained when the acids which enter into the fats are taken up. It is obtained from the fats by boiling them with an alkali like caustic soda or caustic potash, or by heating with steam.

**Properties.**—Glycerin is a thick, colorless liquid with a sweetish taste. It attracts moisture from the air, and is hence used to keep surfaces moist.

ALDEHYDES.

**Formic Aldehyde, Formal,** $CH_2O$.—This is made by passing a mixture of air and the vapor of methyl alcohol over a heated platinum or copper spiral. It is manufactured on the large scale, and comes into the market in solution under the name *formalin*. It is used in the manufacture of some valuable dyes and as a preservative and disinfectant.

**Acetic Aldehyde, Ordinary Aldehyde,** $C_2H_4O$.—This compound is formed by oxidizing ordinary alcohol, the change being represented by this equation:

$$C_2H_6O + O = C_2H_4O + H_2O.$$

Aldehyde is a volatile liquid with a characteristic penetrating odor. When left to itself, and especially when treated with a number of other things, it is converted into another substance of the same composition. This is called *paraldehyde*. A determination of the molecular weight of the substance by the method of Avogadro has shown that it must be represented by the formula $C_6H_{12}O_3$. The change from aldehyde to paraldehyde must, therefore, be represented thus:

$$3C_2H_4O = C_6H_{12}O_3.$$

Paraldehyde is used in medicine.

**Chloral,** $C_2Cl_3HO$, is a compound formed by the action of chlorine on alcohol. It is related to aldehyde, as

chloroform is related to marsh-gas, that is to say, it is a trichlorine substitution-product. It is a colorless liquid. With water it forms a crystallized compound, *chloral hydrate*, $C_2Cl_3HO + H_2O$, which is easily soluble in water, and crystallizes from the solution in colorless prisms. Taken internally in doses of from 1.5 to 5 grams, it produces sleep. In larger doses it acts as an anæsthetic.

### ACIDS.

**Formic Acid,** $CH_2O_2$.—This acid occurs in nature in red ants, in stinging-nettles, in the shoots of some of the varieties of pine, and elsewhere. It is a colorless liquid. Dropped on the skin, it causes pain and produces blisters.

**Acetic Acid,** $C_2H_4O_2$.—This is the acid contained in vinegar, and the value of vinegar is due to its presence. It is formed from alcoholic liquids by exposing them to the air, in consequence of the presence of a microscopic organism which is contained in what is commonly known as "mother of vinegar." The formation of acetic acid from alcohol is due to the action of oxygen as represented in the equation

$$\underset{\text{Alcohol}}{C_2H_6O} + O_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + H_2O.$$

But oxygen alone does not effect the change. When the ferment is present the oxidation takes place. Acetic acid is also obtained by distilling wood. Hence the names *pyroligneous acid* and *wood-vinegar*.

**Properties.**—Acetic acid is a clear, colorless liquid. It has a very penetrating, pleasant, acid odor, and a sharp taste. The pure substance acts upon the skin like formic acid, causing pain and raising blisters.

**Uses.**—Acetic acid is extensively used, chiefly in the dilute form known as vinegar. It is used in calico-printing in the form of iron and aluminium salts. With iron it gives hydrogen, which is needed in the manufacture of certain compounds used in making dyes.

**Salts of Acetic Acid.**—The best-known salts of acetic acid are *lead acetate*, $Pb(C_2H_3O_2)_2$, commonly called *sugar*

*of lead;* and *copper acetate*, $Cu(C_2H_3O_2)_2$, a variety of which is known as *verdigris*.

**Fatty Acids.**—Formic and acetic acids are the first members of an *homologous series* (see p. 662). Some of the more important members are named in the following table:

| | | | |
|---|---|---|---|
| Formic acid..... | $CH_2O_2$, | Butyric acid ..... | $C_4H_8O_2$, |
| Acetic " ..... | $C_2H_4O_2$, | Palmitic " ..... | $C_{16}H_{32}O_2$, |
| Propionic " ..... | $C_3H_6O_2$, | Stearic " ..... | $C_{18}H_{36}O_2$. |

They are called *fatty acids* for the reason that many of them are obtained from fats.

**Butyric Acid,** $C_4H_8O_2$, is of special interest because it is obtained from butter by boiling with caustic potash. It occurs also in many other fats. There is a *butyric-acid ferment* contained in putrid cheese which has the power of converting sugar into butyric acid.

**Palmitic Acid,** $C_{16}H_{32}O_2$, is obtained from many fats, but palm-oil is especially rich in it.

**Stearic Acid,** $C_{18}H_{36}O_2$, is the acid contained in the fat known as *stearin*. The so-called " *stearin candles* " are made of a mixture of palmitic and stearic acids.

**Soaps.**—Soaps are the alkali salts of the acids contained in fats, especially of palmitic and stearic acids. Fats are compounds of these acids with glycerin. When the fats are boiled with an alkali, as caustic soda, the corresponding salts of the acids are formed, while the glycerin is set free. The potassium and sodium salts of palmitic and stearic acids are the soaps.

**Use of Soap.**—The cleansing power of soap depends upon the fact that it dissolves the oily film of the surface of the skin and thus facilitates the removal of the foreign substances commonly known as dirt.

**Action of Soap on Hard Waters.**—As has been explained, a hard water is one that contains salts in solution. *Temporary hardness* is that which is caused by calcium carbonate held in solution in the water by carbon dioxide. *Permanent hardness* is caused by calcium sulphate or magnesium salts. The calcium and magnesium salts of palmitic and stearic acids are insoluble in water. There-

fore, when soap is added to a hard water these insoluble salts are precipitated and give the water a hard feeling. In attempting to wash the hands with soap in a hard water they become covered with a thin layer of the insoluble salts which prevents them from rubbing freely over each other, and makes them feel sticky. Before the soap can do any good all the lime-salt must be precipitated. The action in the case of temporary hardness is represented by the equation

$$\underset{\text{Soap.}}{2NaC_{16}H_{31}O_2} + CaCO_3 = \underset{\text{Calcium Palmitate.}}{Ca(C_{16}H_{31}O_2)_2} + Na_2CO_3.$$

In the case of permanent hardness it is represented by the equation

$$2NaC_{16}H_{31}O_2 + CaSO_4 = Ca(C_{16}H_{31}O_2)_2 + Na_2SO_4.$$

**Relations of the Soap Industry to other Industries.**—A great chemist and philosopher has said that the quantity of soap used in a country is a measure of the civilization of that country. Certain it is that soap is only used by civilized people, and that by them it is used in enormous quantities. In many farm-houses a primitive method for the manufacture of soap is practised, consisting in treating refuse fats with the lye extracted from wood-ashes. A soft soapy mass is thus obtained known as "soft-soap." Fats form the starting-point in the manufacture of all soap. These are generally treated with caustic soda. Caustic soda is made from sodium carbonate by the action of lime; and from sodium chloride by electrolysis. Further, as has been seen, sodium carbonate is made from common salt mostly by the Le Blanc process, which requires sulphuric acid. Thus the manufacture of sulphuric acid and of sodium carbonate is intimately related to the manufacture of soap.

**Oxalic Acid,** $C_2H_2O_4$.—This acid occurs very widely distributed in nature, as in the *sorrels*, which owe their acid taste to the presence of acid potassium oxalate, $KC_2HO_4$; and as the ammonium salt in guano. It is probably one of the first substances formed from carbon dioxide in the

plant. It is manufactured by heating wood shavings or sawdust with caustic soda and caustic potash. Oxalic acid is an active poison. It is used in calico-printing, and in cleaning brass and copper objects.

**Lactic Acid,** $C_3H_6O_3$.—Lactic acid is made by the fermentation of sugar by means of the *lactic-acid ferment.* The reaction caused by the ferment is represented by the equation

$$C_6H_{12}O_6 = 2C_3H_6O_3.$$

**Malic Acid,** $C_4H_6O_5$.—This acid is very widely distributed in the vegetable kingdom, as in apples, cherries, etc.

**Tartaric Acid,** $C_4H_6O_6$.—Tartaric acid occurs very widely distributed in fruits, sometimes uncombined, sometimes in the form of the potassium or calcium salt; as, for example, in grapes, berries of the mountain-ash, potatoes, cucumbers, etc., etc. It is prepared from "cream of tartar" This is acid potassium tartrate, which is formed when grape-juice ferments.

**Citric Acid,** $C_6H_8O_7$.—Citric acid, like malic and tartaric acids, is very widely distributed in nature in many varieties of fruit, especially in lemons. It is also found in currants, whortleberries, raspberries, gooseberries, etc., etc. It is prepared from lemon-juice: 100 parts of lemons yield $5\frac{1}{2}$ parts of the acid. It is a solid, crystallized substance, soluble in water. It is frequently used for the purpose of making lemonade without lemons, and there is no objection to its use for this purpose.

### ETHERS.

**Ether,** $C_4H_{10}O$.—Ordinary ether is the best-known representative of the class of compounds called *ethers.* It is formed from ordinary alcohol by treating it with sulphuric acid and distilling. The result of the action which takes place is represented by the equation

$$\underset{\text{Alcohol,}}{2C_2H_6O} = \underset{\text{Ether.}}{C_4H_{10}O} + H_2O.$$

Ether is a liquid that boils at a low temperature and

takes fire and burns readily. Inhaled it produces insensibility to pain. It is extensively used as an *anæsthetic*.

ETHEREAL SALTS OR ESTERS.

**Action of Acids upon Alcohols.**—When an acid acts upon an alcohol it is neutralized, though not as readily as when it acts upon a base. The product is a substance which resembles a salt and is called an ethereal salt or ester. Thus when nitric acid acts upon alcohol this reaction takes place:

$$C_2H_6O + HNO_3 = C_2H_5NO_3 + H_2O.$$

The product $C_2H_5NO_3$, called ethyl nitrate, is an ethereal salt. The alcohol acts as if it were a substance like caustic potash and made up thus: $C_2H_5OH$. The resemblance between its action and that of caustic potash is shown by the equations

$$KOH + HNO_3 = KNO_3 + H_2O, \text{ and}$$
$$C_2H_5OH + HNO_3 = C_2H_5NO_3 + H_2O.$$

**Saponification.**—When an ethereal salt is boiled with a caustic alkali it is decomposed, the products being an alcohol and an alkali salt. Thus when ethyl nitrate is boiled with caustic potash, potassium nitrate and alcohol are formed:

$$C_2H_5NO_3 + KOH = C_2H_5OH + KNO_3.$$

This process is called *saponification*, because the most important example is furnished by soap-making.

