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CHEMISTRY IN THE SERVICE OF MAN

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INTRODUCTION TO PHYSICAL CHEMISTRY
PRACTICAL PHYSICAL CHEMISTRY

CHEMISTRY IN THE SERVICE OF MAN

BY

ALEXANDER FINDLAY

EMERITUS-PROFESSOR OF CHEMISTRY, UNIVERSITY OF ABERDEEN

WITH PORTRAITS, DIAGRAMS AND ILLUSTRATIONS

"*He that enlarges his curiosity after the works of Nature demonstrably multiplies the inlets to happiness.*"

JOHNSON, *Rambler*, No. 5.

SEVENTH EDITION

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TO
MY WIFE

PREFACE TO THE SEVENTH EDITION

THIRTY-ONE years ago, when the preface to the first edition of this book was written, the author regarded it as his duty to emphasise how greatly we, as a nation, had thitherto failed to recognise the intimate and vital dependence of our social and national prosperity on a knowledge and appreciation of the facts and principles of science, and not least of chemistry, and on their application in industry. At the present time, we have every right to look back with a feeling of satisfaction —but certainly not of complacency, for much still remains to be done—on the great advances which have been made in this country during the past three decades in the encouragement and promotion of scientific research and in the application of science to the improvement of old and the development of new industries. Moreover, although this book is concerned with the advance of chemical science not only in this country but throughout the world, and with the service which chemistry has rendered to mankind, we, in this country, can feel proud of the part which British chemists have played in the general advance of the science no less than of its applications to the advantage of our industries and the material welfare of the people.

In times of war men are inclined to think of the work of chemists as being directed solely to destructive ends, but the discoveries of chemists are contributions to knowledge and, in themselves, are neither beneficent nor maleficent. It is in man's power and it is his responsibility, the responsibility of each individual citizen, to use these discoveries aright. The magnitude of the power which chemists have placed in the hands of men is a challenge to their moral greatness ; and the greater the power the greater is man's opportunity for its right use and for high endeavour. The frightfulness of

the atomic bomb, by which all men were appalled, should be a constant warning and should strengthen the admonition : " Turn back, O Man, forswear thy foolish ways."

Great as have been the suffering and destruction of life brought about by the misuse of the discoveries of chemists, very much greater have been the relief from suffering and the saving of life which their discoveries have made possible. Let the reader turn to page 321 and let him try to compute the sum of misery, suffering and loss of life from which mankind has been saved by the anæsthetics, antiseptics, drugs and insecticides which we owe to the ability, trained intellect, scientific imagination and persistent endeavour of the chemist. It is no exaggeration to say that the health and well-being of the people are more fundamentally dependent on the chemist than on the physician.

In the following pages, also, it has been sought to give some account of the advances which have been made in elucidating the constitution of the atom and in opening up the prospect of the beneficent utilisation of atomic energy, as well as of the recent achievements of chemists in other fields of social and industrial importance : light alloys, plastics, vitamins, hormones, etc.

While we should all be grateful for the many material benefits which chemical science has provided and for the service which it has rendered, and can in increasing measure still render, to industry, one must not fail to encourage or be niggardly in promoting the advance of science by investigations which are " motivated solely by a desire to increase knowledge " ; for the material benefits which derive from science are, as Cuvier said, " applications of verities of a superior order, not sought with a practical intent, verities which their authors have pursued for their own sake, impelled solely by an ardour for knowledge." Moreover, in our eagerness to achieve results of material value we must not lose sight of the idealism of science and of the intellectual satisfaction which its study can give. For the community as a

whole it is of importance not so much that its individual members should acquire a knowledge of the practical applications of science as that they should become imbued with the spirit of science, the passion for truth and the forming of judgments on the basis of ascertainable facts, the spirit of co-operation, of tolerance, of charity and of unselfishness, which are the spirit of true scientific endeavour. The study of science ministers to the satisfaction of the intellectual need of the human mind to understand more fully the phenomena of nature, which become not less but more wonderful the more fully we learn their meaning. The interpretations of science, moreover, do not destroy but give significance to the beauty of nature.

A. F.

66 MANOR WAY,
BECKENHAM, KENT.
March 1947.

PREFACE TO THE FIRST EDITION

WHEN the writer was invited to deliver the Thomson Lectures before the United Free Church College, Aberdeen, at the end of the year 1915, he felt that, as a teacher of chemistry, he could attempt no higher task than that of giving to his hearers, who made no claim to chemical knowledge, some account of what the science of chemistry, both in its general principles and in its industrial applications, has accomplished for the material well-being and uplifting of mankind; and the lectures which were then delivered form the basis of the present work.

The reasons which prompted the choice of subject are, of course, not far to seek. The crisis through which this and other European countries are now passing has brought home to us how greatly we, as a nation, have hitherto failed to recognise the intimate and vital dependence of our social and national prosperity on a knowledge and appreciation of the facts and principles of science, and not least of chemistry, and on their application in industry. All the industries of the country on which not only the comfort but even the life of the people depend—the great manufacturing industries, and agriculture, the greatest industry of all—claim tribute of chemistry. And yet we, as a nation, have done much less than the responsibilities of our civilisation demanded to promote and encourage the development of chemical knowledge; we have even, indeed, largely failed to avail ourselves of that tribute which science is so willing to pay. To the work of laying the foundation of pure science, on which the superstructure of successful industrial achievement must be raised, British chemists have, according to the measure of their numbers, contributed an honourable share; but the people as a whole, being ignorant of science, have mistrusted and

looked askance at those who alone could enlarge the scope of their industries and increase the efficiency of their labours. And so we have witnessed in the past an appalling and needless waste of our national resources, and in too many cases industries have languished and succumbed, or, even when born under conditions of great promise, have remained dwarfed and stunted in growth. In 1862, the German chemist, Hofmann, at that time a Professor of Chemistry in London, could utter the prophecy : " England will, beyond question, at no distant day, become herself the greatest colour-producing country in the world, nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, and her fossil substitutes for quercitron and safflower to China, Japan, and the other countries whence these articles are now derived." But, alas ! that prophecy has not yet been fulfilled, and the industry of synthetic dyes, an industry which above all others depends on the fostering and encouragement of chemical research and on the highest scientific efficiency, has found a home elsewhere amid more congenial surroundings.

But there are now welcome signs that the country is awakening to a sense of past deficiencies, and already the Government has taken a first short step in the direction of encouraging and assisting scientific and industrial research. But if the national effort is really to become effective and to exert a lasting influence, something more is necessary, something which is, perhaps, more difficult of achievement than Governmental aid. The mental outlook and the attitude of the people as a whole towards science must be changed, and the scientific habit and a spirit of trust in science must be cultivated ; and we must also attract in much larger numbers into the ranks of scientific workers men of equal mental calibre to and capable of taking the same wide outlook as those who are at present attracted into the higher ranks of the legal profession or into the Civil Services. Science stands

for efficiency *in all the activities of life*, and the neglect of science spells waste and industrial decay. It is for the country to choose the path which it will follow, but in making their choice let the people bear in mind the words spoken by the King when Prince of Wales : " Does not experience warn us that the rule of thumb is dead, and the rule of science has taken its place ; that to-day we cannot be satisfied with the crude methods which were sufficient for our forefathers, and that those great industries which do not keep abreast of the advance of science must surely and rapidly decline ? "

But we must learn to appreciate science not merely on account of its utilitarian value as a means of increasing wealth and material prosperity. From the material point of view, doubtless, " science is the knowledge most worth," and in the case of most people, perhaps, interest in science centres round its industrial or economic utility. *Nisi utile est quod facias, stulta est gloria* (" All useless science is an empty boast ") is a sentiment which will find a wide if not a universal acceptance, but we must beware of interpreting the usefulness of science in too narrow a spirit. The study of science possesses a cultural value which is quite independent of the utility of its applications ; and as an instrument of culture, as a means of coming into closer relations with Nature and the Infinite, science claims a fuller and more widespread recognition.

At a time of awakening interest in science, the author hopes that the present attempt to give a readily intelligible account of some of the more important general principles and theories of chemical science and of their applications may afford to the general reader some idea of the world's indebtedness to the chemist, and may also stimulate the interest of, at least, the younger students of chemical science by presenting to them a picture of that land into a fuller possession of which they one day hope to enter.

My thanks are due to the publishers, Messrs. Longmans, Green & Co., for permission to use Figures 1, 2, 9, and 10,

taken from works published by them ; and I desire, also, to express my indebtedness to my wife for her assistance not only in preparing the manuscript for publication, but also in reading the proof-sheets.

A. F.

Y GLYN,
LLANFARIAN,
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CHEMISTRY IN THE SERVICE OF MAN

CHAPTER I

INTRODUCTION

CHEMISTRY is a branch of science which deals with matter, or with the material universe which is revealed to us by our senses. It studies the different kinds of substances found in the world, whether in the living animal and vegetable organisms, or in the non-living mineral matter of the universe. Chemistry investigates the composition and specific properties of these substances, the methods of their preparation, the changes which they undergo, and their behaviour, not only in relation to what are called physical forces (heat, light, electricity, etc.), but also in relation to other substances; and it studies also how, from the materials already known, new materials, whether useful or ornamental, may be obtained. Through a knowledge of chemistry one may learn how to prepare, artificially, substances which are normally the products of the vital activity of animal and vegetable organisms, or how to prepare substitutes for these naturally occurring substances. Chemistry, further, occupies itself with the question of how materials already manufactured can be manufactured more economically, or be replaced by more suitable materials; and it helps us to understand how the natural and, it may be, irreplaceable resources of the world can be economised. On the science of chemistry, in fact, more than on any other branch of organised knowledge, depend the material well-being and comfort of man.

But the end and aim of chemistry is not merely material.

Chemistry offers its contribution also to the deeper interests of the human mind. Occupied as he is with the study of material substances and of the marvellous transformations which he is able to bring about in them, the thinking chemist is forced to look beneath the surface of things and to seek an answer to the fundamental questions relating to the ultimate constitution and structure of matter, and to the forces which govern the changes and transformations which he observes in his laboratory, or which are wrought out in the larger laboratory of Nature. The study, not merely of the *products* but also of the principles and laws underlying the *processes* of chemical change, forms the work of the modern chemist. In its wider sweep, chemistry ignores the conventional and artificial frontiers which mark it off from the other branches of science, more especially physics ; and in the last half-century there have been no more fruitful regions of experimental and speculative activity than those common territories where the sciences of chemistry and physics and chemistry and biology overlap.

Chemistry, moreover, possesses a cultural value apart from its applications. Its study is not only a means of cultivating the mind and of training and strengthening the scientific habit of thought, but it also brings us into closer relations with and gives a fuller understanding of the physical universe in which we live. In attempting, therefore, a brief and necessarily incomplete survey of chemistry in the service of man, I shall endeavour not merely to recount some of the manifold ways in which chemistry has revolutionised life and has contributed, on the material side, to a civilised existence ; but I shall try, also, to indicate, if I cannot do more, some of the principles which underlie chemical change, and to recount some of the achievements of chemists and physicists who, during the present century, with amazing insight and experimental skill, have been making known to us the invisible texture of what Carlyle called " the Time-vesture of the Eternal," the material universe.

The Constitution of Matter

The question of the constitution of matter is one which has occupied the minds of thinking and reasoning men from the earliest beginnings of philosophic enquiry; and in the philosophic epoch of the development of our knowledge of the material universe, one cannot but recognise the pre-eminence of ancient Greece. Men of other races and of earlier civilisations had doubtless speculated on the problem of the ultimate constitution of matter, but it was in Greece that the streams of thought flowing from Chaldea, from India and from Egypt, met and mingled, settled and became clarified. It is in ancient Greek philosophy that we find formulated most clearly many of the problems which face the modern man of science, and it was by the Greek philosophers that the first important attempts were made at their solution. These philosophers, it is true, could not make any very marked advance in their knowledge of the physical universe, and their theories remained to a great extent unfruitful, simply because their knowledge of facts was too slight and there was no possibility of testing the validity of their theories by experiment. Nevertheless, channels of thought were cleared by them and lines of advance were opened for others who through difference of temperament and outlook, as well as by growth of knowledge, were perhaps more fitted to travel along them.

Many and varied were the views which were held, and although the study of these will always prove interesting, it must be borne in mind that the considerations which governed the speculations of many of the ancient philosophers were quite different from those by which the modern scientist feels himself bound. To many of the Greek philosophers, the fact that our eyes make things manifest to us was no proof that those things exist. By them, intuition, a very valuable gift indeed, and reason were made the all-sufficient grounds of knowledge; and they sought to explain the

universe merely by the exercise of a vigorous imagination and a rigorous logic. One cannot therefore wonder that they sometimes lost touch with reality. As has been said : " The intellectual vigour of the philosophers of antiquity, indeed, was capable of the grandest and most comprehensive views of Nature, and often conducted them to the most sublime truths, but in attempting perpetually to soar above the vulgar paths of observation and experience, they speedily became confounded in the mists of error and conceit."

In the philosophy of ARISTOTLE, based on that of EMPEDOCLES, we find the conception of one primordial matter, *æther*, which acted as the carrier of certain essential qualities which were taken to be hotness, coldness, wetness, dryness ; and the combination of these qualities in pairs was supposed to give rise to the four elements or primary forms of matter, *fire* (hot and dry), *air* (hot and wet), *earth* (cold and dry), *water* (cold and wet). The elements were regarded not as material things but rather as the combinations of the essential qualities ; and by the union of these in different proportions the different substances were considered to have been formed. This conception of the constitution of matter dominated science until the time of ROBERT BOYLE in the seventeenth century ; and the idea of the existence of four " elements " (fire, air, earth, water) lingers on, in popular thought, even to the present day.

During a period of many centuries before the beginning of the Christian era, Egyptian craftsmen had acquired great skill and expertness in the extraction and working of metals, and had achieved much success in the surface-colouring of metals and in the production of alloys which counterfeited the appearance of gold and silver. In Alexandria, in the early years of the Christian era, Egyptian technical knowledge became united with Greek philosophic speculation and with the astrological and mystical views of the Chaldeans ; and from Alexandria this body of knowledge, speculation and mysticism passed to Syria and Persia, and later, in the

seventh century, to Arabia. To the Greek word, *chemia*,[1] applied to the art of making or counterfeiting gold and silver, the Arabs prefixed the article *al*, and so gave us the term *alchemy*.

Alchemy was, from the very beginning, not only an art but a philosophy, and the philosophic basis of alchemy is to be found in the Aristotelian doctrine of the essential unity of matter, and the view that matter is merely the carrier or embodiment of certain qualities which could be removed from one form of matter and transferred to another form of matter. The belief in the transmutability of matter, in the transmutability, for example, of lead into gold, followed naturally from the Aristotelian theory.

The alchemists also reasoned much by analogy and were thereby often led woefully astray. Thus it was thought that just as in the case of animals birth and growth occur, so also in the mineral world metals were thought of as being generated and growing in the earth ; and just as a chicken grows from an egg, so

> The same we say of lead, and other metalls,
> Which would be gold, if they had time.
> . . . for 'twere absurd
> To think that nature, in the earth bred gold
> Perfect i' the instant. Something went before.[2]

How absurd these views would seem to be ; and yet, although the alchemists were misled by a false analogy, recent work on artificial transmutation (p. 41) shows that the idea of " growth " in minerals is not so fantastic as at one time it appeared to be.

The production of gold, the perfect and complete metal, was regarded, then, as being the end and aim of Nature's striving[3] ; and it was the aim of the alchemists to hasten

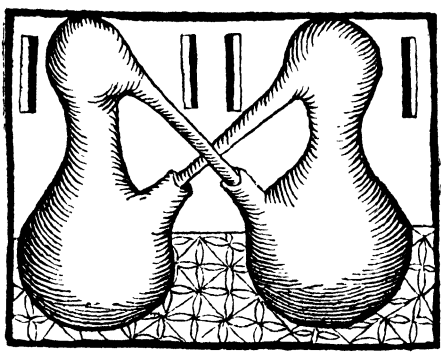
[1] This word is probably derived from chemi (meaning black), the ancient name given to Egypt on account of the dark colour of its soil.

[2] Ben Jonson : *The Alchemist*.

[3] The occurrence of gold and silver in association with base metals, such as copper and lead, was held to support the view that base metals grow into the metals silver and gold.

the process of growth of imperfect or base metals into gold by means of a medicine or transmuting agent called the philosopher's stone, the elixir, the magisterium, etc. To obtain this, all the kingdoms of nature—animal, vegetable and mineral—were ransacked; and materials of all kinds were calcined, boiled, fused and distilled.

Alchemy, then, was a philosophy of nature, and to many of the scholars of the Middle Ages, such as ALBERTUS MAGNUS and ROGER BACON, it made chiefly an intellectual appeal. There were many others, however, for whom



A sixteenth-century twin "pelican," or circulatory vessel, for the prolonged heating of liquids.

avarice and cupidity were the loadstars, and in the fifteenth and sixteenth centuries, especially, alchemy passed into the hands of visionaries and swindlers. Europe swarmed with rogues and tricksters, and it is they who have caused alchemy to be associated in men's minds only with deceit, quackery and charlatanism.

Although the alchemists failed in their endeavour to transmute the base metals into gold, yet by their unceasing labour they laid the foundations of present-day chemistry. To the alchemists we owe the preparation of substances of supreme importance in chemical science, such as sulphuric acid or oil of vitriol, hydrochloric acid or spirit of salt, nitric

acid or *aqua fortis*, *aqua regia* the solvent of gold, and many others. In the sixteenth century, moreover, alchemy acquired a nobler aim and ideal under the influence of that erratic genius and rebel against convention and tradition—Philippus Aureolus Bombastus von Hohenheim, generally known as PARACELSUS, who was born at Einsiedeln in Switzer-

THE ALCHEMIST.
After a painting by A. van Ostade (1661). (*National Gallery, London.*)
On the sheet of paper lying on the floor, the artist, with ironic humour, has painted the words, *oleum et operam perdis*—thou labourest in vain.

land in 1493, and died at Salzburg in Austria in 1541. Paracelsus taught that the true aim of alchemy should be, as the handmaid of medicine, the curing of human illness and disease, and that the preparation and study of the properties of drugs should be the main object of the chemist. A new era in chemistry was thereby inaugurated, known as the period of *iatrochemistry* or medical chemistry.

The teachings of Paracelsus not only turned men's minds from the obsession of gold-making and "the deceitful and mischievous art of alchemy," but led also to the preparation and study of many new materials. Iatrochemistry acted as

ROBERT BOYLE.
From the painting after F. Kerseboom.
(*National Portrait Gallery, London.*)

the bridge between the alchemy of the fifteenth and the beginnings of an exact science of chemistry in the seventeenth century. The philosophy of Aristotle held sway in the minds of men and as a dogma of the Church throughout the Middle Ages, but from time to time protests were raised against the doctrine of the four elements; and the overthrow of this philosophy was completed in the seventeenth century by

the Hon. ROBERT BOYLE,[1] of whom it has been said that "he was the father of chemistry and brother of the Earl of Cork."

Pure substances, as Boyle pointed out, can be divided into two classes. In the one class are those which have, so far, resisted all attempts to decompose them, or to break them down into substances simpler than themselves. These substances, according to Boyle, are the true *elements*, and this definition of an element is still retained. The definition, it should be noted, does not postulate the impossibility of decomposition, but insists merely on the fact that the possibility, if it exists, has not so far been realised.[2]

In the second class of pure substances are placed those which, by one means or another, can be resolved into simpler substances. These more complex substances are called *compounds*. Thus, for example, if the red substance known as red precipitate or oxide of mercury is heated in a glass tube, a gas is given off which has the property that it will cause a glowing splint of wood to re-ignite; and, at the same time, metallic mercury is deposited in shining droplets on the cooler portions of the tube. The red substance has thus been decomposed into metallic mercury and a gaseous substance, to which the name of oxygen has been given. This red substance, therefore, is a compound of mercury and oxygen.

In spite of most laborious and prolonged efforts, chemists have hitherto not succeeded in reducing the number of the elements to less than ninety. Of these ninety elements, a list of which, for convenience of future reference, is given below, all the substances in the known universe are built up.

[1] Robert Boyle, the youngest son of the first Earl of Cork, was born at Lismore, Ireland, in 1627, and died in 1691. He was the author of *The Sceptical Chymist*, the publication of which marks the beginning of chemistry as a science.

[2] Although this definition may still serve for most purposes, the phenomena of radioactivity and the existence of isotopes, to which reference is made in the following chapter, show the need of a new definition.

List of the Elements

Atomic number		Symbol	Atomic weight
1.	Hydrogen	H	1·008
2.	Helium	He	4·003
3.	Lithium	Li	6·94
4.	Beryllium	Be	9·02
5.	Boron	B	10·82
6.	Carbon	C	12·01
7.	Nitrogen	N	14·008
8.	Oxygen	O	16·00
9.	Fluorine	F	19·00
10.	Neon	Ne	20·183
11.	Sodium	Na	22·997
12.	Magnesium	Mg	24·32
13.	Aluminium	Al	26·97
14.	Silicon	Si	28·06
15.	Phosphorus	P	30·98
16.	Sulphur	S	32·06
17.	Chlorine	Cl	35·457
18.	Argon	A	39·94
19.	Potassium	K	39·096
20.	Calcium	Ca	40·08
21.	Scandium	Sc	45·10
22.	Titanium	Ti	47·90
23.	Vanadium	V	50·95
24.	Chromium	Cr	52·01
25.	Manganese	Mn	54·93
26.	Iron	Fe	55·85
27.	Cobalt	Co	58·94
28.	Nickel	Ni	58·69
29.	Copper	Cu	63·57
30.	Zinc	Zn	65·38
31.	Gallium	Ga	69·72
32.	Germanium	Ge	72·60
33.	Arsenic	As	74·91
34.	Selenium	Se	78·96
35.	Bromine	Br	79·92
36.	Krypton	Kr	83·7
37.	Rubidium	Rb	85·48
38.	Strontium	Sr	87·63
39.	Yttrium	Yt	88·92
40.	Zirconium	Zr	91·22
41.	Niobium	Nb	92·91
42.	Molybdenum	Mo	95·95
43.	Masurium[1]	Ma	—
44.	Ruthenium	Ru	101·7
45.	Rhodium	Rh	102·91
46.	Palladium	Pd	106·7
47.	Silver	Ag	107·88
48.	Cadmium	Cd	112·41
49.	Indium	In	114·76
50.	Tin	Sn	118·70
51.	Antimony	Sb	121·76
52.	Tellurium	Te	127·61
53.	Iodine	I	126·92
54.	Xenon	Xe	131·3
55.	Caesium	Cs	132·91
56.	Barium	Ba	137·36
57.	Lanthanum	La	138·92
58.	Cerium	Ce	140·13
59.	Praseodymium	Pr	140·92
60.	Neodymium	Nd	144·27
61.	Illinium[1]	Il	—
62.	Samarium	Sa	150·43
63.	Europium	Eu	152·0
64.	Gadolinium	Gd	156·9
65.	Terbium	Tb	159·2
66.	Dysprosium	Dy	162·46
67.	Holmium	Ho	164·94
68.	Erbium	Er	167·2
69.	Thulium	Tm	169·4
70.	Ytterbium	Yb	173·04
71.	Lutecium	Lu	174·99
72.	Hafnium	Hf	178·6
73.	Tantalum	Ta	180·88
74.	Tungsten	W	183·92
75.	Rhenium	Re	186·31
76.	Osmium	Os	190·2
77.	Iridium	Ir	193·1
78.	Platinum	Pt	195·23
79.	Gold	Au	197·2
80.	Mercury	Hg	200·61
81.	Thallium	Tl	204·39
82.	Lead	Pb	207·21
83.	Bismuth	Bi	209·0
84.	Polonium	Po	—
85.[1]	—	—	—
86.	Radon	Rn	222
87.	Francium	Fr	—
88.	Radium	Ra	226·05
89.	Actinium	Ac	—
90.	Thorium	Th	232·12
91.	Protoactinium	Pa	231
92.	Uranium	U	238·07

[1] The occurrence in nature of elements 43 and 61 has not been confirmed. Isotopes (p. 36) of these elements and also of 85 have been produced artificially. See also p. 45.

Only about twenty of the elements occur free or uncombined in Nature; and the amounts in which the different elements exist vary very greatly. Of all the elements found in the earth, the seas and the air, oxygen and silicon are by far the most abundant, as the following analysis shows :—

CHEMICAL COMPOSITION OF TERRESTRIAL MATTER

(Earth, Air and Sea)

	per cent.		per cent.
Oxygen	50·02	Potassium	2·28
Silicon	25·80	Magnesium	2·08
Aluminium	7·30	Hydrogen	0·95
Iron	4·18	Titanium	0·43
Calcium	3·22	Chlorine	0·20
Sodium	2·36	Carbon	0·18
			99·00

From the numbers in this table one learns that the two elements, oxygen and silicon, in the free or in the combined state, constitute together three-quarters of the whole of terrestrial matter, by weight, so far as this is accessible to direct investigation.

If one considers the composition merely of the earth's crust accessible to investigation, the average values do not differ greatly from those given above. There is, however, evidence to show that the composition of the interior of the earth is very different from that of the crust; and, from investigations of different kinds, the conclusion has been drawn that beneath the crust of the earth there occur zones diminishingly rich in silicates and increasingly rich in iron, and that there is lastly a core consisting essentially of iron and nickel.

THE ATOMIC THEORY

Underlying the philosophy of Aristotle was the idea that matter is continuous, that it is capable of infinite subdivision; but with the overthrow of the doctrine of the four elements of Aristotle there was revived another ancient

hypothesis which had been put forward in the fifth and fourth centuries B.C., by LEUCIPPUS, DEMOCRITUS, and EPICURUS. According to the doctrine of these philosophers, a doctrine which comes nearer to modern scientific views than any other system of philosophy of the ancient world, and which has been preserved and expounded for us by the Roman poet LUCRETIUS, matter is made up of indivisible particles, the " atoms " or the " first-beginnings of things," which are immutable and eternal. These " first-beginnings " are in constant motion, travelling through void. " Of this truth which I am telling," writes Lucretius,[1] " we have a representation and picture always going on before our eyes and present to us : observe whenever the rays are let in and pour the sunlight through the dark chambers of houses, you will see many minute bodies in many ways through the apparent void mingle in the midst of the light of the rays, and as in never-ending conflict skirmish and give battle, combating in troops and never halting, driven about in frequent meetings and partings, so that you may guess from this what it is for first-beginnings of things to be ever tossing about in the great void." By the coming together of these atoms the substances constituting the material world were regarded as being formed ; and the diversity of substances was held to be due to differences in the size and shape of the atoms composing the substances. " Now mark and next in order apprehend of what kind and how widely differing in their forms are the beginnings of things, how varied by manifold diversities of shape. . . . The things which are able to affect the senses pleasantly consist of smooth and round elements ; while all those, on the other hand, which are found to be bitter and harsh, are held in connection by particles that are more hooked, and for this reason are wont to tear open passages into our senses."

These views must seem crude to the modern mind, and even NEWTON, at the end of the seventeenth century, could

[1] Lucretius : *De rerum natura*, translation by Munro.

not greatly refine them. Thus he expressed the view : " It seems probable to me that God, in the beginning, formed matter in solid, massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which He formed them ; and that those primitive particles, being solids, are incomparably harder than any porous bodies compounded of them ; even so very hard as never to wear or break in pieces, no ordinary power being able to divide what God Himself made one in the first creation."

The great authority of Newton gave powerful support to the atomic conception of matter, but it was not till the beginning of the nineteenth century that this fundamental hypothesis was developed into a theory by which the observed phenomena and the laws of chemical combination could be *quantitatively* explained or co-ordinated. It was only after this had been done, however, that the general hypothesis of the atomic constitution of matter could become of any real value in science, and nothing has influenced the progress of chemistry so much as the achievement of this by the Manchester schoolmaster, JOHN DALTON.[1]

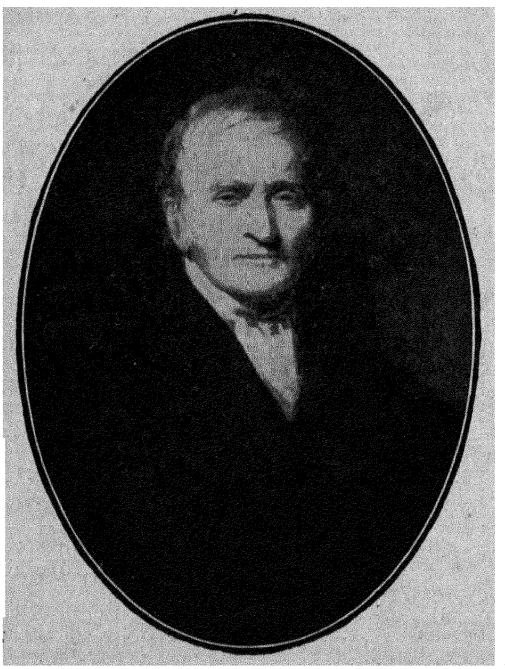
To the older philosophers, the atoms or indivisible particles into which matter could be divided all consisted of the same primordial material, although differing in size and shape. The atoms of Dalton, however, differed in their nature. In the case of any particular element, the definition of which has already been given, the atoms were assumed to be all exactly alike in their properties, including, of course, their mass ; but they differed from the atoms of every other element.

Further, according to Dalton, a compound is formed by the combination of atoms of different kinds ; and since the nature of the compound will necessarily depend on the

[1] John Dalton, the son of a hand-loom weaver in Cumberland, was born in 1766. After teaching for some years in a Manchester school he became a private tutor. The atomic theory, on which his fame mainly rests, was formulated in 1803 and published in 1807. He died in 1844.

number and kind of the atoms present, *the composition of the compound must be definite.* This is the first fundamental law of chemistry, the *law of constant proportions.*

And still further. Since the fundamental assumption of the atomic theory is that atoms are indivisible, that they cannot be broken up into anything smaller, it follows that



JOHN DALTON.

if one particular element A combines with another element B to form compounds containing different proportions of A and B, these different proportions stand to one another in the ratio of integral, or whole, numbers. That is to say, we can have the compounds A + B, A + 2B, 2A + B, 2A + 3B, etc., where A and B represent atoms of the elements A and B. Here, then, we have the explanation

of the second fundamental law of chemistry, the *law of multiple proportions*.

At first Dalton made no distinction between the smallest particle of an element and the smallest particle of a compound. Both were called atoms. But it is clear that this must cause difficulty, because although the atom of an element may be regarded as indivisible, the atom of a compound must still be capable of being split up into smaller particles, namely the atoms of the component elements. A new name was therefore introduced in 1811 by the Italian physicist, AVOGADRO, who called the smallest particle of a compound a *molecule*. The molecule of a compound, therefore, consists of a number of elementary atoms. We have, then, the definition that an atom is the smallest particle of an element which can enter into the composition of a molecule, or which can take part in chemical exchange. It is, so to speak, the smallest coin in chemical currency. A molecule, on the other hand, is the smallest particle of a substance *which can exist in the free state*.

It does not, however, follow that the atom and molecule of an element mean the same thing. In some cases they do, and the atoms of such elements as argon and helium, for example, can exist in the free state, by reason of the fact that they possess no power of combination. But in very many cases the free atoms of an element combine together to form aggregates of like atoms, so that the molecule of an element, or the smallest particle of the element capable of free existence, may consist of two or three or even of four atoms combined together.

The atomic theory of Dalton, modified by the conception of molecules, served to co-ordinate or explain the fundamental laws of chemistry, the laws of definite and of multiple proportions; and on the basis of this theory the superstructure of modern chemistry was largely built.

Symbols and Formulæ.—In the table given on p. 10 it will be seen that opposite each element is a letter or group of

letters, by means of which one can represent shortly the particular element. Each of these *symbols*,[1] as they are called, represents an atom or one atomic proportion by weight of the particular element; and since a compound is regarded as being formed by the combination of atoms, one can conveniently represent the *molecule* of a compound by writing the symbols of the constituent atoms side by side. Thus, NaCl represents a compound of sodium and chlorine, the molecule of which consists of one atom of sodium and one atom of chlorine; CO, similarly, represents a compound of carbon and oxygen, and so on. Frequently, however, the molecule of a compound is formed by the combination of elements in more than one atomic proportion, and so one writes, for example, H_2O, which is the *formula*[2] for water; a formula which indicates that the molecule of water consists of two atoms of hydrogen and one atom of oxygen. The formula NH_3, similarly, which is the formula for ammonia, indicates that the molecule of this compound consists of three atoms of hydrogen united with one atom of nitrogen.

The use of these symbols and formulæ is a great convenience and renders much assistance to the chemist in understanding and in representing chemical changes; and they will be employed to some extent in the following pages. They will, however, be used to assist the understanding, not to burden the memory.

To one point more we must refer. According to the

[1] These symbols were introduced early last century by the Swedish chemist, Berzelius, who used the initial letter of the Latin name to represent the element. Where the name of more than one element began with the same letter, a second letter was added as a distinguishing mark. By using the Latin names of the elements, the symbols were rendered international; and one can thus understand why, in certain cases, the symbols are not obvious abbreviations of the English name of the element. Thus, we have, Sb=antimony (stibium); Cu=copper (cuprum); Au=gold (aurum); Fe=iron (ferrum); Pb=lead (plumbum); Hg=mercury (hydrargyrum); K=potassium (kalium); Ag=silver (argentum); Na=sodium (natrium); Sn=tin (stannum).

[2] One speaks of the *symbol* of an element and the *formula* of a compound or of a molecule.

atomic theory of Dalton, the atoms of a particular element are all exactly alike, and different from the atoms of other elements. If the atoms have definite properties, however, they must also have a definite mass or weight. Although, on the basis of various experimental investigations, the absolute masses of atoms have been calculated (p. 26), it is clear that one cannot handle these infinitesimally small particles of which many millions are contained in the tiniest piece of matter which can be seen even with the help of a microscope ; one cannot place these atoms on the scale pan of a balance and ascertain their weight. It is, however, comparatively easy to determine the *relative* weights of the atoms, and such determinations constitute one of the greatest achievements of science which followed in the train of Dalton's atomic theory. These relative weights are what are called the *atomic weights* of the elements, and their values, referred to the value 16·00 as the atomic weight of oxygen, are given in the table on p. 10. By the introduction of these atomic weights, a new and extended meaning is given to chemical symbols and formulæ. The symbol, Na, for example, not merely represents the element sodium, but stands for one atomic proportion or 22·997 parts by weight of sodium ; and the formula, NaCl, is not merely a convenient shorthand symbol for the compound sodium chloride (which is the chemical name for common salt), but it stands for one molecular proportion by weight, or $22{\cdot}997 + 35{\cdot}457 = 58{\cdot}454$ parts by weight of sodium chloride, the numbers 22·997 and 35·457 being the atomic weights of sodium and chlorine respectively. It will be clear, also, that the *molecular weight* of a compound, which is equal to the sum of the atomic weights of the elements forming it, is the weight of a molecule relatively to the weight of an atom of the standard element, oxygen, taken as 16·00.

Valency.—Although atoms can combine with one another to form a compound or compounds, it has been established that elementary atoms do not possess an unlimited power of

combination. The atoms of two different elements may combine in more than one proportion, but not in every proportion. Hydrogen and chlorine, for example, can combine together only atom for atom : an atom of hydrogen cannot combine with more than one atom of chlorine, and an atom of chlorine cannot combine with more than one atom of hydrogen. On the other hand, an atom of the metal calcium can combine with two atoms of chlorine to form the compound calcium chloride ($CaCl_2$) ; an atom of aluminium can combine with three atoms of chlorine to give $AlCl_3$; and an atom of carbon can combine with four atoms of chlorine to form carbon tetrachloride, CCl_4. The atoms of different elements, therefore, have a certain combining capacity, or have a certain *valence*[1] or *valency*, as it is called ; and since one atomic proportion of hydrogen is never known to combine with more than one atomic proportion of any other element, the combining capacity or valence of hydrogen is taken as the standard and put equal to unity. Chlorine, an atom of which can combine with only one atom of hydrogen, is also said to have unit valence or to be univalent. Oxygen, an atom of which can combine with two atoms of hydrogen (as in water, H_2O), is said to be bivalent ; nitrogen, an atom of which can combine with three atoms of hydrogen (as in ammonia, NH_3), is said to be trivalent ; carbon, an atom of which can combine with four atoms of hydrogen, is said to be quadrivalent ; and so on.

The doctrine of valency, first clearly stated by Sir EDWARD FRANKLAND in 1852, was put forward as an empirical doctrine, and it is only in comparatively recent years that a theoretical basis has been found for it in the conception of the electronic constitution of matter which will be discussed in the next chapter.