**Fats.**—The fats are ethereal salts in the formation of which glycerin, as the alcohol, and three acids take part. The three acids are palmitic and stearic acids, already mentioned, and *oleic acid*, $C_{18}H_{34}O_2$. Although the composition of these substances is comparatively complex, the way they act upon one another is simple, and is the same as the action of nitric acid upon alcohol in forming ethyl nitrate. The fats, then, are the palmitate, stearate, and oleate of *glyceryl*, which bears to glycerin very much the same relation that ethyl, $C_2H_5$, bears to alcohol. When

a fat is boiled with caustic soda, glycerin and the sodium salts of the acids contained in the fat are formed.

Butter consists of ethereal salts of glycerin and several fatty acids, among which are palmitic, stearic, and butyric. *Oleomargarin* is an artificial butter made from other fats than that of milk.

**Ethereal Salts as Essences.**—The ethereal salts generally have pleasant odors, and it is to their presence that many fruits owe their flavors. Some of the compounds are now made artificially and used instead of the fruit-extracts Thus the *ethyl salt of butyric acid* is used under the name of *essence of pineapples*, and the *amyl salt of valeric acid* under the name of *essence of apples*.

**Nitroglycerin.**—Among the more important ethereal salts of glycerin are the *nitrates*. Two of these are known, *viz.*, the *mono-nitrate*, $C_3H_5\begin{cases} O.NO_2 \\ OH \\ OH \end{cases}$, and the *trinitrate*, $C_3H_5(O.NO_2)_3$, the latter being the chief constituent of *nitroglycerin*. Nitroglycerin is prepared by treating glycerin with a mixture of concentrated sulphuric and nitric acids. It is a pale yellow oil insoluble in water. At $-20°$ it crystallizes in needles. It explodes very violently by concussion. It may be burned in an open vessel, but if heated above 250° it explodes. *Dynamite* is infusorial earth* impregnated with nitroglycerin. Nitroglycerin is the active constituent of a number of explosives.

RELATIONS BETWEEN THE COMPOUNDS TREATED OF.

**Comparison of the Formulas.** On comparing the formulas of the hydrocarbons of the marsh-gas series (see p. 662) with those of the simplest alcohols and the fatty acids, it will be seen that these compounds are all related in a simple way. Below are the formulas of a few of the hydrocarbons, alcohols, and acids:

* That is to say, earth made up of the microscopic, flinty shells which constitute the fossil remains of certain minute and simple plants.

| Hydrocarbons. | Alcohols. | Acids. |
|---|---|---|
| $CH_4$ | $CH_4O$ | $CH_2O_2$ |
| $C_2H_6$ | $C_2H_6O$ | $C_2H_4O_2$ |
| $C_3H_8$ | $C_3H_8O$ | $C_3H_6O_2$ |
| $C_4H_{10}$, etc. | $C_4H_{10}O$, etc. | $C_4H_8O_2$, etc. |

Each of these series is an homologous series.

**Alcohols.**—Alcohols have been shown to be derived from the hydrocarbons by the replacement of one or more hydrogen atoms by oxygen and hydrogen, OH, called *hydroxyl*, or from water by replacing one of the hydrogen atoms of the water by a compound of carbon and hydrogen. An alcohol, then, is a hydroxide, just as a metallic base is; only, instead of consisting of a metal in combination with hydrogen and oxygen, it consists of a compound of carbon and hydrogen in combination with hydrogen and oxygen. Thus:

| Metallic Bases. | Alcohols |
|---|---|
| K(OH) | $CH_3(OH)$ |
| Na(OH) | $C_2H_5(OH)$ |

**More Complex Alcohols.**—Just as lime is a more complex base than caustic potash, as shown by the formulas KOH and $CaO_2H_2$ or $Ca(OH)_2$, so there are more complex alcohols than ordinary alcohol. A good example is furnished by glycerin, $C_3H_8O_3$, which has been shown to be a hydroxide corresponding to aluminium hydroxide, $Al(OH)_3$, a fact represented by the formula $C_3H_5(OH)_3$. It may be called glyceryl hydroxide, the complex, $C_3H_5$, being known as glyceryl.

**Radicals or Residues.**—The compounds of hydrogen and carbon contained in the alcohols are called *radicals* or *residues*. We may say that an alcohol is water in which a radical has been substituted for half of the hydrogen:

| | |
|---|---|
| HOH | $C_2H_5OH$ |
| Water. | Ordinary alcohol. |
| HOH | OH |
| HOH | $C_3H_5$ { OH = $C_3H_8O_3$. |
| HOH | OH |
| Water. | Glycerin. |

**Acids.**—Just as the alcohols have been shown to be derived from water, so the organic acids have been shown to be derived from carbonic acid. Carbonic acid itself is not known. But the carbonates are derived from an acid of the formula $H_2CO_3$, or $CO\begin{cases} OH \\ OH \end{cases}$. If, in this acid, a hydroxyl is replaced by a radical, as, for example, by ethyl, $C_2H_5$, a substance of the formula $CO\begin{cases} C_2H_5 \\ OH \end{cases}$ or $C_3H_6O_2$ is the result. If methyl, $CH_3$, is introduced in place of ethyl, the product is $CO\begin{cases} CH_3 \\ OH \end{cases}$ or $C_2H_4O_2$, which is acetic acid. In a similar way all the organic acids are derived from carbonic acid.

## EXPERIMENTS.

### Fermentation.

Experiment 248.—Dissolve about 150 grams commercial grape sugar in 1½ liters of water in a flask. Connect the flask by

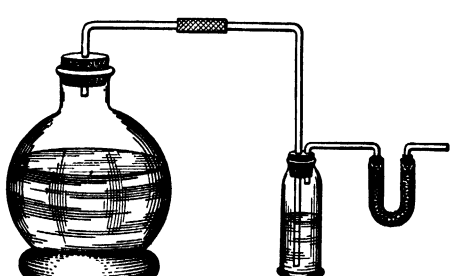


Fig. 81.

means of a bent glass tube with a cylinder or bottle containing clear lime-water. The vessel containing the lime water must be provided with a cork with two holes. Through one of these passes the tube from the fermentation-flask ; through the other a tube connected with a vessel containing solid caustic potash, the object of which is to prevent the air from acting upon the lime-water. The arrangement of the apparatus is shown in Fig. 81. Now add to the solution of grape-sugar a little fresh brewers' yeast ; close the connections and allow to stand. Soon an evolution of gas will begin, and, as this

passes through the lime-water, a precipitate will be formed which can be shown to be calcium carbonate.

## Aldehyde.

Experiment 249.—In a small flask put a few pieces of potassium bichromate, $K_2Cr_2O_7$, and pour upon it a few cubic centimeters of moderately concentrated sulphuric acid. To this mixture add slowly a few cubic centimeters of ordinary alcohol. Notice the odor.

## Soap.

Experiment 250.—Put a piece of lard the size of a grape in an evaporating-dish. Add a few (4 or 5) cubic centimeters of alcohol and 10 drops of a 50 per cent solution of sodium hydroxide. Heat gently and stir the contents of the dish. Boil until the odor of alcohol has disappeared. Evaporate to dryness. Is the residue soluble in water? If not add a little more alcohol and sodium hydroxide and repeat the boiling. The fat should be saponified and the product should be a soap.

## Hard Water.

Experiment 251.—Make some hard water by passing carbon dioxide through dilute lime-water until the precipitate first formed is dissolved again. Filter. Make a solution of soap by shaking up a few shavings of soap with water. Filter. Add the solution of soap to the hard water. Is a precipitate formed? Rub a piece of soap between the hands wet with the hard water.

Experiment 252.—Make some hard water by shaking a liter or two of water with a little powdered gypsum. Perform with it the same experiments as those first performed with the water containing calcium carbonate.

## CHAPTER XXXV.

### OTHER COMPOUNDS OF CARBON.

**The Carbohydrates.**—The carbohydrates form an important group of carbon compounds including the most abundant substances found in the vegetable kingdom. Besides carbon, they generally contain hydrogen and oxygen in the proportions to form water. Hence they are called carbohydrates. The chief compounds included under this head are *grape-sugar or glucose, cane-sugar, starch, cellulose, gum* and *dextrin.*

**Grape-sugar, Glucose, Dextrose,** $C_6H_{12}O_6$.—Dextrose occurs very widely distributed in the vegetable kingdom, particularly in sweet fruits. It is found also in honey and, further, in the liver and the blood. It is formed from several of the carbohydrates by boiling them with dilute mineral acids, or by the action of ferments. Its formation from cane-sugar takes place according to this equation, equal quantities of dextrose and levulose being formed:

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

Its formation from starch is represented by this equation:

$$\underset{\text{Starch.}}{C_6H_{10}O_5} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6}.$$

**Manufacture of Dextrose or Glucose.**—Dextrose is prepared on the large scale from corn-starch in the United States, and from potato-starch in Germany. The change is usually effected by boiling with dilute sulphuric acid. The acid is afterwards removed by treating with chalk, and filtering. The filtered solution is evaporated either to a syrupy consistency, and sent into the market under the names "glucose," "mixing-syrup," etc.; or to dryness, the solid product being known as "grape-sugar."

**Properties.**—Dextrose crystallizes from concentrated solutions, and as seen in commercial "granulated grape-sugar" looks very much like granulated cane-sugar. It is sweet, but not as sweet as cane-sugar. It is estimated that the sweetness of dextrose is to that of cane-sugar as 3:5. Under the influence of yeast it ferments, yielding mainly alcohol and carbon dioxide. Putrid cheese transforms it into lactic acid, and then into butyric acid.

**Levulose, Fruit-sugar,** $C_6H_{12}O_6$.—This form of sugar occurs with dextrose in fruits; and is formed by the action of dilute acids or ferments on cane-sugar, which breaks up according to the equation

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

As cane-sugar is found in unripe fruits, it is probable that the change represented in the equation takes place during the process of ripening.

**Cane-sugar,** $C_{12}H_{22}O_{11}$.—This well-known variety of sugar occurs very widely distributed in nature—in sugar-cane, sorghum, the Java palm, the sugar-maple, beets, madder-root, coffee, walnuts, hazel-nuts, sweet and bitter almonds; in the blossoms of many plants, etc., etc.

**Sugar-refining.**—Sugar is obtained mainly from the sugar-cane and beets. In either case the processes of extraction and refining are largely mechanical. When sugar-cane is used, this is macerated with water to dissolve the sugar. Thus a dark-colored solution is obtained. This is evaporated, and then passed through filters of bone-black by which the color is removed. The clear solution is then evaporated in open vessels to some extent; and, finally, in large, closed vessels called "vacuum-pans," from which the air is partly exhausted, so that the boiling takes place at a lower temperature than is required under the ordinary pressure of the atmosphere. The mixture of crystals and mother-liquors obtained from the "vacuum-pans" is freed from the liquid by being brought into the "centrifugals." These are funnel-shaped sieves which are revolved rapidly, the liquid being thus thrown by

centrifugal force through the openings of the sieve, while the crystals remain behind and are thus nearly dried. The final drying is effected by placing the crystals in a warm room.

**Molasses.** — The mother-liquors obtained from the "centrifugals" are further evaporated, and yield lower grades of sugar; and, finally, a syrup is obtained which does not crystallize. This is *molasses.*

**Properties of Sugar.** — Sugar crystallizes from water in large well-formed prisms. When heated to 210°-220°, it loses water, and is converted into a substance called *caramel,* which is colored more or less brown. When boiled with dilute acids, cane-sugar is split into equal parts of dextrose and levulose. The mixture of the two is called *invert-sugar.* Yeast gradually transforms cane-sugar into dextrose and levulose, and these then undergo fermentation. Cane-sugar does not ferment.

**Sugar of Milk, Lactose,** $C_{12}H_{22}O_{11}+H_2O$.—This sugar occurs in the milk of all mammals. It is obtained in the manufacture of cheese. Cow's milk consists of water, caseïn, butter, sugar of milk, and a little inorganic material, in about the following proportions:

| | |
|---|---|
| Water | 87 per cent. |
| Caseïn | 4 " |
| Butter | 3½ " |
| Sugar of milk | 4½ " |
| Mineral matter | ½ " |
| | 100 |

Cheese is made by adding rennet to milk, which causes the separation of the caseïn. The sugar of milk remains in solution, is separated by evaporation, and purified by recrystallization. It has a slightly sweet taste, and is much less soluble in water than cane-sugar.

**Souring of Milk.**—Sugar of milk ferments under certain circumstances, and is transformed mostly into lactic acid. The souring of milk is a result of this fermentation. The lactic acid formed coagulates the caseïn; hence the thickening.

**Cellulose,** $C_6H_{10}O_5$.—Cellulose forms, as it were, the groundwork of all vegetable tissues. It presents different appearances and different properties, according to the source from which it is obtained; but these differences are due to substances with which the cellulose is mixed; and when they are removed, the cellulose left behind appears to be the same thing, no matter what its source may have been. The coarse wood of trees and the tender shoots of the most delicate plants consist essentially of cellulose. Cottonwool, hemp, and flax consist almost wholly of cellulose.

**Properties.**—Cellulose does not crystallize, and is insoluble in all ordinary solvents. It dissolves in concentrated sulphuric acid. If the solution is diluted and boiled, the cellulose is converted into dextrin and dextrose. It will thus be seen that rags, paper, and wood, all of which consist largely of cellulose, might be used for the preparation of dextrose or glucose, and consequently of alcohol.

**Gun-cotton, Pyroxylin, Nitrocellulose.**—Cellulose has some of the properties of alcohols; among them the power to form ethereal salts with acids. Thus, when treated with nitric acid it forms several nitrates, just as glycerin forms the nitrate known as nitroglycerin (which see). The nitrates are explosive, and are used for blasting under the name *gun-cotton*.

**Collodion.**—A solution of gun-cotton in a mixture of ether and alcohol is known as *collodion solution*, which is much used in photography. When poured upon any surface, such as glass, the ether and alcohol rapidly evaporate, leaving a thin coating of gun-cotton. It is also used in surgery as a covering for wounds.

**Celluloid.**—Celluloid is an intimate mixture of gun-cotton and camphor. As it is plastic at a slightly elevated temperature, it can easily be moulded into any desired shape. When cooled it hardens.

**Paper.**—Paper in its many forms consists mainly of cellulose. The essential features in the manufacture of paper are, first, the disintegration of the substances used.

This is effected partly mechanically and partly by boiling with caustic soda. Then the resulting mass is converted into pulp by means of knives placed on rollers. The pulp, with the necessary quantity of water, is then passed between rollers. Rags of cotton or linen are chiefly used in the manufacture of paper; wood and straw are also used.

**Starch,** $C_6H_{10}O_5$.—Starch is found everywhere in the vegetable kingdom in large quantity, particularly in all kinds of grain, as maize, wheat, etc.; in tubers, as the potato, arrowroot, etc.; in fruits, as chestnuts, acorns, etc.

**Manufacture of Starch.**—In the United States starch is manufactured mainly from maize; in Europe, from potatoes. The processes made use of are mostly mechanical. The maize is first treated with warm water; the softened grain is then ground between stones, a stream of water running constantly into the mill. The thin paste which is carried away is brought upon sieves of silk bolting-cloth, kept in constant motion. The starch passes through with the water as a milky fluid. This is allowed to settle and the water then drawn off. The starch is next treated with water containing a little alkali, the object of which is to dissolve gluten, oil, etc. The mixture is now brought into shallow, long wooden runs, where the starch is deposited, the alkaline water running off. Finally, the starch is washed with water, and dried at a low temperature.

**Properties.**—Starch in its usual condition is insoluble in water. If ground with cold water it is partly dissolved. If heated with water the membranes of the cells of which the starch is composed are broken, and the contents form a partial solution. On cooling, it forms a transparent jelly called *starch-paste*. By dilute acids and ferments starch is converted into dextrin, maltose, and dextrose.

**Flour.**—Wheat flour, which may serve as an example of flour in general, contains water, starch with a little sugar and gum, *gluten*, and a small quantity of mineral matter. The finest flour contains about 10 per cent of gluten and

70 per cent of starch. Gluten is a substance that resembles in many respects the white of eggs, or egg-albumin.

**Bread-making.**—The chemical changes which take place in bread-making are of special interest. Bread is made by mixing the flour with water and a little yeast. The dough thus prepared is put in a warm place for a time, when it *rises*. The rising is a result of fermentation caused by the yeast. A part of the starch contained in the flour is converted into sugar, and this is then converted into alcohol and carbon dioxide by fermentation. The alcohol passes off for the most part, and the carbon dioxide in striving to escape from the thick gummy dough fills the mass with bubbles of gas, making it light and porous. When the loaf is put into the oven the gases contained in it expand, making it still lighter; then the fermentation is checked by the heat and no further chemical change takes place except on the surface, where the substances are partly decomposed and converted into a dark-colored product, the crust.

### A FEW COMPOUNDS FROM COAL-TAR.

**Aromatic Compounds.**—The fact that benzene, $C_6H_6$, toluene, $C_7H_8$, and other hydrocarbons are obtained from coal-tar has already been mentioned (p. 660). These hydrocarbons are the starting-points for the preparation of a large number of compounds of carbon which are commonly called the "aromatic compounds," as many of them have pleasant aromatic odors.

**Nitrobenzene,** $C_6H_5NO_2$.—This substance is formed by treating benzene with nitric acid:

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

It is a yellow liquid with a pleasant odor like that of the oil of bitter almonds. It is much used under the name *artificial oil of bitter almonds.*

**Aniline,** $C_6H_5NH_2$.—When nitrobenzene is treated with a solution from which hydrogen is given off the oxygen is extracted and replaced by hydrogen:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

The product is the substance known as aniline. It is a colorless liquid. When it together with a similar substance, known as toluidine, is treated with mercuric chloride, $HgCl_2$, or arsenic acid it is converted into the dye *magenta*, which is the substance from which most of the aniline dyes are prepared.

**Aniline Dyes.**—Of these a large number are in use. They are all derivatives of rosaniline, of which magenta is a salt. Aniline dyes of a great many different colors are made, some of them of great beauty.

**Phenol, Carbolic Acid,** $C_6H_6O$.—This familiar substance is contained in coal-tar, and is extracted from it by treating with caustic soda in which the carbolic acid dissolves. When pure it crystallizes in beautiful, colorless, rhombic needles. It has a peculiar, penetrating odor, and is poisonous. It is much used as a disinfectant.

**Trinitrophenol, Picric Acid,** $C_6H_3O(NO_2)_3$, is made by the action of nitric acid on phenol. Picric acid is a lemon-yellow, crystalline substance, used as a yellow dye and as an explosive.

**Explosives.**—All explosives contain nitrogen, and their explosiveness depends on the instability of compounds of nitrogen and oxygen and on the great stability of molecular nitrogen, which last—with other substances—is the product of all explosives.

Explosives are of two types, *instantaneous* and *progressive*. Suitable dilution of an instantaneous explosive renders it less violent.

The most important instantaneous explosives are nitroglycerin, dynamite in its many forms of dilution, and blasting gelatin, which is the most violent explosive known. It is made by mixing about 95 parts of nitroglycerin with 5 parts of gun-cotton; it is a gelatinous mass.

The most violent explosions are initiated by the explosion of a cap of mercury fulminate. The *character* of an explosion depends on the character of the initial shock.

*Progressive explosives* are common black gunpowder, nitro-cellulose powders, and picric acid powders. *Gunpowder* is now mostly replaced for blasting purposes by dynamite and blasting gelatin, and for cannon and small-arm purposes by the powders just mentioned.

*Nitro-cellulose powders.*—Gun-cotton is "colloided" by dissolving it in a mixture of alcohol and ether, and evaporating the solution: a tough amorphous solid or colloid remains. This in granulated form is a "*smokeless powder*."

As nitro-cellulose has too little oxygen to oxidize the carbon completely, either nitro-glycerin or metallic nitrates are generally added to supply the oxygen, in making smokeless powders.

*Cordite*, the English smokeless powder, is a mixture of colloided gun-cotton with nitroglycerin and vaseline. The smokeless powder used for small-arms by the army of the United States contains colloided gun cotton and potassium nitrate or barium nitrate.

Picric acid and ammonium picrate are also utilized as smokeless powders. The French mellinite and the English lyddite * are both chiefly picric acid.