One of the greatest of scientists, Lord KELVIN, said : " I often say that if you can measure that of which you speak, and can express it by a number, you know something of your

[1] From the Latin *valere*, to be worth.

subject; but if you cannot measure it, your knowledge is meagre and unsatisfactory." And it is because Dalton's theory is a quantitative theory, or capable of quantitative expression, that it was possible for the hypothesis of the discontinuous or atomic constitution of matter to become the foundation stone of modern physical science; and it is by the introduction of mathematics and by the quantitative treatment of chemical phenomena that modern chemistry is mainly distinguished from the chemistry of a hundred years ago.

Modern Scientific Method

In so far as philosophic views were founded, as many of the Greek views regarding the constitution of matter were founded, on observations of facts, even when the observations were faulty, one need not be surprised that the vigorous imagination and keen intellect of the Greeks should formulate views or theories regarding the constitution of matter which find their counterpart in modern scientific theory. That, notwithstanding their intellectual powers, the assertion could be made, as it was made by Whewell, that "the whole mass of the Greek philosophy shrinks into an almost imperceptible compass when viewed with reference to the progress of physical knowledge," is due to the fact that the aims and methods of Greek philosophy were so different from the aims and methods of modern science. The Greek philosophers sought for a general philosophic doctrine or formula which should throughout be consistent with itself and should embrace not merely the phenomena of the material universe, but should also include the activities of thought, of life and of conduct. Starting from a postulate or premiss based, it might be, on an observation of fact or on an analogy (often false), a comprehensive philosophy was developed by the exercise of a rigorous logic; but not even Aristotle, in spite of the principles he himself laid down, principles which are at the foundation of the inductive and

experimental methods of modern science, tested his conclusions on the touchstone of fact. In modern science, which has developed from the time of FRANCIS BACON in the early part of the seventeenth century, one has adopted a less comprehensive aim and a more experimental method.

The first step in the building up of knowledge by the scientific method is to ascertain the facts by observation and experiment. Thus, in order to learn how the volume of a gas is altered by pressure, a certain mass of the gas must be subjected to a series of different pressures, and at each pressure the volume of the gas must be measured. In this way, Robert Boyle found that *the volume of a gas is inversely proportional to the pressure* (Boyle's law). If the pressure is doubled, the volume is halved. This *generalised statement* of observed facts is called a *scientific law*, or *law of nature*. Such a law, it should be emphasised, merely summarises, in a general statement or formula, a relationship which has been observed in a certain number of cases. A scientific law, therefore, differs from a civil law in being merely descriptive, not prescriptive ; and the enunciation of a scientific law by the generalisation of experimentally determined facts—the arguing from particular cases to a general or universal relation—is called *induction*. It forms the second stage in the building up of the scientific edifice.

The method and aim of science, however, does not consist merely in the " ordering of nature " in descriptive laws. It seeks also to correlate or " explain " the laws ; and so, with the general laws as a starting point, scientific imagination is called upon to frame an *hypothesis* or conception regarding the fundamental nature of things. This hypothesis must, of course, be in harmony with all the facts already known and it must be such that the general laws, obtained inductively from experiment, follow as necessary consequences from the hypothesis. When the *deductions* from the hypothesis are found to be in harmony with the inductively derived laws, the hypothesis takes rank as a *theory*.

An hypothesis or theory makes it possible not only to co-ordinate or correlate the various known laws—to explain these laws, as one says—but also to predict new and undreamt-of laws. It not only gives satisfaction to the mind by producing coherence and order among diverse phenomena, but it opens up vistas of new knowledge, suggests new tests of its own validity and spurs one on to fresh endeavour. Before the new laws obtained deductively from an hypothesis or theory are accepted, however, *they must be subjected to verification by experiment.* With the continual necessity, therefore, of experimental investigation and testing of deductions from theory, it will readily be understood that

"Science moves, but slowly slowly, creeping on from point to point";

and the building up of the edifice of science is a slow and laborious task.

CHAPTER II

RADIOACTIVITY AND ATOMIC STRUCTURE

ALTHOUGH the atomic theory, formulated by Dalton in 1803, was generally accepted as a guiding principle in physical science, it was regarded by some merely as a convenient "working hypothesis," useful but not necessarily representing actual fact. No direct, experimental proof of the objective reality of atoms existed. Investigations, however, belonging mainly to the present century, have contributed, from several different directions, towards establishing the atomic theory in a position of unassailable strength, and have furnished a proof of the objective reality of atoms or discrete particles as constituting the fundamental basis of matter. By the phenomena of diffusion, more especially diffusion of gases (Chap. XIII); by the Brownian movement observed in the case of minute particles in suspension (Chap. XIII); by the phenomena of radioactivity, and even by the blue colour of the sky, the discontinuous structure of matter is made manifest and the existence of atoms or discrete particles established with a probability amounting to a certainty.

To Dalton, as to Newton, the atoms were "solid, massy, hard, impenetrable particles," incapable of sub-division; but during the greater part of the nineteenth century the ground was being prepared for a revision of this view. To this work of preparation attention may be given for a moment.

As the determinations of atomic weights increased in number, it was observed that most of the values, when referred to the atomic weight of hydrogen as unity, were either whole numbers or very nearly whole numbers. This remarkable fact gave rise to the view, first put forward in 1816 by WILLIAM PROUT, a physician and Lecturer on Chemistry in London, that the atoms of different substances

are made up of various amounts of some primordial matter, and that this primordial matter is hydrogen. This view, however, did not meet with general acceptance, because it was found that the deviation of the atomic weights of a number of the elements from whole multiples of the atomic weight of hydrogen could not be explained as due to experimental error. Many chemists felt, however, that although they could not accept Prout's view, it contained some element of truth ; and this feeling was strengthened when, in 1901, the Hon. R. J. STRUTT, now Lord RAYLEIGH, by applying the law of probabilities, showed that " the atomic weights tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence." How nearly the hypothesis of Prout agrees with present-day views regarding the constitution of the atom will become clear in the sequel.

Periodic Law.—Although Prout's hypothesis was not accepted by chemists, the study of the atomic weights of the elements brought to light a number of regularities and relationships which pointed to the existence of some genetic connection between the elements ; and of these regularities the most important was that discovered by the Russian chemist, MENDELÉEFF, and by the German chemist, LOTHAR MEYER, in 1869 and 1870, the so-called *periodic law.* It was observed by these chemists that when the elements are arranged in the order of their atomic weights, there is a periodic recurrence of properties. Thus, leaving hydrogen and helium out of account for the present, and starting with lithium, we have the series,

lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, neon,

and then the series,

sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, argon,

in which the properties of the elements are similar to those of the corresponding members of the former series ; that is,

sodium is similar to lithium, magnesium to beryllium, and so on till we come to argon which has properties similar to those of neon. After argon, which is similar to helium and neon, there comes the element potassium,[1] and so a new series is begun. Now, however, as the diagram (Fig. 1) shows, new types of elements occur and the period becomes longer; so

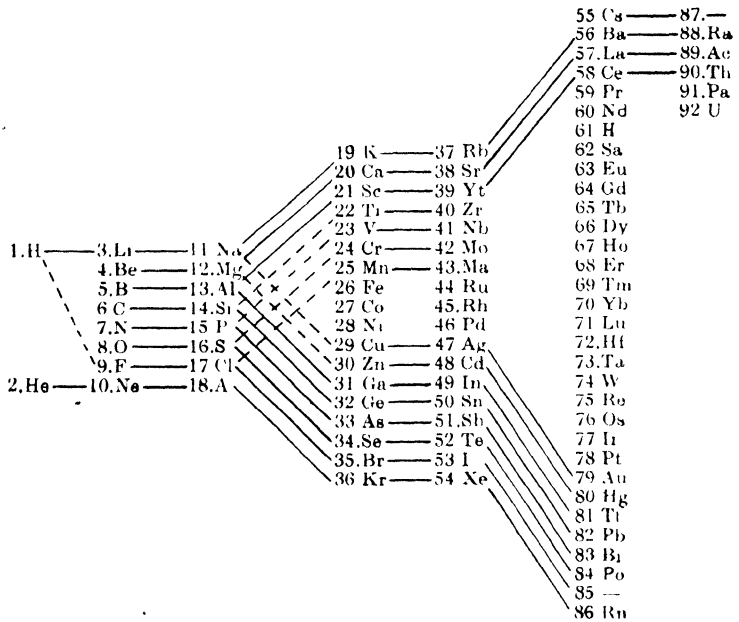


FIG. 1.—PERIODIC CLASSIFICATION OF THE ELEMENTS.

that, from potassium, which corresponds to lithium and sodium on the one hand, to krypton, which corresponds to neon and argon on the other hand, there is a period not of eight but of eighteen elements. This is followed by another period of eighteen elements from rubidium to xenon, and then there is a jump to a still longer period of thirty-two elements (one of which is still not definitely characterised).

[1] Argon is placed before potassium, although the latter has the smaller atomic weight. This is one of the anomalies of the Mendeléeff periodic classification, and will receive its explanation later.

A fragmentary period of six elements completes the table. Owing to the periodicity of properties, elements of similar or analogous character fall into corresponding places in the various periods, and, in the diagram, the members of these " natural families " or groups of related elements are joined together by full drawn lines. Dotted lines join elements which are less closely related than are the members of the " natural families."

The periodic law has proved a most valuable guide in chemical investigation, and so uniform is the variation of properties from element to element that Mendeléeff was

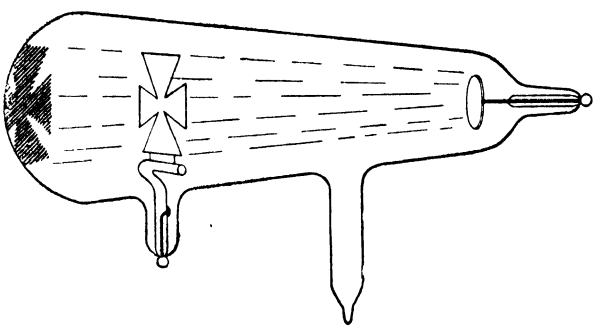


FIG. 2.—CROOKES TUBE.

able to predict the properties of several elements, then unknown, with what was later found to be surprising accuracy.

Recognition of the essential validity of the periodic law greatly stimulated speculation and investigation into the nature and genesis of the elements, and during the nineteenth century evidence was accumulating that the older views regarding the nature of the atoms must be revised. Modern investigation has now amply proved that the atom of the chemist, the unit of chemical exchange, can no longer be regarded as the unit of sub-division of matter. On the contrary, the atom is now known to be a complex structure built up of much smaller particles, the nature and arrange-

ment of which have been, for a number of years, the subject of experimental investigation.

Cathode Rays.—The new light which, during the present century, has been shed on the problem of the constitution of matter came first from an unexpected direction, namely, from a study of the discharge of electricity through highly rarefied gases. In 1859, it was discovered by the German physicist PLÜCKER, that when an electric discharge is allowed to take place in a highly evacuated glass tube, a peculiar radiation is projected from the negative electrode or *cathode*, as it is called ; and this radiation excites a phosphorescent light in the glass of the tube opposite the cathode. This radiation, moreover, known as the *cathode rays*, travels in straight lines, and if a solid object is placed in the path of the rays, a shadow is cast (Fig. 2). Moreover, by using a concave cathode, whereby the rays can be brought to a focus, a metal can be raised to incandescence, or even melted, under the fury of the bombardment by the cathode rays. These phenomena were studied more fully by Sir WILLIAM CROOKES who, in 1879, surmised that the cathode rays were composed of extremely small particles or corpuscles ; and in 1897, Sir JOSEPH J. THOMSON, while Professor of Physics in the University of Cambridge, proved that they consist of negatively charged particles which travel with the enormous velocity of from 10,000 to 100,000 miles per second, the latter velocity being such that the particles would engirdle the earth four times in the space of a second.

The mass of these negatively charged particles or *electrons*, as they are called, is exceedingly small and equal only to one eighteen-hundred-and-fortieth ($\frac{1}{1840}$) of the mass of the hydrogen atom, the lightest atom or lightest particle of matter hitherto known.[1] In this way, the existence of

[1] The mass of a hydrogen atom has been calculated to be $1{\cdot}67 \times 10^{-24}$ gram (*i.e.* 1·67 divided twenty-four times by 10), and the mass of an electron is therefore $9{\cdot}11 \times 10^{-28}$ gram. In other words, it would take about one million million million million atoms of hydrogen to make up the weight of 1 gram (15·4 grains).

particles very much smaller than the chemical atom was discovered; and since it was found that these electrons are given off by substances under various conditions, as, for example, when a body is raised to incandescence,[1] the conception of the electronic constitution of matter, *i.e.* of the atom, arose.

From another direction, also, further impressive evidence was soon obtained that the atom is no longer to be thought of as a single, indivisible, unchangeable particle, but as a vibrant microcosm, a complex system possessing enormous potential energy and capable, in certain cases at least, of undergoing an amazing and spontaneous transformation into atoms of a different kind.

Radioactivity.—The property of radioactivity was discovered in 1896 by the French physicist, HENRI BECQUEREL, who found that the compounds of uranium continuously and spontaneously emit " rays " or radiations which have the power of passing through wood, paper and other opaque materials, and of affecting a photographic plate in a manner similar to the X-rays which had shortly before been discovered by the German physicist, RÖNTGEN. Further investigation of radioactive phenomena by Professor PIERRE CURIE and his wife, MARIE SKLODOVSKA CURIE, in Paris, led to the discovery, in 1898, of the much more highly radioactive element radium, which occurs, to the extent of about one part in 10,000,000, in the uranium-containing mineral, pitchblende. From this mineral, by a long and laborious process, Mme. Curie later prepared the salt of radium, radium chloride, a white substance similar in appearance to common salt. Although the element radium has been isolated, and has been found to resemble, in its chemical properties, the metals calcium and barium, it is in the form of its chloride that it is generally employed; and when, in ordinary language, one speaks of radium, it is to this salt, radium chloride, that one generally refers.

[1] As in the " valve " used in wireless telephony.

Small amounts of radium are still obtained from its original source, the pitchblende deposits at Joachimstal in Bohemia, as well as from deposits of carnotite occurring in the States of Colorado and Utah in America, but it was the Katanga Mines in the Belgian Congo that, until about 1930, furnished almost the whole of the world's supply of radium. In that year, however, large deposits of pitchblende were discovered on the shores of the Great Bear Lake in Northern Canada, and, since 1933, ever-increasing quantities of radium have been produced there. The El Dorado Mine of Northern Canada has become one of the richest radium-producing mines in the world.

Radium is a substance which must be handled with care, for, if kept for a short time near the body, it cauterises the skin and produces a sore which is difficult to heal. It is used extensively in the treatment of cancer and other malignant growths.

The investigation of the radioactive elements, uranium, thorium and radium, has shown that the atoms of these elements are continuously giving out positively and negatively charged particles, the so-called alpha and beta rays; and they are the source, also, of ethereal vibrations, the gamma rays, which are similar in nature to the X-rays. The beta rays, or negatively charged electrons, and, more especially, the gamma rays, are highly penetrating,[1] but the alpha rays, which are positively charged particles of atomic dimensions (p. 31), are easily stopped by a sheet of note-paper, or even by a few centimetres[2] of air. These alpha particles, however, contain much more energy than the electrons and are much more effective in breaking up the molecules of the atmospheric gases, whereby the air is rendered a conductor for electricity. These alpha rays are, of course, all stopped by

[1] It is these very penetrating rays that destroy the unhealthily growing cells in cancer.

[2] A centimetre is rather less than half an inch; 2·54 centimetres (cm.) = 1 inch.

the walls of the glass or metal tube in which, ordinarily, the small quantities of radium salt are sealed up.

The three most important radio-elements are, as has been mentioned, uranium, thorium and radium, but electrical measurements have shown that these elements give rise to a large number of other radio-elements which have a much more transient existence. Thus, radium gives rise to a gas, *radon* or radium emanation, which is itself radioactive and can be observed, like radium, to glow in the dark; and thorium, also, gives rise to a radioactive gas, thorium emanation. These gases, however, when removed from the original material, gradually lose their radioactive property and disappear; but just as fast as the separated emanation disappears, just so fast is fresh emanation produced by the original radium or thorium, spontaneously and always at the same rate, unaltered by anything that man can do. Nor is this all. From the radium and thorium whole series of radioactive substances are produced successively, *e.g.* radium, radon, radium A, radium B, etc., down to radium G, which is identical with lead. These different members of a radioactive series, which are obtained, for the most part, only in unweighable amounts, are distinguished from one another and identified by the rate at which the radioactive power diminishes or "decays." Thus, the radioactive power of radium falls to half its value in a period of 1590 years, whereas the corresponding time for radon is 3·825 days, and for radium A, 3·05 minutes.

On account of its high radioactive power, an indication of which is given by its short "life," radon is now very generally employed in radio-therapy in place of, or in addition to, radium (radium chloride).

One of the disintegration products of thorium, known as mesothorium-1, is obtained in considerable quantities as a by-product of the incandescent gas-mantle industry. Mesothorium-1 loses half its radioactivity in $5\frac{1}{2}$ years, so that its life is comparatively short; but for that very reason

highly active preparations can be obtained. The commercial mesothorium is largely employed in the manufacture of luminous paints, which can be applied, for example, to the hands of watches and so make it possible for the time to be read in the dark.

Although the fact of radioactivity is now familiar to all, the phenomena of radioactivity were, in the closing years of the nineteenth century, startling in their unexpectedness; and they were bewildering and inexplicable until, in 1902, ERNEST RUTHERFORD (afterwards Lord Rutherford) and FREDERICK SODDY put forward their now universally accepted hypothesis of *atomic disintegration.* According to this hypothesis, the atom of a radioactive element is a complex system of particles which undergoes spontaneous change, or explodes, as it were, with projection at a very high velocity of negatively charged electrons (the so-called beta rays), and of heavier, positively charged particles or alpha rays. Not all the atoms, however, of a radioactive substance undergo disintegration at one moment; only a certain definite fraction of the atoms reach the condition of instability at the same time, and the fraction is different for each radioactive element. In the case of radium, for example, only about one atom out of every hundred thousand million breaks up each second.

In the case of uranium, the process of disintegration is a very slow one, otherwise the element would have already disappeared from the earth. Of the uranium existing at the present time, half will have disappeared by transformation into other elements, including radium, only at the end of rather less than five thousand million years. On the other hand, half the radium now existing will have disappeared at the end of 1590 years, and half of what then remains will have disappeared at the end of a further period of 1590 years. Fresh amounts of radium, however, are being slowly produced by the parent element uranium. The radioactive gas, radon, when separated from the parent radium, rather rapidly disappears—half of it goes in less than four days (*see*

p. 29), and half of what is then left disappears in another four days, and so on. Just as fast as the separated radon disappears, however, fresh radon is produced by the original radium, and so the supply is kept up.

Other radioactive elements similarly undergo disintegration and become transformed into other elements, as we have already seen (p. 29).

A striking confirmation of the correctness of the disintegration hypothesis of radioactivity and of the complexity of atoms was obtained when Sir WILLIAM RAMSAY and Lord RUTHERFORD showed, by direct experiment and in different ways, that the positively charged alpha particle which is expelled from radioactive substances is in fact a positively charged helium atom, or a helium atom which has lost two electrons. Not only did Rutherford isolate the alpha particles and show that on losing their electrical charge by taking up electrons they form ordinary helium, but he also succeeded in counting the number of alpha particles emitted by a given weight of radium, by allowing the particles to pass through a small hole and impinge on a fluorescent screen. At each impact of an alpha particle, a little flash of light was produced,[1] and by counting the number of flashes the number of particles passing through the opening was obtained. Since the number of alpha particles expelled from a given weight of radium can be counted, and since each alpha particle becomes a helium atom, it is possible, by measuring the volume of helium produced by a given weight of radium in a given time, to calculate the number of helium atoms (or molecules) in a given volume of the gas. The number obtained by Lord Rutherford, namely, twenty-seven trillion five hundred thousand billion ($2{\cdot}75 \times 10^{19}$), in 1 cubic centimetre at 0° C. (32° F.), is in good agreement with the value deduced from measurements of an entirely different kind.[2]

[1] This fact was made use of by Crookes in the construction of the small instrument known as the spinthariscope.

[2] In the above statement, a billion is taken as a million million, and a trillion as a million billion.

According, moreover, to a well-known theorem of Avogadro, *equal volumes of all gases when under the same pressure and at the same temperature, contain the same number of molecules.* It follows, therefore, that at 0° C. and under standard atmospheric pressure (76 cm. of mercury), 1 cubic centimetre of any and every gas will contain $2{\cdot}69 \times 10^{19}$ molecules, to use a more accurate number than that obtained by Lord Rutherford.

Atomic Structure.—The striking proof of the complexity of the chemical atom which was afforded by electrical and radioactive phenomena gave a great impetus to the formation of definite views regarding the inner structure or constitution of what was formerly thought of as indivisible. Since negatively charged electrons constitute part of the atom (p. 27), and since the atom as a whole is electrically neutral, it follows that there must be an amount of positive electricity within the atom equal to the total negative charge carried by the electrons. How, then, is the structure of the atom to be conceived ?

Experiment showed that when alpha rays, from radium, for example, were passed through a gas, most of the tracks were straight lines ; some showed a slight bending, while a very few showed a sharp deflection. A similar behaviour was also found when alpha rays were passed through thin metal foil, *e.g.* gold leaf. In this case, some of the alpha rays were thrown back almost on their own tracks. From a study of these results, Lord Rutherford suggested that the positive electricity in the atom is concentrated in a very minute *nucleus*, in which, also, almost the whole mass of the atom is supposed to be resident. Around this minute positively charged nucleus the negative electrons are arranged in the form of concentric rings or orbits, like a sun ringed round with planets. This atomic model, the general correctness of which has been confirmed by all later work, was a brilliant inference from experimentally determined data.

And what is the nature of the positively charged nucleus ?

The atoms or nuclei of radioactive elements emit, on disintegrating, alpha particles or positively charged helium nuclei, as well as beta rays or negatively charged electrons. In the case of the heavy atoms of the radioactive elements, therefore, we seem to have a proof that the positively charged nucleus of the helium atom is one of the units of nuclear structure ; but since the mass of the helium atom (or nucleus) is nearly four times that of the hydrogen atom, the helium nucleus must itself be regarded as complex. The conclusion, therefore, is reached that the positively charged nucleus of the hydrogen atom, the lightest atom, is the simplest, positively charged unit of atomic structure. This unit is called a *proton.*

The proton was for long regarded as being the unit of positive electricity, but in 1933 it was found that there can be produced, under certain conditions, a particle which has the same mass as the electron, but which has a positive instead of a negative charge. This particle, therefore, to which the name *positron* has been given, must be regarded as the unit of positive electricity, just as the electron is the unit of negative electricity. It exists as some sort of structural unit in the nucleus of the atom.

Besides the positively charged protons and positrons and the negatively charged electrons, the investigations of physicists have revealed the presence in the atom of uncharged particles or *neutrons*, produced by the firm combination of a proton and an electron. Such particles have been liberated, for example, by the bombardment of atoms of beryllium and of boron by alpha rays (p. 42), and have proved to be most valuable missiles in bringing about the artificial disintegration of atomic nuclei.

Modern investigations of the structure of the atom, therefore, have extended enormously the limit of sub-division of matter ; and the atom now takes the form of a very open-spaced system of particles, the diameters of which are very small compared with that of the system as a whole, or of the atomic domain as it has been called. The hydrogen

atom, according to the modern view, consists of a positively charged nucleus, a minute speck of positively charged matter (the proton), round which, at a relatively very great distance, there circles a negatively charged electron. The structure of an atom of hydrogen, therefore, has been compared with that of the solar system, and it has been pointed out that since the diameter of the earth is one twenty-thousandth of the diameter of its orbit round the sun, one can think of a hydrogen atom as a system in which the earth represents an electron circling round a nucleus (much smaller than itself), at a distance equal to twice the distance of the earth from the sun. The atom, therefore, is mainly void, a thing of specks and spaces, mainly spaces ; and one can readily understand how a positively charged alpha particle can pursue a straight path *through* the atoms of matter and be only occasionally deflected by a near approach to, or collision with, the massive, positively charged nucleus (p. 32).

The atom of helium, the element of next higher atomic weight to hydrogen, has a nucleus which carries two positive charges, and round this nucleus there circle, therefore, two electrons. This helium nucleus, since its mass is four times that of the hydrogen atom, is to be regarded as being made up of two neutrons and two protons, the resultant nucleus, therefore, carrying two positive charges. The atoms of the elements of higher atomic weight, similarly, are to be regarded as constituted of positively charged nuclei, built up of protons and neutrons, encircled by rings of planetary electrons ; and the important discovery has been made that *as one passes from element to element, the number of positive charges on the nucleus and, therefore, the number of planetary electrons surrounding the nucleus, increases by single units.*

Atomic Number.—The number of excess positive charges on the nucleus, which determines the number of planetary electrons, is of much importance, because it is on these planetary electrons that the chief chemical and physical properties of the elements depend. One of the great advances made in

modern times has been the recognition of the fact that the number of excess positive charges on the atomic nucleus is the same as the serial number or *atomic number*, as it is called, of the element in the periodic classification given on p. 24. For the determination of the atomic number several methods are now available. In the case, therefore, of uranium, the element of highest atomic weight occurring in nature,[1] the atomic number of which is 92, the atom consists, it is believed, of a complex nucleus carrying an excess positive charge of 92 units, surrounded by rings or shells of 92 electrons.

The recognition of the fact that the properties of an element depend on the atomic number, rather than on the atomic weight of the element, enables one to take account of the anomalies occurring in the Mendeléeff classification (p. 23), namely, that argon must, on account of its chemical properties, be placed before potassium, and similarly tellurium before iodine, although the atomic weights are in the reverse order. When the elements are arranged in the order of their atomic numbers, instead of their atomic weights, these anomalies disappear, and argon and tellurium fall into their proper places (p. 24). Generally, it is true, the atomic numbers and atomic weights follow the same order, but not always ; and for the periodic recurrence of chemical properties it is the atomic number which is of importance. The periodic law (p. 23), therefore, must now be stated in the form : *The properties of the elements vary in a periodic manner with the* ATOMIC NUMBER.

The existence of a series of integral atomic numbers throws important light on the number of elements still to be discovered. On arranging the elements serially in order of the atomic numbers, as in the table on p. 10, it is found that only two gaps occur, indicating that between hydrogen and uranium only two elements remain to be discovered. Experimental evidence of the existence of these has been

[1] Artificially produced elements of higher atomic weight are now known (p. 45).

obtained, although the elements have not been definitely characterised (p. 10).

Although there appears to be justification for the view that the ultimate structural units of the nuclei of all atoms are protons and neutrons, the fact that in the explosive disruption of radioactive atoms, helium nuclei (alpha rays) are ejected, suggests that the helium nucleus of two neutrons and two protons is a particularly stable complex; and the helium nucleus, therefore, appears to be a very important secondary structural unit of the more complex atoms.

Isotopes.—Since 1913, great advances in our knowledge of the constitution of matter have been made. By electrical methods, introduced and developed by Sir J. J. THOMSON and F. W. ASTON of the University of Cambridge, the mass of the positive nuclei, and therefore the mass of the atoms,[1] of different elements has been determined; and it has been shown that if the atomic weight of oxygen be represented by the number 16, the atomic weights of all other atoms are to be represented by whole numbers,[2] *e.g.* the atomic weight of helium by 4, of carbon by 12, of nitrogen by 14, etc. These numbers are identical with the atomic weights as determined by chemical methods. In the case of those elements, however, which yield fractional atomic weights when determined chemically, Aston showed that the element, as it exists in nature, is not simple, but consists of a mixture of different atoms, the masses of which are represented by whole numbers. Thus the atomic weight of chlorine, determined by chemical methods, is 35·46 (the atomic weight of oxygen being 16). By the method of *positive ray analysis*, as it is called, Aston showed that ordinary chlorine is a mixture of atoms having atomic weights 35 and 37 respectively, mixed together in the proportion of about 3 to 1. The two varieties of atoms are chemically indistinguishable and are called

[1] The mass of the electrons may be neglected.

[2] Slight divergences may be found, the explanation of which, however, cannot be discussed here.

isotopes. The existence of isotopes, first realised in the case of radioactive elements, will readily be understood when one remembers that the atomic weight depends on the mass of the nucleus, whereas the chemical properties of the element depend on the number of planetary electrons or the number of excess positive charges on the nucleus. By adding one proton and one electron, or one neutron, to the nucleus of a given atom, the mass of the atom will be increased by one, but the positive charge on the nucleus, and therefore the chemical properties, will remain unchanged. In the case of the two isotopes of chlorine, the atomic number of which is 17, the nucleus of one consists of 18 neutrons and 17 protons, while the nucleus of the other consists of 20 neutrons and 17 protons. Most of the elements have been found to exist in isotopic forms, the separation of which is generally very difficult.

In 1932, the very interesting and rather startling discovery was made by Professor H. C. UREY and his fellow-workers in America that ordinary hydrogen is a mixture of two isotopes, the lighter having the atomic weight 1 and the heavier the atomic weight 2, the nucleus, in this case, consisting of one neutron and one proton. For the lighter isotope the name hydrogen has been retained, and the heavier isotope has been christened *deuterium* (symbol D). Whereas the isotopes of the elements of higher atomic weight differ only slightly from one another in their properties, deuterium differs quite markedly from hydrogen, as, indeed, one might expect from the fact that its atomic weight is twice that of hydrogen. Deuterium is chemically less reactive than hydrogen, and the compounds which it forms are less reactive than the corresponding hydrogen compounds. " Heavy water " or deuterium oxide, D_2O, the analogue of the hydrogen compound H_2O, has a density (1·11) which is 11 per cent. greater than that of the hydrogen oxide, and it cannot replace the hydrogen compound in the animal organism. Tadpoles, for example, will die if placed in " heavy water." Ordinary water is not pure hydrogen oxide,

H_2O, but contains deuterium oxide, D_2O, to the extent of about 1 part in 6500.

The fact that elements exist in different isotopic forms is not only of great interest in connection with the theory of atomic structure, but is becoming increasingly important for certain branches of chemical and medical research, because of the use of such isotopes as so-called *tracer elements*. The isotopes of an element, although chemically identical, can be distinguished by physical methods; and this is more especially the case when the isotopes are radioactive. They are thereby labelled. If, therefore, a foodstuff, for example, or a compound containing, say, carbon, nitrogen or phosphorus, is prepared from a naturally rare or artificially prepared isotope of the ordinary element and is introduced into the body, the track of that compound through the body can be followed. By this means it has been shown, for example, that phosphorus introduced into the body in a meal, finds its way into the bones within a few hours.

Some of the isotopes are stable, but many radioactive isotopes, with a comparatively short life, are now being produced in considerable quantities not only by means of the cyclotron (p. 42), but, more especially, in the apparatus used for the production of atomic bombs (p. 44). These radioactive isotopes, of which the most important are C 14, S 35, P 32, I 131, where the numerals are the atomic weights, promise to be of great value not only as tracer elements but also, it may be, for the treatment of disease. An artificially prepared radioactive isotope of phosphorus, for example, has been used in the treatment of leukæmia.

Planetary Electrons.—As one passes from element to element, we have seen, the number of planetary electrons increases, at each step, by unity, and as their number increases, the planetary electrons are regarded as grouping themselves on the surface of concentric spheres or shells. Except in the case of helium, which has only two planetary electrons, the

maximum degree of stability is reached when the number of electrons in the outermost shell reaches eight, forming what is known as an *octet*. When more planetary electrons are added, as when one passes from neon to sodium, a new ring of electrons begins to be formed. This is built up by the successive addition of one electron until one comes to argon with its outermost ring of eight electrons.

It may be noted that although the number of electrons in the outermost orbit never exceeds eight, the number in the inner orbits may rise to thirty-two. Thus, in the case of the element radon, which belongs to the helium family (Fig. 1, p. 24) and has the atomic number 86, the numbers of electrons in successive orbits, from the nucleus outwards, are 2, 8, 18, 32, 18, 8.

According to present views, it is the electrons of the outermost shell which are involved in chemical combination, and chemical combination may be regarded as an expression of the tendency of an atom to lose or gain electrons so as to form the most stable system with an outermost shell of eight electrons, such as exists in the case of the rare gases, except helium. As these elements have the most stable outermost shell of eight electrons, they show no tendency either to gain or to lose electrons ; they are chemically inactive and have zero valency. The sodium atom has one electron in the outermost shell, and it readily gives up this electron so as to form a system having the arrangement of the nearest inert gas, neon (*see* p. 24). Chlorine, on the other hand, which has an outermost shell of seven electrons, readily takes up one electron to complete the octet, thereby forming a system which has the arrangement of the inert gas argon. Combination between sodium and chlorine, therefore, readily occurs by the transfer of one electron from the sodium atom to the chlorine atom ; and since the sodium atom thereby becomes positively charged and the chlorine atom negatively charged, the two atoms are held together by electrostatic attraction. Sodium and chlorine are said to be univalent

elements. Similarly, calcium can give up and oxygen can take up two electrons, and are therefore said to be bivalent. Valency thus appears as a measure of the number of planetary electrons which an atom has in its outermost shell in excess of or in defect of eight.

In many cases, however, combination between atoms depends not on the giving and receiving of electrons, but on the SHARING of one or more pairs of electrons, so that each atom has eight electrons in its outermost shell.

From the preceding discussion it will be evident how very nearly the hypothesis of Prout agrees with the now generally accepted views regarding the constitution of the atoms of different elements. Although the atoms of the elements are not to be regarded as built up of hydrogen atoms but rather of hydrogen nuclei (protons) and electrons, the idea underlying the two views is essentially the same; and as a result of recent investigations and deductions one is beginning to see more clearly something of the order and unity which run through the whole series of diverse elements known to the chemist. One is also getting glimpses of that evolutionary process through which the material universe has passed since the time of which Ovid speaks in his well-known lines:

> Ere earth and sea and covering heavens were known,
> The face of nature, o'er the world, was one;
> And men have called it Chaos; formless, rude,
> The mass; dead matter's weight, inert and crude;
> Where in mix'd heap of ill-compounded mould,
> The jarring seeds of things confusedly roll'd.

By the investigations of the twentieth century the atomic or discontinuous constitution of matter has been established beyond any reasonable doubt; and in the process our views regarding the ultimate units of matter have undergone a change. To quote the words of the eminent French physicist, JEAN PERRIN: "Atoms are no longer eternal, indivisible entities, setting a limit to the possible by their irreducible simplicity; inconceivably minute though they be, we are

beginning to see in them a vast host of new worlds. . . . Nature reveals the same wide grandeur in the atom and the nebula, and each new aid to knowledge shows her vaster and more diverse, more fruitful and more unexpected, and, above all, unfathomably immense."

Transmutation of Elements.—The knowledge which has been gained regarding the constitution of matter, and more especially the discovery of the phenomena of radioactivity, place in a new light the question of the transmutation of the elements, the achievement of which was one of the great aims of the mediæval alchemist.

Whether the elements such as we know them at the present day represent the halting points in a process of disintegration of more complex elements, or of integration from simpler units of matter, they appear to consist, for the most part, of stable atomic systems. In the radioactive elements, however, we have atomic systems which pass spontaneously into a condition of instability and undergo a process of disintegration into simpler atomic structures. In this way, a transmutation, not of lead to gold but of radium or of thorium to lead, may be said to take place. This process of transmutation, however, is quite uncontrollable by man.

It was in 1919 that the first artificial transmutation of one element into another, by the disintegration of atomic nuclei, was effected by Lord RUTHERFORD. Atoms, as we have seen, are very open-spaced structures, and when atoms of nitrogen were bombarded by alpha particles, liberated, for example, by the radioactive disintegration of radium, most of the particles passed in a straight line through the open structure of the atom. Some, however, of the particles, which are projectiles of great kinetic energy, registered direct " hits " against the nucleus of the nitrogen atoms, and, in fact, penetrated into the nucleus of the nitrogen atoms. An unstable structure was thereby produced which immediately broke up with the emission of a proton and the production of a stable oxygen isotope of atomic weight 17. A number

of other light elements could be similarly "transmuted." The important discovery was also made by Sir JAMES CHADWICK, working in Rutherford's laboratory, that by the bombardment of the element beryllium with alpha particles, carbon was formed with the emission, not of protons, but of swift, penetrating, uncharged particles, or *neutrons*. These neutrons are very efficient agents for the disintegration and transmutation of atoms, for, owing to the absence of an electric charge, they are not repelled by the nucleus and so can more readily enter into it. The unstable structure produced then breaks up into atoms of a different kind. Such transmutations may, in fact, be actually taking place in many naturally occurring minerals. Rapidly moving protons and deuterons (positively charged nuclei of deuterium), their motions greatly accelerated by a powerful electric field, as in the apparatus known as a cyclotron, have also been used for the purpose of bringing about artificial transmutations, some of which may in the future prove to be of much value. By the bombardment of atoms of the elements with these different missiles—alpha particles, neutrons, protons, deuterons—many transformations have been effected, and even new radioactive elements have been obtained which may some day be used as a substitute for radium in radio-therapy. The experiments of the old alchemists, based on vague and ill-defined speculation, ended in failure; the experiments of the new alchemists, founded on definite and experimentally verified views, have ended in a brilliant success. Lead, it is true, has not been changed to gold, but something of much greater importance has been achieved. The modern alchemists, who have pursued their investigations with the sole purpose of increasing knowledge and have thereby revealed to us the nature and structure of the atom, have, by their discoveries, opened up visions of great storehouses of energy which may be used to transform the whole material life of man.

Sub-atomic Energy.—The particles forming the nucleus of

an atom are held together by very powerful forces, and when the nucleus undergoes radioactive transformation great stores of energy are set free. Each disintegration of an atomic nucleus is accompanied by a decrease of mass, which is partially converted into energy ;[1] and so great is the energy produced by the decrease of mass that one ounce of matter transformed entirely into heat energy would, it has been calculated, be sufficient to convert nearly a million tons of water into steam. The energy liberated, therefore, in atomic nuclear reactions is enormous compared with that set free by a corresponding number of atoms in even the most intense chemical reactions, in which only the outer shells of planetary electrons are engaged. The radioactive transformations, however, are uncontrollable by man.

The discovery that the atoms of matter are vast storehouses of potential energy stirred the imagination and gave rise to the belief that in the complex systems of particles constituting the atoms of matter, there must exist inconceivably great, untapped and formerly unsuspected reservoirs of energy, compared with which the energy of combustion of all our fuel reserves is quite trifling. If one could only gain control of sub-atomic energy, or could control the process of atomic disintegration so as to bring it about at will, then, it was thought, untold stores of energy would be available to carry on the work of the world when the reserves of coal should be exhausted ; or which, in the hands of the evilly disposed, would suffice to shatter the globe. Until 1939, however, neither the former hope nor the latter fear appeared to be well founded.

Although the disintegration of atomic nuclei had been effected by Lord Rutherford in 1919, only one out of many thousands of the bombarding particles brought about disintegration of atomic nuclei. From each successful collision, it is true, energy was gained, but the total energy used up in

[1] It was shown by Einstein, as long ago as 1905, that, according to the theory of relativity, there is no essential difference between mass and energy. The continual emission by the sun of energy in the form of heat is considered to be due to a loss of mass.

producing the bombarding particles was far greater than the energy released from the relatively few successful collisions. Moreover, unlike the chemical process of combustion, for example, the atomic disintegrations were not self-propagating, for the energy released by one nuclear disintegration did not suffice to bring about the disintegration of the neighbouring nuclei. There seemed to be little hope, therefore, that one would be able to gain useful energy from the atoms by artificial processes of atomic transformations.

Early in 1939, the outlook was entirely altered. In that year it was discovered that when the atoms of uranium, and especially the isotope of atomic weight 235, were bombarded by neutrons,[1] the uranium nuclei do not disintegrate like those previously studied, but undergo "fission," or split into two parts of nearly equal mass. Not only was this process accompanied by the liberation of a large amount of energy, but other neutrons were also released which could then bring about the fission of neighbouring uranium nuclei. For the first time, as the result of investigations carried out by physicists in a number of different countries, there seemed to be an experimental basis for the hope that the store of atomic energy might be usefully released; for, once the fission of uranium nuclei had been initiated in a few atoms, the neutrons produced would bring about the fission of other atoms. A chain process would thus be established which would propagate itself throughout the mass of uranium with great velocity and with the liberation of a large amount of energy. The energy required to start the chain is very small compared with the total energy liberated.

It has been found, moreover, that when the uranium isotope, U 238, is bombarded by neutrons which have a velocity (and therefore an energy) intermediate between that required to bring about the fission of U 238 and U 235, a new nucleus is produced with a mass number of 239. This loses two electrons in successive steps and gives rise to the

[1] Produced, for example, by mixing beryllium with radium (p. 42).

two elements not found in nature, *neptunium* (atomic number 93) and *plutonium* (atomic number 94); and the latter element, when bombarded by neutrons of low velocity, also undergoes fission with release of neutrons.[1]

Everyone is now aware how through the ability and co-operative labours of a large number of scientists, drawn from different allied countries, and the expenditure of £500,000,000, there was accomplished in 1945 what is probably the greatest achievement of scientific genius of all time, the liberation of the great stores of energy locked up in the atoms of matter. That this achievement should have to announce itself to the world through the bursting of an atomic bomb over Hiroshima on 6th August 1945, creating destruction equal to that produced by 20,000 tons of high explosive, is one of the tragedies of our time and of our civilisation. We may well bear in mind the words contained in the statement issued by Mr. Winston Churchill: "This revelation of the secrets of nature, long mercifully withheld from man, should arouse the most solemn reflections in the mind and conscience of every human being capable of comprehension. We must indeed pray that these awful agencies will be made to conduce to peace among the nations, and that instead of wreaking measureless havoc upon the entire globe, they may become a perennial fountain of world prosperity."

With the bursting of the first atomic bomb, a new epoch in the world's history and in the history of human civilisation began; and one can only speculate, vaguely, perhaps, but hopefully, on the possibilities for good opened up for the world, when the stores of sub-atomic energy are liberated, not with world-shattering violence, but as a steadily flowing stream controlled and directed for the use and benefit of mankind.

[1] Elements with atomic numbers 95 (Americium, Am) and 96 (Curium, Cm) have also been produced artificially.

CHAPTER III

THE GASES OF THE ATMOSPHERE

THE composite nature of atmospheric air, which from earliest times had been regarded as an element, was first demonstrated, in 1674, by the English physician, JOHN MAYOW, who showed that when a substance is burned in air enclosed in a vessel standing over water, the volume of the air is diminished, and that in the residual gas combustion will no longer take place. Subsequent investigations, belonging in some cases to comparatively recent times, have shown that atmospheric air is a mixture of a number of different gases in proportions which remain remarkably constant. The gases normally present in air are : nitrogen, oxygen, carbon dioxide, water vapour, and a group of gases, known as the rare gases, the most abundant of which is argon. Besides these normal constituents, other gases and also solid particles, derived from local sources, may be present as impurities.

As the result of analysis it has been found that the average composition of purified air, free from carbon dioxide and water vapour, is as follows :

	Per cent. by volume.	Per cent. by weight.
Nitrogen . .	78·06	75·5
Oxygen . .	21·00	23·2
Rare gases. .	0·94	1·3

Nearly four-fifths of the air, by volume, therefore, consists of nitrogen, and one-fifth of oxygen. Normally, there are about three parts of carbon dioxide in ten thousand parts of air by volume.

Nitrogen was first obtained, in 1772, by a botanist, DANIEL RUTHERFORD, who burned phosphorus in a vessel containing air, and removed, as is now known, the oxygen

which is present. At the present day, very large quantities of nitrogen are obtained industrially by the distillation of liquid air, the production of which will be described later (p. 58). Although it plays a very important *rôle* in the economy of nature, nitrogen is a very inert or chemically inactive element at the ordinary temperature, and supports neither combustion nor life. It was first called *azote.*

The discovery of *oxygen,* in 1773–1774, we owe to CARL WILHELM SCHEELE, a Swedish apothecary who was recognised as one of the foremost chemists of the time, and to JOSEPH PRIESTLEY, an English Unitarian Minister and amateur of science, and one of the most versatile and intellectually active men of the eighteenth century. Both these investigators obtained oxygen by decomposing, by heat, red oxide of mercury, a compound of mercury and oxygen, but the gas is now best prepared on a small scale by heating a mixture of potassium chlorate and manganese dioxide. On an industrial scale, the gas is produced mainly by the distillation of liquid air, but a certain amount is also obtained by a process of electrolysis which will be discussed in Chap. XII.

The most conspicuous property of oxygen is the readiness with which it combines with other substances, as shown, for example, in the vigour with which it supports combustion. A merely glowing strip of wood bursts into flame when introduced into oxygen, and phosphorus burns in the gas with dazzling brightness. At the present time, oxygen finds extensive application not only in medicine, in cases of difficult respiration, but also in industry for the production of high temperatures by means of the oxy-hydrogen blowpipe (p. 110) and the oxy-acetylene blowpipe (p. 114).

Carbon dioxide, which is normally present in air only in very small amounts, may escape in considerable quantity through fissures in the earth in volcanic regions, as in the Poison Valley of Java. It occurs also dissolved in many mineral waters, from which it may escape with effervescence. Artificial aerated waters are produced by dissolving carbon

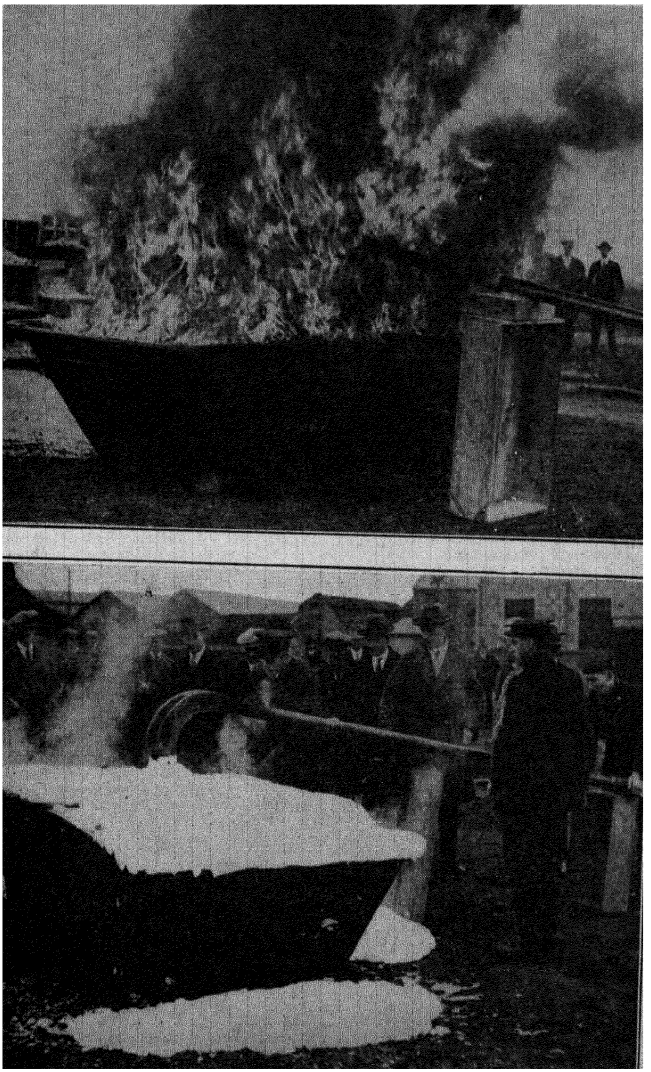
dioxide in water under pressure. The gas is one and a half times as heavy as air.

Carbon dioxide is formed in large quantity in many natural and industrial processes, as when coal burns and when limestone or chalk is heated for the production of quicklime. It is also formed abundantly in the process of fermentation for the production of alcohol, and also when an acid is brought in contact with chalk, soda, or other carbonate. Owing to the fact that carbon dioxide does not support combustion, it is used to extinguish fires. Some portable fire-extinguishers are filled with a solution of sodium bicarbonate and contain also a quantity of acid in a glass tube which can be broken by means of a plunger. By the action of the acid on the bicarbonate of soda, carbon dioxide is formed and partly dissolves in the water. On opening the nozzle, the solution of carbon dioxide is ejected by the pressure of the gas. The effectiveness of the arrangement can be increased, as in the Foamite Firefoam apparatus, by adding to the liquid in the extinguisher, glue, liquorice or some other material which is capable of forming a foam or froth. When the mixture is ejected from the apparatus, a stiff foam, containing carbon dioxide, is produced, which effectively " blankets " or smothers the fire. In the " Fire-foam " apparatus the carbon dioxide is produced, not by the action of an acid, but by the action of a solution of aluminium sulphate on sodium bicarbonate.

When carbon dioxide is passed into lime water (a solution of slaked lime or calcium hydroxide in water), a turbidity is produced owing to the fact that the gas reacts with the calcium hydroxide and forms insoluble calcium carbonate. This is clearly represented by the *chemical equation* :

$Ca(OH)_2$	+	CO_2	=	$CaCO_3$	+	H_2O
Calcium hydroxide.		Carbon dioxide.		Calcium carbonate.		Water

This reaction is used as a *test* for carbon dioxide.



Courtesy of Aberdeen Journals, Ltd.

Extinguishing an Oil-fire by means of Foamite Firefoam.

Carbon dioxide can be liquefied, and the liquid is placed on the market in steel cylinders. On allowing the liquid to be discharged through the nozzle of the cylinder into a cloth bag, rapid evaporation of the liquid takes place and the temperature is thereby lowered to such an extent that the liquid freezes to a snow-like solid. This solid passes into gas without melting and gives a temperature of -79° C. ($-110{\cdot}2^\circ$ F.).[1] It is therefore largely used as a refrigerant in the manufacture, for example, of ice cream. Owing to the fact that the solid carbon dioxide is surrounded by a layer of gas, the solid may, notwithstanding its very low temperature, be lightly placed in contact with the skin without any harm resulting. If, however, the carbon dioxide snow is pressed against the skin, painful " burns " will be produced and the skin destroyed. Carbon dioxide snow is also used, instead of ice, in railway refrigerator cars, blocks of compressed solid carbon dioxide being placed on the floor of the car. The cold heavy gas, which is formed by sublimation, gradually rises, filling the whole car and overflowing through vents at the top. This carbon dioxide snow—"drikold " or " dry ice " as it is sometimes called—is found to be as effective as more than ten times its weight of ordinary ice. Cartons of ice cream are also frequently packed in small quantities of carbon dioxide snow and the cream can thus be kept frozen for considerable periods of time.

Since oxygen is being removed from and carbon dioxide is continually being poured into the air owing to the respiration of animals, the combustion of coal and other fuels, processes of fermentation and other industrial operations, the question arises : How does Nature achieve the degree of constancy

[1] In scientific work, temperature is always measured on the Centigrade scale. On this scale, the melting-point of ice is represented by 0°, and the boiling point of water by 100°. On the Fahrenheit scale, the corresponding temperatures are 32° and 212°. For the conversion of temperature on the Centigrade scale to temperature on the Fahrenheit scale, one can make use of the formula :—

$$t^\circ F. = \frac{t^\circ C. \times 9}{5} + 32.$$

in the composition of the air which is so remarkable? Large quantities of carbon dioxide are, in the first place, removed from the air by solution in rain and in the water of the rivers and oceans. Further, as was shown by de Saussure early in the nineteenth century, the green leaves of plants take up carbon dioxide and water vapour from the air, and, through the radiant energy of sunlight and in presence of the chlorophyll or green colouring matter in the leaves, these substances are used to build up, step by step, various complex compounds, such as sugar, starch and cellulose. During this process, moreover, there is set free and given up to the air a quantity of oxygen equal in volume to the carbon dioxide removed. The green vegetation on the earth's surface, therefore, plays a very important part in maintaining the constancy of composition of the air.

The *Rare Gases* of the atmosphere, under which name are included helium, neon, argon, krypton and xenon, form a group of related elements, the discovery of which is one of the most romantic episodes in the history of chemistry.

In 1785, the Hon. HENRY CAVENDISH, a man noted for his great ability no less than for his extreme shyness and hatred of publicity, described before the Royal Society in London experiments which are at the very root of the discovery of the rare gases. Cavendish showed that when electric sparks are passed through air, combination of nitrogen and oxygen takes place; and if a solution of potash is present in the vessel of air, nitre or saltpetre is formed. By adding further quantities of oxygen and continuing to pass the sparks, the nitrogen could be removed, and any excess of oxygen could be absorbed by a solution of *liver of sulphur* (potassium sulphide). As a result of his experiments, however, Cavendish found that no matter how long the passage of electric sparks was continued, there always remained a small bubble of gas, equal to about 1 per cent. of the [illegible] which did not combine with the oxygen. Littl[illegible] that in that bubble of gas five hitherto unknow[illegible] contained,

chemists assumed that the gas was only nitrogen; and for over a hundred years the importance of Cavendish's experiment was overlooked, and the little bubble of gas, so big with scientific interest, was ignored. Until 1893, therefore, chemists everywhere believed that dry air, freed from incidental impurities, consists solely of oxygen (21·0 per cent.), and nitrogen (79·0 per cent.), together with a minute amount of carbon dioxide (about 3 parts in 10,000 of air); and so confident were chemists that they knew all about the composition of the atmosphere that the announcement of the discovery of a new element in the air, made by the late Lord RAYLEIGH and Sir WILLIAM RAMSAY at the Oxford meeting of the British Association in 1894, was received with incredulity. The story of that discovery is the story of skilful and accurate experiment, and of clear and logical reasoning.

The late Lord Rayleigh, Cavendish Professor of Physics in the University of Cambridge, while engaged in the accurate investigation of the density of different gases, found that "atmospheric nitrogen," or the gas left after removal of the oxygen from the air, had a somewhat greater density than nitrogen obtained from one of its compounds. The difference was not great, being only about 1 part in 230, but it was much greater than the possible errors of the determination. Lord Rayleigh announced his results early in 1893, and invited the help of chemists in explaining the discrepancy. With the permission of Lord Rayleigh, the late Sir William Ramsay[1] joined in the investigation and, making use of the fact that magnesium combines with nitrogen to form a nitride, Ramsay passed "atmospheric nitrogen" repeatedly over a red-hot mixture of magnesium and quicklime, and obtained a small quantity of residual gas which did not combine with the metal. Lord Rayleigh, also, repeated the experiment of Cavendish, but on a much larger scale, and

[1] Perhaps the m[illegible] of British chemists since the time of Sir Humphry Davy, [illegible]asgow in 1852, he became Professor of Chemistry at Ur[illegible], London (1887-1912) and was awarded the Nobel Prize [illegible] 1904. He died in 1916.

instead of a small bubble he obtained no less than two litres [1] of gas which did not combine with oxygen. The density of the residual gas obtained by Ramsay and by Lord Rayleigh was found to be about 20, compared with the value of 14 for nitrogen. The gas was subjected to chemical and physical treatment of every imaginable kind, but it underwent no change; and attempts to cause it to combine with other substances were entirely unsuccessful. It was a quite inactive and inert element, the first such element to be discovered, and it received, in consequence, the name *argon* (Greek *a*=not, *ergon*=work). Since atoms of argon can exist in the free state, the molecule of argon is the same as the atom. Argon is said to be monatomic.

Argon, which forms rather less than one per cent. of air by volume and which was, at first, of purely scientific interest, is now obtained commercially in large quantities from liquid air, and finds an important industrial application in filling incandescent electric lamps of the "half-watt" type. Owing to the presence of the gas, the tungsten filament of the lamp can be heated to a much higher temperature, and a brighter light can therefore be obtained, without dispersion of the metal and blackening of the bulb taking place.

When an electric discharge is passed through a mixture of argon and mercury vapour contained, under reduced pressure, in a glass tube, a bright blue light is emitted. This fact is made use of for the production of illuminated signs.

For the identification of the rare gases, all of which are chemically quite inert, use is made of the spectroscope. When white light from an incandescent solid body is allowed to pass through a prism, it is found that the light is drawn out into a rainbow band of colour, known as a *spectrum*. In the case of the light emitted by an incandescent gas, however, the spectrum consists not of a continuous band of colour, but of isolated lines of colour, each line occupying a certain definite position and corresponding with light of a

[1] A litre or 1000 cubic centimetres (c.c.) is equal to 1·76 imperial pints.

certain definite wave-length. Since each gas gives its own characteristic spectrum or arrangement of lines, it is easy, by determining the position of the lines, with the aid of a spectroscope, to identify a gas.

In 1868, the French astronomer, Professor JANSSEN, and the English astronomer, Sir NORMAN LOCKYER, while examining the spectrum of the sun's photosphere during an eclipse, observed a yellow line which they could not find in the spectrum of any known terrestrial substance. Lockyer, therefore, concluded that it must be due to some extra-terrestrial element to which he gave the name of *helium* (from *hēlios*, the Greek word for sun). The element remained unknown on the earth until the year 1895, the year after the discovery of argon, when it was isolated by RAMSAY from the uranium-containing mineral, cleveite. That a gas was given off by this mineral on treatment with acid was already known, but the gas was thought to be nitrogen. On examining the spectrum of the gas, however, Ramsay at once saw that the gas was neither nitrogen nor argon ; and examination of the spectrum of the gas by Sir WILLIAM CROOKES showed that the gas was none other than the helium of Lockyer and Janssen.

Investigation of this new gas showed that it is an element with the atomic weight 4·00, and that, like argon, it is chemically inert and incapable of forming any compounds. As in the case of argon, also, the molecule consists of only one atom. It is the most difficult of all gases to liquefy, and it boils, under atmospheric pressure, at a temperature of −268·7° C. (−515·7° F.).

Helium is now known as a disintegration product of radioactive substances, and it is consequently found in most radioactive minerals. It has also been found in certain naturally occurring waters, *e.g.* in the mineral springs of Bath, and it occurs in air to the extent of about 1 part in 200,000 by volume. The main source from which it is obtained is the natural gas which escapes from the earth in

certain parts of the world, more especially in the State of Texas, in North America, where many millions of cubic feet of helium are produced annually.

The natural gas, which comes to the separation building under a pressure of 650 lbs. per square inch, is cooled and allowed to expand. The lowering of temperature which is thereby produced serves to liquefy most of the natural gas, whereas the helium is collected in the gaseous form. The liquid is again allowed to pass into gas and the cold gas so obtained serves to cool down the incoming gas. The natural gas, freed from helium, is used for heating and illuminating purposes.

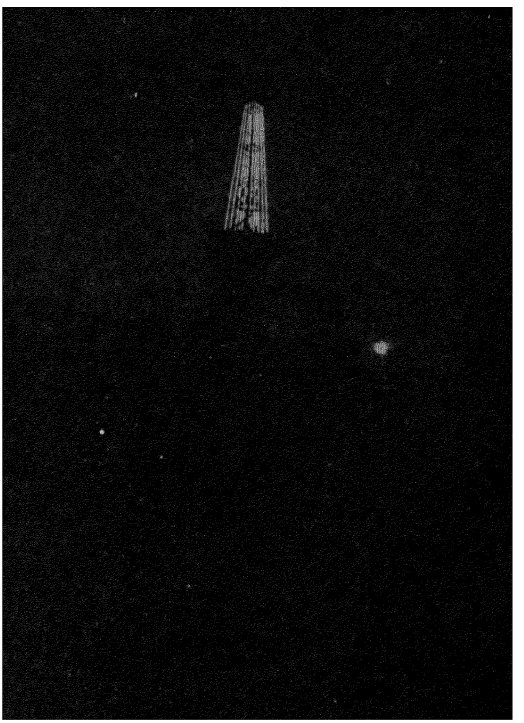
Helium is used for filling balloons, and for this purpose it possesses the great advantage over hydrogen of not being inflammable. Although the density of helium is twice that of hydrogen, its lifting power is not much less, because the lifting power depends only on the difference between the density of the air and that of the gas. Taking the densities of hydrogen, helium and air as 1, 2 and 14·4 respectively, the lifting power of hydrogen and of helium will be as 13·4 is to 12·4. That is to say, the lifting power of helium is 92·5 per cent. of the lifting power of hydrogen.

Helium also finds use in the treatment of respiratory diseases and for the production of artificial breathing atmospheres for caisson workers and divers working at great depths. If, in these cases, divers are supplied with ordinary air, nitrogen dissolves in considerable quantities in the blood under the existing high pressure; and if the diver were brought rapidly to the surface, the dissolved nitrogen would pass out of solution and cause death by a blocking of the blood vessels with gas. To avoid this, a long period of gradual decompression is necessary. If, however, the diver is supplied with a mixture of oxygen and helium, the period of decompression can be very greatly reduced, as the solubility of helium is much less than that of nitrogen.

Under the influence of an electric discharge, the gas emits

a pale yellow light, and is used in the construction of illuminated signs.

Owing to the discovery of the monatomic elements, argon



NEON LIGHTHOUSE.

[From *The Approach towards a System of Imperial Air Communications*, by permission of the Controller of H.M. Stationery Office.]

and helium, which are chemically inert and may therefore be regarded as having zero valency, a new family of elements had to be inserted in the periodic classification. Since, moreover, helium preceded the metallic element lithium,

and argon the element potassium, it seemed probable that other similar elements should exist which would take their places in front of the elements sodium, rubidium, and caesium (Fig. 1, p. 24). In 1896, therefore, a systematic search for the missing elements was commenced by Sir WILLIAM RAMSAY and Dr. MORRIS W. TRAVERS, and was pursued with such energy and ability that in a short time three new elements were obtained from the air, namely, *neon*, *krypton* and *xenon*. The identity of these gases was established by means of the characteristic spectra which they give; and the determination of their atomic weights showed that they were the elements sought for. In the space of a few years, therefore, no fewer than five new elements, present in the air, were discovered; and the series of the rare gases was completed some years later by the discovery of radon, the radioactive gas or "emanation" given off by radium.

Besides helium and argon, neon, which occurs in the air to the extent of only fifteen parts per million, has already found practical application for filling "Osglim" lamps (night lights and emergency lights), and neon tubes, used for testing the sparking plugs of motor cars and in the construction of illuminated signs. Under the influence of the electric discharge, the gas glows with a brilliant rose colour.

Since the light emitted by neon lamps has a great power of penetrating mist and fog, such lamps are also used for lighthouses at air-ports.

Krypton and xenon, also, are now being used in place of argon for filling electric lamp bulbs. Such lamps are said to be one-third more efficient than those containing argon. Krypton occurs to the extent of one part per million, and xenon to the extent of one part per eleven million parts of air.

In modern times, owing to the great development of the nitrogen industries, more especially the synthetic production

of ammonia (p. 207), a cheap source of nitrogen, as well as of hydrogen, has become essential. As we shall learn in the sequel, various sources of industrial hydrogen are now available.

For the purpose of obtaining nitrogen, the method which is most frequently employed in industry is the distillation of liquid air. Liquid air, of course, consists of a mixture of liquid nitrogen (together with argon, etc.) and liquid oxygen, which boil at $-196°$ and $-183°$ C. ($-319°$ and $-296{\cdot}5°$ F.) respectively. Just as the different hydrocarbons in crude petroleum can, as will be pointed out later, be separated by fractional distillation, so also, in the case of liquid air, one can separate the nitrogen from the oxygen. As nitrogen boils at a lower temperature than oxygen, it distils off first, and can, by suitable arrangements, be obtained free from oxygen.

The production of liquid air is now a very simple matter, and has developed into an industry of enormous proportions, many millions of gallons of liquid air being produced daily in the different factories of the world. The principle on which the process of liquefaction depends is that when highly compressed air is allowed to expand rapidly, its temperature falls; and the amount by which the temperature is lowered on expansion is all the greater the lower the temperature of the compressed gas previous to the expansion.

The industrial application of this principle is due mainly to a German and to an English engineer, von Linde and W. Hampson, and their process will be understood from Fig. 3. Air under a pressure of about 150 atmospheres, and free from moisture and carbon dioxide, enters the apparatus at A, and passes, as shown by the arrows, to the central tube, where it sub-divides into a series of three or four tubes, B, of thin copper wound spirally round the central rod D. At the lower end, these tubes pass together into a valve C, at which the compressed air rapidly expands. A lowering of

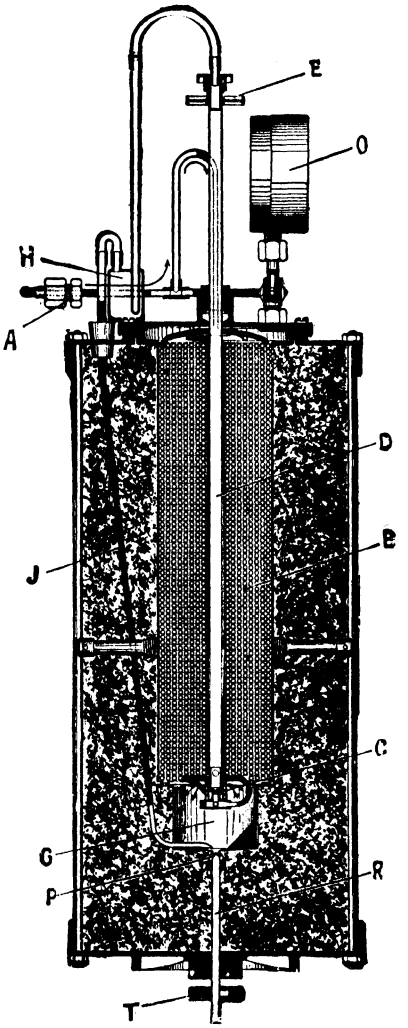


FIG. 3.—HAMPSON APPARATUS FOR LIQUEFYING AIR.

A, tube by which air enters ; B, section through spirals of copper tubing ; C, expansion valve ; D, central spindle ; E, wheel for opening and closing expansion valve ; G, tank in which liquid air collects ; H, gauge to indicate amount of liquid air in G ; J, tube connecting tank with gauge ; O, pressure gauge to indicate pressure at which the air enters the apparatus ; P, valve closing tube R, through which the liquid air is withdrawn ; T, wheel for opening the valve R.

temperature is thereby produced. The cool air now passes upwards over the coils of copper tubing, and so cools down the compressed air which is passing through them towards the expansion valve. In this way the air expanding at the valve gets progressively colder and colder, until at last a point is reached when the lowering of temperature on expansion is so great that the air liquefies. It collects in the tank G, from which it can be drawn off from time to time through the tube R.

The ease with which liquid air can now be produced is not only of great industrial importance, but is also of much value in the furtherance of scientific knowledge. By means of liquid air, one is enabled to extend the scope of scientific investigation to temperatures which otherwise would be inaccessible; and the increase of knowledge which has accrued therefrom is of the highest scientific interest and practical value. The utilisation of this new aid to scientific research was greatly facilitated by the introduction of the well-known Dewar "vacuum vessels." These "vacuum vessels," which are now so familiar under the name of "thermos" flasks, consist of double-walled glass vessels (Fig. 4), the air being removed as completely as possible from the space between the two walls. The "vacuum" by which the vessel containing the liquid air is thus surrounded acts as a very efficient heat insulator, so that although the liquid air is several hundred degrees Fahrenheit colder than the surrounding atmosphere, the heat from the latter is conducted only very slowly to the liquid air, which may thus be preserved for hours without any considerable loss. The efficiency of the vacuum vessel may be considerably increased by silvering the inner walls of the vessel. By this means the passage of radiant heat can to a great extent be prevented.

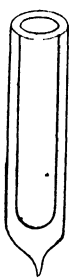


FIG. 4.—DEWAR VACUUM VESSEL.

CHAPTER IV

COMBUSTION AND THE PRODUCTION OF FIRE

ONE of the most typical, most familiar and most important cases of chemical action is that which is observed in the process of combustion or the burning of substances in air. The manner in which the first visible combustion, or fire, was brought about on the earth will doubtless always remain unknown. It may, perhaps, have had its origin in some lightning flash, or in the sparks struck from the flints of primitive man ; or it may have been produced by the self-heating of combustible material, or by the rubbing together of dried wood ; or it may be that, as in the *Song of Hiawatha* :

> Gitche Manito, the mighty,
> . . . . .
> Breathed upon the neighbouring forest,
> Made its great boughs chafe together,
> Till in flame they burst and kindled.

But in whatever way fire was first produced, its importance and value were early recognised, as one can understand from the sanctity with which all primitive peoples have endowed the hearth ; from the Promethean legend of a boon stolen from, not granted by, the gods ; as well as from the later belief of the followers of Zoroaster, that fire is the special abode of divinity.

And even in modern times, although the feeling of reverence or of awe is no longer inspired by a process which can be explained in terms of chemical action, and can be produced at will by the striking of a match, one is not likely to underrate the importance of combustion when it is remembered that our present-day civilisation in all its manifold forms of expression, in manufactures, in railway and steamship transport, in artificial illumination, etc., is based on a process of combustion.

What then is the explanation of this process of combustion? Not so very long ago the view was held that the property of combustibility was due to the presence in the combustible substance of a fiery principle, *phlogiston*;[1] and that when a substance burns, the phlogiston escapes, leaving behind the ash, or calx, as it was called in the case of a metal. Charcoal, which burns leaving practically no ash, was therefore regarded as being almost pure phlogiston. This was the explanation of combustion given, more especially, by the German chemist, STAHL, towards the end of the seventeenth century; and it was not till a hundred years later that the "phlogiston theory" was finally overthrown by LAVOISIER,[2] who died in 1794, a victim of the guillotine, in the troublous times of the French Revolution.

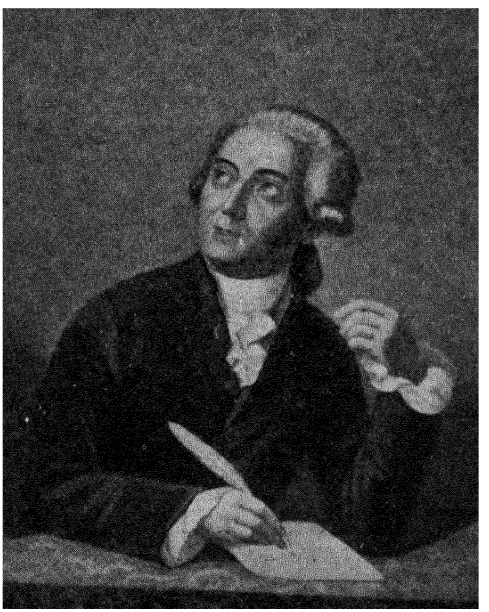
The long life of such an erroneous theory as that due to Stahl may be attributed to the fact that chemistry was, at that time, still largely a qualitative or descriptive science, and it was considered that form rather than weight was the characteristic property of substances. The balance, of course, was known and used, but its importance was not fully appreciated; so that when it was found that the products of a combustion weigh more than the original combustible substance, the upholders of the phlogiston theory sought to defend their position by identifying phlogiston with the "principle of levity." The escape of the "principle of levity" from the body left the body heavier.

Much as one may be inclined to smile at such an explanation, one ought to remember that the phlogiston theory served usefully its day and generation, and satisfied even the modern requirements of a theory, in that it gave an explanation of combustion which satisfied men's minds at the time,

[1] The word is derived from the Greek verb, *phlogizein*, meaning to burn.

[2] Antoine Laurent Lavoisier, the most brilliant of the French chemists of the eighteenth century, was born in Paris in 1743, and made many contributions of the greatest importance to chemistry. He became a member of the *Ferme Générale*, was denounced by Marat as acting contrary to the commonweal, and was beheaded on 8th May 1794.

and also inspired a large amount of fruitful investigation. Who can say that even some of our most cherished theories may not be considered by the unthinking a hundred years hence to be equally worthy of derision? The phlogiston theory, however, long outlived its usefulness, and the



ANTOINE LAURENT LAVOISIER.

tenacity with which it maintained itself is an instructive illustration of the difficulty which most minds have of freeing themselves from the authority of a long-held theory; and it conveys a lesson, which is not unnecessary even at the present day, that a theory from being a helpful guide may readily become an oppressive tyrant. As LIEBIG wrote many years ago, after having himself been a victim of the misfortune to which he refers: "No greater misfortune

could befall a chemist than that of being unable to shake himself free from the power of preconceived ideas, and, yielding to the bias of his mind, of seeking to account for all phenomena which do not fit in with these ideas by explanations which have no basis in experiment."

The irresistible force of facts, however, was gradually increasing, and after the discovery of the gas oxygen by Priestley and by Scheele, in the year 1774, Lavoisier was able to put forward a new interpretation of the process of combustion of substances in air; and with that interpretation, modern chemistry was born.