**Oil of Bitter Almonds, Benzoic Aldehyde,** $C_7H_6O$.—This substance occurs in combination with amygdalin, which is found in bitter almonds, laurel-leaves, cherry-kernels, etc. Amygdalin belongs to the class of compounds known as *glucosides*, which break up into glucose and other substances. Amygdalin itself, under the influence of *emulsin*, which occurs with it in the plants, breaks up into oil of bitter almonds, hydrocyanic acid, and glucose:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\substack{\text{Oil of}\\\text{bitter}\\\text{almonds}}}{C_7H_6O} + \underset{\substack{\text{Hydrocy-}\\\text{anic acid}}}{CNH} + \underset{\text{Glucose}}{2C_6H_{12}O_6}.$$

It is prepared from bitter almonds, which yield about 1.5 to 2 per cent. It is a liquid with a pleasant odor. It is made artificially from coal-tar, and was at one time used in the artificial preparation of indigo.

**Benzoic Acid,** $C_7H_6O_2$.—Benzoic acid occurs in gum benzoin and in the balsams of Peru and Tolu, and is made artificially from coal-tar by oxidizing toluene,† $C_7H_8$.

**Balsams and Odoriferous Resins.**—The balsams of Peru and Tolu are thick fragrant fluids which are obtained from certain trees in South America and elsewhere by cutting the bark. Benzoin is a similar substance. These as well as myrrh, frankincense, and other substances of the kind are used for their odors. The odors are intensi-

* In the last war in South Africa after some of the battles the hands and faces of the combatants were seen to be colored yellow. This must have been due to the picric acid contained in the lyddite used by the English.

† The name toluene comes from the fact that this hydrocarbon was first obtained from the balsam of Tolu.

fied when the substances are heated. They are largely used as *incense.*

**Gallic Acid,** $C_7H_6O_5$.—Gallic acid occurs in sumach, in Chinese tea, and many other plants. It is formed by boiling tannin or tannic acid with sulphuric acid. It is prepared from gall-nuts by fermentation of the tannin contained in them. It is closely related to tannin or tannic acid.

**Tannic Acid, Tannin,** $C_{14}H_{10}O_3$.—This substance occurs in gall-nuts, from which it is readily extracted. It is soluble in water. Its solution gives a dark, blue-black color with iron salts. Tannin is used extensively in medicine, in dyeing, in the manufacture of leather and of ink.

**Tanning.**—The process of tanning consists in treating hides, from which the hair has been removed, with an infusion of hemlock or oak bark, or of sumach-leaves, in which there is tannic acid. The acid combines with certain parts of the hides, forming insoluble compounds which remain in the pores, converting the hides into leather.

**Indigo.**—In several plants which grow in the East and West Indies, in South America, Egypt, and other warm countries, a substance called *indican* occurs. When this is treated with dilute mineral acids or certain ferments, it breaks up into indigo-blue and a substance resembling glucose. The principal ingredient of commercial indigo is indigo-blue. Indigo-blue is now prepared artificially by a somewhat complicated method.

**Naphthalene,** $C_{10}H_8$.—This hydrocarbon is contained in coal-tar in large quantity. It is a beautiful, white, crystallized substance much used in the preparation of dyes and for protecting woollen fabrics from moth, the well known moth balls consisting of impure naphthalene.

**Anthracene,** $C_{14}H_{10}$.—Anthracene like naphthalene is obtained from coal-tar. Its chief use is in the preparation of artificial alizarin.

**Alizarin,** $C_{14}H_8O_4$.—Alizarin is the well-known dye obtained from madder-root. For some years it has been

made artificially from anthracene, and the cultivation of madder has been given up. Madder-root was used for dyeing "Turkey-red." Artificial alizarin is almost exclusively used for this purpose at present.

**Glucosides.**—Glucosides are substances that occur in nature in the vegetable kingdom. They break down into sugar and other compounds under the influence of ferments and dilute acids. Amygdalin has already been mentioned. This breaks down into oil of bitter almonds and dextrose. Indican, which yields indigo and dextrose, is another example.

**Myronic Acid,** another glucoside, is found in the form of the potassium salt in black mustard-seed. When treated with myrosin, which is contained in the aqueous extract of white mustard-seed, potassium myronate is converted into dextrose and oil of mustard.

**Alkaloids.**—These compounds occur in plants, and are frequently the parts of the plants which are most active when taken into the animal body. They are hence sometimes called the *active principles* of plants. Many of these substances are used in medicine. They all contain nitrogen and in some respects resemble ammonia. Only a few of the more important alkaloids need be mentioned here.

**Quinine.**—This valuable alkaloid is obtained from the outer bark of certain trees which grow in Peru. The bark is known as Peruvian bark.

**Cocaine** is found in cocoa-leaves. Its hydrochloride has come into prominence in medicine, owing to the fact that a small quantity of its solution placed upon the eye or the gums or injected beneath the skin causes insensibility to pain.

**Nicotine** occurs in tobacco-leaves in combination with malic acid.

**Morphine, Codeine** and **Narcotine** are the principal alkaloids found in *opium*, which is the evaporated sap that flows from incisions in the capsules of the white poppy before they are ripe.

# INDEX.


Acetone, 357.
Acetylene, 364, 662, 664; series, 662.
Acheson process, 356.
Acid, 168.
Acid, acetic, 357, 660, 668; antimonic, 335; arsenic, 329; arsenic, experiments with, 351; arsenious, 330; benzoic, 684; bichromic, 603; boric, 344; bromic, 204; butyric, 669; carbolic, 683; carbonic, 373; chloric, 156, 158; chloric, experiments with, 160; chlorous, 158; chlorplatinic, 657; chlorsulphuric, 255; chromic, 603, 607; chromic, experiments with, 616; citric, 671; cyanic, 390; disilicic, 405; disulphuric, 247; dithionic, 249; diuranic, 614; ferric, 628; ferrihydrocyanic, 640; ferrohydrocyanic, 640, 641; fluosilicic, 401; fluosilicic, preparation of, 408; formic, 668; fuming sulphuric, 247; gallic, 685; hydrazoic, 290; hydriodic, 207; hydrobromic, 202; hydrobomic, experiments with, 216; hydrochloric, 56, 137; hydrochloric, experiments with, 146; hydrochloric, formation of, 146; hydrochloric, preparation of, 146; hydrocyanic, 389; hydrofluoric, 212; hydrofluoric, experiments with, 219; hydronitric, 290; hydrosulphurous, 249; hypobromous, 204; hypochlorous, 157; hyponitrous, 296; hypophosphoric, 326; hypophosphorous, 327; hyposulphurous, 249; iodic, 208; iodic, experiments with, 218; lactic, 671; malic, 671; manganic, 214, 617, 623; metaaluminic, 532; metaboric, 344; metachromous, 604; metantimonic, 312, 335; metaphosphoric, 312, 325; metarsenic, 312, 329; metastannic, 588, 591; metavanadic, 342; molybdic, 612; muriatic, 56; myronic, 686; nitric, 56, 291; nitric, experiments with, 304; nitric, preparation of, 304; nitric, red fuming, 295; nitric, reduction of, 305; nitrohydrochloric, 295; nitrosylsulphuric, 239; nitrous, 295; nitrous, experiments with, 306; nitrous, normal, 296; Nordhausen sulphuric, 247; oleic, 672; orthoantimonic, 311, 335; orthoarsenic, 311; orthoboric, 344; orthophosphoric, 311, 321; orthovanadic, 342; osmic, 654; oxalic, 670; palmitic, 669; pentathionic, 249; perbromic, 264; perchloric, 157; perchloric, preparation of, 161; perchromic, 618; periodic, 210; permanganic, 214, 617, 624; persulphuric, 250; perthiosulphuric, 233; phosphomolybdic, 612; phosphoric, 321; phosphoric, experiments with, 348; phosphoric, gla-

cial, 325; phosphoric, "insoluble," 510; phosphoric, "reverted," 510; phosphoric, "soluble," 510; phosphorous, 326; picric, 683; propionic, 669; prussic, 389; pyroantimonic, 312, 335; pyroarsenic, 312, 329; pyroligneous, 357, 660, 668; pyrophosphoric, 312, 325; pyrosulphuric, 247; pyrovanadic, 342; selenic, 256; selenous, 256; silicic, 403; silicic, experiments with, 409; silicic, insoluble, 405; silicic, normal, 403; stannic, 590; stearic, 669; sulphantimonious, 338; sulpharsenious, 332; sulphocyanic, 391; sulphuric, 56, 237; sulphuric, experiments with 258 sulphuric, normal, 247; sulphuric, solid, 247; sulphurous, 248; sulphurous, experiments with, 259; sulphydric, 232; tannic, 685; tartaric, 671; telluric, 257; tellurous, 256; tetraboric, 344, 484; tetrahydroxylsulphuric, 246; tetrathionic, 249; thiosulphuric, 249; triazoic; 290; trithionic, 249; tungstic, 613; vanadic, 342.
Acids, 107, 162; basicity of, 172, 176; constitution of, 170; definition of, 168; dibasic, 173; fatty, 669; monobasic, 173; nomenclature of, 182; organic, 675; pentabasic, 173; polyphosphoric, 326; polysilicic, 405; polystannic, 591; salt, 173; strength of, 180; tetrabasic, 173; tribasic, 173; trisilicic, 406.
Acids of antimony and arsenic, constitution of, 311.
Acids of chlorine, 158.
Acids of nitrogen, 281.
Acids of phosphorus, constitution of, 311.
Acids of sulphur, constitution of, 238.
*Acidum phosphoricum glaciale*, 325.
Acker process, 477.
Actinium, 616.
Affinity, chemical, 9; coefficients of, 419.
Agate, 402.
Air, 265; analysis of, 266, 276; and life, 271; pure, 272; impure, 272.
Air-gas, 378.
Alabandite, 622.
Alabaster, 507.
Albite, 474. 537.
Alcohol, 660; denatured, 666; ethyl, 665; methyl, 357, 660, 665.
Alcohols, 665, 674.
Aldehyde, acetic, 667, 676; benzoic, 684; formic, 667.
Aldehydes, 667.
Algaroth, powder of, 339.
Alizarin, 685.
Alkalies, 162, 443.
Alkali metals, 460.
Alkaline earths, 497.
Alkaloids, 686.
Allanite, 600.
Allotropy, 123.
Allylene, 662.
Alum, 461, 535; burnt, 536; shale, 536.
Aluminates, 531.
Aluminium, 527; alloys, 540; bronze, 530, 547; chloride. 530; chloride, preparation of, 542; hydroxide, 531; oxide, 533; silicates, 537; sulphate, 534.
Alums, 534.
Alunite, 536.
Amalgamation process for silver, 554.
Amalgams, 577.
Amethyst, 402.
Amides, metal, 286.
Ammonia, 279, 281, 282; composition of, 286; determination of composition of, 303;