It was known that air consists of two parts or constituents, an " active " part which enables a substance to burn and an " inactive " part (azote or nitrogen), in which combustion does not take place. During a visit to Paris in 1774, Priestley, while dining one day with Lavoisier, mentioned his discovery of a gas, now known as oxygen (p. 47), in which a candle burned much better than in common air. Lavoisier at once conceived the idea that this new gas represents the portion of the air which combines with a metal and gives rise to the calx; and the explanation of combustion was thus to be found in the chemical combination of the burning substance with the oxygen of the air. The correctness of this idea was proved by quantitative experiment and the actual weighing of the substances.[1]

The calx of mercury (now known as oxide of mercury) was first produced by heating a weighed amount of mercury in a retort which communicated with a known volume of

[1] It may, perhaps, be remarked in passing, that it was Lavoisier who, owing to the constant use which he made of the balance and the importance which he attached to its indications, established the fundamental law of physical science, the *law of the conservation of matter* or *conservation of mass*, which states that in no chemical action is matter either created or destroyed; the sum of the masses of the reacting substances is equal to the sum of the masses of the products formed. The matter can be changed in form; it cannot be altered in quantity. All later experimental investigation, even the most recent, carried out with all the care and refinement of accuracy of which the modern balance is capable, has served only to confirm this law discovered by Lavoisier.

air contained in a bell-jar standing over mercury (Fig. 5). The mercury in the retort was heated on a charcoal furnace for twelve days at a temperature just below its boiling-point. At the end of this time a quantity of the red calx of mercury, 45 grains in all, had formed on the surface of the metal, and the volume of the air in the bell-jar had diminished by 7–8 cubic inches. The residual gas in the bell-jar did not support life or combustion.

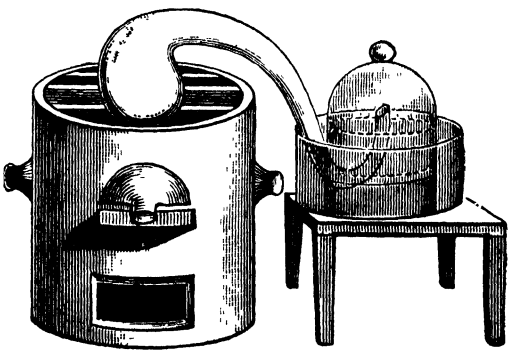


FIG. 5.—LAVOISIER'S EXPERIMENT OF HEATING MERCURY IN AIR.

The red calx of mercury was then heated to a higher temperature, and Lavoisier found that from 45 grains of the calx, 41 grains of metallic mercury were formed and 7–8 cubic inches of a gas (oxygen) were evolved.

It was thus shown by Lavoisier that when a metal or other substance is burned in air, the oxygen of the air combines with the metal or burning substance. In other words, *the process of combustion is a chemical reaction between the burning substance and the oxygen of the air, the process being accompanied by emission of heat and, it may be, light.* A flame, however, is formed only when the burning substance is a gas at the temperature of the combustion. The nitrogen of the air takes no part in the process, but acts merely as a diluent which moderates the vigour of the combustion.

Since combustion in air is due to a chemical reaction between the burning material and oxygen, a process which is known as *oxidation*, the vigour of combustion can be increased by increasing the rate at which oxygen is supplied to the burning material; and this is what one does when one blows a fire with a bellows. Conversely, combustion can be stopped by preventing access of oxygen to the burning material, as happens when one uses, for example, the Foamite fire extinguisher (p. 48). Similarly, the Pyrene fire extinguisher, largely used on motor cars, is filled with a liquid, carbon tetrachloride, which when squirted on burning material forms a heavy vapour. This vapour effectually "blankets" the fire and prevents access of atmospheric oxygen to the burning material.

If, however, the explanation of combustion which has just been given is correct, the question arises: Why does a combustible material not take fire when it is exposed to the air? Coal gas, for example, may be allowed to escape from the burner, or a candle or piece of wood or coal may be left exposed to the air, or even to pure oxygen, without any apparent change taking place; and in order that they shall exhibit the phenomenon of combustion, that is, in order that they shall undergo the process of oxidation, or combination with oxygen, with production of heat and light, it is necessary to heat the materials up to a certain temperature, called the *ignition-point*. Combustion then goes on of itself. The explanation of this fact is that the velocity or vigour of every chemical change is increased by raising the temperature. At the ordinary temperature, the oxidation of the candle or the coal takes place so slowly that no change is apparent even over long periods of time. If, however, the temperature of the combustible material is raised, the rate at which it reacts with the oxygen of the air rapidly increases, and consequently the production of heat which accompanies the reaction also rapidly increases, and the temperature rises progressively. When this reaches a certain point, the

ignition-point, the reaction takes place with such rapidity that the heat which is produced by the process of oxidation is sufficient to raise the substances to incandescence and also to maintain the burning substance at a temperature above the ignition-point. The process of combustion is thus enabled to proceed continuously.

On the other hand, if the burning substance is cooled sufficiently, the temperature is lowered to below the ignition-point, and so the combustion ceases. A simple experiment which can be carried out by anyone will serve to demonstrate

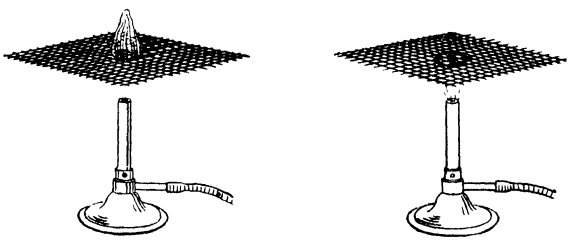


FIG. 6.—EXTINCTION OF FLAME BY WIRE GAUZE.

this important truth. If a piece of metal wire gauze is held at a distance of half an inch or an inch above a burner from which coal gas is issuing, and if a light is then applied to the gas *above the gauze*, it will be found that the flame of burning gas is arrested by the gauze and does not pass through to the burner (Fig. 6); for the wire gauze conducts the heat of the flame away so rapidly that the temperature is lowered to below the ignition-point of the gas. Only after the gauze has become quite hot does the gas below the gauze become ignited. Similarly, if the gauze is brought down on a flame of burning gas, the flame is extinguished at the gauze. The gas itself, however, passes through, as can be shown by bringing a light to the upper surface of the gauze, when the gas will take fire.

The cooling power of wire gauze received, early last century, an application of the highest importance in the miner's safety lamp invented by Sir HUMPHRY DAVY. This

lamp has undergone a striking change and marked improvement since the time of its first invention, and the modern safety lamp (Fig. 7) shows little sign of the means whereby safety is secured. On careful examination, however, it is seen that all the holes through which air can pass to the flame, or the hot air and products of combustion can pass out, are protected by fine wire gauze. Although, therefore,

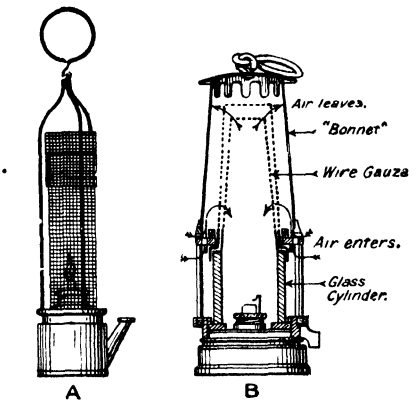


FIG. 7.—MINER'S SAFETY LAMP.

In the old form of lamp, the flame was surrounded by a closed cylinder of wire gauze which considerably diminished the light emitted by the lamp ; but in the modern type, a cylinder of glass is inserted, whereby the efficiency of the lamp is greatly increased.

the combustible gas, the " fire-damp," can pass through this gauze and can burn inside the lamp, the flame cannot pass through the gauze and be communicated to the explosive mixture of fire-damp and air in the mine.

Warning of the presence of the dangerous fire-damp is given to the miner through the luminous flame of the lamp becoming crowned by a " cap " of pale blue flame. The greater the amount of fire-damp the larger is the cap.

The process of combination with oxygen which, as we have seen, is the essential feature of the combustion process in air, may, however, go on appreciably even at temperatures

below the ignition-point. Thus, when metallic iron is exposed to moist air, it rusts. This rust is oxide of iron, a compound of iron and oxygen; and the process of rusting is therefore a process of oxidation, a process of combustion, against which it is necessary to protect, by paint or other means, all iron structures exposed to the air, if we would have them last. The rusting of iron is said to be a process of *slow combustion*, because the temperature does not rise to the point of incandescence. Slow combustion can be demonstrated more strikingly with the metal aluminium, which combines with oxygen more vigorously than iron does. When finely divided aluminium is heated in the air, as, for example, when aluminium powder is blown through a flame, it burns with a very bright light; but when exposed to the air at the ordinary temperature, the metal remains apparently unchanged. As a matter of fact it rapidly combines with the oxygen of the air, but the coherent film of oxide which is formed on the surface protects the metal from further attack, and therefore no change is apparent. By coating the surface of the metal with mercury, however, a liquid amalgam or alloy of mercury and aluminium is produced, and the formation of a coherent film of aluminium oxide is thereby prevented. The aluminium is consequently no longer protected from the continued action of the oxygen of the air. In this case it is observed that the aluminium undergoes oxidation quite rapidly, the oxide forming a moss-like growth on the surface of the metal. The heat which is produced by the oxidation, although quite marked, is dissipated so quickly that the temperature does not rise to the point of incandescence, and so no light is seen.

Processes of slow combustion, or combustion unaccompanied by the emission of light, are going on continually within our bodies, and are the source of the heat by means of which the temperature of the body necessary for health is maintained. When air is drawn into the lungs, the oxygen passes or diffuses through the thin walls of the blood vessels,

and combines with the hæmoglobin present in the red blood corpuscles. On the other hand, carbon dioxide passes from the venous blood into the air-spaces of the lungs and is expelled in the expired air. The oxygen, in the form of oxy-hæmoglobin, is carried by the blood to all parts of the body, and oxidises or burns the tissues and assimilated food materials with production of carbon dioxide and water, the former being then conveyed by the blood back to the lungs and so got rid of. Oxygen, then, is necessary for respiration as well as for combustion in air, and, although prolonged inhalation of pure oxygen would be harmful by producing too rapid oxidation in the body, the gas is frequently administered in cases of difficult breathing due to pneumonia or other diseases of the lungs.

The presence of carbon dioxide in expired air is readily shown by blowing through a tube into clear lime water (a solution of slaked lime in water). The liquid very speedily becomes turbid owing to the separation of insoluble carbonate of lime, formed by the combination of carbon dioxide with the slaked lime (p. 48).

In the processes of putrefaction and decay, also, we have examples of slow combustion in which animal and vegetable material is oxidised by the oxygen of the air, with the co-operation of various micro-organisms; and efficient aeration, as in a rushing and tumbling stream, is an excellent means of purifying water from all kinds of organic contamination.

Under favourable conditions, the process of slow combustion may pass into rapid combustion with production of light. For, if the heat which is produced by the combination of the oxygen with the combustible material is prevented from being dissipated, the temperature will go on rising gradually, and as the temperature rises, the vigour of the combustion, or chemical combination, increases. More and more heat, therefore, is produced in a given time, the temperature rises more and more rapidly until, finally, it reaches the ignition-point of the combustible material. The slow

combustion passes into rapid combustion, and the combustible material takes fire without the application of external heat; in other words, it undergoes *spontaneous combustion*. In this way arise, for example, the so-called " gob " fires, in spaces from which coal has been removed and where coal-dust and fine coal remain behind; so also may fire break out in coal bunkers and in other confined spaces in which combustible matter, like oily cotton waste, is stored without proper ventilation. Such spontaneous combustion will, of course, take place with special readiness in the case of readily inflammable substances, or substances which have a low ignition-point, such as phosphorus. Thus if this substance is dissolved in the liquid known as carbon disulphide, and if the solution is then poured on a sheet of filter paper, or thin blotting-paper, the carbon disulphide soon evaporates and leaves the phosphorus on the paper in a finely divided state. The oxygen of the air rapidly unites with the phosphorus, and the heat which is thereby developed soon raises the temperature to the ignition-point of the phosphorus, and rapid combustion sets in.

Although the most familiar examples of combustion are those which take place in air, the term combustion must not be restricted only to such cases. Combustion, in its widest meaning, is a process of chemical action in which so much heat is generated that the burning substance becomes incandescent and emits light; and such a process may occur even when no air or oxygen is present. Thus, for example, the gas hydrogen will burn not only in air, with production of the substance water, but it will also burn in the gas chlorine with formation of the compound known as hydrogen chloride or hydrochloric acid gas. And similarly, other cases of combustion are known which do not depend on the presence of oxygen, and are not processes of oxidation.

Even when the combustion is due to the combination of the combustible material with oxygen, to a process of oxidation as we have called it, the oxygen need not be

present in the gaseous form, but may be yielded up by some compound containing it. Various well-known substances, such as chlorate of potash (potassium chlorate), $KClO_3$, and saltpetre (potassium nitrate), KNO_3, can act as suppliers of oxygen in this way, and the use of such substances for promoting combustion has long been known. *Touchpaper*, for example, the slow-burning paper which is so familiar in connection with fireworks, is prepared by soaking paper in a solution of saltpetre and allowing it to dry. The saltpetre is in this way deposited in the fibres of the paper, and renders the latter more readily combustible. Such paper does not require the presence of gaseous oxygen for its combustion, but will burn in an atmosphere of nitrogen or other inert gas. In the case of gunpowder, also, which will be discussed at a later point, saltpetre is similarly made use of as a reservoir of oxygen.

The process of combustion by means of combined oxygen has also been turned to very good account for the production of high temperatures and for the purpose of obtaining certain metals from their oxides. The metal aluminium, we have seen, reacts energetically with oxygen, and it combines with great vigour not only with gaseous oxygen but also with the oxygen contained in compounds. If, then, oxide of iron is mixed with powdered aluminium and the mass strongly heated at one point by means of a special ignition mixture, the aluminium combines with the oxygen of the iron oxide; and so much heat is thereby generated that a temperature of nearly 3000° C. (about 5400° F.) is produced. This reaction forms the basis of the so-called *thermit* process, a process which has become familiar through its application to the welding of tramway rails and to the repair, *in situ*, of broken castings, shafting, etc. The mixture of iron oxide and aluminium is ignited and the molten iron which is produced in the process and raised to a high temperature by the vigour of the reaction is run into a mould formed round the ends of the rails or fractured

metal. The rails are thus raised to such a high temperature that they can be readily welded by pressure, or the fracture is filled with fresh iron and a solid joint effected.

The very high temperature produced by the combustion of aluminium has led to the use of thermit mixture in incendiary bombs designed to be dropped from aeroplanes or airships, the bombs being furnished with a special mechanism by means of which the mixture can be ignited automatically.

The intense heat produced by the oxidation of aluminium has also been made use of in certain high explosives used for military purposes. The best known of these is *ammonal*, which consists of a mixture of aluminium powder with ammonium nitrate and trinitrotoluene (or T.N.T.). When this mixture explodes, the aluminium is oxidised by the ammonium nitrate, and the temperature of the explosion is thereby greatly raised (see also p. 135).

In order to bring about combustion, it is necessary, as we have seen, to raise the temperature to a certain point, the ignition-point. Nowadays this causes no difficulty; and it may be regarded as not the least of the services which chemistry has rendered to man, that it has put it within his power to obtain fire at will, with a minimum both of trouble and expense. From the primitive method of rubbing two dried sticks together to the use of the flint and steel, and from the latter to the modern safety-match, is indeed an advance the importance of which for our modern civilisation it would be difficult to estimate and impossible to over-estimate.

One of the characteristics of chemical action, as we have seen it exemplified in the process of combustion, is the production of heat, but it was not till early in the nineteenth century that practical suggestions were made for the employment of such means of producing fire. One of the earliest of these suggestions which had a certain measure of success was made, about 1810, by a Frenchman named CHANCEL, who tipped strips of wood with a mixture of potassium chlorate and sugar, bound together by means of

gum. When this composition was dipped into concentrated sulphuric acid (oil of vitriol), the sugar took fire and burned at the expense of the oxygen contained in the potassium chlorate; and this combustion was then communicated to the wood splint. These matches were sold as late as the middle of last century. About the beginning of 1827, JOHN WALKER, an English apothecary, invented a match the tip of which consisted of a mixture of potassium chlorate and sulphide of antimony, and this mixture could be ignited by being drawn between folds of glass paper. These matches, known as "friction lights," and later as lucifers, were the first friction matches used.

But there is a substance the use of which for matches is at once suggested both by its name and by its properties, the readily inflammable substance *phosphorus*, which was discovered as long ago as 1669, and is prepared at the present day by heating to a high temperature in an electric furnace a mixture of calcium phosphate, silica (sand), and coke. From the readiness with which this substance ignites, it was only natural that attempts should be made to utilise it as a convenient fire-producer. Such attempts were, at last, successful, and phosphorus-tipped matches, known as Congreves, were in almost universal use until near the end of the nineteenth century.[1] The tips of these matches consisted, essentially, of a mixture of phosphorus and some substance rich in oxygen, such as potassium chlorate, or red lead (oxide of lead), bound together with gum or glue, and coloured with various pigments. As fire-producers these matches were a great advance on those which had gone before. But for every advance a certain price has to be paid, and for the phosphorus match mankind found the price

[1] Even as early as 1786, an Italian had brought out in Paris "le briquet phosphorique," which consisted of a bottle coated internally with phosphorus, and matches tipped with sulphur. When one of the matches was rubbed against the inside of the bottle so as to remove a little of the phosphorus, and was then brought into the air, the phosphorus took fire. Such a match was used by Faraday as late as 1827.

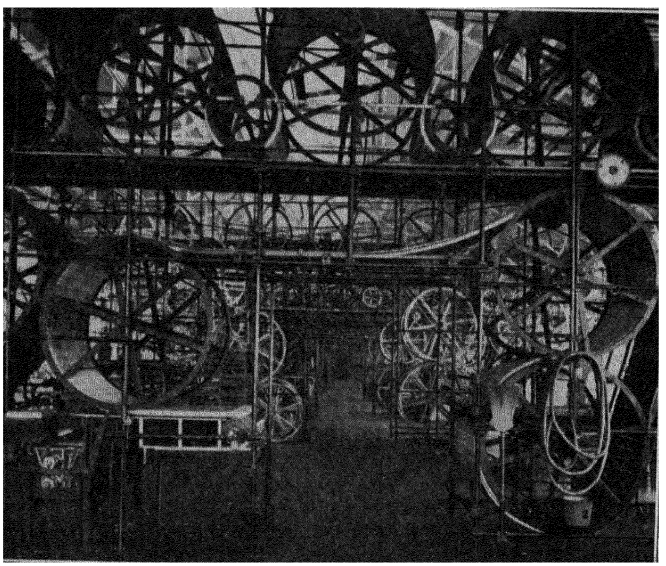
too heavy. The accidental fires due to the ready inflammability of the phosphorus, and the general danger of its unrestricted use; the number of deaths, accidental or intentional, produced by phosphorus poisoning; and the terrible disease, known as "phossy jaw," or necrosis of the jaw-bone, which attacked the workers in the match factories, led to a ban being placed on what had been hailed as a boon; and the use of ordinary white or yellow phosphorus [1] has, in all civilised countries, been forbidden by law.

The element phosphorus, however, occurs not only in the readily inflammable and poisonous white variety, but also in a totally distinct form, that of a dark red powder known as *red phosphorus*. Such physically distinct forms of an element are frequently spoken of as *allotropic modifications*.

Since red phosphorus, which is produced by heating white phosphorus in closed vessels to a temperature of about 240° C. (464° F.), is much less readily inflammable than white phosphorus and is also non-poisonous, attempts were made to utilise it for the manufacture of matches. Difficulties were at first encountered, but these were overcome by a German chemist about the middle of last century; and his invention, first taken up in Sweden, led to the introduction of the so-called Swedish or *safety match*. In these matches the red phosphorus is not incorporated in the match head, but is used in the composition with which the rubbing surface is coated. The match tip consists of a mixture of sulphide of antimony and an oxidising substance such as potassium chlorate, red lead, or potassium dichromate; and sulphur and charcoal are sometimes added. This mixture will not take fire when rubbed on a rough surface, but only when rubbed on the specially prepared surface coated with a paste of red phosphorus mixed, sometimes, with sulphide

[1] Pure phosphorus is a white, translucent, wax-like substance which can be cut with a knife. When exposed to sunlight it becomes yellow or even red in colour owing to its conversion into the so-called red phosphorus.

of antimony and powdered glass. Moreover, in order to diminish the risk of accidental fire through the glowing wood of a used match, safety matches are soaked in a solution of alum, sodium phosphate, ammonium phosphate, or some other salt. The charred wood of the match is thereby



Courtesy of Bryant & May Ltd.

MACHINE FOR MAKING MATCHES.

The splints of wood, fixed in holes in an endless metal band, are carried through a bath of melted paraffin to impregnate the wood, and then over the surface of the match composition contained in a trough on the left. As the band travels on, the matches are given time to dry before being pushed out of the holes in the band.

strengthened, and the match ceases to glow almost immediately after being blown out.

When the use of white phosphorus was forbidden, the attention of chemists was directed to the discovery of other materials which might be used instead, and a non-poisonous match was produced which possessed the advantage of the

old phosphorus match, of striking on any rough surface. In the case of this " strike anywhere " match, the tipping composition consists of a mixture of sulphide of phosphorus and potassium chlorate, or other oxidising material, bound together with glue, and powdered glass is also sometimes added to increase the friction and so facilitate the inflammation of the match head.

To render the wood of the match more readily inflammable and so allow of the combustion passing on from the tip to the wood, the latter is impregnated with paraffin wax, although, sometimes, as in the case of some Continental matches, sulphur is employed instead.

In the case of *vesuvians*, the match head consists of a mixture of powdered charcoal and nitre, to which some scenting material, such as gum benzoin or sandalwood, is added. This head is then tipped with a striking mixture such as has already been described.

The making of matches, once a " dangerous occupation," has now passed from the handworker to the machine, which not only cuts the blocks of wood into splints of proper size and shape, but tips them with the inflammable mixture and packs them into boxes, which it also makes and labels. A single machine can thus turn out over 5,000,000 matches in a day. Only by such means could the almost incredible number of matches be produced which are turned out annually by the match factories of the world.

Although the ordinary match forms by far the most usual means of obtaining fire and light, one must not fail to mention the now familiar " petrol lighters." When an alloy of iron and the metal cerium is rubbed against a piece of steel, small particles of the alloy are rubbed off and take fire in the air. If the sparks so produced are allowed to come into contact with the vapour of petrol, or similar volatile liquid, the latter takes fire and a flame is obtained. In this apparatus we have, in a refined form, the flint and steel of olden days.

Ceria, or oxide of cerium, is now produced in large quantity as a by-product of the manufacture of incandescent gas-mantles (p. 111), and is derived mainly from monazite sand, valuable deposits of which are found in Brazil and also in Travancore, India. It was while investigating how the accumulations of ceria might be utilised that AUER VON WELSBACH discovered, early in the present century, the peculiar property of the iron-cerium alloy which led to the above application.

The pyrophoric cerium-iron alloy has also found use in tracer shells and tracer bullets. The friction of the air, as the shell or bullet speeds on its way, causes a small piece of the alloy, attached to the shell or bullet, to take fire and so trace out the path of flight.

CHAPTER V

FUELS AND ILLUMINANTS

Solid Fuels

Until comparatively recent times, down, say, to the seventeenth century, wood was the almost universal fuel; but since coal first began to be mined, it has become, in an ever-increasing degree, the immediate source of the energy on the utilisation and transformation of which our present-day civilisation depends, and it now occupies a position of unquestioned pre-eminence.

Coal consists of the fossil remains of early, luxuriant vegetations. Through an age-long process the cellulose, of which the woody fibre essentially consists, has become converted, under the influence of high temperature and pressure, into more highly carbonised compounds, the proportion of hydrogen and oxygen becoming diminished owing to the formation of gaseous substances such as carbon dioxide and marsh gas. From the figures given in the following table, one can

	Carbon.	Hydrogen.	Oxygen	Calorific value B.Th U. per lb.
Cellulose $(C_6H_{10}O_5)_n$	44·5	6·2	49·3	7,500
Wood (dry)	50·0	6·0	44·0	8,600
Peat (Irish)	60·0	5·9	34·1	9,900
Lignite	67·0	5·2	27·8	11,700
Bituminous coal	88·4	5·6	6·0	14,950
Welsh steam coal	92·5	4·7	2·7	15,720
Anthracite	94·1	3·4	2·5	

recognise the gradual carbonisation of cellulose, the materials peat, lignite or brown coal, bituminous coal and anthracite representing progressive stages in the natural process.[1]

[1] It must be noted that wood, peat and coal are not definite chemical compounds, and that the composition of the different kinds of coal may vary considerably. The numbers given in the table, therefore, are only approximate values representing, as it were, the composition and calorific

The process of carbonisation is accompanied by a diminution of the amount of gaseous and volatile matter which the fuel can yield on being heated, and this markedly affects the manner in which the different materials burn. Dry wood, we know, burns readily and with a bright and cheerful flame, whereas anthracite, which represents the most advanced stage in the natural process of carbonisation of woody fibre, is ignited only with difficulty, and burns with a very small and not strongly luminous flame.

It is not, however, the cheerfulness with which the fuel burns that concerns us here, but the all-important question of how much heat is given out in the process of combustion. It is the " calorific value " of the fuel that claims our attention just now.

When one examines the different solid fuels from this point of view, it is found, as the figures in the last column of the table on p. 79 show, that with the progressive carbonisation, the heat-producing power of the fuel increases, so that among all the solid fuels, anthracite stands pre-eminent. A British thermal unit [1] represents the amount of heat required to raise the temperature of one pound of water through 1° F., and the numbers in the table show that whereas one pound of dry wood will give out, on burning, about 8,600 units,[2] an equal weight of bituminous or household coal will yield about 14,900, while Welsh steam coal and anthracite will give 15,700 units. On this fact depends the great value of anthracite as a fuel.

Although wood is still used to some extent as a fuel, more

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value of an average member of the different classes. Moreover, other substances, more especially compounds of nitrogen and sulphur, are present, besides carbon, hydrogen and oxygen; but although, under certain conditions, these substances may give rise to important and sometimes undesirable by-products, their influence on the fuel-value of the combustible materials is very small.

[1] Heat energy is very frequently measured also in calories, a calorie being the amount of heat required to raise 1 gram of water through 1° C. A British thermal unit is equal to 252 calories.

[2] Under ordinary conditions the calorific value is considerably less than this owing to the presence of 15–20 per cent. of moisture.

especially in domestic heating, it cannot, on account of its price and low heat-producing power, find general adoption. The value of wood, in fact, as a material for constructional purposes and as a source of cellulose (for the manufacture of paper, rayon or artificial silk, etc.) and other products is much greater than its value as a fuel.

In the great peat deposits of the world,[1] also, there exists an enormous potential supply of fuel, but although peat has a local importance as a domestic fuel, the cost of removing the large amount of water which it contains has hitherto proved an effective barrier to its commercial exploitation as an industrial fuel.

When one considers the very great variations in the calorific value of different kinds of coal, it will at once be clear that it is rather irrational to buy coal merely by weight, without regard to the amount of heat which the coal can give out. It is true that the existence of different kinds of coal having varying quality or calorific value is recognised to some extent by a variation in the price charged; but what is, perhaps, not sufficiently recognised is that there may be considerable variation in the heat value of even the same kind of coal, or of coal drawn at different times from the same mine. Clearly, then, the price paid should be related to the heat-producing value of the coal, and this is the basis on which, to an increasing extent, large consumers of coal contract for their supplies.

The world's supply of coal, on which our present-day industrial civilisation depends, is being used up incomparably more quickly than fresh coal is being formed; and the question, how most efficiently to utilise the irreplaceable coal reserves is therefore exercising the minds of the scientific leaders of industry in all countries. The problem of coal economy and coal utilisation, moreover, must not be re-

[1] The area of peat moors in Europe has been estimated at 140,000,000 acres, and in Ireland alone the available peat has been estimated as equal to 2,500,000,000 tons of coal.

garded merely from the point of view of the use of this mineral as a fuel or as the source of other fuels (oil or gas), for it must not be forgotten that coal, in the hands of the chemist, is also the ultimate source of very valuable chemical products—dyes, drugs, plastics, explosives, etc.—derived from the product of its distillation, coal tar. From coke and steam, moreover, a gas (water-gas) is produced which, as we shall learn later, is not only an important fuel but also the raw material from which substances of great industrial and economic value are obtained.

Whereas, in industry, the necessity for the efficient utilisation of coal as a fuel is generally recognised, it must be confessed that the use of raw coal in the open domestic fire-place, so common in Great Britain, is a most wasteful method of heating. When fresh coal is put on a fire, a process of " dry distillation " takes place with production of gas and tarry products, which, undergoing a partial decomposition with separation of carbon (soot), give rise to clouds of smoke. Thereby, it has been shown, as much as a third of the heat value of the coal is lost. With the ordinary open fire-place only about one-fifth of the heat of the burning coal becomes effective in heating the room.

But if the open fire is wasteful, one will not willingly consent to give it up, and against its wastefulness one may place its efficiency in promoting ventilation and the hygienically advantageous manner of heating by radiation. Moreover, its comfortable appearance, " the wee bit ingle blinkin' bonnily," is something which has a value of its own, not recognised perhaps by science, but which doubtless reacts powerfully on the temperament and character of the people. Attempts therefore have been made to produce a fuel which can be burned in the open fire and which avoids the waste accompanying the production of smoke. By carrying out the distillation of coal in retorts one can avoid the most wasteful part of the process of burning coal in the open fire, for the illuminating gas, ammonia and tar which

are produced are collected, and the *coke* which is left behind can be used as a smokeless fuel. Although the ordinary coke of the gas works, obtained by distilling coal at a temperature of about 1100° C. (2012° F.), is such that it cannot be burned as readily as coal in the open fire—although great advances in this direction have recently been made—it has been found that by carrying out the distillation at a temperature of about 500° C. (932° F.), the residual coke still contains sufficient volatile matter to enable it to burn readily and without smoke in the ordinary grate. Considerable quantities of this low-temperature coke, having a calorific value of 13,500 B.Th.U., are now produced under various names (coalite, fuelite, etc.), and the greatly increased production and use of such a smokeless fuel calls for serious consideration.

Not only does the use of raw coal as a fuel involve the loss of by-products, but it is also accompanied by the production of much smoke by which the atmosphere is polluted and the health of the people prejudicially affected. What could be more depressing to the spirits of the people in our large towns than the want of sunlight and the appearance of " the sombre houses hearsed with plumes of smoke " ? In some industrial areas it has been shown that the available sunlight, the great minister of health, is reduced by as much as 40 per cent., owing to the presence of smoke in the air ; and no less than 400–500 tons of soot fall per square mile per annum.

Moreover, besides the lowering of vitality and the predisposition to disease, brought about by a smoky atmosphere and absence of sunlight, great material damage is also done, and great monetary loss is caused owing to the increased cost of cleaning and larger laundry bills. Although the use of raw coal in our industries can be dispensed with only slowly, it is highly desirable that in the domestic fire-place, which after all is mainly responsible, in Great Britain, for the production of smoke and soot, raw coal will soon cease

to be burned. The poet will then no longer be able to exclaim :

> Look ! where round the wide horizon
> Many a million-peopled city
> Vomits smoke in the bright air.

In recent years improvements have been introduced in the design and use of appliances for burning solid fuel for domestic heating, cooking, etc. These make it possible to burn coal and other solid fuels with greater ease and efficiency, and with the emission of less smoke.

Coal also contains small quantities of compounds of sulphur, and when the coal is burned an acid oxide of sulphur, sulphur dioxide, is formed. This has a harmful action on vegetation, stone and metal work, etc. It is therefore necessary, when coal is burned in very large quantities in a restricted area, as in the large power stations at Battersea and Fulham, London, to remove the sulphur dioxide from the flue gases before their emission into the air. This is done by spraying the flue gases with a slurry or fine suspension of lime or chalk in water. The flue gases are then discharged into the air practically free from smoke, grit and sulphur dioxide.

Solid Illuminants

At the present time when, by the mere touch of the finger on a button, a flood of brilliant light can instantly be obtained, it is difficult to realise what must have been the conditions of life when man had to be content with the smoky flame of the pine torch or of the rush dipped in olive oil. When, also, one thinks of the old guttering candle, with its constant need of "snuffing," one can appreciate how great has been the advance in the direction of artificial illumination ; and practically the whole of this advance has taken place since the beginning of the nineteenth century.

The production of light depends in all cases, with the exception of electric light, on the process of combustion in air, and it is therefore only what one would expect, that man first made use of those naturally occurring substances and materials which can be burned without requiring previous special treatment. Thus the vegetable oils, such as olive oil and rape-seed oil, furnished, from a very early period, the main light-giving material; and at a later date, the need of a vessel to contain the oil was done away with by using the solid animal fats, in the form of candles.

For the earliest candles a solid animal fat was employed, such as ox-fat or tallow, and the candle was made by repeatedly dipping the wick into the melted tallow. At first, the wick was made from the dried pith of the rush (whence was derived the name *rushlight*), but later, wicks of cotton fibre were employed. From the manner in which they were made, these candles were called *dips*.

During the nineteenth century the manufacture of candles was greatly improved owing to the elucidation of the chemical nature of fats and oils by the French chemist, CHEVREUL. Animal and vegetable fats and oils, it was shown, are all compounds of the familiar substance *glycerine*, $C_3H_5(OH)_3$, with various acids, such as *palmitic acid* ($C_{15}H_{31}\cdot COOH$), *stearic acid* ($C_{17}H_{35}\cdot COOH$) and *oleic acid* ($C_{17}H_{33}\cdot COOH$). The first two acids are solids, and give rise to solid fats; but oleic acid is a liquid, and the glycerine compound derived from it is also a liquid and the main constituent of olive oil.

In the making of the modern candle, the fat or tallow is first boiled with acidified water in order to separate the fibrous matter from the fat, and the latter is then subjected to the action of superheated steam, whereby the fat is decomposed into glycerine and the acids with which it was combined—stearic, palmitic and oleic acids. After purification, the mixture of acids is distilled, and the solid acids separated from the liquid oleic acid by pressing. The solid

thus obtained consists mainly of stearic acid or stearin, and forms, generally with the addition of a small quantity of solid paraffin or paraffin wax, the material of the ordinary stearin candle of the present day. This candle has the advantage over the old tallow dip, in being harder and cleaner to handle, in having a better appearance—white and opaque—in showing no tendency to bend or to gutter, and in burning with a bright and smokeless flame.

The paraffin wax, to which reference has just been made, is itself also largely used for making candles. It is a white material which is obtained by distilling oil shale and brown coal or lignite, and is also extracted from American, Galician and especially from Burma or Rangoon petroleum. It consists of a mixture of compounds which contain only hydrogen and carbon, and are therefore called *hydrocarbons*, and belongs, therefore, to an entirely different class of compounds from the fats or the fatty acids, all of which contain oxygen.

The wax candles formerly so highly prized were made of beeswax; and spermaceti, a compound obtained from the oil of the sperm whale, was also used in the manufacture of candles. The hard China wax, produced by a coccus, a small insect similar to the wood-louse, and various kinds of vegetable wax are also used for candle-making in China and Japan.

Although the materials of which candles are made are, of course, combustible, it should be remembered that they do not burn unless the temperature is raised to a point sufficiently high to cause them to pass into vapour; and it is the vapour which burns and so gives rise to the flame. When a candle is lit, the heat of the flame melts a quantity of the solid candle. This liquid then rises up the wick by what is known as capillary action—just as one can mop up water with a piece of blotting-paper—and is then vaporised and ignited by the heat of the flame.

In the old tallow candles, the wick required to be snuffed from time to time; that is, the unburnt end of the wick had

to be removed with a pair of special scissors. The reason for this is as follows. Immediately surrounding the wick of the candle there is the unburnt vapour of the candle material, and this vapour cuts the wick off from contact with the atmospheric oxygen. Consequently, although the wick becomes charred by the heat of the flame, it is not consumed, because the oxygen of the air is not allowed access to it. The charred wick, therefore, continues to increase in length, and there is conducted up into the flame more of the liquid fuel than can properly be consumed. The flame then burns dim and emits a large amount of smoke.

The necessity for snuffing, however, is now obviated by the use of twisted or flat-plaited wicks. As the candle burns, the end of the wick, as every one may see by looking at a burning candle, curls or bends outwards to the edge of the flame, and coming, in this way, into contact with the oxygen of the air, it burns away, and so no snuffing is required.

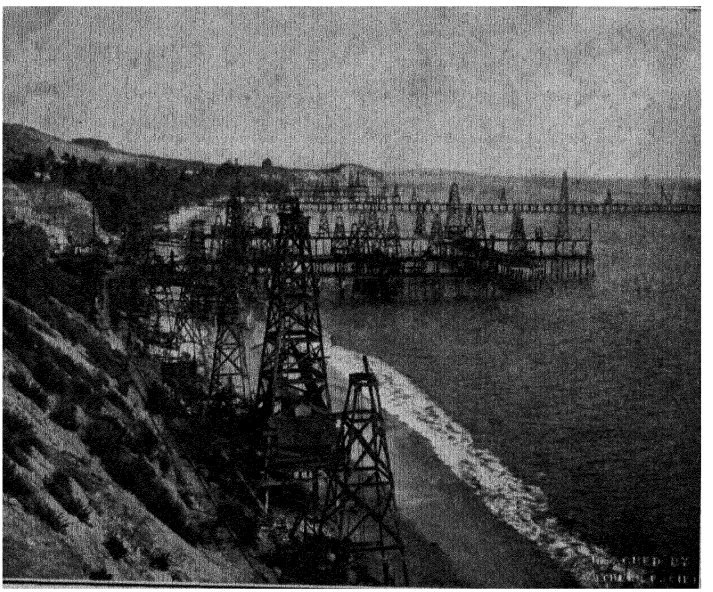
Liquid Fuels and Illuminants

The occurrence of a natural mineral oil has been known from a very early period, and " slime " or bitumen (formed from mineral oil or petroleum,[1] as it is now called, by the loss of its more volatile constituents) was used as a mortar by the builders of the Tower of Babel. Classical writers, also, record the presence of oil in various regions and describe its use both as an embrocation and as an illuminant. In the region of Baku on the Caspian Sea, moreover, the " Holy Fire " of the burning oil and of the gas which accompanies it was, in ancient times, a place of pilgrimage of the Persian Guebers or fire-worshippers.[2]

[1] The word petroleum means " rock oil."

[2] In the hills near Kirkuk in Iraq lies a shallow depression where inflammable gas, escaping from the crust of the earth, burns continuously, night and day, with dancing, flickering flames. This spot, known locally as the " Fiery Furnace," may have been the scene of the " trial by fire " to which Shadrach, Meshach and Abednego were subjected by Nebuchadnezzar.

In America, exudations of mineral oil had long been known and the oil had, by reason of its medicinal and curative properties, been used both internally and externally. It was, however, only in 1859 that the first oil-well was drilled in Pennsylvania for the purpose of winning the oil for use as an illuminant and lubricant. The increasing demand for



Courtesy of Southern Pacific Company

OIL WELLS NEAR SUMMERLAND, CALIFORNIA.

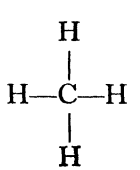
oil, for use more especially as a fuel, has, during the present century, led to the development and exploitation of many new oil-fields in different parts of the world. In 1938, the world production of petroleum amounted to 270,000,000 tons, nearly two-thirds of this being produced in the United States.[1]

[1] During the past decade oil has been obtained in England, more especially from wells near Eakring in Nottinghamshire. The amount produced down to 1945 was about 400,000 tons. The life of this oil-field is put at from ten to twenty years.

Of the origin of petroleum, little can be asserted with confidence, but it is generally considered that the oil has been formed by the gradual decomposition, under bacterial action, of deposits of marine animal and vegetable matter. The oil occurs in pools between layers of impervious rock, and is associated with a gas, the pressure of which is, in some cases, sufficient to force the oil up through the bore-pipe so as to form a mighty fountain.

Although the petroleum from different oil-fields may vary greatly in composition, it consists, in all cases, essentially of a mixture of *hydrocarbons*, or compounds which contain carbon and hydrogen only. For the most part, the hydrocarbons belong to what is known as the methane or paraffin series (*see below*), but other hydrocarbons, known as *naphthenes*, may also be present in varying amounts. These compounds contain a lower proportion of hydrogen and are more akin to the so-called *aromatic* hydrocarbons (benzene, toluene, etc.), which are contained in coal-tar (Chap. XV). Small amounts of these aromatic hydrocarbons are also present in certain types of petroleum.

METHANE, or marsh gas, is the lowest member of a long series of hydrocarbons, all of which have similar chemical properties and composition. The molecule of methane consists of one atom of carbon to which four atoms of hydrogen are united; and since an atom of carbon is never found to combine with more than four atoms of hydrogen, the carbon is said to be saturated, and methane is spoken of as a *saturated hydrocarbon*. Diagrammatically, one can represent the molecule of methane thus:



or, more simply, by the formula CH_4.

Methane is the inflammable gas which rises in bubbles when one stirs the mud of decaying vegetation at the bottom of a stagnant pool—hence the name *marsh gas*; and it is also the gas which, produced during the formation of coal,[1] escapes from the coal-beds during mining and which, mixed with the air of the mine, constitutes the explosive mixture, *fire-damp*. Methane, moreover, is the main constituent of the " natural gas " which escapes from the earth in various oil-bearing regions (p. 99).

Large quantities of methane are produced by bacterial action on the sludge formed in the processes of sewage purification which are being introduced by an increasing number of local authorities. In one installation, more than a million cubic feet of gas, containing 70 per cent. of methane, are produced daily. Since methane finds many important uses not only as a fuel but also in chemical industry, for the production of carbon black (p. 125), hydrogen (p. 194), methanol, etc., waste of it should be avoided and increased production and utilisation should be encouraged.

The element carbon is remarkable among all the elements in the property that its atoms can combine with one another so as to form " chains " of carbon atoms, and give rise to a series of compounds which may be represented by the formulæ:

$$CH_3—CH_3 \text{ (ethane)}, \quad CH_3—CH_2—CH_3 \text{ (propane)},$$
$$CH_3—CH_2—CH_2—CH_3 \text{ (butane)}, \text{ etc.}$$

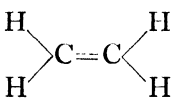
A large number of such compounds are known, and it will be observed that the composition of each of them can be represented by the formula C_nH_{2n+2}. Owing to their

[1] The total quantity of methane which might be made available from the coal mines in Great Britain alone is very large. One mine is stated to produce as much as 10 million cubic feet of gas, containing 80–90 per cent. of methane, per day. As a motor fuel, this is equivalent to about 60,000 gallons of petrol.

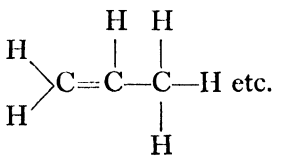
chemical inertness, the hydrocarbons belonging to this series are spoken of as *paraffins*.[1]

As the proportion of carbon in the compounds increases, the hydrocarbons become less and less volatile, and boil, therefore, at higher and higher temperatures; and when the number of carbon atoms in the molecule is greater than sixteen, the compounds are solid at the ordinary temperature.

It may also be mentioned here that besides the saturated hydrocarbons, other hydrocarbons are known which contain a lower proportion of hydrogen, and are therefore said to be *unsaturated*. Thus, if two hydrogen atoms are removed from each of the compounds of the methane series, hydrocarbons are obtained which can be represented by the formulæ:



C_2H_4 (Ethylene)



C_3H_6 (Propylene)

These constitute another series of hydrocarbons, known by the name of the first member ethylene. Some of these hydrocarbons occur in natural gas and also in the gas produced in the "cracking" of oil (p. 95), and they are the raw materials for the production of "polymer petrol" (p. 98) and for the manufacture of solvents and other substances of great value.

Hydrocarbons are also known which contain a still lower proportion of hydrogen, or higher proportion of carbon, for example acetylene, C_2H_2 or $HC{\equiv}CH$, the first member of a series having the general formula C_nH_{2n-2}.

Crude Petroleum is generally a thick yellow, brown, or black liquid, which shows a green fluorescence. After the gaseous hydrocarbons which may be dissolved in it have

[1] From the Latin *parum* (little) and *affinitas* (affinity).

been removed, the petroleum has to be refined or purified and then submitted to *fractional distillation*, in order to separate it into portions adapted for different purposes.

The crude petroleum is heated in a still and the vapour led into a high tower fitted with perforated transverse plates, at which condensation of the vapour takes place. The constituents of higher boiling point condense at the lower, hotter plates, and the vapour of the more volatile constituents bubbles through the liquid and condenses at successively higher levels. By tapping off the condensed liquid at different heights of the tower, a series of " fractions " of different boiling-points can be obtained.[1]

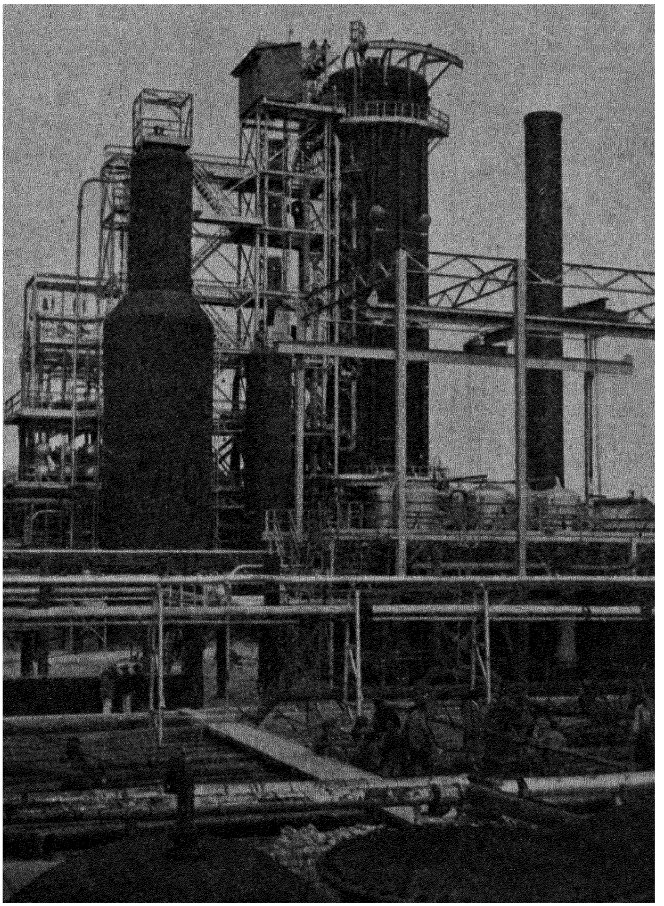
The most volatile fraction, which distils over up to a temperature of about 70° C. (158° F.), is called petroleum ether and is largely used as a solvent and as a local anæsthetic owing to the cold produced by its evaporation. The next fraction, with a distilling temperature between 70° and 120° C. (248° F.), is called gasoline or petrol, and is used as a motor spirit and also for illuminating purposes (petrol-air gas). At a higher temperature, from 120° to 150° C. (302° F.), there is obtained a fraction called petroleum benzine[2] or benzoline, which is used as a solvent and as a " dry-cleaning " agent for the removal of oil and grease stains.

The fraction condensing between 150° and 300° C. (300° and 570° F.) constitutes burning oil or kerosine,[3] or paraffin oil; that condensing between 250° and 340° C. (482° and 644° F.) constitutes solar oil or gas oil, which is used in Diesel engines. The distillation of the less volatile residues is then carried out under reduced pressure and oils of various grades are obtained and are used as lubricating oils and for burning under boilers. From the highest fractions of all one obtains vaseline and, in some cases, solid

[1] The temperatures at which the different fractions are collected may vary in different refineries.

[2] Not to be confused with benzene obtained from coal-tar.

[3] This spelling, with the termination -ine in place of -ene, has been adopted by international agreement.



Courtesy Anglo-Iranian Oil Co. Ltd.

A MODERN PETROLEUM DISTILLATION UNIT.

The main fractionating tower (122 feet high) is on the right, with the primary flash tower for the removal of the most volatile constituents in the centre and the vacuum column on the left.

paraffin, which is used for making candles, water-proofing paper, and other purposes.[1] A final residue of pitch is obtained.

Nearly all crude petroleum oils contain compounds of sulphur, and compounds of nitrogen are also frequently present. These pass over into the various "fractions" obtained by distillation and have to be removed by suitable chemical treatment before the finished products are placed on the market.

Since paraffin oil, or kerosine, contains a relatively large proportion of carbon, its vapour burns with a smoky flame, owing to incomplete combustion, unless there is a liberal supply of air. When this oil is used as an illuminant, therefore, the flame is surrounded by a chimney whereby a draught of air is created, and oxygen is thus brought in larger amount to the flame; and in the case of lamps with a circular wick, a tube must also be provided through which air can pass to the *inner* surface of the flame.

In the early days after the introduction of mineral oil as an illuminant, explosions and fires were not infrequent, and these led to the introduction of special legislation to regulate the use of such oil. The accidents which occurred were due mainly to the insufficient removal of the more volatile constituents of the petroleum, and these, mixing with the air in the oil reservoir of the lamp, formed an explosive mixture which became ignited by the flame. To obviate such risks, it has been enacted that only such oil shall be used as does not give off an inflammable vapour below a certain temperature. This is tested by heating the oil in a special apparatus under specified conditions, and determining the temperature at which, on passing a light over the mouth of the vessel containing the oil, a flash of flame is

[1] It is of interest to note that in the Kettleman Hills, California, a well was tapped which gave an oil consisting almost entirely of volatile hydrocarbons, and a natural gas consisting mainly of methane. Over 100,000 gallons of gasoline and 90,000,000 cubic feet of gas were obtained daily.

seen. This is known as the flash-point of the oil, and in Great Britain it has been enacted that the flash-point of burning oil must not be below 73° F., when determined by what is known as the " closed " test.

Until well into the present century, petroleum was of importance chiefly as a source of illuminants and lubricants. For some time now, however, owing to the development of the internal combustion engine and the increasing use of the oil-fired steam boiler, the value of petroleum depends mainly on its being a source of fuel supply. Since 1 lb. of fuel oil, the higher boiling fractions of petroleum, has a calorific value of about 19,500 B.Th.U.—about one and a quarter times greater than anthracite—and since oil possesses many advantages over coal in the matter of cleanliness, control of consumption, stowage room, etc., its use as a fuel, especially for ocean steamers, has greatly increased.

It is, however, in the use of gasoline or petrol as a fuel for the internal combustion, motor car and aeroplane engine that the greatest developments have taken place; and as the gasoline fraction obtained by the distillation of petroleum is quite insufficient to meet the demand, large quantities of motor spirit have to be produced by the " cracking " of gas oil and even of kerosine, for which now there is a relatively reduced demand. By heating these oils under pressure to a temperature of 380° C. (716° F.), or more, the relatively large molecules are broken down into the simpler molecules of the hydrocarbons which constitute gasoline or petrol. This process is facilitated by the presence of aluminium chloride which acts as a catalyst (*see* Chap. IX). The spirit obtained by cracking contains also unsaturated hydrocarbons (p. 91), as well as iso-paraffins[1] and so-called aromatic hydro-

[1] In the iso-paraffins the carbon atoms are joined together so as to form not a *straight* but a *branched* chain, as is shown by the formula for iso-octane:

$$\begin{array}{l} CH_3 \quad\quad CH_3 \\ CH_3{\cdot}\dot{C}{\cdot}CH_2{\cdot}\ \dot{C}H{\cdot}CH_3 \\ \quad\ \dot{C}H_3 \end{array}$$

carbons (benzene, toluene, etc.). These are of value because they help to prevent the unpleasant phenomenon of "knocking," which is due to the passing of the relatively slow wave of combustion into the relatively very rapid wave of explosion in the gasoline-air mixture in the engine cylinder. Detonation or explosion takes place when the compression of the gasoline-air mixture exceeds a certain value for a given fuel.

Since the efficiency of the internal combustion engine increases with the degree of compression of the fuel-air mixture in the cylinder before firing, it is of advantage to use a fuel which has little tendency to detonate on compression, or which has, as it is said, a high anti-knock (or high octane) value.[1] The tendency of a motor spirit to knock varies with the composition and nature of the hydrocarbons of which the spirit is made up, and great advances have been made in recent years in the production of motor fuels of high octane number by blending the gasoline obtained by the distillation of petroleum with "cracked" spirit, benzene (benzole) or lead ethyl, $Pb(C_2H_5)_4$, spoken of popularly as "Ethyl." By blending petrol with up to 40 per cent. of isopropyl ether (produced from propylene), a motor fuel with an octane number of 100 can be obtained. Through the introduction of these improved motor fuels, the motor car engineer has been able, during the past decade, to design his engine so as to increase the compression ratio from about 4 : 1 to 6·5 : 1. The efficiency has thereby been very greatly increased.

The natural reserves of oil are not inexhaustible, and the question arises whether any substitute can be obtained. Fortunately, the outlook is full of hope.

[1] The anti-knock value of a motor spirit is determined by comparison with the anti-knock value of known mixtures by volume of the two hydrocarbons, normal heptane (C_7H_{16}) and iso-octane (C_8H_{18}) having the formula $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}C{\cdot}(CH_3)_3$. A motor fuel which has the same anti-knock properties as a mixture of 70 volumes of octane and 30 volumes of heptane is said to have an octane number of 70. "Ethyl petrol" has an octane number of 80. The higher the octane number, the smaller is the tendency to knock.

In Scotland, ever since 1860, mineral oil has been obtained by heating a carbonaceous shale, called *oil shale*. From one ton of this shale one can obtain about thirty gallons of oil from which, by distillation, motor spirit, illuminating oil, fuel oil, lubricating oil and solid paraffin can be obtained. Since enormous deposits of oil shale occur in many different countries, it will be possible to obtain abundant supplies of oil fuel—at a greater cost it may be than at present—when the oil wells shall have ceased to flow.[1]

From coal, also, fuel oil may be obtained, and is being obtained, by various processes. By the low temperature carbonisation (distillation) of bituminous coal (p. 83) a tar is produced from which one can obtain, by fractional distillation, motor spirit, fuel and lubricating oils, similar to those obtained from petroleum ; whereas by the high temperature distillation of coal (p. 104) a tar is produced from which benzene (or benzole)[2] is obtained. Although benzene is not used as a motor spirit by itself, mixtures of benzene with petrol and also with alcohol are extensively employed. The addition of benzene to petrol increases the anti-knock value.

Motor spirit can also be produced, and has been produced in very large amounts, by the hydrogenation of coal, a process developed originally by the German chemist, F. BERGIUS. Ground coal, made into a paste with oil for convenience of handling and treatment, is subjected to the action of hydrogen at a temperature of 420°–500° C. (788°–932° F.), and under a pressure of about 200 atmospheres. The coal is thereby converted, by the action of heat and the taking up of hydrogen, into gaseous hydrocarbons (methane, ethane, propane, butane),[3] petrol, middle oils and heavy oil.

[1] Since 1940, petrol has been produced commercially at Glen Davis in Australia from oil shale, a yield of 100 gallons of oil being obtained per ton of shale. It is planned to produce 30,000,000 gallons of oil per annum.

[2] The term benzole is applied to various commercial mixtures of benzene hydrocarbons (benzene, toluene, etc.).

[3] The propane and butane are separated and compressed into cylinders for use as a gaseous fuel (" Calor Gas ") in country districts, while the other hydrocarbons can be used for the production of hydrogen (p. 194).

The heavy oil is used for making the ground coal into a paste and the middle oils, in the form of vapour, are passed with hydrogen through heated tubes in the presence of molybdenum sulphide as catalyst. The oils are thereby " cracked " and partially hydrogenated, and the spirit so obtained is added to the petrol to produce a motor fuel with an octane number of 71–73. By the use of suitable catalysts, whereby the various reactions can not only be accelerated but also have their course directed, control is obtained of the nature of the oils formed. With tin as catalyst, in presence of hydrochloric acid gas, 180 gallons of motor spirit can be obtained by the hydrogenation of one ton of bituminous coal.

Petrol is also produced by the hydrogenation of coal-tar creosote (a process used in England) and of the tar produced in the low temperature carbonisation of coal (p. 83). Moreover, increasingly large quantities of high-grade petrol are now also being produced from natural gas (p. 99) and from refinery gas, formed in the process of " cracking " oils. These gases, which are available in enormous quantities,[1] consist partly of saturated and partly of unsaturated hydrocarbons. The saturated hydrocarbons can be decomposed by heat, with formation of unsaturated hydrocarbons of the ethylene type. These unsaturated hydrocarbons, when passed at a temperature of about 450° F. and under a pressure of about 14 atmospheres over a catalyst, pyrophosphoric acid, undergo *polymerisation*, two or more simple molecules uniting together to form more complex molecules. In this way motor spirit (" polymer petrol ") of a high octane number, and even iso-octane itself, can be obtained, suitable for blending with and improving the anti-knock properties of ordinary petrol.

In 1925, F. FISCHER and H. TROPSCH, in Germany, found that water-gas (p. 107), in presence of a suitable catalyst (*e.g.* cobalt and thorium) and at a temperature of about 400° F., is converted into a mixture of liquid and

[1] In 1938, the annual production of cracked gas amounted to 300,000,000,000 cubic feet.

gaseous hydrocarbons. The low-boiling fraction of the liquid has a low anti-knock value and must be improved by the addition of lead ethyl, benzole, or the " polymer petrol " just described; but the higher-boiling fraction, on being " cracked," gives good yields of high anti-knock motor spirit.

From water-gas, also, high-grade, viscous lubricating oils can be produced, with the help of aluminium chloride as catalyst.

In various ways, therefore, research chemists have succeeded in producing motor fuel and lubricating oils from coal, directly or indirectly, and from natural and oil refinery gases; and they have so greatly improved the products that a gallon of petrol will, to-day, do twice as much work as a gallon did ten or fifteen years ago.

In addition to the mineral oils, alcohol or spirits of wine (Chap. XVII) is also used to some extent as a fuel for motor-car engines. Natalite, for example, is a mixture of alcohol and ether and is produced as a motor fuel in Natal, South Africa; and mixtures of alcohol with benzene and with petrol are also used as motor fuels. Although the calorific value of alcohol is not so high as that of gasoline, higher compressions can be used without detonation, or " knocking," taking place, and the increase of efficiency of an internal combustion engine with compression is so great, that it may compensate for the lower calorific value of the alcohol. The possibility of a great extension in the use of alcohol as a motor fuel in the future must not be overlooked.

Although petroleum is chiefly valuable as being a source of supply of fuels and lubricants, it has now also gained a position of major importance as a raw material for the production of compounds of great value (*see* Chap. XV).

Gaseous Fuels and Illuminants

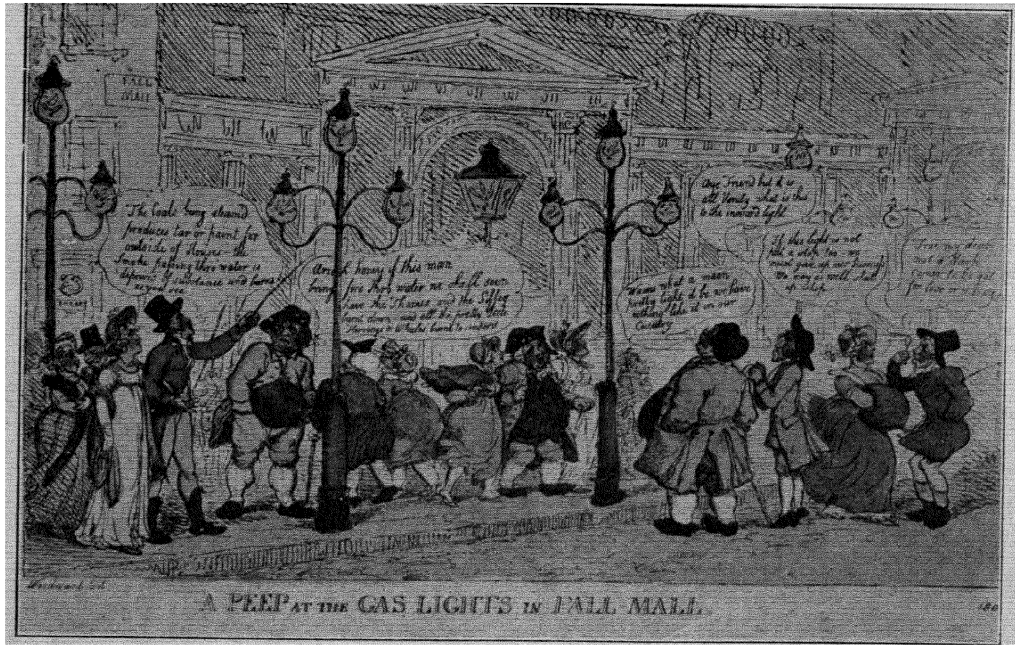
In various countries (the United States, Russia, Rumania, Canada, and others) great reservoirs of " natural gas " are

found, unassociated with oil, and this gas has been used for many years, in the United States, not only for illuminating purposes but also as a fuel for steel manufacture, for the melting of glass, and for other industrial purposes.[1] Its use for the production of motor spirit has just been discussed. As a fuel, natural gas is of great importance on account of its high calorific value of over 1000 B.Th.U. per cubic foot. This is twice as great as the calorific value of the gas obtained by the high temperature distillation of coal. In the United States, many million cubic feet of gas are daily conveyed many hundreds of miles through pipes to industrial centres.

Although natural gas has a very great value in the countries where it is found, the most important gases used at the present day for the production of heat and light are those which are obtained, by one process or another, from coal, and more especially the gas which is obtained by heating coal in closed vessels or " retorts," out of contact with the air. That a combustible gas can be produced in this way was observed about 1688, by John Clayton, a Yorkshire clergyman, who later became Dean of Kildare ; but it is to a Scotsman, William Murdoch, that belongs the credit of having developed the process for the production of an illuminating gas for general use.[2] That was towards the end of the eighteenth century, but it was only after the lapse of ten or twelve years that the gas began to be publicly and generally used. The introduction of gas for street lighting was due to a Moravian, Winzer or Winsor, and through his efforts Pall Mall in London was lighted by gas on 28th January 1807, and created quite a sensation. By 1816

[1] It is estimated that the available world supply of natural gas (mainly methane) is about ten million tons a year.

[2] William Murdoch, who was born at Lugar in Ayrshire, in 1754, was associated with the engineering firm of Messrs. Boulton & Watt, Birmingham. In 1792 he lighted his house at Redruth, in Cornwall, with coal-gas, and it was at the works of Boulton & Watt at Soho, Birmingham, that coal-gas was first used (in 1798) on a large scale as an illuminant.



A Peep at the Gaslights in Pall Mall.
(After a drawing by Woodward.)
Engraved by Rowlandson.

the greater part of London was lighted by gas. The great change which was thereby effected in the appearance of the towns and in the comfort of the people is described by a writer in the early nineteenth century: "We all remember the dismal appearance of our most public streets previous to the year 1810; before that time, the light afforded by the street lamps hardly enabled the passenger to distinguish a watchman from a thief, or the pavement from the gutter. The case is now different, for the gas-lamps afford a light little inferior to daylight and the streets are consequently divested of many terrors and disagreeables, formerly borne with because they were inevitable."

Coal is not a definite chemical substance, but a complex mixture of substances, the nature of which is not yet definitely known. The essential elementary constituents of coal are carbon, hydrogen and oxygen, but the elements nitrogen and sulphur also occur in small amounts; and when coal is heated in closed retorts, or "distilled" as one says, there is obtained not only the gas which is used for illuminating and heating purposes, but also considerable quantities of ammonia and of tar, and there remains in the retort a residue of coke. Down to the middle of last century the ammonia and the tar were regarded as by-products of little value, but, as we shall learn more fully later, they have since then become materials of great importance;[1] while, owing to the great developments of the iron and steel industry, the demand for coke has, in recent times, become so great that many millions of tons of coal are now distilled annually for the production, primarily, not of gas, but of coke.[2]

Although the nature of the products as well as their

[1] Owing to the great developments which have taken place in the industrial production of synthetic ammonia (Chapter x), the importance of gas-works ammonia has again greatly diminished.

[2] During the period 1936-38, about forty million tons of coal were carbonised annually in Great Britain, half for the production of 300,000,000,000 cubic feet of gas, and half for the production of metallurgical coke.

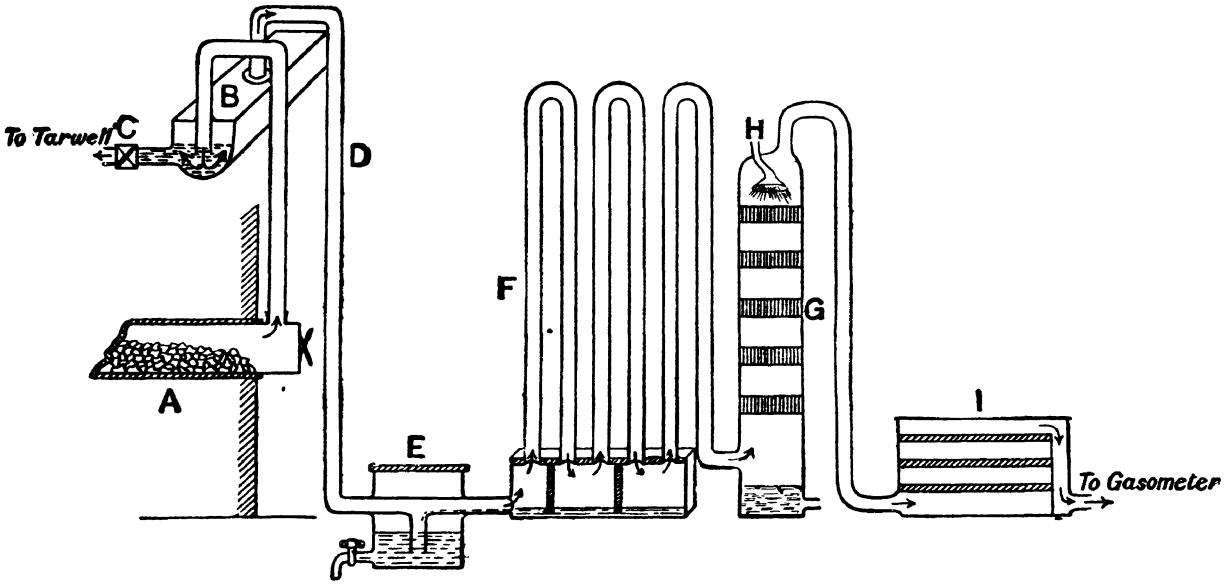


FIG. 8.—DIAGRAM OF GAS-MANUFACTURING PLANT.

A, retort in which coal is heated; B, the hydraulic main; C, outlet for the tar; D, gas pipe; E, tank in which the ammoniacal liquor collects; F, cooling pipes; G, scrubber in which traces of ammonia are removed by trickling water, supplied through the sprinkler H; I, purifying boxes for removing carbon dioxide and sulphuretted hydrogen.

relative amounts depend on the kind of coal distilled and on the temperature at which the process is carried out, one may say that, under the general conditions met with in gas works, the main products obtained and their relative amounts are as follows :

	Approximate quantity formed from 1 ton of coal
1. Illuminating gas	11,000 cubic feet.
2. Coal-tar	120 lbs.
3. Ammonium sulphate	25 ,,
4. Coke	1,500 ,,

In the manufacture of illuminating gas, the coal is heated in large fire-clay retorts, placed horizontally or vertically, at a temperature of 1000°–1100° C. (1832°–2012° F.), and the products of decomposition are led away by a pipe the mouth of which dips under the surface of water contained in what is known as the hydraulic main (Fig. 8). Here, part of the water and of the coal-tar condense, while the gaseous products pass away to a series of cooling pipes, exposed to the air, in which a further condensation of water vapour and of tar takes place. The ammonia present in the gas dissolves for the most part in the water produced, and the remainder is removed by passing the gas through " scrubbers." The gas still contains a number of substances the presence of which would be deleterious, the more important of these being sulphuretted hydrogen (hydrogen sulphide) and carbon dioxide. The sulphuretted hydrogen is harmful because it gives rise, in the burning gas, to sulphur dioxide (the pungent gas formed when sulphur burns in air), which exercises a destructive action on plants, metal work, etc. ; and the presence of carbon dioxide is objectionable because it lowers the heating and illuminating power of the gas. To free the gas from these impurities, therefore, it is passed, first of all, through a series of boxes containing trays covered with slaked lime which combines with and so removes the carbon dioxide ; and then through another series of boxes containing hydrated oxide of iron (*e.g.* bog iron ore), which

removes the sulphuretted hydrogen, by forming with it the compound, sulphide of iron. By introducing a small and regulated amount of air into the gas at this stage, the sulphide of iron is continuously oxidised to iron oxide and free sulphur. When the amount of free sulphur reaches about 60 per cent. of the iron oxide, the latter loses its efficacy, but this " spent oxide " still has its uses, for it is sold to the manufacturer of sulphuric acid, who utilises it in the manner we shall learn later.

Besides hydrogen sulphide, other substances—carbon disulphide, naphthalene and hydrocyanic acid (prussic acid)—are also removed from coal-gas and form or give rise to by-products of value. Among the by-products obtained is ammonium thiocyanate, NH_4CNS, which, on being heated, forms the compound *thiourea*, $CS(NH_2)_2$. This compound is used in the production of synthetic plastics (p. 335).

After undergoing the various processes of purification, the illuminating gas passes to the gas-holder, and is then ready for distribution to the consumers. Although the composition of the gas supplied by different works is by no means the same, nor invariable even in the case of the same works, the following numbers may be taken as representing an average composition of illuminating gas.

COMPOSITION OF COAL-GAS

Hydrogen	56 per cent.	by volume.
Methane	22·8 ,,	,,
Unsaturated hydrocarbons (Ethylene, etc.)	2·5 ,,	,,
Carbon monoxide	10·9 ,,	,,
Carbon dioxide	1·3 ,,	,,
Nitrogen	6 ,,	,,
Oxygen	0·5 ,,	,,

Coal-gas, then, as we see, is a mixture of a number of gases, and of these carbon dioxide, nitrogen and oxygen represent what we may call impurities; they act merely as diluents and lower the illuminating power of the gas.

Of the combustible gases present in coal-gas, hydrogen burns with a non-luminous, scarcely visible flame; carbon monoxide, with a non-luminous flame of a bright blue colour;[1] and methane, with a flame which has only a slight illuminating power. Ethylene, however, burns with a strongly luminous flame, and it is to this gas, and to the other unsaturated hydrocarbons present in small amounts, that the luminosity of a coal-gas flame is mainly due. Among the unsaturated hydrocarbons present, there may be mentioned benzene (or benzole, to give it the name by which it is known in commerce), the vapour of which burns with a luminous flame and with the production of a large amount of soot.

What, then, is the explanation of the luminosity of the flame of burning coal-gas, or of a candle, or of petroleum? The answer is that which was given long ago by Sir HUMPHRY DAVY: The luminosity is due to the decomposition of the hydrocarbons with liberation of particles of carbon which are then raised to incandescence by the heat of the burning gases. The presence of this finely divided carbon can, indeed, be readily shown by bringing a cold object into the luminous part of the flame; it becomes coated with soot. These carbon particles, however, do not escape into the air, but on reaching the edge of the flame where they come into contact with the oxygen of the air, they are completely burned to the invisible gas carbon dioxide. And so, on examination, one sees in these flames three zones: an inner non-luminous zone of unburnt gas or vapour; a luminous zone in which the carbon particles are raised to incandescence; and a very faint outer zone surrounding the flame, in which complete combustion of the carbon particles takes place.

From the explanation which has just been given, it will readily be understood that the luminosity of a flame will be

[1] The lambent blue flame seen on the top of a clear-burning coal fire is due to the combustion of carbon monoxide. It is an exceedingly poisonous gas.

increased by increasing the proportion of carbon-yielding substances in the burning gas ; and hydrocarbons, and more especially unsaturated hydrocarbons, which contain a relatively large proportion of carbon, will be the most effective substances to use. By such additions it is possible to " enrich " a poorly luminous gas, a fact which is made use of at the present day in many of the larger gas-works.

Not only can a combustible gas be manufactured by the distillation of coal, but when steam is passed over white-hot coke, a gas is obtained which is a mixture of hydrogen and carbon monoxide :

$$C + H_2O = CO + H_2$$

Carbon (coke) and water give carbon monoxide and hydrogen.

Although this gas mixture, known as *water-gas*, has no illuminating power, it can be manufactured at a small cost, and after being enriched by the addition of unsaturated hydrocarbons, obtained by the decomposition or " cracking " of oil at a high temperature, it is added (as *carburetted water-gas*) to the gas obtained by the distillation of coal. Water-gas is also frequently added without enrichment to coal-gas, so as to give a cheaper gas of lower illuminating power.

Formerly when coal-gas was used almost entirely as an illuminant, gas-producing companies had to supply gas of a certain minimum illuminating power ; but at the present time coal-gas is employed mainly as a domestic and industrial fuel for the production of heat. The illuminating power standard has therefore been abandoned in Great Britain, and gas-producing companies may supply gas of varying quality, but the charge to the consumer may be made only on the basis of the heat-value of the gas. Greater freedom is thus given to the producer, and the consumer pays for the amount of heat energy or the number of *therms* he receives, 1 therm being equal to 100,000 B.Th.U.