experiments with, 301; preparation of, 301; process for soda, 483.
Ammoniacal liquor, 282, 361, 488.
Ammonium alum, 537; amalgam, 289, 577; chloride, 282, 488; chlorostannate, 590; diuranate, 615; group, 284; hydrosulphide, 490; hydroxide, 285; nitrate, 490; magnesium arsenate, 525; magnesium phosphate, 324, 525; phospho-molybdate, 612; salts, 284, 486; salts, formation of, 302; sodium phosphate, 324; sulphate, 282, 490; sulphide, 488; sulphide group, 230, 488; sulphide, yellow, 490.
Ampere, 150; his hypothesis, 88.
Amygdalin, 684.
Anatase, 399, 406.
Anhydrides, 209.
Anhydrite, 507.
Aniline, 682; dyes, 683.
Anions, 149.
Annealing of glass, 514; of iron, 637.
Anode mud, 545.
Anthracene, 660, 685.
Antimony, 332; acids of, 311; and its compounds, experiments with, 351; blende, 337; oxychlorides, 339; oxychlorides, experiments with, 352; pentachloride, 338; pentasulphide, 338; pentoxide, 337; salts of, 336; sulphides, experiments with, 352; tetroxide, 337; trichloride, 338; trioxide, 335; trisulphide, 337.
Antimonyl salts, 336; sulphate, 336.
Apatite, 314, 508.
Aqueous tension, 47.
*Aqua regia*, 295.
Aragonite, 505.
*Arbor Saturni*, 594.
Argentic chloride, 558; nitrate, 560.
Argentous chloride, 557.
Argon, 274.
Aromatic compounds, 682.
Arrhenius, 424.
Arsenic, 321; acids of, 311; and its compounds, experiments with, 350; disulphide, 331; pentasulphide, 332; pentoxide, 331; sulphides, experiments with, 351; trichloride, 332; trioxide, 330; trioxide, experiments with, 351; trisulphide, 332.
Arsenical pyrites, 328.
Arsenides, 327.
Arseniuretted hydrogen, 328.
Arsenopyrite, 645.
Arsine, 328, 350.
Atomic theory, 83, 410; weights, 16, 19, 86; weights and specific heat, 426.
Atoms, 83, 88, 410.
Aurates, 562.
Aureoline, 127.
Auric chloride, 565; compounds, 561; hydroxide, 561; oxide, 561.
Aurous chloride, 565; compounds, 561; oxide, 561; sulphide, 565.
Avogadro's hypothesis, 88.
Azote, 262.

Babbitt's metal, 595.
Baking powders, 484.
Balsams, 684.
Banca tin, 588.
Barff's process, 638.
Barite, 517, 519.
Barium, 517; carbonate, 519; chloride, 518; chromate, 610; dioxide, 518; ferrocyanide, 640; hydroxide, 518; oxide, 518; peroxide, 518; phosphates, 520; sulphate, 519; sulphide, 519.
Barometer vacuum, 117.
Barytes, 452.
Base, 168.

Bases, 107, 162, 168; acidity of, 173; constitution of, 170; definition of, 168; diacid, 173; monacid, 173; nomenclature of, 183; triacid, 173.
Basic-lining process, 635.
Battery, storage, 597.
Bauxite, 528.
Bell-metal, 547.
Bengal-fire, 517.
Benzene, 334, 660, 662, 682; series, 662.
Benzine, 661.
Benzoin, 684.
Berthollet, 129.
Beryl, 521.
Beryllium, see Glucinum.
Bessemer process, 634.
Binary compounds, 434, 449.
Birkeland, 292.
Bismuth, 339; and its compounds, experiments with, 352; basic nitrates of, 340; dichloride, 341, 352; dioxide, 341; nitrate, 339; oxychloride, 341; pentoxide, 341; peroxide, 341; salts, 340; subnitrate, 340; sulphate, 339; trichloride, 341; trioxide, 340; trisulphide, 341.
Bismuthyl salts, 340.
Blast furnace, 630.
Black ash, 482.
Black-lead, 355.
Bleach, 503.
Bleaching by chlorine, 133; by sulphur dioxide, 252; powder, 157, 502.
Block-tin, 588.
Blowpipe, 385; experiments with, 393.
Bluestone, 549.
Blue vitriol, 549, 550.
Bog iron ore, 642.
Bone-black, 359; filters, 360, 365.
Bone-oil, 660.
Bones, distillation of, 660.
Bonds, 96.
Boracite, 344, 525.
Borax, 344, 484; anhydrous calcined, 485.
Borocalcite, 344, 516.
Boron, 342; experiments with, 352; hydride, 343; nitride, 343, 345; phosphate, 345; salts of, 345; trichloride, 343.
Boryl potassium tartrate, 345.
Boussingault, 268.
Boyle's law, 42, 45.
Brass, 546, 571.
Braunite, 618, 620.
Bread-making, 682.
Bricks, 540.
Brimstone, 222, 223.
Britannia metal, 333, 589.
Bromides, experiments with, 456.
Bromine, 201; hydrate, 202; preparation of, 216; water, 202.
Bronze, 547, 589.
Brookite, 399, 406.
Brown iron ore, 630, 642.
Bumping, 105.
Bunsen, 268, 473, 494.
Bunsen burner, 387.
Burning, 36.
Butane, 662.
Butter, 673; of antimony, 338.
Butylene, 662.
*Butyrum Antimonii*, 338.

Cadmium, 574; carbonate, 575; chloride, 574; sulphate, 574; sulphide, 575.
Cæsium, 473.
Calcium, 499; borates, 516; carbide, 516; carbonate, 505; chloride, 500; chloride, preparation of, 526; cyanamide, 515; fluoride, 501; hydroxide, 501; manganite, 622; nitride, 516; oxide, 501; phosphates, 508; salts, experiments with, 526; silicate, 511; sulphate, 507; sulphide, 515.
Calc-spar, 367, 505.
Calomel, 578.
Calorie, 40.
Calorimeter, 40.
Calorimetric value, 379.

Candle, standard, 382.
Cane-sugar, 678.
Caramel, 679.
Carat, 565.
Carbohydrates, 677.
Carbon, 353; experiments with, 365; amorphous, 356; bisulphide, 390; chemical conduct of, 362; dioxide, 367; dioxide, experiments with, 378; dioxide, relations to life, 372; experiments on reducing power of, 366; monoxide, 375; monoxide, experiments with, 379; silicide, 407.
Carbonates, 373, 454; acid, 374; experiments with, 459; normal, 374; primary, 374; secondary, 374.
Carbonyl chloride, 377.
Carborundum, 407.
Carnallite, 202, 461, 463, 465, 473, 522.
Carnelian, 402.
Caro's reagent, 250.
Cassiterite, 587, 591.
Cast iron, 632; gray, 632; white, 632.
Catalyser, 78.
Catalysis, 77; negative, 79.
Catalytic action, 78.
Cations, 149.
Caustic potash, 464; soda, 478.
Cavendish, 54.
Celestite, 516, 517.
Celluloid, 680.
Cellulose, 677, 680.
Cement steel, 637.
Cementite, 636.
Cements, 515; hydraulic, 515; Portland, 515.
Cerite, 600.
Cerium, 399, 600, 601.
Cerussite, 593.
Chalcedony, 402.
Chalcocite, 544, 552.
Chalk, 367, 499, 505, 506.
Chance process for recovery of sulphur, 482.
Charcoal, 356; absorption of gases by, 359, 365; animal, 359; filters, 359.
Charcoal-kiln, 357.
Charring process, 356.
Chemical action, 7, 29.
Chemical analysis, 658.
Chemical change, 2; caused by heat, 26; by electric current, 27.
Chemical energy, 41.
Chemical equations, 22.
Chemical reactions, 22; cause of, 416; kinds of, 413; ideal, 417.
Chemical work, 41.
Chemistry, 3; organic, 354, 659.
Chili saltpetre, 205, 291, 292, 466, 478.
Chloral, 667; hydrate, 668.
Chlorates, 452.
Chlor-aurates, 562.
Chlorides, 132, 134, 436; double, 440; experiments with, 456; general properties of, 439.
Chlorination process, 563.
Chlorine, 129; acids of, 158; dioxide, 159; experiments with, 145; preparation of, 131; heptoxide, 159; hydrate, 136, 146; liquid, 136; monoxide, 159; trioxide, 159.
Chloro-acids, 440.
Chloroform, 664.
Chlorostannates, 590.
Chlorplatinates, 657.
Choke-damp, 372.
Chromates, 607; experiments with, 616.
Chrome alums, 606.
Chrome iron ore, 603.
Chrome yellow, 611.
Chromic chloride, 604; compounds, 603; hydroxide, 605; iron, 533, 603; oxide, 606; sulphate, 606.
Chromite, 533, 603.
Chromites, 605.
Chromium, 257, 602; trioxide, 609.
Chromous compounds, 603.
Chrysoberyl, 532

Cinnabar, 576, 581.
Clay, 397, 528, 538.
Coal, 360; anthracite, 360; bituminous, 360; distillation of, 659; hard, 360; soft, 360.
Coal-gas, 381, 392.
Coal-tar, 361, 659.
Cobalt, 646; sulphide, 648.
Cobaltic hydroxide, 647; oxide, 647.
Cobaltite, 647, 648.
Cobaltous chloride, 647; cyanide, 648; hydroxide, 649.
Cocaine, 686.
Codeine, 686.
Coke, 358.
Colemanite, 344, 516.
Collodion, 680.
Colloid, 405.
Colloidal solution, 405.
Columbite, 342.
Columbium, 342.
Combination, 8, 22; by volume, law of, 77; direct, 413.
Combining weights, 15, 16, 86.
Combustion, 37; experiments on, 52.
Compound, chemical, 8, 10, 28.
Concentration, 109.
Concrete, 515.
Conductivity, 178.
Conductor, 148.
Condy's liquid, 626.
Constitution, 94, 412.
Constitutional formulas, 94.
Contact action, 78.
Copper, 543; and its salts, experiments with, 566; acetate, 669; alloys, 546; basic carbonate, 551; metallurgy of, 544; native, 544; plating, 552; pyrites, 446, 544, 552; ruby, 544, 548.
Copperas, 644.
Coral, 499.
Cordite, 684.
Corrosive sublimate, 579.
Corundum, 533.
Cotunnite, 595.
Coulomb, 150.
Critical points, 43.
Crocoisite, 593, 604.
Cryolite, 212, 474, 528.
Crystalloid, 405.
Cupric arsenite, 551; carbonates, 551; chloride, 548; hydroxide, 549; nitrate, 551; oxide, 549; sulphate, 549; sulphide, 552.
Cuprite, 548.
Cuprous chloride, 547; chloride, preparation of, 566; hydroxide, 548; oxide, 548; sulphide, 551.
Cyanides, 389, 391.
Cyanogen, 388; constitution of, 391; experiments with, 395.