Coal-gas, produced by high temperature carbonisation, has a calorific value of about 480–520 B.Th.U. per cubic

foot; while that produced by low temperature carbonisation has a value of 800–1000 B.Th.U. per cubic foot. The calorific value of water-gas, which is largely used as an industrial fuel, alone or mixed with coal-gas, is about 280 B.Th.U. per cubic foot.

The gas, *carbon monoxide*, which forms one of the constituents of water-gas, differs from the other oxide of carbon, carbon dioxide, to which reference has already been made (p. 48), not only in being a combustible gas but also in being intensely poisonous. This is due to the fact that the gas combines with the hæmoglobin, or oxygen-carrying constituent of the blood, to form a very stable, bright-red compound, carboxy-hæmoglobin, which is no longer able to take up oxygen from the air entering the lungs. The presence of 1 volume of carbon monoxide in 5000–10,000 volumes of air will cause headache, while if 1 per cent. of carbon monoxide is present, unconsciousness and death will occur in a few minutes. Many cases of poisoning by carbon monoxide have occurred owing to its presence in illuminating gas and in the products of imperfect combustion in stoves or in the engines of motor cars, from which it passes out in the exhaust. In cases of necessity, protection against the gas can be obtained by wearing a mask containing a mixture of the oxides of manganese, copper, cobalt and silver—a mixture known technically as *hopcalite*. In the presence of this mixture, or even of a specially prepared manganese dioxide alone, carbon monoxide is oxidised by atmospheric oxygen to carbon dioxide.

When coal-gas is used as a fuel for heating purposes, it is important that combustion takes place rapidly and completely without the separation of carbon particles, and this result is secured if the coal-gas, before being burned, is mixed with a suitable amount of air. The molecules of the combustible gas then find oxygen with which they can combine, ready at hand, so to say, and combustion takes place rapidly and completely without the separation of carbon

particles; the flame is therefore non-luminous, but much hotter than the ordinary luminous flame. This principle was made use of by the German chemist BUNSEN in the burner which goes by his name, and is applied in gas fires, gas cookers, etc. (Figs. 9 and 10). In the Bunsen burner, the gas issues from a jet which is surrounded by a wider tube, near the foot of which holes are pierced through which air is drawn into the burner by the uprush of gas. The gas thereby becomes mixed with air, the amount of which necessary to ensure complete combustion can be regulated by enlarging or diminishing the size of the air openings. If too much air is admitted to the gas, the mixture becomes explosive, and the flame strikes back to the jet where the gas enters the burner. If this occurs, the gas must be at once turned out, as incomplete combustion takes place and products of a very poisonous character are formed. These, fortunately, betray their presence by a powerful and unpleasant odour.

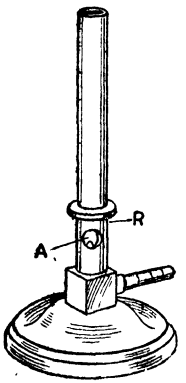


FIG. 9.—BUNSEN BURNER.

A, air-hole by which air can pass into the tube and mix with the gas which enters at the small jet seen through the opening. The supply of air can be regulated by means of the movable ring R.

In gas fires, burners of the same type as the Bunsen burner are employed, and the long, hot gas flames which are formed raise to a high temperature special "radiants" of fire-clay and asbestos, which then radiate heat into the room. Such gas fires have in recent years been improved in construction so that their ventilating efficiency and their emission of radiant heat have been greatly increased, and they have now lost practically all their former unhygienic properties.

If the luminous coal-gas flame is supplied with oxygen instead of with air, a higher temperature can be obtained; for the nitrogen of the air acts as a diluent and so cools down

the flame. One cannot, however, in this case make use of the ordinary burner, for the mixture of oxygen and coal-gas is explosive, and the flame would at once "strike back." A burner of special construction is therefore employed which allows of a jet of oxygen being blown into the gas as it burns at the mouth of the burner, and one thus obtains what is known as the oxy-coal-gas blowpipe flame (Fig. 11). If this flame is allowed to impinge on a highly refractory material like quicklime, the latter is raised to a brilliant incandescence, producing the well-known lime-light. (Nowadays the oxide of the rare metal zirconium is largely used in place of lime.)

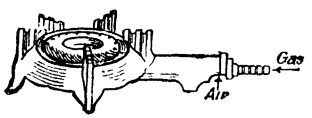


FIG. 10.—GAS COOKER, CONSTRUCTED ON THE PRINCIPLE OF THE BUNSEN BURNER.

If hydrogen is used in place of coal-gas, a still higher temperature, up to about 2000° C. (3632° F.), can be obtained, and the high temperature produced by means of the oxy-hydrogen flame has found an interesting and important application in the manufacture of artificial gems, such as rubies and sapphires. These gems consist essentially of oxide of aluminium (alumina), a substance which occurs naturally as corundum, and, in an impure state, as emery. It is a very refractory substance, but it can be melted in the oxy-hydrogen blowpipe flame. When a mixture of 97·5 per cent. of alumina and 2·5 per cent. of oxide of chromium is heated in the blowpipe flame, it is fused, and, on cooling, solidifies to a ruby-red solid. It *is* a ruby, identical in physical and chemical properties with the natural gem; and it differs from the latter solely in minute irregularities of internal structure detectable only by the eye of the expert. In the manner described, artificial rubies weighing as much as eighty carats, or over half an ounce avoirdupois, have been obtained. These artificial rubies, on account of their great hardness, are now manufactured in large quantities for use in the bearings of watches and for other purposes.

Sapphires can be obtained in a similar manner by fusing a mixture consisting of alumina and small quantities of the oxides of titanium and iron.

For a number of years the position of coal-gas as an illuminant has been vigorously assailed by electricity, and

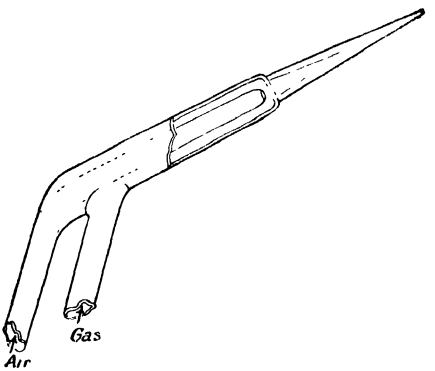


FIG. 11.—BLOWPIPE.
When the gas is burning at the mouth of the wider tube, air or oxygen is blown into the flame through the inner tube.

it is very doubtful if the industry could have maintained itself even as it has done but for the invention of the now familiar incandescent mantle. This invention, it is important to bear in mind, was not due to any conscious desire or well-directed search for a means to improve the illuminating efficiency of gas, but to a purely scientific investigation of the oxides of the so-called rare metals which was carried out by AUER VON WELSBACH in 1884. In the course of his investigations, von Welsbach was struck by the fact that some of the oxides of the rare metals emit an exceptionally brilliant light when incandescent; and at once his mind grasped the potentialities of the fact. A scientific discovery, however, is one thing; to make that discovery of practical utility is quite another; and in the present case, as in all cases, a large amount of patient and careful investigation had to be

carried out before the incandescent mantle could be made a commercial success and be brought to its present state of perfection.

To make the discovery of practical utility, " mantles " or " stockings " of woven cotton, artificial silk (p. 144), or ramie fibre (fibre produced from a plant of the nettle class), are soaked in a solution containing the nitrates of thorium and cerium[1] in the proper proportions. These mantles are then dried and incinerated, whereby the fibre is burned away and the nitrates are converted into a mixture of the oxides of the metals, which form a skeleton work preserving the shape of the mantle. To protect the fragile mantle from injury during transport, it is dipped in collodion. When the mantle is suspended in the hot, non-luminous flame of a special burner constructed on the principle of the Bunsen burner, it is raised to incandescence and emits a brilliant white light. From a careful investigation it was found that the best results are obtained when the oxides are present in the proportion of 99 per cent. of thoria (thorium oxide) to 1 per cent. of ceria (cerium oxide). Neither thoria itself nor ceria itself has much light-giving power; and any variation in the proportions of the two oxides from those given is accompanied by a diminution in the light-giving power of the mantle. The part played by the small quantity of ceria in the mantle is, therefore, a very important one, for which, however, no completely satisfactory explanation has yet been found.

The most plausible explanation so far advanced is that the particles of ceria are embedded in a badly conducting mass of thoria, which allows of the ceria being heated up to a point of brilliant incandescence; and further, the ceria possesses the property of accelerating the combustion of the gas, so that the combustion is concentrated or focused on

[1] The chief source of these elements is a mineral known as monazite, which is found in various parts of the world, but more especially in Brazil and at Travancore, India.

the small particles of ceria. As a consequence, the temperature of these particles rises above the average temperature of the mantle, and the brightness of the incandescence is thereby increased. This action of the ceria is spoken of as a *catalytic* action, about which we shall have more to say later. Ceria, however, is a substance which radiates heat rapidly, and if present in the mantle in larger amounts, the loss of heat by radiation is so great that the catalytic action is more than counterbalanced, and the illuminating power of the mantle is diminished.

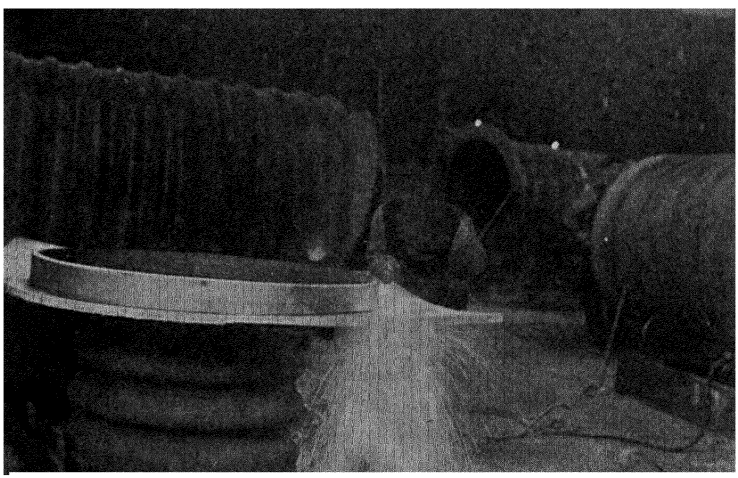
The invention of the incandescent mantle completely revolutionised the gas industry. Not only could a very bright light, rivalling that of the electric incandescent lamp, be obtained, but the cost of production of the gas was lowered because it was found that equally good results could be obtained with a gas of poorer quality, that is, of lower illuminating power. Gas manufacturers, therefore, were able to use cheaper coal, and, by carrying out the distillation at a higher temperature, were able to obtain a larger volume of gas from the coal. Although the illuminating power of this gas when burned in a flat flame is lower than formerly, the temperature produced in the Bunsen flame and therefore the incandescence of the mantle are not greatly affected.

Incandescent mantles are employed not only with coal-gas but also with a combustible mixture of petrol vapour and air; and petrol-air gas is now largely installed in houses in country districts remote from centres of coal-gas manufacture.

One other illuminant must be mentioned, the use of which depends on the process of combustion in air, namely, *acetylene*, a gas which is readily obtained by the action of water on a compound of calcium and carbon, known as calcium carbide.[1] This substance is obtained by heating to a high

[1] Acetylene can also be produced by the pyrolysis, or decomposition at high temperature, of methane; and owing to the enormous supplies of methane which are available from petroleum and natural gas, the production of acetylene from this substance may, in the future, assume great importance.

temperature a mixture of quicklime (calcium oxide) and carbon in the form of anthracite or coke. The preparation is carried out in a special type of furnace in which the high temperature necessary is obtained by means of the electric arc,[1] and owing to its use for the production of acetylene, calcium cyanamide (Chap. x), and other substances, calcium carbide is now manufactured in large quantities.



Courtesy of British Oxygen Co.

CUTTING STEEL BY OXY-ACETYLENE FLAME.

Acetylene is an unsaturated hydrocarbon having a relatively large proportion (over 92 per cent.) of carbon, as is shown by its formula C_2H_2. Under ordinary conditions the gas burns with a luminous and very smoky flame, but by using a special burner which ensures the admixture with the gas of a small amount of air, a white, intensely luminous flame is obtained.

By injecting oxygen into a flame of acetylene, a tem-

[1] A temperature estimated at about 3000° C. (about 5400° F.) can, in this way, be obtained.

perature of about 3480° C. (6300° F.) can be obtained, and this fact has received important applications. If, for example, the oxy-acetylene flame is allowed to impinge on a piece of iron or steel, the metal is heated locally to redness, and if a fine jet of oxygen is then directed against the red-hot metal, the iron is oxidised to oxide of iron which melts in the intensely hot blowpipe flame, and flows away like water. By this means one can cut through even large steel rods, shafts, or girders as easily as a knife will cut through cheese, and with a cut almost as fine. One of the first applications to be made of the oxy-acetylene blowpipe flame was to cut through the dense tangle of iron girders formed by the collapse of the buildings in the fire at the Brussels Exhibition of 1910, and so to allow of their removal. Acetylene is also very extensively used for the welding of metals.

Owing to the readiness with which compressed or liquid acetylene may undergo explosive decomposition, the gas is generally dissolved in a solvent, *acetone*, under pressure, and the solution stored and transported in steel cylinders. These cylinders contain a porous, absorbent material which acts as a carrier for the solvent, acetone, and increases the storage capacity of the cylinder. The danger of explosion is also thereby diminished.

Besides being used in the manner described above, large quantities of acetylene are also used for the production of acetic acid (Chap. XVII), of ethyl alcohol, of butyl alcohol (p. 354), synthetic rubber (p. 341), etc. Acetylene, in a concentration of about 1 per cent., is also used to accelerate the ripening of peaches, oranges and other fruits. The manufacture of calcium carbide and the production therefrom of acetylene is, therefore, an industry of very great importance.

CHAPTER VI

MATTER, ENERGY AND EXPLOSIVES

THE consideration of the process of combustion, controlled and utilised for the production of heat and light, leads to a realisation of the fact that in the chemical reactions and transformations which take place, one is not dealing merely with material things. In the case of the burning candle, oil, or coal-gas, it is not the combustible substances (stearin, paraffin, hydrogen, methane, etc.), nor the products of combustion (carbon dioxide and water vapour), which interest us primarily, but the immaterial light, the ethereal vibrations to which the process of combustion gives rise. So also, passing on to the consideration of combustible substances as fuels, and of the process of combustion as a source of heat, we again recognise that our interest is focused not on the material nature of the combustibles, but on their efficiency as heat-producers. Heat, however, is a form of energy, and can be converted into other forms of energy, such as mechanical energy, and can perform what we call work ; and so it is really in their power of doing work that we see the value of combustibles. The combustible substances together with the oxygen of the air represent so much *potential energy*, and the process of combustion is like the downward rush of the waterfall in being a process by which potential energy becomes available for doing work. In the recognition of the supreme importance of energy, in the establishment of the law of the conservation of energy and of the laws governing the mutual transformation of the different forms of energy, we see one of the greatest achievements of nineteenth-century physical science ; and if one would grasp the spirit of modern chemistry, one must learn to regard a chemical change or reaction not merely as

involving some material transformation but as representing a flow of energy out of or into the substances undergoing the change. "Real gain," as Sir William Ramsay said in his presidential address to the British Association in 1911, "real gain, real progress consists in learning how better to employ energy —how better to effect its transformation"; and it is by the utilisation of energy and by the methods of applying and transforming energy, that the nineteenth and twentieth centuries are so strongly marked off from the centuries which preceded them.

At the present day by far the greatest part of the energy necessary for the continuance of vital activity, as well as for carrying on the industrial life of the world, is derived from the energy of combustion of carbon, and of its compounds. Through the oxidation of carbonaceous food by means of the oxygen taken in through the lungs, the vital activity of the animal organism is maintained, and the inert carbon dioxide produced in the process is sent into the atmosphere in the expired air. But the carbon does not thereby cease to be available, for, as has already been pointed out (p. 51), the green plants, absorbing the radiant energy of sunlight, transform and utilise the carbon dioxide for the purpose of building up their own structures and producing compounds like starch and sugar, which again become the food and the source of energy of animals. In the case, therefore, of the element carbon which constitutes the basic element of all life, there is a continual circulation in nature, whereby the mutual preservation of the animal and vegetable worlds is secured. The green plants act as transformers of the radiant energy of sunlight into the potential energy of combustible substances.

The synthetic or building up processes which thus take place in the green plant were imitated by Professor E. C. C. BALY in the Chemical Laboratories of the University of Liverpool. It was found that carbon dioxide and water when exposed to light, in presence of a suitable catalyst[1] (a material

[1] For example, ferric oxide, to which a small amount of thorium oxide has been added. See also Chapter IX.

which accelerates a reaction without itself entering into the products of change), combine to form compounds of a sugar-like character, called generally carbohydrates (p. 137). The "yield" or proportion of carbohydrate so far obtained is very small; but the artificial synthesis resembles in several points the natural synthesis in the plant. The process is one which is at present of no practical utility, but its purely scientific interest and importance are very great.

Although the association of energy with chemical change is very obvious in the process of combustion, it is also found in all chemical changes. Every chemical system, every collection of substances which can spontaneously undergo chemical change, represents a certain amount of potential energy, and the material change which is observed, and which constitutes what is called a chemical reaction, is merely the outward sign of the conversion of so much potential energy into active energy—heat energy, or some other form of energy. Moreover, whenever a chemical change or reaction occurs, the heat which is given out, the so-called heat of reaction, is, for a given weight of the reacting materials and under specified conditions, constant and definite in amount.

But it must not be thought that all chemical change is accompanied by an *evolution* of heat. In some cases, the initial substances possess less energy than the final products, and the chemical change therefore takes place with *absorption* of heat. Energy, that is to say, must be supplied to the initial substances in order that they may pass into the final products of change. One distinguishes, therefore, between *exothermal* reactions or reactions accompanied by evolution of heat, and *endothermal* reactions or reactions accompanied by absorption or taking in of heat energy.

This way of regarding chemical change as being the outward and visible sign of energy change is very instructive; for it is clear that if we can make a substance take up energy—if we can, as it were, pump energy into a substance—we can thereby alter the amount of energy of which that

substance is the carrier, and so change its nature. This fact is clearly illustrated by the behaviour of the familiar substance, oxygen.

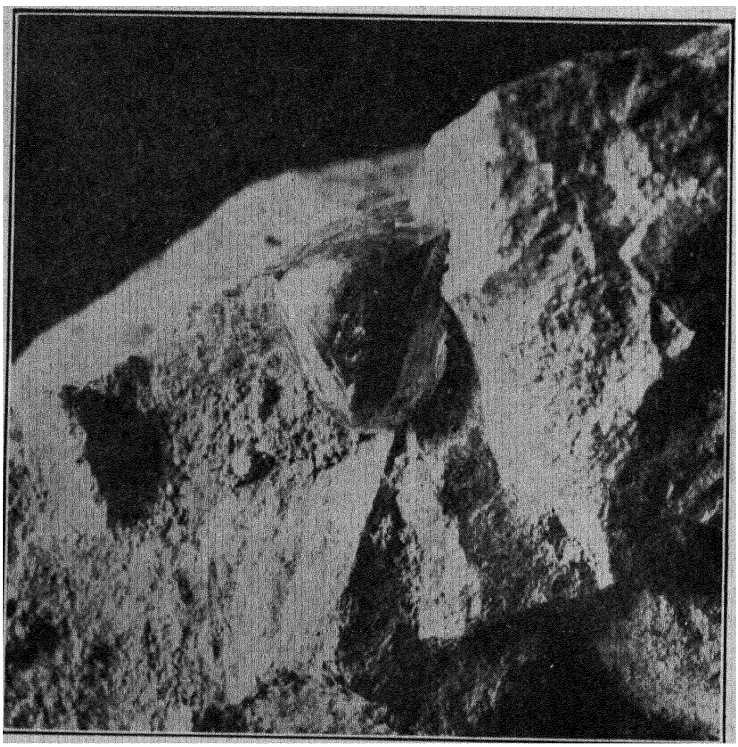
The molecule of oxygen consists of two atoms, O_2, but when the gas is subjected to the action of an electric discharge under particular conditions, it takes up or absorbs some of the energy of the discharge and passes into a gas which, on account of its powerful and characteristic smell, received the name of *ozone* (Greek *ozo*, I smell). The material change, the chemical change, which accompanies the absorption of energy, is the addition of a third atom of oxygen to the molecule of that gas, so that the molecule of ozone consists of three atoms of oxygen, O_3. Since ozone contains more energy than ordinary oxygen, it is a more active oxidising agent, and for this reason it is used for the purification of water and other bactericidal purposes, and for bleaching wax, starch, flour, ivory and other substances.

At Niagara Falls, large quantities of ozone are used in the production of vanillin, the sweet-smelling constituent of vanilla pods, by the oxidation of oil of cloves (p. 330).

In white phosphorus and red phosphorus (p. 75), and in the three forms of carbon—charcoal, graphite and diamond —we have further examples of elements existing in different, so-called *allotropic*, forms containing different amounts of energy. That the three forms of carbon, which differ so markedly in appearance and physical properties, are associated with different amounts of energy, is shown by the fact that when equal weights are burned different amounts of heat are evolved. The applications and uses of the different forms of carbon, however, do not centre round their calorific values, but round other properties of quite a different character.

Diamond is a crystalline form of carbon which is now found mainly in South Africa, the Congo and Gold Coast, and is greatly valued as a gem. The crystals, generally in the form of octahedra, may occur either embedded in a

rocky matrix, known in South Africa as blue ground, from which they are recovered by crushing and washing, or in loose alluvial deposits. Diamond has a high index of refraction and, consequently, when suitably cut, scintillates



Courtesy of De Beers Consolidated Mines Ltd

DIAMOND CRYSTAL IN BLUE GROUND.

and flashes in varied colours. It is the hardest of all substances and therefore finds important use as a cutting, drilling and polishing material. For this purpose the impure black diamonds, known as *carbonado* or *bort*, are largely employed.

Graphite is also a crystalline form of carbon, deposits of which are found especially in Ceylon and Madagascar. It

has a greasy or unctuous feel and is extensively used as a lubricant. Unlike diamond, graphite is soft and has long been used for the manufacture of lead pencils. For this purpose, the graphite is ground to a fine powder and mixed with various amounts of clay or powdered retort carbon in order to produce pencils of different hardness. On account of its resistance to heat, graphite is used for making crucibles. It is also a moderately good conductor of electricity and is

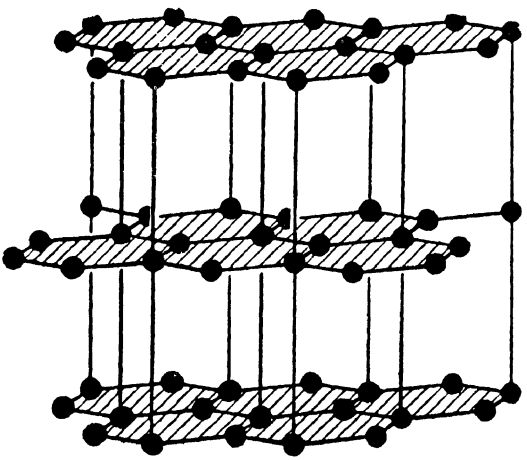


FIG. 12.—ARRANGEMENT OF THE CARBON ATOMS IN GRAPHITE.

employed in the construction of dry cells and of electrodes for use in electro-chemical industry (Chap. XII). As we shall learn later, graphite is now manufactured artificially in large amount.

The marked differences in the properties of diamond and graphite are due to differences of crystalline structure, or arrangement of the carbon atoms in the crystal. In graphite, as is shown by examination with X-rays, the crystal consists of layers of carbon atoms, the atoms in each layer being arranged in the form of hexagons lying in one plane ; and the different parallel layers are relatively far apart (Fig. 12). The forces acting between adjacent layers are much less than those between the atoms of the same layer, and the different

layers can therefore move past one another relatively easily. This explains the soft, unctuous feel of graphite and its use as a lubricant.

In diamond there are also layers of carbon atoms arranged in hexagons. The atoms in a given layer, however, are not all in one plane, but have a zig-zag arrangement, so that the layers have, as it were, a corrugated surface (Fig. 13). The atoms in adjacent layers, moreover, are as near together as

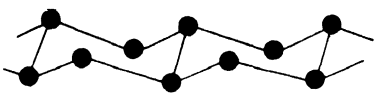


FIG. 13.—LAYER OF CARBON ATOMS IN DIAMOND.

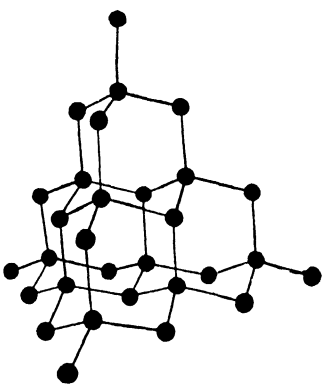


FIG. 14.—ARRANGEMENT OF CARBON ATOMS IN DIAMOND.

the atoms in a given layer (Fig. 14). The crystal is therefore more compact than graphite, and the adjacent layers, being near together and "corrugated," do not readily move past one another. Hence the hardness of diamond.

Charcoal, an amorphous or non-crystalline form of carbon, is obtained by heating wood, bone, coco-nut shell and other carbonaceous matter in a closed vessel, or retort, out of contact with the air; and at the present day large quantities of wood are "distilled" not only for the production of charcoal but also for the sake of the other products formed.

When wood is heated in retorts, volatile products—wood tar, wood spirit or methyl alcohol,[1] acetic acid, acetone, and various gases—pass off and charcoal remains in the retort. The gases are used for heating the retorts.

Charcoal is very porous and possesses in a very high degree the property of condensing on its surface, or *adsorbing*, different gases and vapours, and for this reason may be used for removing foul or noxious gases from the air. It finds important application in the construction of gas masks for protection against poisonous gases, and it is also largely used for removing gasoline vapour from the " natural gas " which escapes from many oil wells. The adsorptive power of charcoal is greatly increased by lowering the temperature; and this fact is made use of for the purpose of producing high vacua. The vessel to be exhausted is connected with a tube containing charcoal cooled in liquid air. At this low temperature, the air is very completely condensed on the surface of the charcoal.

Charcoal also finds a very wide use for the decolorising of liquids, *e.g.* sugar molasses.

The " pyroligneous acid " or aqueous distillate from wood was until 1925 the main source of methyl alcohol (or methanol as it is now frequently called), acetic acid and acetone, all of which are important substances in industry. Methyl alcohol, however, is now produced in very large amounts from water-gas (p. 193), acetic acid is produced from acetylene (Chap. XVII), and acetone is produced by a fermentation process (Chap. XVII), as well as from ethyl alcohol and from acetic acid. As a result of these developments, which well illustrate how in chemical science and industry there can be no standing still, the wood distillation industry has been dealt a serious blow.

From a very early time, charcoal has been used as a fuel

[1] Crude wood-spirit, which contains a number of substances besides methyl alcohol, is extensively used in Great Britain for the purpose of denaturing spirits of wine (ethyl alcohol).

as well as in metallurgy, and in all the forests of Europe the "coallier" or charcoal-burner was a well-known and picturesque figure. Although most of the charcoal is now produced in retorts, a certain amount is still produced by the primitive, centuries-old and very wasteful method of the "pit," a certain preference being shown by some industries for such forest-burned charcoal. In constructing a pit, logs

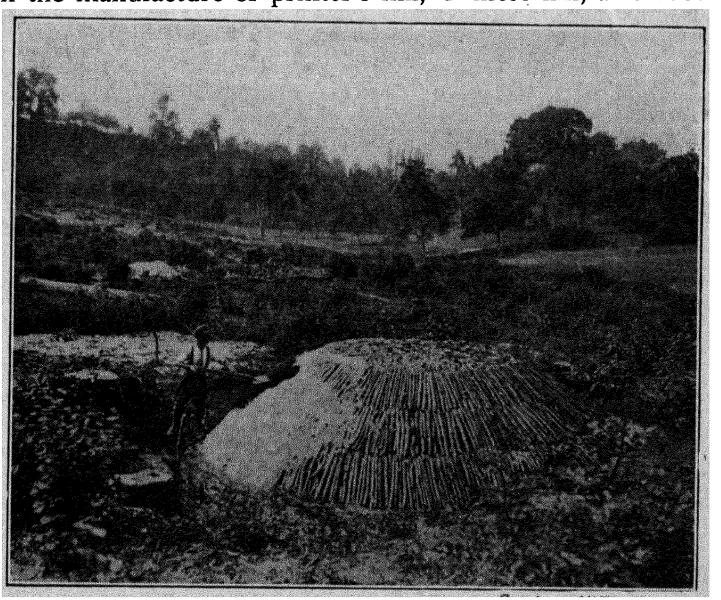
Courtesy of "The Times."

CHARCOAL-BURNING AT LONGHOPE, FOREST OF DEAN.
Making the chimney before piling up the lengths of wood.

of wood are built up in tiers round a central chimney or flue, covered with shavings or brushwood, and cemented down with earth or turf, to prevent access of air. A fire is lighted in the central chimney, and the burning carefully watched and adjusted, so as to prevent excessive combustion and to bring about even "coaling." After the smoke has ceased to escape, all the air vents are closed to exclude air, and the mass is left to cool down. By this method, the heat of

combustion of part of the wood serves to carbonise the rest.

Carbon black, *lampblack*, or soot, another form of amorphous carbon, is produced by the combustion, in a limited supply of air, of coal-tar residues and also by burning natural gas and methane against a cold surface. It is used in the manufacture of printer's ink, Chinese ink, and boot-



Courtesy of "The Times."

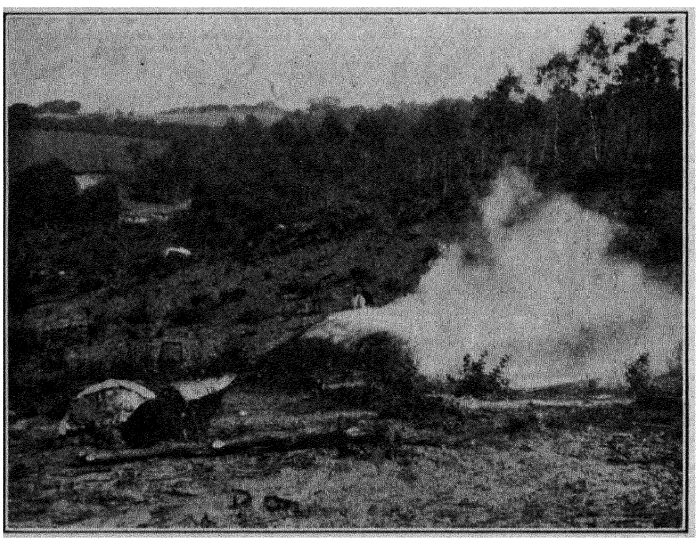
CHARCOAL-BURNING AT LONGHOPE, FOREST OF DEAN.

The " pit," built in three tiers of cordwood round the chimney, being covered with shavings and earth.

blacking. It is most extensively employed, however, in the manufacture of rubber tyres, because when mixed with the rubber it gives increased toughness, elasticity and durability. By this means, a fourfold increase in the mileage of a motor car tyre can be obtained.

The idea that a spontaneously occurring chemical change

represents the conversion of so much potential energy into other forms of energy, can perhaps be most vividly realised from a consideration of the materials known as *explosives*. In the case of the explosives actually in use, the chemical process which occurs is essentially one of very rapid combustion, with production of gaseous substances occupying



Courtesy of "The Times."

CHARCOAL-BURNING AT LONGHOPE, FOREST OF DEAN.
The pit in action.

a volume which, at the temperature of the explosion, is, perhaps, 15,000 to 20,000 times as great as that of the explosive itself.

As early as the seventh century, we read, a rapidly burning mixture, known as Greek Fire, was used by the inhabitants of Constantinople in their defence of the city against the Moslems, and, even as late as the thirteenth century, rapidly burning mixtures of sulphur, pitch, naphtha and other substances which " came flying through the air like a winged

long-tailed dragon, about the thickness of a hogshead, with the report of thunder and the velocity of lightning," were used by the Moslems in the crusades. When and by whom the first real explosive, *gunpowder*, was invented is unknown, although the invention has frequently, but erroneously, been attributed to Roger Bacon in the thirteenth century. During the nineteenth century, more especially, man strove to discover new explosives of greater and greater power, to learn how better to utilise and control the transformation of the enormous stores of potential energy contained in explosives, and to make them work for him both in peace and in war. Some idea of the advance which has been made is gained when we compare the artillery used by the English at the battle of Crécy in 1346, when the guns " threw little balls of iron to frighten the horses," with the modern large gun which can hurl a projectile of nearly a ton in weight to a distance of thirty miles.

Gunpowder is a mixture of potassium nitrate or saltpetre, charcoal and sulphur, and its action as an explosive depends on the rapid combustion of the sulphur and charcoal at the expense of the oxygen contained in the saltpetre. The composition varies in different countries and according to the use to which the explosive is to be put, but generally gunpowder consists of about 75 per cent. of saltpetre, 10 per cent. of sulphur, and 15 per cent. of charcoal. Although in modern times great improvements have been made in gunpowder, these improvements have been of a physical or mechanical and not of a chemical nature. In the manufacture of black powder, the constituents are finely ground, mixed together and the mixture passed through a fine-mesh sieve of copper or brass wire. To secure thorough mixing or incorporation, the mixture, kept in a moist state, is ground in a mill under heavy edge-runners. The cake so produced is broken up into pieces and then subjected to a pressure of, perhaps, 400 lbs. per square inch whereby a hard mass is obtained. The press-cake is then granulated by passage between rollers

with pyramidal teeth of different sizes, and the grains polished or glazed in rotating wooden drums. Finally, the gunpowder is dried by air at a temperature of about 40° C. (104° F.). The violence of the powder as a blasting explosive can be varied by altering the density and size of the grains. Increase of density and coarsening of the grains make the powder slower.

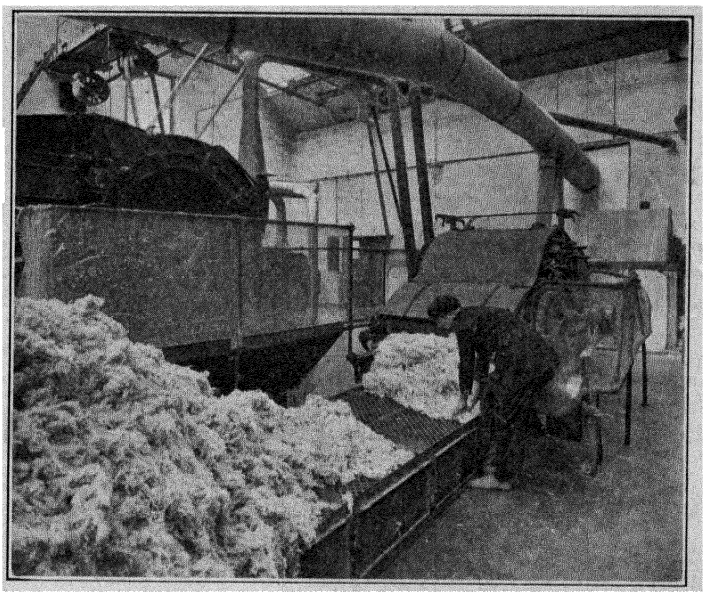
While still largely used in connection with the beneficent operations of mining and also for pyrotechnic displays, gunpowder is no longer employed as a propellant for military or naval purposes.[1] Its use has been given up not only on account of the large volume of smoke produced in the explosion, which by speedily hiding everything from view prevents the effective use of quickfiring guns, but also because explosives of very much greater power and efficiency have been discovered.

The first great advance in the chemistry of explosives took place with the discovery of *gun-cotton*, in 1846, by CHRISTIAN FRIEDRICH SCHÖNBEIN, Professor of Chemistry in the University of Basle. Cotton consists, essentially, of the chemical substance cellulose, which is, as we have seen (p. 79), a compound of carbon, hydrogen and oxygen. When this is acted on by a mixture of nitric and sulphuric acids, various compounds of cellulose with nitric acid are formed, the composition and properties of which depend on the strength of the acid mixture and the temperature and duration of reaction. The compounds so formed, strictly called cellulose nitrates, are more popularly called *nitro-celluloses*. Since not only cotton but also purified wood fibre or wood pulp and other vegetable fibres consist *essentially* of cellulose, such materials can also be used, and are to a certain extent used in the production of nitro-cellulose, as we shall learn more fully in the following chapter. For the production of explosives cotton is almost exclusively

[1] It is, however, still used for the bursting-charge of shrapnel, for filling the rings of time-fuses for shells, etc.

employed, and in its preparation and treatment great care is exercised.