Dalton, 13; his atomic theory, 83; his law, 45.
Daniell cell, 570.
Datholite, 344.
Davy, 129, 462.
Deacon's process, 130.
Decomposition, 8, 23; direct, 415; double, 23, 413, 415.
Decrepitation, 476.
De la Bastie glass, 514.
Deliquescence, 107, 116.
Dephlogisticated muriatic acid, 129.
Developers in photography, 559.
Dextrin, 677.
Dextrose, 677.
Dialyser, 404.
Dialysis, 404.
Diamond, 355.
Diaspore, 531.
Didymium, 342, 601.
Diffusion, 58; experiments on, 69.
Dimorphism, 224.
Dissociation, 105, 320, 421; electrolytic, 166, 423; of dissolved substances, 166, 424.
Distillation, 116; destructive, 357; dry, 357.
Dolomite, 367, 521.
Double chloride, 440.
Dowson gas, 378.
Drinking-water, bad, 114.
Drummond light, 79.

Dulong, 429.
Dumas, 268; his study of combustion of hydrogen, 72; method for determining the specific gravity of vapors, 98.
Dyes, adjective, 536; substantive, 536.
Dynamite, 673.

Earthenware, 540.
Efflorescence, 107, 116, 479.
Eka-aluminium, 584.
Eka-boron, 541.
Eka-silicon, 587.
Electric current, 148; energy required to electrolyze different electrolytes, 208; units, 150.
Electrodes, 149.
Electrolysis, 148, 423; primary and secondary products of, 151.
Electrolytes, 149.
Electrolytic dissociation, 166, 423.
Electrolytic process for chlorine, 131.
Electromotive force, 570.
Electro-negative ions, 166.
Electrons, 86.
Electro-positive ions, 166.
Electrotypes, 552.
Elements, 6, 16; acid-forming, 144; base-forming, 144, 169; replacing power of, 96; symbols of, 16, 19.
Emanation, 616.
Emerald, 521.
Emery, 533.
Emulsin, 684.
Energy, 1; chemical, 41; conservation of, 5; stored up in plants, 373.
Enstatite, 405.
Epsom salt, 521, 524.
Equations, chemical, 22.
Equilibrium, 419.
Erbium, 526.
Essence of apples, 673; of pineapples, 673.
Esters, 672.
Etching on glass, 213, 219.
Ethane, 662.
Ether, 671.
Ethereal salts, 672.
Ethers, 671.
*Ethiops martialis*, 582.
Ethylene, 364, 662, 664; series, 662.
Eudiometer, 73.
Eudiometric method, 73, 268; experiments, 82.
Euxenite, 541.
Eyde, 292.
Explosives, 683.

Faraday, 136; his laws, 150, 151.
Fats, 672.
Feldspar, 406, 455, 461, 528, 537.
Ferment, butyric-acid, 669; lactic-acid, 671; nitrifying, 291.
Fermentation, 660, 666, 675; acetic-acid, 666; alcoholic, 666; lactic-acid, 666.
Ferric chloride, 639; chloride, preparation of, 651; compounds, 628; ferrocyanide, 640, 641; hydroxide, 642; hydroxide, soluble or colloidal, 643; oxide, 643; phosphate, 645; sulphate, 645; sulphate, preparation of, 651.
Ferri-potassium ferrocyanide, 640.
Ferrochromium, 604.
Ferrous ammonium sulphate, preparation of, 651; carbonate, 644; chloride, 639; compounds, 628; ferricyanide, 640, 641; hydroxide, 641; phosphate, 645; sulphate, 644; sulphate, preparation of, 651; sulphide, 643.
Ferrous-ferric oxide, 642.
Fertilizers, 511.
Fire-damp, 662.
Flame, 382; oxidizing, 384; reactions, 492; reducing, 384.
Flames, 382; luminosity of,

386; structure of, 384.
Flash light, 522.
Flint, 402.
Flint-glass, 513.
*Flores zinci*, 572.
Flour, 681.
Fluorine, 211.
Fluor spar, 212, 499, 501.
Flux, 212, 501, 507.
Fool's gold, 645.
Formal, 667.
Formalin, 667.
Formulas, constitutional, 94; molecular, 93, 411.
Frank, 515.
Frankincense, 684.
Franklinite, 568, 642.
Frazer, 426.
Fruit-sugar, 678.
Fuel gases, 377.
Fulminating mercury, 582.
Fumaroles, 344.
Fusel oil, 666.

Gadolinite, 541, 600.
Gahnite, 532, 568.
Galena, 593, 598.
Galenite, 446, 554, 593, 598.
Gallium, 584.
Galvanized iron, 571.
Garnet, 511.
Gas, normal, 90.
Gases, kindling temperature of, 382, 392; measurement of volume of, 44.
Gasoline, 661.
Gay-Lussac, 45, 129; law of, 43; tower, 241.
Generator gas, 378.
German silver, 547, 649.
Germanium, 587; chloride, 587.
Gersdorffite, 649.
Glass, 512; Bohemian, 513; Jena, 513.
Glauber, 137, 478.
Glauber's salt, 479.
Glover tower, 240.
Glucinum, 521.
Glucose, 677.
Glucosides, 684, 686.
Gluten, 681.
Glycerin, 667.
Gold, 561; alloys, 565; amalgam, 565, 578; colloidal, 565; metallurgy of, 562; plating, 566; sulphide, 565.
Goldschmidt's welding process, 530.
Graham, 61.
Gram-molecular weights, 164.
Granite, 537.
Grape-sugar, 677.
Graphite, 355.
Greenockite, 574.
Green vitriol, 550, 644.
Guldberg, 418.
Gum, 677.
Gun-cotton, 680.
Gun-metal, 547.
Gunpowder, 467.
Gypsum, 452, 499, 507.

Halogens, 200.
Hardness, permanent, 506, 508, 669; temporary, 506, 669.
Hard water, 506; experiments with, 676.
Hauerite, 622.
Hausmannite, 618, 620.
Heat of combustion, 39; of condensation of steam, 105; of decomposition, 41; of fusion of ice, 105; of neutralization, 167; of vaporization of water, 105; specific, law of, 427.
Heavy spar, 452, 517, 519.
Helium, 275, 616.
Hematite, 630, 643.
Heptane, 662.
Hexane, 662.
Homologous series, 662.
Homology, 662.
Hornblende, 521.
Horsetail, 402.
Hydragillite, 531.
Hydrates, 106, 183; vapor pressure of, 106.
Hydraulic cement, 515; mining, 562.
Hydrazine, 281, 290.
Hydrocarbons, 364, 660; experiments with, 366; for-

mation of, 659; substitution products of, 663.
Hydrochloric acid hydrate, 141.
Hydrogen, 54; amount evolved when a known weight of a metal is dissolved in an acid, 66; burning of, 72; chemical properties of, 59, 69; dioxide, 125; dioxide, experiments with, 127; peroxide, 125; persulphide, 233; preparation of, 63; sulphide, 227; sulphide, experiments with, 235; sulphide group, 230; sulphide in chemical analysis, 230.
*Hydrogenium*, 61.
Hydrogen-valence, 196.
Hydrolysis, 175.
Hydrosulphides, 232, 448.
Hydroxides, 107, 443; experiments with, 457; formation from oxides, 254.
Hydroxyl, 674.
Hydroxylamine, 281, 290.
Hydroxyl-ammonium salts, 290.
Hypochlorites, 452.

Iceland spar, 505.
Ice-machine, 283.
Illuminants, 388.
Illuminating gas, 381.
Illumination, 381.
Incense, 685.
Indican, 685.
Indigo, 685.
Indium, 584.
Infusorial earth, 402, 673.
Ink, sympathetic, 647.
Invert-sugar, 679.
Iodic anhydride, 209.
Iodides, experiments with, 456.
Iodine, 204; bromide, 211; chloride, 211; experiments with, 217; pentoxide, 209; trichloride, 211; starch test for, 218; tincture of, 206.
Iodoform, 664.
Ionisation, 149; measurement of, 178; of bases, 177; of salts, 171.
Ions, 111, 149, 166.
Iridium, 654; chloride, 654.
Iron, 629; allotropic forms of, 636; disulphide, 645; galvanized, 571; metallurgy of, 630; ores, 630; pyrites, 446, 645.

Kainite, 465, 471, 521.
Kaolin, 528, 538.
Kelp, 205.
Kerosene, 661.
Kieserite, 465, 479, 521, 523.
Kindling temperature, 37; of gases, 382, 392.
Kinetic theory of gases, 42; applied to liquids, 103.
King's yellow, 332.
Kipp's apparatus, 50.
Kirchhoff, 473, 494.
Knietsch, 243.
Krypton, 275.