Gun-cotton, which is defined as a nitro-cellulose with more than 12·3 per cent. of nitrogen and not less than 85 per cent. insoluble in a mixture of ether and alcohol (two

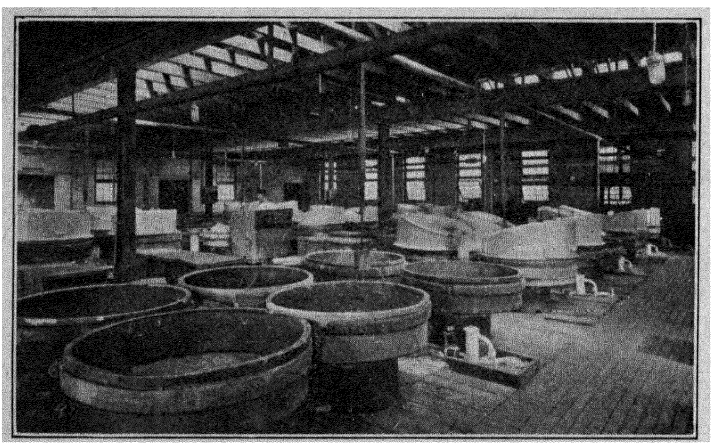


Courtesy of Imperial Chemical Industries Ltd. (Nobel Section).

TEASING COTTON PREPARATORY TO NITRATION.

volumes of ether to one of alcohol), is prepared from cotton linters, or the short fibres which are left after the cotton used for textile purposes has been removed from the cotton seed. The linters, after being freed from dust, are boiled with a solution of caustic soda (sodium hydroxide or NaOH), in order to remove natural oil and non-cellulosic matter, and then bleached. The bleached linters are then opened in a teasing machine and subjected for a period of about two and a half hours to the action of a mixture of

nitric and sulphuric acids, an operation frequently carried out in shallow, earthenware pans. After nitration, the waste acid is allowed to run off at the bottom of the pan while water is run on to a perforated plate which rests on the top of the cellulose. The nitrated cotton is then very thoroughly washed and boiled, to render it more stable.



Courtesy of Imperial Chemical Industries Ltd. (Nobel Section).

PANS FOR NITRATING CELLULOSE.

When ignited, loose gun-cotton burns with great rapidity, but not so rapidly as to constitute an explosion. The molecule of gun-cotton, however, which, as one might say, is almost bursting with energy, is in a very unstable condition, and when subjected to a shock, as, for example, when a little fulminate of mercury or lead azide is caused to detonate near it, it suddenly decomposes and gives rise to a large volume of gaseous substances—nitrogen, oxides of carbon and water vapour. Since these gases are all colourless, and as no solid materials are formed, gun-cotton explodes without production of smoke.

As an explosive, gun-cotton possesses the very important property that it can be used wet. This wet gun-cotton will

not take fire when a light is applied to it, but when subjected to the shock of a fulminate of mercury or lead azide detonator, it explodes just as readily as when it is dry. Thus, torpedoes and sea-mines are charged with rolls of moist gun-cotton which have been subjected to a high pressure (six tons per square inch) and so compressed into hard blocks.

The disruptive effect of gun-cotton is very great by reason of the rapidity with which the decomposition of the substance takes place. Thus, whereas a couple of pounds of gunpowder require about a hundredth of a second for complete combustion, the same weight of gun-cotton undergoes decomposition in about one fifty-thousandth part of a second. It is on this fact that the shattering or disruptive effect, the " brisance," depends. It is this fact also which makes gun-cotton, which is very valuable as a " high " or " disruptive " explosive, unsuitable for use as a " low " or " propulsive " explosive in guns. It would simply burst the gun. For effective propulsion, it is necessary to have a rapid and increasing *push* behind the projectile, not an instantaneous increase of pressure.

Although gun-cotton cannot be employed as a propellant, the advantages attaching to a smokeless explosive are so obvious that attempts were made to overcome the difficulties due to the rapid rate of explosion. These attempts to " tame " the gun-cotton have been entirely successful. Although gun-cotton dissolves only to a slight extent in a mixture of ether and alcohol, nitro-cotton with a lower percentage of nitrogen dissolves completely,[1] yielding a liquid well known under the name of *collodion*. If, then, gun-cotton be mixed with a soluble nitro-cotton and the mixture kneaded with ether-alcohol to form a paste, and if the paste be then granulated by passage through suitable dies, gelatin-like grains are obtained after the ether and alcohol have been

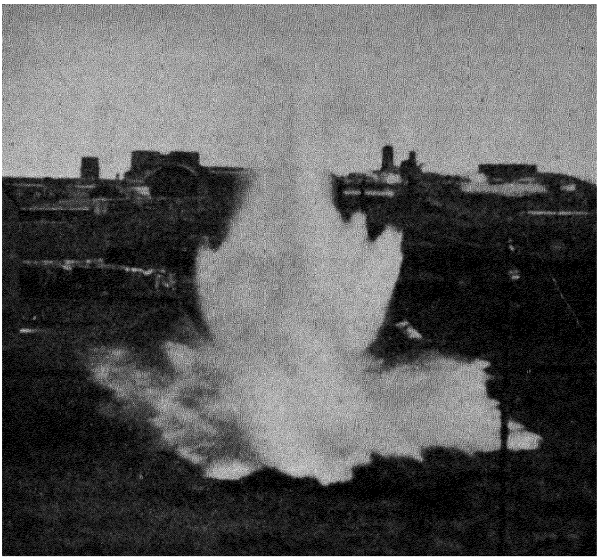
[1] The solubility of nitro-cellulose can be greatly altered by treatment, and a nitro-cellulose with high solubility can be obtained from a nitro-cellulose with low solubility by heating the latter with water under pressure.

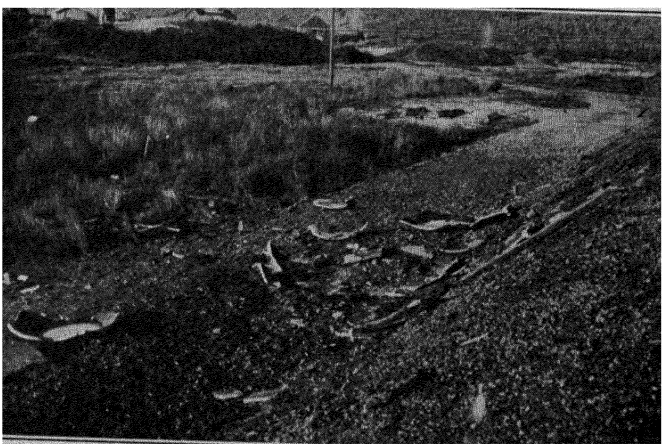
removed by volatilisation. Such gelatinised nitro-cotton is widely used as a smokeless powder for naval and military purposes in Europe and in the United States of America. It was the first smokeless powder to be used for military purposes. To render the material less liable to undergo decomposition with time, a small amount of a stabiliser, *e.g.* diphenylamine, is incorporated in it.

A further advance in the chemistry of explosives was made by the Swedish chemist, ALFRED NOBEL. When glycerine, which, as we have seen (p. 85), is readily obtained from animal or vegetable fats and oils, is treated with a mixture of nitric and sulphuric acids, it behaves similarly to cotton and yields a substance " nitro-glycerine," which is a liquid and very powerful explosive. This substance, discovered by the Italian chemist, SOBRERO, in 1847, and first manufactured on a commercial scale in 1862 by Nobel, was difficult to handle on account of its great sensitiveness to shock, and was the cause of many fatal accidents ; but it was found that if the liquid nitro-glycerine was mixed with kieselguhr, a fine earth composed of the siliceous skeletons of marine diatoms, the explosive could be transported and handled with comparative freedom from danger.[1] In this form nitro-glycerine has been extensively used under the name of *dynamite*, its explosion being brought about by means of a fulminate of mercury detonator.

When about 8 per cent. of nitro-cotton is mixed with 92 per cent. of nitro-glycerine, a tough jelly-like mass is formed known as *blasting gelatin*. That this explosive is more powerful than dynamite, that it is, indeed, one of the most powerful blasting explosives known, will cause no wonder, since the nitro-glycerine is not mixed with an inactive material like kieselguhr, but with a substance which is itself an explosive. Some of the most commonly used blasting agents are the *gelignites*, formed by adding varying pro-

[1] Wood-flour or wood-meal, burnt cork, charcoal and other materials are also used as absorbents in place of kieselguhr.





Courtesy of Imperial Chemical Industries Ltd. (Nobel Section).

BREAKING UP A LARGE CAST-IRON POT.

A large cast-iron pot which was to be broken up was filled with water and a charge of blasting gelatin, submerged in the water, was exploded. The upper picture shows the fountain of water following on the explosion ; the lower, fragments of the pot.

portions of such materials as potassium nitrate, ammonium nitrate, wood-meal, chalk, to the blasting gelatin.

The British service powder, *cordite*, is prepared by mixing a " paste " of gun-cotton (65 per cent.) and nitro-glycerine (30 per cent.) with acetone, and adding a quantity of vaseline (5 per cent.).[1] The mixture is then forced by hydraulic pressure through a die into the form of a thread or cord. Hence the name cordite. After evaporating off the acetone, the cordite forms a horn-like material which is very insensitive to shock and safe to handle. The " taming " action of gelatinisation on two of the most powerful explosives is one of the most important and remarkable discoveries in this branch of science; and nitro-cotton, gelatinised in one way or another, is now the basis of all propulsive ammunition.

Although gun-cotton is extensively employed as a high explosive, more especially in torpedoes, other explosives derived from the products of distillation of coal are employed in shells. Of these explosives the two most important and most used are *picric acid* and *trinitrotoluene*.

When carbolic acid or phenol, to give it its scientific name, is treated with a mixture of nitric acid and sulphuric acid there is formed trinitrophenol or picric acid. As ordinarily obtained, it is a faintly yellow crystalline substance, which was long used as a yellow dye for silk. As an explosive it goes by various names, such as melinite, lyddite, dunnite, pertite, and shimosite.

Picric acid, however, has now been largely superseded by another explosive which is derived from the hydrocarbon toluene, and is called trinitrotoluene, or T.N.T., or *trotyl*. This substance also is a solid, and can be subjected with impunity to very rough usage; a bullet, even, may be fired into the mass without producing any effect. When detonated,

[1] Vaseline lowers the temperature of the explosion and so reduces the erosion of the gun-barrel, and it also increases the stability of the cordite when stored.

however, trinitrotoluene explodes with a violence not much inferior to picric acid, but as the oxidation of the carbon in the compound is by no means complete, dense black clouds of carbonaceous matter are produced. In order to secure more perfect combustion and, at the same time, to reduce the amount of T.N.T. required, ammonium nitrate, a substance containing a large proportion of oxygen, is now generally added. In this way the British service high explosive, *amatol*, a mixture of eighty parts of ammonium nitrate with twenty parts of T.N.T., is obtained. A mixture of T.N.T. and aluminium powder, known as *tritonal*, was used during the war for filling the bombs known as " block busters."

The compound, *cyclonite*, referred to by the Research Department at Woolwich as R.D.X., is an explosive which in blasting power and *brisance* is greatly superior to any other explosive hitherto used for bursting charges. Cyclonite is not produced from coal tar but from methanol (p. 193), now manufactured mainly from water-gas. By the oxidation of methanol there is produced *formaldehyde* (H·CHO)—sold in solution as a disinfectant under the name of formalin—which reacts with ammonia to form a compound known as hexamine. By the action of concentrated nitric acid on this compound, cyclonite $(CH_2{\cdot}N{\cdot}NO_2)_3$ is obtained ; a compound in which the CH_2 and the $N{\cdot}NO_2$ groups are arranged alternately in the form of an hexagonal " ring." A mixture of T.N.T., R.D.X. and aluminium powder, known as *torpex*, was used during the war as the most effective under-water explosive for the destruction of U-boats.

It is, one must remember, not merely or even mainly for the purpose of strengthening man's arm in war that explosives have found an application ; they have also, through their use in mining and by rendering possible such great engineering works as the Suez Canal and the Panama Canal, and the removal, in 1885, of the reefs known as Hell Gate in the channel of the East River, New York, played an important part in the peaceful progress of civilisation. Through the

labours of chemists a wide range of explosives has been obtained to satisfy the very varied demands of industry and engineering ; and even in the piping times of peace, hundreds of thousands of tons of explosives are produced for mining, blasting and sporting purposes.

CHAPTER VII

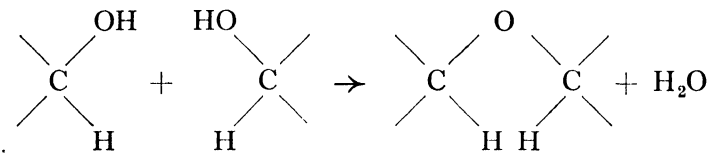
CELLULOSE AND CELLULOSE PRODUCTS

We have seen in a previous chapter how the woody material of plants has, by the age-long action of natural forces, become converted into the most valuable of all fuels, coal; and we have also seen how cotton can, by the action of nitric acid, be transformed into one of the most powerful of explosives. We must now consider very briefly how the chemist has, in other ways, succeeded in changing the aspect and nature of the cellulose, of which cotton and wood fibre essentially consist, so as to produce other materials which can be fashioned into articles of utility and of beauty, ministering to the wants, the comfort and even the luxury of man.

The chemical substance cellulose belongs to a group of compounds consisting of carbon, hydrogen and oxygen, in which the hydrogen and oxygen are present in the proportion of two atoms of the former to one of the latter. Since this is the proportion in which these two elements combine to form water, it was thought, erroneously, that cellulose and the other compounds belonging to that group were compounds of carbon with water, and so the name *carbohydrate* was applied to them. The different sugars, such as glucose and sucrose (cane and beet-root sugar), and also starch and a number of other substances, belong to the class of the carbohydrates; and in cellulose the carbon, hydrogen and oxygen are united in the proportions of six atoms of carbon, ten atoms of hydrogen, and five atoms of oxygen ($C_6H_{10}O_5$).

The molecule of cellulose is very large and may be regarded as built up of several hundreds of molecules of glucose,

$C_6H_{12}O_6$,[1] formed into a chain by a process of *condensation*; that is, by the elimination of a molecule of water between each pair of glucose molecules. Thus :

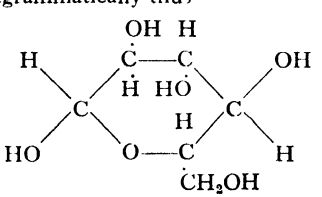


Cellulose is therefore represented by the formula $(C_6H_{10}O_5)_n$ where n is more than 100.

The purest naturally occurring form of cellulose is cotton, the hairy material which covers the seeds of various species of the cotton plant (*Gossypium*). When this has been chemically treated with alkalies and bleaching agents, and with acids, in order to remove various organic and mineral impurities, the product constitutes what is called cellulose. This is one of the most important and valuable substances in present-day civilisation, being employed in the manufacture not only of cotton and linen textile materials, but also of explosives, of paper, and of other substances, to some of which we shall refer later. Its great value for the manufacture of paper depends mainly on the fibrous character of naturally occurring cellulose, and also on the fact that it is a very stable substance and is not acted on by the atmosphere nor by most of the other substances with which it ordinarily comes into contact.

The cotton fibre is to be regarded as made up of a bundle of long-chain molecules, arranged parallelwise, with forces of

[1] Represented diagrammatically thus



attraction holding these bundles together. It is on the existence of long-chain molecules, packed closely side by side, that the strength of a fibre depends.

Less than a hundred years ago, when the production of paper was hampered by a Government duty, and before education had created the present demand for cheap newspapers and cheap books, paper was manufactured entirely from cotton and linen rags. But nowadays the supply of these is quite inadequate to meet the demand, and recourse is had to the less pure forms of cellulose which constitute the skeletal frame-work of all plant structures. Large quantities of more or less pure cellulose, therefore, are produced at the present day from straw, various grasses (especially esparto grass), and from wood, for use in the different industries of which cellulose is the basis.

Of these different sources of cellulose, wood is by far the most important. Wood fibre consists mainly of a compound of cellulose with lignone, encrusted frequently with resinous matter, and in order to isolate the cellulose this compound must be decomposed. Formerly this was done by boiling the wood, in the form of shavings or chips, with caustic soda (giving rise to " soda pulp "), but this substance has now been very largely replaced by calcium bisulphite (or acid sulphite of lime),[1] the wood being boiled with the liquor under a pressure of several atmospheres. Not only is the wood fibre thereby broken up chemically with production of cellulose, but the latter is also bleached to some extent by the sulphite. The cellulose is now separated from the sulphite liquor, washed and beaten with water so as to break down the fibres into small shreds, in which form it constitutes *wood pulp* (" sulphite pulp ").

For the treatment of resinous woods, more especially, a mixed solution of caustic soda and sodium sulphate is used, the pulp so obtained being known as " sulphate pulp."

[1] This substance is formed by passing sulphur dioxide into milk of lime (suspension of slaked lime or calcium hydroxide in water).

This pulp is employed in the manufacture of a strong wrapping paper (Kraft paper).

Pulp is produced, however, not only by chemical but also by mechanical means, the wood being ground to powder on rapidly revolving, wet grindstones. In this " mechanical pulp," however, the cellulose is not separated from the lignone and the resins in the wood ; it is not of a strictly fibrous nature and does not felt together readily. It is suitable, however, for mixing with other paper-making, fibrous material, especially cotton, for the production of a cheap paper. Owing to the presence of non-cellulosic matter in the ground wood, this paper turns yellow in a comparatively short time (owing to oxidation), and undergoes disintegration. It is suitable, therefore, only for ephemeral literature.

Of the paper at present manufactured, by far the largest proportion is made from wood pulp.

For the manufacture of paper, the cotton rags, grass, or crude wood pulp (" half stuff ") are disintegrated in " potchers " and bleached by means of chlorine or bleaching powder. The disintegrated fibres are then placed with water in " beaters " where they are cut and frayed into short fibrillæ by means of rotating blades, so that they may felt together better in the later process of paper-making. Dyes, also, are added at this stage if a coloured paper is desired.

When the fibres have been sufficiently broken down, they are suspended in water and run in a uniform stream over an endless band of wire gauze, through which the water drains away ; and the fibres are caused to felt together by giving a vibratory motion to the band of gauze. The web of felted fibres is now carried between rollers which press out the excess of water, and then between heated rollers in order to dry the paper.

The paper so obtained is loose in texture and of the nature of blotting paper ; and to make it suitable for writing or printing it must be sized. For this purpose it is passed

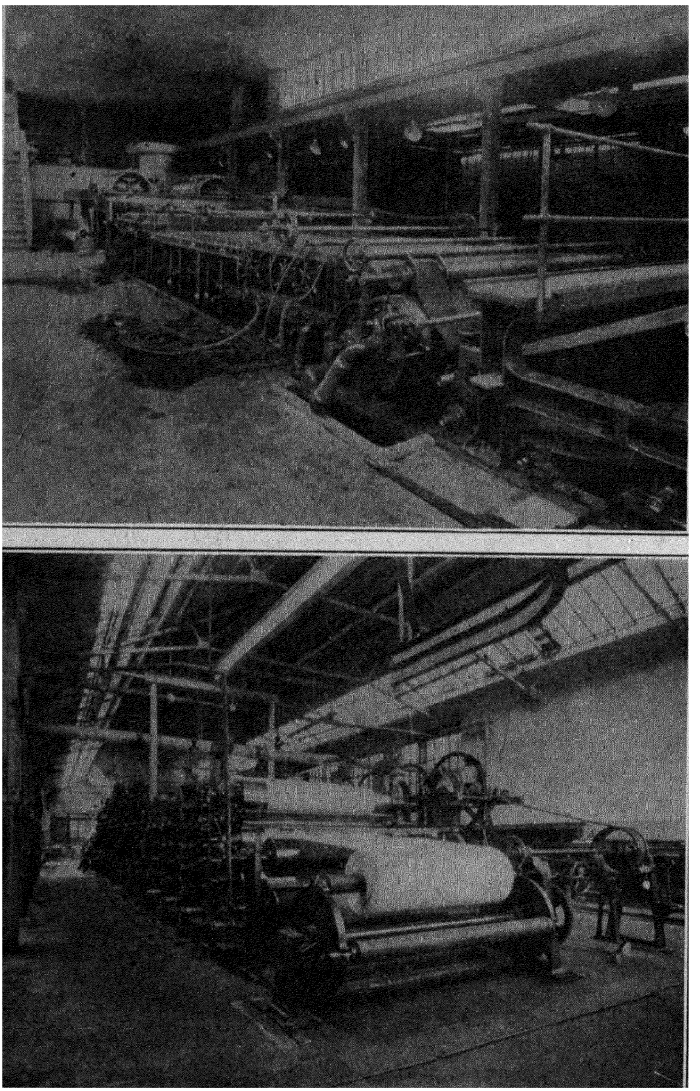
through solutions of alum and of rosin soap (p. 237), whereby a compound of rosin and aluminium is formed which binds the fibres together and prevents the ink from running. The addition of the sizing materials may also be made to the pulp before making into paper. In the case of finer papers, the paper may be sized by passage through a solution of

Courtesy of A. Pirie & Sons, Ltd.

BEATERS FOR DISINTEGRATION OF FIBRES.

gelatin. Sometimes, also, powdered gypsum, white clay, titanium oxide, or similar substances are added to the paper pulp in order to " load " or give body to the paper, fill up its pores, and allow of a more highly glazed surface being obtained by calendering, or rolling between hot rollers.

By immersing paper for a short time in a fairly concentrated solution of sulphuric acid, the cellulose is converted into a gelatinous mass which fills up the pores of the paper, and on being thoroughly washed, the paper is found to be parchmentised, or converted into a non-porous material



Courtesy of A. Pirie & Sons, Ltd.

PAPER-MAKING MACHINE.

Upper ; wet end : Lower ; dry end.

resembling parchment (prepared skin of the sheep or she-goat). Such *parchment paper* can also be prepared by immersing paper in a solution of zinc chloride; and by compressing together a number of sheets of such parchment paper, the compressed fibre, or "hard fibre," so largely used in the manufacture of travelling cases and trunks and as an insulating material for electricity, is obtained.

When one adds ammonia to a solution of bluestone or copper sulphate, a pale blue solid, copper hydroxide, is formed; and if this solid is dissolved in ammonia, a clear deep-blue coloured liquid (a solution of cuprammonium hydroxide) is produced. This liquid has the important property that it can dissolve cellulose, and by coating paper with the solution obtained and then immersing it in acid, the cellulose is thrown out of solution as a gelatinous mass which coats the paper and renders it waterproof. In this way *Willesden paper* is prepared.

As long ago as the seventeenth century, threads "resembling silk" were being sold in England, and Dr. ROBERT HOOKE, in 1664, put forward in his *Micrographia* the

> perhaps but a ſmall part of the ſubſtance, yet being ſo highly impregnated with the colour, as to be almoſt black with it, may leave an impreſſion ſtrong enough to exhibite the deſir'd colour. A pretty kinde of artificial Stuff I have ſeen, looking almoſt like tranſparent Parchment, Horn, or Iſing-glaſs, and perhaps ſome ſuch thing it may be made of, which being tranſparent, and of a glutinous nature, and eaſily mollified by keeping in water, as I found upon trial, had imbib'd, and did remain ting'd with a great variety of very vivid colours, and to the naked eye, it look'd very like the ſubſtance of the Silk. And I have often thought, that probably there might be a way found out, to make an artificial glutinous compoſition, much reſembling, if not full as good, nay better, then that Excrement, or whatever other ſubſtance it be out of which, the Silk-worm wire-draws his clew. If ſuch a compoſition were found, it were certainly an eaſie matter to find very quick ways of drawing it out into ſmall wires for uſe. I need not mention the uſe of ſuch an Invention, nor the benefit that is likely to accrue to the finder, they being ſufficiently obvious. This hint therefore, may, I hope, give ſome Ingenious inquiſitive Perſon an occaſion of making ſome trials, which if ſucceſsfull, I have my aim, and I ſuppoſe he will have no occaſion to be diſpleas'd.
>
> PASSAGE FROM HOOKE'S *Micrographia*

suggestion that it might be possible to make an " artificial glutinous composition " resembling silk. This suggestion was realised in 1883 by Sir JOSEPH WILSON SWAN, who was the first to produce filaments by squirting solutions of nitro-cellulose and the first to de-nitrate the filaments produced. The incentive which led Swan to his invention was the demand for a continuous filament for use in the recently introduced electric light bulbs ; but Swan also soon realised the possible uses of these filaments for textile purposes, and gave them the name of " artificial silk."

Swan's process was adapted commercially by the French chemist, Count HILAIRE DE CHARDONNET, who, in 1889, exhibited in Paris a material which, in its general appearance, imitated in a remarkable manner the fibre spun from the glands of the silkworm.[1]

Nitro-cellulose (cellulose nitrate), as we have seen, can, when suitably prepared, be dissolved in a mixture of alcohol and ether, and when the somewhat viscous liquid which is thus obtained is squirted through fine openings, and the jet of liquid allowed to pass through water, thin threads or filaments are formed. By treating these threads with certain solutions, *e.g.* a solution of sulphide of ammonium, the nitrate groups (NO_3), to the presence of which the nitro-cellulose owes its ready inflammability, are removed, and one obtains a regenerated cellulose, the natural structure of which has, however, been destroyed by the treatment to which it has been subjected. Threads or filaments so produced have all the superficial appearance and lustre of silk, and it was by this process that the fibre produced by the silkworm was first imitated and counterfeited in a commercially successful manner.

It was, however, not long before chemists discovered other methods of transforming cellulose into filaments and threads resembling silk. We have already seen that cellulose

[1] True silk belongs to a class of substances known as proteins, and contains nitrogen as well as carbon, hydrogen and oxygen.

dissolves in a solution of blue cuprammonium hydroxide, and when the viscous mass which is thus obtained is squirted into a suitable hardening liquid, threads of a silk-like lustre are also obtained.

The method by which most of the artificial silk, or *rayon*, as it is now called, is made at the present day, the so-called viscose process, was invented by the English chemists, C. F. Cross and E. J. Bevan. As raw material for this process, wood pulp, prepared by the maceration and chemical treatment of wood, is used. This pulp is treated with a solution of caustic soda and then with the liquid called carbon disulphide, whereby a thick syrup-like mass (*viscose*) is obtained. By forcing this viscous material through minute jets, or spinnerets, into a bath containing sulphuric acid, sodium sulphate, zinc sulphate and glucose, the viscose filament is coagulated and reconverted into cellulose. Silky filaments are thus produced which can be spun into threads or yarn suitable for weaving. Although, originally, the popularity of rayon depended mainly on its lustrous appearance, in which it is superior to natural silk, de-lustred rayon, or rayon with a dull lustre, was introduced in 1926 and rapidly gained popularity. To produce a rayon with dull lustre, the viscose is forced through spinnerets into a solution containing a white pigment (*e.g.* titanium oxide).

Although costing very much less than silk, rayon has not been found to enter into direct competition with the natural product; but for use in the production of articles of apparel, whether woven or knitted, of embroideries and laces, imitation furs and tapestries, it has developed for itself, and by reason of its own distinctive properties, a field of usefulness already great and rapidly expanding. So great, in fact, has this field of usefulness already become that the production of rayon in 1938 amounted to no less than 1,900,000,000 lbs., about ten times the production of silk.

Another type of artificial silk has also come into use under the name of *celanese* or *acetate rayon*. Unlike the viscose

rayon, celanese does not consist merely of transformed cellulose, but is a compound of cellulose with acetic acid, cellulose acetate. A viscous solution of cellulose acetate in acetone is forced through spinnerets and the acetone is removed from the issuing filaments by means of warm air. Celanese forms from eight to ten per cent. of the total production of rayon.

When celanese is treated with a dilute solution of alkali, it undergoes hydrolysis (p. 150); the acetate groups are removed and the celanese is reconverted into cellulose. If, at the same time, the fibre is stretched, so as to bring about a favourable arrangement of the long-chain molecules, its strength is so greatly increased that, weight for weight, it is stronger than the strongest steel. Ropes made of this regenerated and stretched cellulose (known as " fortisan ") were used, during the war, for towing gliders carrying airborne troops.

While, in the early days of the rayon industry, the filaments from the spinnerets were spun into yarn, now, nearly half of the total amount of rayon produced is made into *staple fibre* by cutting the filaments into short lengths, like the fibres of cotton or wool. The staple fibre is then spun, either alone or mixed with other natural or artificial fibres, on a cotton or woollen mill, and a yarn obtained with which the textile manufacturer can obtain novel and interesting effects. Staple fibre, also, produced from de-lustred rayon and specially crimped or curled, is used as a wool substitute. Fibres which may be used as wool substitutes and which possess the dyeing properties of wool in varying degrees are also produced, under the name of *rayolana*, by impregnating the viscose filaments with synthetic resins (p. 333); and to other synthetic materials with silk- or wool-like properties, reference will be made later (p. 358). These synthetic fibres are used mainly in admixture with natural fibres, such as cotton and wool, and are to be regarded not as substitutes for silk and wool but as supplementary to these natural

fibres for the production of cheaper fabrics and new effects.

One should not fail to realise that the invention of rayon has not only given rise to an industry of great magnitude and economic importance, but has also brought about social reactions of a very marked character. By making a material, having much of the attractiveness of silk, readily available for textiles of varied character and use, for stockings and other articles of apparel, a profound change has been effected in the taste, outlook and way of life of large sections of the community.

Viscose is used for the production not only of rayon but also of a transparent cellulose film under the registered name of *Cellophane*. From a slit pouring machine a continuous band of viscose is formed which is then passed through a salt and acid solution in order to decompose the viscose. The sheet of transparent cellulose is then bleached with hydrogen peroxide, washed, and dried in warm air. Thin sheets of Cellophane are now much used for wrapping foodstuffs and other materials, and also by druggists for capping the stoppers of bottles. Placed in position while wet, it shrinks greatly on drying and so fits tightly to the bottle.

Cellulose acetate, also, is used not only as a thermoplastic material (p. 149) but also, in the form of sheets reinforced with wire netting, as a substitute for glass, under the names *vimlite* and *windolite*.

The artificial silks described in preceding pages must not be confused with the lustrous material known as *mercerised cotton*, so called after JOHN MERCER, an English calico printer who, in 1844, found that, when cotton is acted on by a solution of caustic soda, the naturally flat, twisted fibres swell to a cylindrical form and become shorter. Forty-five years later, in 1889, H. A. LOWE discovered that when the cotton fibres are tightly stretched during their treatment with caustic soda solution, so that they cannot shrink, they exhibit,

after washing and drying, a silky lustre, due to the reflection of light from the smooth surface of the fibre.

In the middle of last century, the supply of billiard balls was threatened owing to a shortage of elephant tusks ; and an American newspaper offered a prize of $10,000 for the most successful ivory substitute. Working under this incentive, two brothers HYATT, of Albany, N.Y., in 1869, made use of the fact, discovered in 1865 by ALEXANDER PARKES of Birmingham, that if camphor is added to a mixture of nitro-cellulose and alcohol, a hard, horn-like material is obtained which can readily be fashioned, while hot, into articles of various shapes and forms. To this material the name celluloid was given.[1] Although naturally of a clear gelatin-like appearance, celluloid can easily be dyed various colours, can be rendered opaque by the addition of different substances, and can, by special treatment, be made to imitate not only such materials as bone and ivory, but also amber, tortoise-shell, marble and agate. Light in weight and not readily breakable, celluloid is used for the manufacture of photographic films, combs, knife-handles, soap-boxes, and other articles of common use too numerous to mention. It is, however, a material the use of which is not altogether free from danger, since the basis of celluloid is the highly inflammable nitro-cellulose. It has, indeed, given rise to many disastrous conflagrations. To start the combustion of the celluloid, it is not necessary to bring it into contact with a naked flame. Contact for a short time with an incandescent electric-light bulb may be sufficient to start the combustion, and fires have even been caused by the accidental focusing of the sun's rays on articles of celluloid exhibited in shop windows.

Although the dangerous inflammability of celluloid can be reduced by the addition of various salts, dextrine, and

[1] Soon after the introduction of celluloid a similar material was produced in England under the name *xylomte*.

similar substances, the discovery of a material having the many good qualities of celluloid, but free from the dangers attending its ready inflammability, is clearly one of great importance. The acetate of cellulose, when mixed with suitable plasticisers, yields a material called *cellon* or *lumarith*, which resembles, and is even superior to, celluloid in its general properties, and is not inflammable. It is more elastic than celluloid, is used as a substitute for gutta-percha, vulcanite, etc., and is also used for making the bristles of hair-brushes, for the production of the imitation horse-hair of which ladies' hats are frequently made, and for the manufacture of cinematograph films. In the form of a thick viscous solution it is employed as a flexible varnish for wood, paper and metal, for enamelling aeroplanes, and as an insulating covering for electrical conductors.

But we have not yet exhausted the uses to which this most valuable substance cellulose can be put through the ingenuity of the chemist. If instead of mixing the nitro-cellulose with camphor so as to produce celluloid it is mixed with a drying oil, like linseed oil, and with colouring matters, and is then spread on a fabric, a sort of " oil-cloth " is obtained ; and on passing this between suitably cut rollers, the material is grained and a very good *imitation leather* is produced. Such imitation leathers, like *Rexine* for example, are now used very extensively for the upholstering of furniture and for other purposes. It is widely used for the upholstery of motor cars, for which purpose the world's total supply of leather would be quite inadequate.

At the present time, also, nitro-cellulose is very extensively employed for the production of *collodion* (a solution of nitro-cellulose in a mixture of ether and alcohol), for use in pharmacy and as a dip for incandescent mantles (p. 111). It is also used for the preparation of aeroplane dopes and of lacquers and enamels for wood, leather and metal. For the production of these lacquers and enamels, which are widely used for the finishing of motor-car bodies, etc., the nitro-

cellulose is dissolved in a suitable solvent, and to the solution there are added a diluent, a gum or resin (dammar, mastic, shellac, etc.),[1] a plasticiser and a pigment. The resin is added in order to give gloss, hardness and impermeability to the film, and the plasticiser, in order to prevent the film from becoming too brittle. After application, the lacquer rapidly dries and the film obtained is characterised by its hardness, toughness and resistance to scratching and rubbing. The production of satisfactory lacquers is a work of great complexity, and success has been obtained only as the result of prolonged research, deep knowledge and rigid scientific control.

The introduction of these nitro-cellulose lacquers has created a demand for a large number of solvents of different volatility, such as ethyl acetate, acetone, butyl acetate, amyl acetate, ethyl lactate, butyl lactate, etc., and for plasticisers such as triphenyl phosphate, tricresyl phosphate, diethyl phthalate. As a result of this demand, substances which formerly were laboratory products of purely scientific interest are now produced on a large scale for industrial application.

It has already been stated that the cellulose molecule may be regarded as built up of glucose molecules, with elimination of water. It is found, therefore, that when cellulose is heated under pressure with dilute acid, it undergoes *hydrolysis*, or is *hydrolysed*, as it is said ; that is, water is taken up and the molecule of cellulose is decomposed into its constituent glucose molecules. In recent years this process has found successful industrial application in the production of alcohol from sawdust and other wood waste. The wood waste, moistened with dilute sulphuric acid, is placed in a closed digester and steam is passed in until the pressure rises to six or seven atmospheres. The cellulose is rapidly hydrolysed,

[1] Synthetic resins of the type of bakelite (Chap. XVI) are also largely used.

and the glucose formed passes into solution. In Switzerland, the hydrolysis of the cellulose is carried out with cold, concentrated hydrochloric acid in vessels constructed of a highly resistant material known as *prodorite* (a pitch cement); and hydrolysis also takes place to a certain extent in the process of producing sulphite pulp (p. 139). The glucose solution obtained in these processes, after removal of the acid, is subjected to fermentation (Chap. XVII), and alcohol is formed. In view of the economic value of alcohol, the process promises to become of increasing importance in the future. In Sweden the alcohol produced from the sulphite pulp liquors is used, mixed with petrol (75 per cent.), as a motor fuel.

By the acid hydrolysis of wood there are also formed acetic acid and a sugar known as *xylose*, $C_5H_{10}O_5$, which is suitable as a foodstuff for diabetics. Great possibilities are thereby opened up for the development and economic utilisation of forests and forest products.