Lactose, 679.
Lamp-black, 358.
Lanthanum, 542, 600.
*Lapis lazuli*, 539.
Laughing-gas, 297.
Lavoisier, 32, 266.
Laws of Bunsen and Kirchhoff, 494; of Charles, 45; of combination by volume, 77; of conservation of energy, 5; of definite proportions, 12 410; of Dulong and Petit, 429; of indestructibility of matter, 4, 410; of multiple proportions, 13, 410; of specific heats, 427.
Lea, 556.
Lead, 592; and its compounds, experiments with, 601; acetate, 668; carbonate, 598; chloride, 595, 601; chromate, 611; iodide, 595, 601; metallurgy of, 593; molybdate, 612; nitrate, 598; oxide, 595; peroxide, 596, 601; sesquioxide, 595; suboxide, 595; sugar of, 596, 668; sulphate, 599; sulphide, 446,

598; tetrachloride, 595; tree, 594.
Lead-pencils, 355.
Le Blanc process for soda, 481.
Leonite, 471.
Lepidolite, 473, 486.
Levulose, 678.
Lewes, 387.
Lignite, 360.
Lime, 501; air-slaked, 501; chloride of, 157, 503; slaked, 501; superphosphate of, 509.
Lime-kiln, 501.
Lime-light, 79.
Limestone, 367, 499, 505.
Lime-water, 501.
Linking of atoms, 412.
Linnæite, 648.
Liquid-oxygen, 120.
*Liquor Ferri chlorati*, 639; *Ferri sesquichlorati*, 639.
Litharge, 595.
Lithium, 486; carbonate, 486; chloride, 486; phosphate, 486.
Loadstone, 642.
Lubricating oils, 661.
Lunar caustic, 560.
Lydite, 684.

Magenta, 683.
Magnalium, 540.
Magnesia, 523; *alba*, 524; *usta*, 523.
Magnesio-ferrite, 533.
Magnesite, 521, 524.
Magnesium, 521; and its salts, experiments with, 526; borates, 525; carbonate, 524; chloride, 523; chloride, preparation of, 526; hydroxide, 523; nitride, 525; oxide, 523; phosphates, 525; silicates, 525; silicide, 525; sulphate, 523.
Magnetic oxide of iron, 533, 642.
Magnetite, 533, 630, 642.
Malachite, 544, 551.
Malaria, 273.
Manganates, 623.
Manganese, 214, 617; and its compounds, experiments with, 627; black oxide of, 214, 618, 620; dioxide, 214, 618, 620; disulphide, 622; heptoxide, 216, 626; salts, preparation of, 627; tetrachloride, 619; tetrafluoride, 619; trichloride, 619.
Manganic compounds, 617; oxide, 620; sulphate, 522.
Manganite, 618, 620.
Manganous chloride, 618, 627; compounds, 617; hydrosulphide, 622; hydroxide, 620; sulphate, 622; sulphide, 622.
Manganous-manganic oxide, 620.
Marble, 367, 499, 505.
Marcasite, 645.
Marl, 506, 538.
Marsh-gas, 364, 662.
Marsh's test for arsenic, 334, 351.
Mass action, 418.
Mass, influence of, 418.
Matches, safety, 318, 469.
Matte, 544.
Matter, 1; composition of, 5; law of indestructibility of, 4, 410.
Meerschaum, 521.
Mellinite, 684.
Mendeléeff, 187, 541, 584, 587; tables of, 188, 189.
Mercuric chloride, 579; compounds, 567, 575; cyanide, 582; diammonium chloride, 583; iodide, 580; nitrate, 582; nitrate, preparation of, 585; oxide, 581; sulphide, 581.
*Mercurius solubilis Hahnemanni*, 583.
Mercurous ammonium chloride, 583; chloramide, 583; chloride, 578; compounds, 567, 575; iodide, 580; nitrate, 582; nitrate, preparation of, 585.
Mercury, 575; and its salts, experiments with, 585; metallurgy of, 576.

Meta-arsenates, 329.
Metallic properties, 431.
Metallurgy, 433.
Metals, 144, 169, 431; properties, 434.
Metaphosphates, 324, 445.
Metastannates, 591.
Metathesis, 23, 415.
Meteorites, 629, 649.
Methane, 364, 662; series, 662.
Meyer, Lothar, 187, 541; natural system of elements, 191.
Meyer, Victor, method for determining the specific gravity of vapors, 99.
Mica, 511, 528, 537.
Microcosmic salt, 490.
Milk, souring of, 679.
Minerals, 433.
Miner's safety lamp, 383, 663.
Minium, 597.
Mixing syrup, 677.
Mixtures, mechanical, 10, 28.
Moissan, 355, 449, 451.
Molasses, 679.
Molecular formulas, 93, 411; weights, 89.
Molecules, 88, 411.
Molybdates, 612.
Molybdenite, 612.
Molybdenum, 257, 611.
Morley's determination of the ratio between the atomic weights of hydrogen and oxygen, 73.
Morphine, 686.
Morse, 426.
Mortar, 514.
Mosaic gold, 592.
Murium, 129.
Myrosin, 686.
Myrrh, 684.

Naphtha, 661.
Naphthalene, 660, 685.
Narcotine, 686.
Nascent state, 124.
Neodymium, 342, 601.
Neon, 275.
Neutralization, 162; experiments on, 185.
Newton's metal, 340.
Niccolite, 649.
Nickel, 648; alloys, 649; carbonyl, 650; cyanide, 649; plating, 649.
Nickelic hydroxide, 649.
Nickelous hydroxide, 649; oxide, 649.
Nicotine, 686.
Niobium, 342.
Nitrates, 451; formation of, 280; formation of, in the soil, 280, 291.
Nitre, 262.
Nitric oxide, 298; experiments with, 307.
Nitrides, 286.
Nitrification, 291.
Nitrifying ferment, 291.
Nitrobenzene, 682.
Nitrocellulose, 680; powders, 683.
Nitrogen, 262; acids of, 281; boride, 345; experiments with, 275; iodide, 301; oxides, 281; pentoxide, 300; peroxide, 299; peroxide, experiments with, 308; preparation of, 263, 275; relations to life, 271; trichloride, 301; trioxide, 299; trioxide, experiments with, 308.
Nitroglycerin, 673.
Nitrosyl chloride, 295.
Nitrous oxide, 297; experiments with, 307.
Non-metals, 144, 431.

Octane, 662.
Oil of bitter almonds, 684; artificial, 682.
Olefiant gas, 364, 664.
Oleomargarin, 673.
Oleum, 247.
Olivine, 525.
Opal, 402.
Open-hearth furnace, 635.
Opium, 686.
Ores, 433.
Orpiment, 328, 332.
Orthoclase, 406.
Osmium, 654; peroxide, 654.

Osmond, 636.
Osmotic pressure, 425.
Oxidation, 441; slow, 38.
Oxides, 42, 441; acidic, 209; basic, 209.
Oxidizing agent, 61.
Oxone, 34, 478.
Oxygen, 32; amount liberated from a known weight of potassium chlorate, 48; and acid properties, 181; burning of, 59, 392; chemical properties of, 35, 51; physical properties of, 35, 50; preparation of 43.
Oxygen-valence, 196.
Oxyhydrogen light, 79, 82; blowpipe, 79, 82.
Ozone, 118; in the air, 122.
Ozone-water, 120.

Palladium, 654.
Palladium-hydrogen, 654.
Paper, 680.
Paraffin, 661.
Paraldehyde, 667.
Paris green, 551.
Park's method of separating silver from lead, 554.
Passive state of iron, 638.
Pattison's method of separating silver from lead, 554.
Peat, 360.
Pentane, 662.
Periodates, 210.
Periodic law, 187, 413.
Permanent white, 519.
Permanganates, 623, 624.
Petalite, 486.
Petit, 429.
Petroleum, 659, 661.
Pfeffer, 425.
Phenol, 683.
Philosopher's wool, 572, 584.
Phosgene, 377.
Phosphate rock for fertilizers, production of, 511.
Phosphates, 323, 455; acid, 323; neutral, 323; normal, 323, 455; primary, 323, 455; secondary, 323, 445; tertiary, 323.
Phosphine, 318; experiments with, 347; liquid, 319.
Phosphorescence, 316.
Phosphoric anhydride, 327.
Phosphorite, 314, 499, 508.
Phosphorous anhydride, 327.
Phosphorus, 314; acids of, 311; experiments with, 346; oxychloride, 321; pentachloride, 320; pentachloride, preparation of, 349, pentoxide, 327; red, 317; trichloride, 319; trichloride, preparation of, 348; trioxide, 327.
Phosphuretted hydrogen, 318.
Photography, 559.
Photometer, 382.
Physical change, 2.
Physics, 3.
Pig iron, 632.
Pinchbeck, 547.
Pink salt, 590.
Pitch-blende. 613.
Placer mining, 562.
Plaster of Paris, 115, 507.
Platinic chloride, 657; sulphide, 658.
Platinous chloride, 657; sulphide, 658.
Platinum, 655, 658; alloys, 657; black, 656; metals, 653; spongy, 656.
Plumbago, 355.
Plumbates, 597.
Plumbites, 596.
Pollux, 473.
Polonium, 616.
Porcelain, 538, 539.
Potash, 461, 472; water-glass, 473.
Potassium, 461; alum, 535; bichromate, 608; bromide, 463; carbonate, 471; carbonate, acid, 472; carbonate, extraction from wood-ashes, 495; chlorate, 156, 468; chlorate, preparation of, 160; chloride, 463; chromate, 608; cyanide, 469; disulphate, 471; ferricyanide, 389, 640, 641; ferrocyanide,

389, 639, 640; fluogermanate, 587; fluoride, 463; hydride, 462; hydrosulphide, 466; hydroxide, 464; hypochlorite, 156; iodide, 463; iodide, preparation of, 495; manganate, 623; manganate, preparation of, 627; nitrate, 466; nitrite, 468; oxide, 465; perchlorate, 157, 469; perchlorate, preparation of, 161; permanganate, 215, 623, 624; permanganate, preparation of, 627; peroxide, 465; phosphates, 472; salts, experiments with, 495; silicate, 473; stannate, 590; sulphate, 470; sulphate, acid, 471; sulphite, 471; sulphite, acid, 471; sulphocyanate, 470.
Praseodymium, 342, 601.
Preparing-salt, 591.
Priestley, 32, 262, 266.
Primary cells, 569.
Printing-ink, 358.
Propane, 662.
Propylene, 662.
Prussian blue, 641.
Prussiate of potash, red, 640; yellow, 389, 639.
Puddling, 633.
Purple of Cassius, 565.
Pyrargyrite, 560.
Pyrite, 630, 645.
Pyroarsenates, 329.
Pyrolusite, 214, 618, 620.
Pyrometric value, 379.
Pyrophosphates, 324, 455.
Pyrosiderite, 642.
Pyroxylin, 680.
Pyrrhotite, 630.

Quartation, 563.
Quartz, 397, 401.
Quartz glass, 403.
Quartzite, 397, 402.
Quaternary compounds, 435.
Quick-lime, 501.
Quinine, 686.

Radicals, 674.
Radioactivity, 615.
Radium, 615.
Ramsay, 62, 274, 275.
Rayleigh, 274.
Raoult's methods for determining molecular weights, 423, 424.
Reaction, chemical, 22.
Realgar, 328, 331.
Red-fire, 517.
Red lead, 596, 597.
Red phosphorus, 317.
Red prussiate of potash, 640.
Reducing agent, 61.
Reduction, 61, 70, 441; by carbon, 364.
Residues, 674.
Respiration, 371.
Reversible reaction, 60.
Reversion of phosphates, 510.
Rhodium, 654; chloride, 654; oxide, 654.
Rhodocroisite, 618.
Rinnmann's green, 574.
Roasting, 432, 448.
Rock-crystal, 402.
Rose's metal, 340.
Rouge, 643.
Rubidium, 473.
Ruby, 533.
Ruby copper, 544, 548.
Rupert's drops, 513.
Rusting, 638.
Ruthenium, 653; oxide, 654.
Rutile, 399, 406.

Safety lamp, 383, 663.
Safety matches, 318, 469.
Sal ammoniac, 282, 488.
*Sal armeniacum*, 282.
Salt, 168.
Salt, common, 475.
Saltpetre, 262, 461, 466; plantation, 466.
Salts, 158, 175; acid, 173; basic, 174, 177; constitution of, 171; decomposition by bases, 443; formation of, 437; formation of, experiments on, 185; neutral, 173, 174; nomenclature of, 183; normal, 173, 174.

Samarium, 541.
Samarskite, 541.
Sand, 397, 402.
Saponification, 672.
Sapphire, 533.
Scandium, 541.
Scheele, 32, 129, 262, 266.
Scheele's green, 551.
Scheelite, 612.
Schlippe's salt, 338, 478.
Schonite, 465, 470.
Schweinfurt green, 551.
Selenium, 233; dioxide, 256; oxides, 255.
Serpentine, 406, 521, 525.
Setting, 507.
Siderite, 630, 644.
Siemens-Martin furnace, 635.
Sieman's regenerative apparatus, 378.
Silica, 397.
Silicates, 397, 455.
Silicides, 407.
Silico-methane, 398.
Silicon, 396; carbide, 407; dioxide, 401; experiments with, 408; hexachloride, 400; hydride, 398; preparation of, 408; tetrachloride, 399; tetrafluoride, 400; tetrafluoride, preparation of, 408.
Silver, 553; and its salts, experiments with, 566; allotropic forms of, 556; alloys of, 557; amalgam, 557, 578; bromide, 558; chloride, 558; cyanide, 560; glance, 560; iodide, 558; metallurgy of, 554; nitrate, 560; oxide, 559; oxidized, 560; peroxide, 560; plating, 557, 566; suboxide, 560; sulphides, 560; tree, preparation of, 566; triazoate, 559.
Slaking, 443, 501.
Smalt, 648.
Smaltite, 647.
Smithsonite, 568, 574.
Smokeless powder, 468, 683.
Soap, action on hard waters, 669; preparation, 676.
Soaps, 669.
Soapstone, 521.
Soda, 480; bicarbonate of, 483; calcined purified, 482; crude, 482; crystallized, 482; feldspar, 474, 537; hyposulphite of, 480.
Soda-water, 370, 484.
Sodium, 474; alum, 537; amalgam, 577; ammonium phosphate, 490; bichromate, 610; borate, 484; bromide, 477; carbonate, 480; carbonate, acid or primary, 483; carbonate, preparation of, by ammonia process, 483; chloride, 475; chloride, commercial methods of electrolysis of, 152; chromate, 610; cyanide, 486; diuranate, 615; ferricyanide, 640; ferrocyanide, 640; fluoride, 477; hydride, 475; hydroxide, 477; iodide, 477; oxide, 478; nitrate, 478; peroxide, 478; phosphates, 484; salts, experiments with, 496; silicate, 485; stannate, 590; sulphantimonate, 478; sulphate, 478; sulphate, experiment on supersatured solution of, 496; thiosulphate, 480.
Soft-soap, 670.
Solder, soft, 589.
Solute, 108.
Solution, 108; as an aid to chemical action, 111; normal, 178.
Solvay process for soda, 483.
Solvent, 108.
Sorrels, 670.
Sparklets, 369.
Spathic iron, 630, 644.
Specific heat, law of, 427.
Specific heat and atomic weights, 426.
Specific gravity of vapours, determination of, 98.
Spectroscope, 494.
Spectrum, absorption, 494; continuous, 493; band, 493.
Specular iron ore, 643.

Spelter, 568.
Sphalerite, 568.
Spiegel iron, 632.
Spinels, 532.
Spirits of wine, 665.
*Spiritus fumans Libavii*, 590.
Spitting of silver, 556.
Spodumene, 486.
Stalactites, 506.
Stalagmites, 506.
Stannic chloride, 590; chloride, preparation of, 601; hydroxide, 590; oxide, 591; sulphide, 591.
Stannite, 588.
Stannous chloride, 589; chloride, preparation of, 601; sulphide, 591.
Starch, 677, 681.
Starch-paste, 681.
Stas, 12, 556.
Stassfurt potash industry, 464.
Stearin, 669; candles, 669.
Steel, 636.
Stibine, 351.
Stibnite, 332, 337.
Stolzite, 612.
Stone-ware, 538.
Storage battery, 597.
Strass, 513.
Stromeyerite, 560.
Strontianite, 516.
Strontium, 516; chloride, 517; hydroxide, 517; nitrate, 517; oxide, 517; sulphate, 517.
Sublimation, 488.
Substitution, 24, 55.
Sugar of lead, 596, 668; of milk, 679; refining, 678.
Sulphantimonates, 338.
Sulphates, 452; experiments with, 458.
Sulphides, 225, 446.
Sulphites, 453; acid, 248.
Sulpho-salts, 449.
Sulphostannates, 592.
Sulphur, 221; acids of, 238; *auratum*, 338; chlorides of, 233; dichloride, 233; dioxide, 250; dioxide, experiments with, 259; flowers of, 222, 223; heptoxide, 250; hexafluoride, 233; hexiodide, 233; hexoxide, 250, 255; insoluble, 225; monochloride, 233; sesquioxide, 250; soluble, 225; stick, 223; tetrachloride, 233; trioxide, 250, 253; trioxide, experiments with, 260; waters, 113, 222, 227.
Sulphuretted hydrogen, 227.
Sulphuric acid hydrates, 244.
Sulphuric anhyride, 253.
Sulphurous anhydride, 250.
Sulphuryl chloride, 255.
Sulphuryl-hydroxyl chloride, 255.
Sulphydrates, 232.
Suspension, 108.
Sylvite, 461, 463, 465.
Symbols of compounds, 20; of elements, 16, 19.
Sympathetic inks, 647.

Tachydrite, 500.
Talc, 521.
Tannin, 685.
Tanning, 685.
Tantalite, 342.
Tantalum, 342.
Tartar, cream of, 671; crude, 461; emetic, 336.
Tellurium, 234; dioxide, 257; monoxide, 257; trioxide, 257.
Tempering of glass, 514; of steel, 636.
Temperatures, methods of obtaining high, 379.
Ternary compounds, 435.
Thallium, 584.
Thénard, 129.
Theory, uses and value of a, 85.
Thermochemistry, 26.
Thomas-Gilchrist process, 634.
Thorite, 399, 405.
Thorium, 399; dioxide, 406.
Thyroiodine, 206.
Tin, 587; and its compounds, experiments with, 601; amalgam, 589; metallurgy of, 588; pest, 588; salt, 589.
Tin-foil, 588.

Tin-stone, 587, 591.
Titanium, 399; dioxide, 399, 406.
Toluene, 660, 662, 682.
Toluidine, 683.
Transition temperature, 224.
Tridymite, 401.
Trinitrophenol, 683.
Tungstates, 613.
Tungsten, 257, 612.
Turkey-red, 686.
Turnbull's blue, 641.
Tuyeres, 630.
Type-metal, 333.

Ultramarine, 539.
Uranates, 614.
Uraninite, 613.
Uranium, 257, 613; oxides, 614; yellow, 615.
Uranous salts, 614.
Uranyl nitrate, 614; sulphate, 614; salts, 614.
Ursol, 127.

Vacuum-pans, 678.
Valence, 94, 412; variations of, 412.
Vanadium, 342.
Van't Hoff, 425.
Vapor pressure of liquids, 103.
Vein mining, 562.
Ventilation, 273.
Verdigris, 669.
Vinegar, 668; mother of, 666, 668.
Vitriol, oil of, 56, 238.
Vitriols, 550.
Vivianite, 645.

Waage, 418.
Water, 101; as a solvent, 110; contamination of, by sewage, 114; determination of composition of, 80; distilled, 115; in organic substances, 101, 115; of crystallization, 101, 106, 115; proof of composition of, 102; purification of, 114, 116; synthesis of, 102; vapor pressure of, 103.
Water-gas, 56, 375, 376.
Water-glass, 473, 485.
Waters, chalybeate, 113; effervescent, 113; hard, 113; natural, 112; sulphur, 113, 222, 227.
Weights, atomic, 16, 19, 86, combining, 15, 16, 86; molecular, 89.
Weldon's process, 131, 621.
Welsbach, Auer von, 601.
Welsbach mantles, 406.
White arsenic, 330.
White lead, 598.
White precipitate, 583; fusible, 583; infusible, 583.
White vitriol, 550, 574.
Window glass, 512.
Winkler, 586.
Witherite, 517, 519.
Wolframite, 612.
Wollastonite, 405, 511.
Wood, distillation of, 660.
Wood's metal, 340.
Wood-spirit, 357, 660, 665.
Wood-vinegar, 668.
Work, chemical, 41.
Wrought iron, 633, 636.
Wulfenite, 593, 612.

Xenon, 275.
Xylene, 660, 662.

Yellow prussiate of potash, 389, 639.
Ytterbium, 541.
Yttrium, 541.

Zeolites, 511.
Zinc, 568; and its salts, experiments with, 584; alloys, 571; amalgam, 571; blende, 572; carbonate, 574; chloride, 571; dust, 568; experiments on burning of, 584; hydroxide, 572; metallurgy of, 568; oxide, 572; solution of, in sodium hydroxide, 584; sulphate, 573; sulphide, 572; white, 572.
Zinc method of separating silver from lead, 554.
Zircon, 399, 405.
Zirconium, 399.