CHAPTER VIII

METALS AND THEIR ALLOYS

CHEMISTS are accustomed to classify the elements into metals and non-metals, and this grouping of the elements, although not always sharply defined, is at least convenient. Ordinarily, one thinks of a metal as being opaque and as showing, in the compact state, a lustre, the so-called metallic lustre; and one thinks also of a metal as being a good or fairly good conductor of heat and electricity. These properties serve by no means satisfactorily to define a metal or to distinguish it from a non-metal, but we need not at present trouble ourselves too much about definitions. There are certain familiar substances which are spoken of as metals, such as gold, silver, iron, copper, aluminium, zinc, lead, etc., and it is these substances that will now be discussed.

Certain metals, more especially gold, occur native or in the free state, and it may therefore be supposed that it was with such metals that primitive man first became acquainted. Gold, probably, was the first metal known, and its natural beauty and the ease with which it can be worked must have attracted primitive man, as it has attracted men throughout all ages, and have led to its use, at an early period, for purposes of personal adornment. The beautiful gold jewellery, bracelets, rings, etc., to be seen in the Museum at Cairo show that the use of gold for ornamental purposes was already well known in Egypt as early as about 3500 B.C. Almost all the other metals, however, occur only in the form of compounds from which the metal must be isolated, and before these metals could be put to use, a knowledge of how they could be extracted from their ores had first to be gained.

The history of the development of human civilisation has frequently been divided into three ages or epochs: the stone age, the bronze age and the iron age; and it has been thought that these three periods followed each other successively. This view is in harmony with what is doubtless the case, that copper and bronze were known and widely used before man had become acquainted with iron or had learned how to extract it in quantity from its ores. There was, however, much overlapping of the different "ages," and, among certain races, iron was in common use at a time when, among other races, bronze was generally employed. At the present day, one may perhaps say that we are still in the iron (or steel) age, although other metals are, year by year, finding an ever-extending application.

In ancient times, seven metals were known, and as these metals were thought by the alchemists to be affected by and to derive their properties from the planets (including the sun), the names of the planets were applied to the metals which were also represented by the astronomical signs of the planets, as shown in the following list:

Metal	*Planet*	*Sign*	*Metal*	*Planet*	*Sign*
Gold	Sun	☉	Lead	Saturn	♄
Silver	Moon	☾	Tin	Jupiter	♃
Copper	Venus	♀	Quick-silver	Mercury	☿
Iron	Mars	♂			

Traces of these old designations are still met with, *e.g.* *lunar caustic* (silver nitrate), but of the old names only one remains in use, namely, mercury.

Gold, Silver and Platinum

These three precious metals are widely used for currency, jewellery and scientific purposes. All occur in the free state, and silver and platinum also occur as compounds associated with other metals.

Gold is very widely distributed, but is produced mainly in South Africa (Transvaal), Russia (U.S.S.R.), the United States of America and Canada. Although, in the past, much gold was obtained from sands and alluvial deposits, most of the gold is now isolated from gold-bearing rock. This rock is crushed by means of " stamps " or heavy steel pestles, and ground in rotary mills.[1] The finely crushed material is washed over large plates covered with corduroy cloth, which retains the heavy gold particles. After these have been washed from the cloth and separated on a rocking table from particles of other material, they are shaken in closed vessels with mercury, and the amalgam so obtained is distilled. The mercury passes off and the gold is left behind. The sands from which the gold has for the most part been separated are treated with a solution of sodium cyanide which dissolves the gold. The cyanide solution is then run into large vats and ribbons of zinc are immersed in the solution. The gold is thereby caused to separate out, while the zinc goes into solution.

Gold is a very malleable metal which can be rolled or beaten out into leaves one ten-thousandth of a millimetre (one two-hundred-and-fifty-thousandth of an inch) in thickness, and can also be drawn into wires of extreme tenuity. The purity or fineness of gold is generally expressed in carats, pure gold having a fineness of 24 carats. Since pure gold is too soft for use, it is alloyed or mixed with copper or silver. British currency gold has a fineness of 22 carats, and consists of a mixture of 22 parts of gold with 2 parts of silver and copper, or 91·67 per cent. of gold, 2 per cent. of silver, and 6·33 per cent. of copper. In Australia, silver is used in place of copper. In the United States currency gold consists of 90 per cent. of gold and 10 per cent. of other metals. The finest quality of jewellery gold is 18 carat gold, or a mixture of 18 parts of gold with 6

[1] The method of extraction described here is that used in the Transvaal, whence nearly a third of the world's annual production is derived.

parts of copper; but lower qualities, especially 15 and 9 carat gold, are also employed. "White gold," now much used for jewellery in place of platinum, is produced by alloying gold with palladium or with nickel.

The best solvent for gold is a mixture of nitric and hydrochloric acids—a mixture called by the alchemists, *aqua regia*. A yellow substance, so-called "gold chloride," crystallises from the solution. It is used for toning photographic prints.

Silver is a metal which also occurs native, more especially in Ontario, Canada; but it is generally found as a sulphide associated with lead or copper, and is produced mainly in Mexico, the United States, South America and Canada. Various methods of a more or less complex kind are employed for the extraction or recovery of silver from its ores.

Silver has long been prized as a jewellery metal on account of its appearance, and it was also used very widely as a currency metal.[1] Formerly, British sterling silver was an alloy containing $7\frac{1}{2}$ per cent. of copper, while the silver coinage of the United States contained 10 per cent. of copper. Now, however, sterling silver contains only 50 per cent. of silver, and is alloyed with 40 per cent. of copper, 5 per cent. of nickel, and 5 per cent. of zinc.[2]

Silver does not combine with oxygen at the ordinary or even at higher temperatures and does not, therefore, tarnish when exposed to pure air. The tarnishing which takes place when silver is exposed to the air, especially of large towns, is due to the presence of sulphur compounds in the air and the formation of silver sulphide. Similarly, "oxidised silver" is not oxidised at all, but "sulphidised" by treatment with a solution of an alkaline sulphide. A film of dark silver sulphide is thereby formed on the surface of the metal.

Silver is the best conductor of heat and of electricity.

[1] Its use for this purpose is now being abandoned.

[2] Owing to the increase in the price of silver, the amount of silver in a half-crown (two shillings and sixpence) was worth three shillings and fourpence in 1920. The present alloy was adopted in 1927.

On account of the fact that they are acted on by light, silver salts, especially the chloride and bromide, are extensively employed in photography. The amount of silver so employed is second only to that used for currency.

Platinum is a metal rather more costly than gold. Formerly most of the world's supply of platinum was obtained from Russia, where the metal was found in the region of the Ural Mountains. At the present time, however, more than half of the total world's production of platinum and the platinum metals (palladium, iridium, rhodium) comes from Canada and less than a quarter from Russia. South Africa, where there are extensive deposits of platiniferous ores, and the Republic of Colombia, South America, also produce notable amounts of these costly metals.

Platinum is a malleable and ductile metal, much valued as a jewellery metal for the setting of diamonds and other gems; and it is largely used in chemical laboratories, on account of its high melting-point and its resistance to attack by chemicals. It finds, also, considerable application in industry as a catalyst, as will be discussed in the following chapter.

Owing to the fact that platinum expands and contracts with change of temperature at nearly the same rate as glass, a wire of this metal can be melted into glass and the latter does not crack on cooling. For this reason, platinum wire used to be employed in making connection between the filament of an electric incandescent lamp and the fittings outside. Owing to its high price, however, it is no longer used for this purpose, its place being taken by the nickel-iron alloy, *platinite* (p. 161). The saving thereby effected has been estimated at about £1,000,000 per annum.

Iron and Steel

Highly valued as gold and silver may be for their beauty and for their use as jewellery and currency metals, and important as the former may be regarded as a basis of values

in international exchange, these metals are of small importance in our present-day civilisation compared with the metal iron. In the words of Rudyard Kipling:

> *'Gold is for the mistress—silver for the maid—*
> *Copper for the craftsman cunning at his trade.'*
> 'Good!' said the Baron, sitting in his hall,
> 'But Iron—Cold Iron—is master of them all'

Yes, master both in peace and in war. We still live in the "iron age," and iron constitutes more than 90 per cent. of the world's total tonnage of metals.

Although the element iron forms about 5 per cent. of the solid crust of the earth, so far as we know it, it occurs, with the exception of small quantities of meteoric iron, only in the form of compounds, more especially with oxygen and with sulphur. Of these, the most important are hæmatite (Fe_2O_3), limonite, a hydrated oxide ($2Fe_2O_3$, $3H_2O$), magnetic iron ore (Fe_3O_4), and the sulphide, iron pyrites (FeS_2), the well-known brass-like mineral sometimes called "fool's gold." This mineral is never used for the production of iron, but large quantities are employed in the manufacture of sulphuric acid. Various red and brown pigments, *ochres*, are prepared from purified hæmatite and limonite.

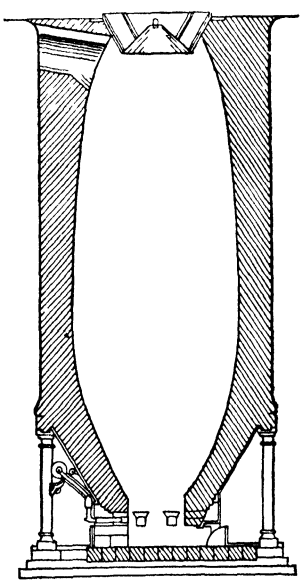


FIG. 15.—DIAGRAM OF BLAST FURNACE.

The extraction of iron from its ores (generally the oxide, Fe_2O_3, or the carbonate, $FeCO_3$) is carried out in the *blast furnace*, a tall structure with a roughly egg-shaped interior (Fig. 15). After fires have been lit and the furnace has been heated up, a mixture of ore, coke (or

coal), and limestone (calcium carbonate) is introduced from the top, and a blast of hot air is blown in through pipes or "twyers" (French, *tuyères*) at the bottom of the furnace. In this way a high temperature is produced; the coke burns and gives rise to carbon dioxide, and this gas in contact with the red-hot coke passes into carbon monoxide, which ascends through the hot mass, combines with the oxygen of the iron ore and so sets free the metal. At the high temperature of the furnace, the metal melts and flows down to the bottom, and at the same time the lime formed by the decomposition of the limestone combines with the silicates (clay) added to or present as impurities in the iron ore, to form a glass-like material or slag. This likewise flows in the molten state to the bottom of the furnace, where it floats on the surface of the molten iron. From time to time the slag is removed and the molten iron run off into moulds, where it solidifies and forms *pig iron*.

The slag which is obtained from the blast furnace and which has been formed by reaction between the limestone added to the ore and the clay (a hydrated silicate of aluminium) with which the ore is generally associated, is used in the manufacture of *Portland cement*, which consists of a mixture of calcium silicate and calcium aluminate (p. 190). This cement when mixed to a paste with water has the property of setting to a hard mass even under water, and is therefore of great value for the construction of piers or other engineering works under or in contact with water. The carbon monoxide, also, which escapes in large quantities from the top of the blast furnace is made use of, partly for burning in furnaces to heat the air of the blast, and partly for the production of power in gas engines.

Pure iron is never used industrially, and all commercial forms of iron are mixtures of iron with larger or smaller amounts of other substances. The three main kinds of commercial iron are *cast iron*, *wrought iron*, and *steel*, and of these, the first is the least pure form of iron. *Cast iron*

is essentially the iron as it comes from the blast furnace, and contains generally from 2 to 5 per cent. of carbon, much of it in the form of graphite, together with other impurities, such as silicon, sulphur and phosphorus, in amounts depending on the ore employed. It is a hard but brittle form of commercial iron.

Ordinary cast iron is readily attacked by dilute hydrochloric and sulphuric acids, but the rate of attack can be reduced to a very remarkable extent by increasing the proportion of silicon. Thus, ware made of a cast iron containing from 12 to 19 per cent. of silicon (*e.g.* tantiron, duriron, ironac, narki) is so acid-proof that it can be used for the evaporation of sulphuric acid. Such cast iron, however, is extremely brittle.

Wrought iron is the purest form of iron used industrially, and is obtained by strongly heating pig iron in a furnace along with hæmatite. This oxide oxidises the carbon and silicon, as well as any phosphorus and sulphur which may be present. Wrought iron is soft and fibrous in structure, and is also tough and malleable, so that it can readily be worked, even at the ordinary temperature.

Steel, by far the most important form of commercial iron, is not a definite substance; there are many different kinds of steel, all of which are alloys of iron with other substances. Ordinary steels are essentially alloys of iron and carbon, the amount of carbon varying from 0·1 to 2·0 per cent. The carbon is present in the form of a compound with iron known as cementite, Fe_3C.

Steel is produced either by the Bessemer or, generally, by the Siemens-Martin open-hearth process, the aim in either case being to remove, by burning or oxidation, the impurities present in pig iron, and more especially the sulphur and phosphorus, the presence of which is very detrimental to the steel. In the Bessemer process, the oxidation is effected by blowing air through the molten metal, and in the open-hearth process by the addition of

oxide of iron or hæmatite. When phosphorus is present in the pig iron, the furnace is lined with magnesite (magnesium carbonate) or with dolomite (double carbonate of calcium and magnesium), with which the oxidised phosphorus combines to form a phosphate known as *basic slag*. This is largely employed as a phosphatic manure in agriculture.

Besides possessing a much greater tensile strength than cast or wrought iron, steel is characterised by the fact that it can be hardened by heating to a fairly high temperature and then cooling in oil or in water. The process is known as *tempering*, and the temper (hardness, elasticity, etc.) produced in the steel depends not only on the composition but also on the temperature to which it is heated and the rate at which it is cooled down. According to the treatment employed, the highly elastic steel of the watch-spring or the hard steel of the cutting tool can be obtained.

The effect of adding other substances to steel has been the subject of intensive investigation by metallurgical chemists, and as a result many new steels possessing distinct and valuable properties have been introduced into the service of man. The addition of chromium, for example, gives hardness to steel, and thus by the addition of about 2 per cent. of chromium one obtains *chrome steel*, which is employed for steel tyres, ball bearings, files, rock-crushing machinery and armour plate. By adding a small amount of nickel to the chrome steel, greater elasticity is given. " Stainless steel," which does not rust or tarnish in contact with food or fruit acids, is a steel containing from 12 to 15 per cent. of chromium. It is extensively used for the manufacture of table cutlery. " Staybrite " steel, containing about 18 per cent. of chromium and about 8 per cent. of nickel, is highly resistant to the corrosive action of sea-water, acids, etc., and is finding increasing use in chemical industry and also for many articles of domestic utility.

Addition of nickel to steel imparts hardness and elasticity, and *nickel steel* is therefore used for armour plate, propeller

shafts, etc. When the percentage of nickel is greatly increased, steels having very valuable and special properties are obtained. Thus, *invar*, a steel containing 36 per cent. of nickel and only 0·2–0·5 per cent. of carbon, has a negligible coefficient of expansion throughout the ordinary range of temperature variation. It is therefore used for the manufacture of measuring rods, surveyors' tapes, instruments of precision, and the pendulums of clocks. A similar alloy, *elinvar*, is used for the balance spring of watches, because its coefficient of elasticity and, therefore, the control which the spring exerts, do not alter with the temperature. *Platinite*, similarly, is a nickel steel containing 46 per cent. of nickel. Its coefficient of expansion, which can be varied by slightly varying its composition, is practically the same as that of glass, and so wires of platinite may be sealed into glass. The alloy consisting of 53·8 per cent. of iron, 29 per cent. of nickel, 17 per cent. of cobalt, and 0·2 per cent. of manganese has a coefficient of expansion (4×10^{-6}) almost identical with that of hard glass. This alloy is therefore very useful for sealing into glass for electrical purposes.

When the amount of manganese, which is normally present in small amounts in all steels, is increased up to, say, 9–14 per cent., a very hard, tough steel is obtained, which is extensively used for rock-crushing machinery, switch-points on railways, burglar-proof safes and steel helmets. As this steel is also non-magnetic, it is used in the construction of those parts of ships which are in the neighbourhood of the compass.

As a cutting tool, ordinary high-carbon steel is quite satisfactory so long as the work is carried out at such a rate that the temperature does not greatly rise; but it is useless for the high-speed cutting of metals, when the cutting tool may become red-hot. Under these conditions, ordinary steel speedily loses its hardness. It was, however, found that by the addition of tungsten or of molybdenum to a chrome steel, an alloy was obtained which retained its hardness even at a red heat. Such high-speed tool steel, which contains, say, 0·6

per cent. of carbon, 4 per cent. of chromium, 14–20 per cent. of tungsten (or 5–6 per cent. of molybdenum), and sometimes also about 1 per cent. of vanadium, is therefore a material of the very highest value in modern engineering practice.

When exposed to moist air, iron readily undergoes oxidation or rusts. When used, therefore, in constructional work, protection of the metal by frequent painting is necessary. In other cases the metal may be coated with zinc (galvanised iron), or with tin (tinplate).

Tungsten, which is obtained from the mineral wolfram, is a metal which fuses only at a very high temperature. It finds a very widespread use in metal filament electric lamps. Tungsten carbides (compounds of tungsten and carbon), alloyed with small amounts of cobalt, known as *carboloy*, are, on account of their diamond-like hardness, superior to tungsten steels for the high-speed cutting of metals.

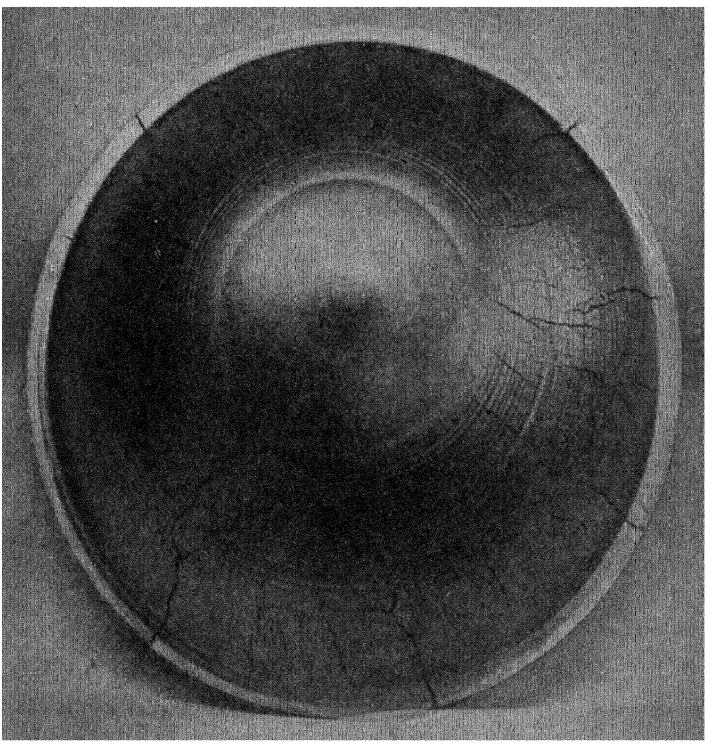
Copper and Non-ferrous Alloys

Copper is one of the metals with which man earliest became acquainted, and the copper mines of Sinai were worked as early as 5000 B.C. Its name is derived from the Latin, *æs cyprium*, later *cuprum*, so called because in Roman times it was largely obtained from the island of Cyprus.

Although copper occurs native, more especially in the region of Lake Superior, it is mainly from its compounds, the sulphide and carbonate, that the metal is at present extracted. It is produced in large quantities in the United States, Chile, Northern Rhodesia and the Belgian Congo.

The chief industrial use of copper is for the construction of wire and cable for the conduction of electricity; and since the conductivity, which is inferior only to that of silver, is greatly diminished even by small amounts of impurity, the metal, as extracted from its ores, must be refined or purified. This is now carried out by electrolysis, so-called *electrolytic copper* being obtained (p. 262).

In association with other metals, copper gives rise to a number of alloys, some of which, the *brasses*, find a very widespread use. Brass is an alloy of copper and zinc, and brasses with different properties are obtained by varying the



Courtesy of H. Moore and S. Beckinsale.

SEASON-CRACKING OF BRASS.

proportions of the two metals. Brasses containing about 30 per cent. of zinc are among the most important, and are used for castings and for cartridge cases. A brass containing 40 per cent. of zinc and known as *Muntz metal* is used in sheathing ships on account of its resistance to corrosion.

Dutch metal is an alloy containing about 20 per cent. of zinc.

Brass and certain other alloys which have been subjected to mechanical stress by being hammered, drawn, or pressed, are liable to undergo what is called "season-cracking." Thus, hard-drawn tubes, cartridges cases, etc., may crack some time after they have been made, more especially when exposed to an atmosphere in which traces of ammonia are present. This liability to crack may, however, be removed by heating the metal to a temperature of 200° to 300° C. (392° to 572° F.). At this temperature the internal stresses are relieved but the hardness of the metal is not destroyed.

Bronzes are alloys of copper and tin, but they sometimes also contain zinc. *Gun metal* is a bronze containing from 8 to 12 per cent., and *bell metal* a bronze containing from 12 to 24 per cent. of tin. Bronze coinage contains 4 per cent. of tin and 1 per cent. of zinc; while *phosphor-bronze*, which is widely used for taps, valves, etc., where corrosion has to be avoided, contains varying proportions of copper, tin, lead and phosphorus.

An alloy consisting of copper and nickel (68 per cent.), known as *monel metal*, has proved of great value on account of its general resistance to corrosion and to the action of sea-water. It is extensively used for condenser tubes in steamships. Losses due to corrosion have thereby been greatly reduced. The alloy, consisting of 54 per cent. of copper, 45 per cent. of nickel, and 1 per cent. of manganese, is used for decorating and ornamental metal work under the name *silveroid*.

When exposed to the action of moist air, copper becomes coated with a green-coloured, basic copper carbonate, called *verdigris*;[1] and the metal readily dissolves in nitric acid with formation of copper nitrate. *Copper sulphate*, the

[1] In the neighbourhood of towns, the patina which forms on copper is mainly a basic copper sulphate.

best known salt of copper, crystallises from solution in deep-blue coloured hydrated crystals, having the formula $CuSO_4$, $5H_2O$, and known popularly as *bluestone*. When added even in small amount to water, it prevents the growth of algæ.

A mixture of copper sulphate solution and milk of lime (slaked lime or calcium hydroxide) is largely used, under the name of *Bordeaux mixture*, for spraying fruit trees and bushes, especially vines, to protect them against insect and fungoid pests. This is the main use to which copper sulphate is put.

The metal *Nickel*, ores of which occur mainly at Sudbury in Ontario, is purified by the Mond process. When carbon monoxide is passed over nickel at a temperature below 100° C. (212° F.), combination takes place and a volatile liquid known as nickel carbonyl is obtained. On heating the vapour of this compound, decomposition takes place ; pure nickel is deposited and carbon monoxide is regenerated, and can be used for the purification of a further quantity of metal. When in a coherent form, nickel is a hard, white, lustrous metal, and is used for the electrodes of sparking plugs for motor-car engines, etc. It is highly resistant to the action of the atmosphere, and for this reason it is used for protecting iron or steel from rust, the metal being deposited by electrolysis (nickel plating). Before being plated with nickel, iron or steel is generally plated with copper.

Nickel is extensively employed as a constituent of many important alloys. Besides those to which reference has already been made, one may mention *white metal* or *German silver*, an alloy of copper, nickel and zinc, which is used as a basis for silver-plated ware, and *nichrome*, an alloy of nickel and chromium with about 23 per cent. of nickel. This alloy, the life of which can be greatly increased by the addition of cerium (up to 1·2 per cent.), is widely used as resistance wire in electric heaters. Nickel currency alloy is an alloy of nickel and copper containing about 25 per cent. of nickel.

Permalloy or *Mumetal* is a nickel-iron alloy containing about 78 per cent. of nickel. It possesses a high value of what is known as magnetic permeability, and if a submarine cable is sheathed with permalloy, attenuation and distortion of the signals are eliminated. By this means, it has been possible to increase the rate of cable communication from 300 to 1500 signals per minute.

Chromium, which, as has been mentioned, forms a constituent of a number of valuable alloys and is now extensively used for the plating of other metals, is obtained by reducing its oxide with aluminium as in the thermit process (p. 72). It is harder than nickel and more resistant to atmospheric action.

Mercury, the heavy, liquid, lustrous metal, the well-known properties of which lend to it a peculiar fascination, is extracted from the naturally-occurring compound, mercuric sulphide (HgS) or *cinnabar*, a substance which, when ground, yields a powder of a bright-red colour (vermilion). When cinnabar is strongly heated in air, the sulphur combines with the oxygen to form sulphur dioxide, and the mercury is vaporised. By condensing the vapour in cold chambers, the liquid metal is obtained. It is widely used in the construction of thermometers and barometers. Its alloys with other metals are called amalgams.

Mercury gives rise to two classes of salts, known respectively as mercurous and mercuric salts. Mercurous chloride (Hg_2Cl_2) or *calomel* is used in medicine and mercuric chloride ($HgCl_2$) or *corrosive sublimate*, a corrosive poison, is used as a germicide.

Tin is one of the metals which were known in ancient times, its alloys with copper constituting one of the earliest known alloys of which we have knowledge, namely, bronze. At least as early as 1000 B.C. the great traders of antiquity, the Phœnicians, obtained this metal from the tin mines of Cornwall, where it was found in the form of its oxide, known as *tinstone* or *cassiterite*. To this fact is due the old

name of Cassiterides or Tin Islands applied to Britain. For a long time the whereabouts of the Cassiterides remained known only to the Phœnicians, and provoked much anxious curiosity on the part of the Romans. So highly, however, was the secret prized that it is recounted that Phœnician sailors, on being followed by a Roman ship, while on their way to Cornwall, ran their ship ashore rather than betray the position of the valuable tin mines.

Now the glory of the Cornish tin mines has departed. More important deposits have in modern times been found in other parts of the world, chief amongst these being those at Perak and Selangor (Malay States), in Bolivia, Nigeria, Siam, and in the islands of Banca and Billiton in the Dutch East Indies. Little, if any, tin is now mined in Cornwall.

Tin is a metal of manifold uses. Its resistance to atmospheric attack has led to its use for coating iron and steel as a protection against rusting. Tinplate, used for making containers, "cans" or "tins," for biscuits, preserved foods, etc., is made by dipping steel sheets in molten tin. The malleability of the metal, owing to which it may be rolled out into thin leaves or foil, has also led to its use as a wrapping for chocolate and other materials. So-called *silver paper* is not silver at all, but the much less valuable metal tin.

In association with other metals tin forms part of a number of alloys. Thus there are known *bronze* (copper and tin); *Britannia metal* and the *Babbitt metals* (tin, antimony, and copper) used for bearings of engines; *pewter* and *solder* (tin and lead).

Except during the warmer summer months, ordinary lustrous tin, or white tin, is not in a really stable condition, but at all temperatures below 13° C. (about 55° F.) is liable to undergo change and pass into a less dense form known as grey tin. At ordinary temperatures this change takes place with extreme slowness, and may, indeed, not take place for centuries; and the change is retarded by the presence even of traces of bismuth, lead, antimony, or

cadmium. At very low temperatures, however, and even during severe winters in European countries, the change may occur with considerable rapidity, and is accelerated by traces of aluminium, zinc, cobalt and manganese. Generally, the conversion of white to grey tin takes place in spots or patches, and owing to the lower density of grey tin, wart-like powdery growths are formed, the appearance of which on the surface of the bright metal has earned for the transformation the name of *tin plague*. In Fig. 16, is shown a picture of a medal, dated 1692, suffering from tin plague. This " plague," moreover, is contagious, for the conversion of white tin to grey tin is stimulated and accelerated by contact with the latter. All articles of tin, organ pipes, medals, pewter pots, etc., are liable to suffer from tin plague, and the results may sometimes be disastrous.

Zinc occurs in many countries, mainly in the form of its sulphide, known as zinc blende, some of the most important deposits being found in the United States, in British Columbia and at Broken Hill, Australia. The zinc is generally associated with other metals in the ore, so that the latter has first to be subjected to a process whereby the zinc ore is concentrated. The zinc concentrate is then treated for the extraction of the metal, which in the crude state is known as spelter.

Zinc is a bluish-white metal, the main uses of which are for the production of brass and for galvanising iron. It is also used in the construction of Leclanché and dry cells. Oxide of zinc is used in surgical dusting powders and ointments and as a pigment under the name of *zinc white*; and a mixture of zinc sulphide and barium sulphate is employed as a pigment under the name of *lithopone*.

Lead is a heavy metal which has been known and used from the earliest times and which also finds wide application at the present day. Owing to its resistance to atmospheric attack and to the action of acids, this metal is employed for roofing purposes, for sulphuric acid plant, for lining vats in which chemical processes are carried out, etc. Its most

Courtesy of Prof. E. Cohen.

FIG. 16.—MEDAL SHOWING TIN PLAGUE.

extensive single use is in the manufacture of storage batteries. Lead is so plastic that it can be squirted, under pressure, through dies into the form of rods and pipes, and lead pipes have been used from very early times for the conveyance of water. Water containing carbon dioxide in solution attacks lead fairly readily, but this action is checked by the presence of carbonates or sulphates of calcium and magnesium. Since these salts are present in what is called " hard " water (Chap. XI), it follows that hard water attacks lead to a much less extent than distilled or than a soft moorland water. Owing to the fact that lead in solution is poisonous, the resistance of this metal to the action of water is of great importance in connection with the use of lead pipes for the conveyance of drinking water. Where the water of a town's supply is very soft, it is necessary to " harden " it somewhat by the introduction of small quantities of lime.

Lead hardened by the addition of a small amount of arsenic is used in the manufacture of shot, and lead hardened by the addition of antimony finds use as *type metal.* Alloys of lead, tin and bismuth, or lead, tin, bismuth and cadmium, are used as *fusible metals,* some of which melt considerably below the boiling-point of water.

Lead combines with oxygen to form a number of oxides, the most important of which are *litharge* (PbO), *red lead* (Pb_3O_4) and *lead dioxide* (PbO_2). Red lead is extensively used in the production of " crystal " glass (Chap XI), as a plumber's cement, and as a pigment, *minium.* Lead dioxide (or lead peroxide as it is sometimes called) forms the material of the positive plate of the lead storage cell (Chap. XII).

Another very important compound of lead is *white lead,* a so-called basic carbonate of lead having the composition, $2PbCO_3$, $Pb(OH)_2$. In the production of this pigment, lead plates are supported in earthenware pots, at the bottom of which is a layer of acetic acid. The pots are placed close together, hundreds of them, on a layer of spent and fermenting tanner's bark, spread on the floor of the building.

The first tier of pots is covered by wooden boards on which a layer of tanner's bark and a second tier of pots are placed; and so on, tier above tier of pots, containing plates of lead and acetic acid. As the bark ferments, heat is liberated and carbon dioxide is evolved. The lead is acted on by the vapour of the acetic acid and forms lead acetate, and this then reacts with the carbon dioxide to form the basic lead carbonate. In twelve or thirteen weeks the whole of the metal is converted into white lead.

Although white lead is valuable as a pigment on account of its covering power, it suffers from the disadvantage that when exposed to air containing sulphuretted hydrogen, it becomes dark owing to the formation of black lead sulphide. The white pigment, *titanium white* (titanium oxide), which has a high opacity, does not darken in sulphurous air and has a lower density than white lead, is now largely used.

Certain other metals, *e.g.* magnesium and aluminium, will be discussed at a later point (Chap. XII).

CHAPTER IX

VELOCITY OF REACTIONS AND CATALYSIS

THE overthrow of the phlogiston theory by Lavoisier towards the end of the eighteenth, and the enunciation of the atomic theory by Dalton early in the nineteenth century, marked the beginning of a new era in chemical science. After that time, the activities of chemists were directed in an increasing degree to the preparation and to the quantitative determination of the composition of new substances and naturally occurring materials, as well also as to the determination of the atomic weights of the elements. Moreover, the study of the compounds of carbon, a branch of science to which the name of Organic Chemistry is applied, began to be developed with an ever-increasing energy ; and in this domain, the problems connected with the constitution of the molecule, that is, with the arrangement of the atoms within the molecule, were so important for the proper understanding of the enormous array of substances which chemists were able to prepare, that such questions exercised, and very properly exercised, a powerful fascination over the workers in that branch of chemistry. The quite wonderful results which were thereby obtained had their value, also, not merely in the domain of theoretical chemistry, but led to some of the most brilliant achievements of practical chemical science—to the preparation of dyes, drugs, perfumes, and many other materials of the greatest industrial and, one may say, human value—so that one need not hesitate to regard such work as amongst the most important in the whole history of the science. By the workers who achieved such splendid success, chemical reactions were regarded entirely or mainly from the material point of view, from the point of view of the substances undergoing change and of the substances produced by the

change. But there is clearly another aspect of the subject which demands attention. Just as we have already recognised that substances are carriers of energy, and that a chemical reaction or chemical change is a mode of transforming chemical energy into other forms of energy, so also in modern chemistry one is concerned not merely with the material *products* of chemical change, but also with the *process* of chemical change itself. Why does a chemical reaction take place, and what are the laws governing the rate at which and the extent to which a chemical reaction proceeds ? These are the questions which *chemical dynamics*, one of the most important branches of modern chemistry, seeks to answer.

Although it is not possible to discuss the subject fully here, the attempt must be made to give some indication of the more general principles in order that one may gain a better appreciation of present-day chemistry and a more intelligent understanding of some of the most recent and economically most important industrial processes, the development and success of which depend on dynamical investigations.

When, in the thirteenth century, the great Dominican monk and Bishop of Regensburg, ALBERTUS MAGNUS—*magnus in magia naturali, maior in philosophia, maximus in theologia*—used the word " affinitas," he merely summed up the views current at that time, that chemical reaction is due to a similarity or kinship between the reacting substances. But although this term affinity or chemical affinity is still in use, it must now be regarded not as signifying any natural resemblance or family relationship, but rather as a force, electrical in nature, which acts between different kinds of matter and which, under certain conditions, brings about a chemical action between them. The existence of this force is postulated in order to account for the fact that chemical change or reaction will take place between substances when thereby potential energy can be converted into work. Chemical affinity, it should be noted, does not

give an *explanation* of chemical change; it is, rather, a measure of the work done by a system when it undergoes change.

One of the most important factors in the process of chemical change is the speed with which it takes place, the velocity of the reaction. That there are great differences in the rates at which chemical change takes place is so obvious as almost to render its emphasis unnecessary. The rusting of iron, the oxidation of aluminium, the burning of wood, the explosion of gun-cotton, are chemical changes which take place with markedly different velocities. This great difference in the rate of reaction we shall be inclined to attribute to differences in the chemical affinity, and in so doing we shall be right, but only partly right; for when one studies the process of chemical change more fully, it is found that the rate of a reaction does not depend merely on chemical affinity, but also on a number of other factors. Of these factors, one of the most important is the *concentration* of the reacting substances, that is, the amount of the substances in a given volume. We shall be able to understand this more readily if we fix our attention, for the present, on reactions between gaseous substances. When a substance is in the state of a gas, its molecules are supposed, according to the kinetic theory (p. 273), to be moving about with great velocity in all directions, and combination or reaction between two substances, A and B, can take place only when molecules of A and B collide or come within each other's sphere of influence. If, then, we have a certain number of molecules of the substance A and a certain number of molecules of B moving about in a given space, an A molecule will collide with a B molecule a certain number of times per second, and the rate of reaction, therefore, will have a certain value. Suppose that the number of B molecules is now doubled. It is clear that in the same unit of time an A molecule will now have double the number of chances of colliding with a B molecule and of entering into reaction

with it, and the rate of reaction will therefore be twice as great as it was originally. Similarly, if the concentration not only of the B molecules, but also of the A molecules be doubled, then it is clear that the rate of reaction will again be doubled; that is, the reaction now takes place four times as fast as it would have done with the original concentrations of the two substances. The speed of a reaction, in fact, is proportional to the product of concentrations of the reacting substances. This law of the dependence of the speed of a chemical change on the concentrations of the reacting substances was discovered by two Norwegian scientists, GULDBERG and WAAGE, and is generally known as the *law of mass action.*

The velocity of chemical change is also very greatly influenced by the temperature, a fact to which we have already alluded (p. 66). Although the speed of different reactions is affected in a different degree by temperature, it may be taken as a convenient approximation that the speed of a reaction is doubled by raising the temperature 10° C. (18° F.). A simple calculation will show what the magnitude of this effect may be. Suppose that a reaction requires one second for its completion at the melting-point of ice, that is at 0° C. (32° F.). At 100° C. (212° F.), the boiling-point of water, the same change would take place in about one-thousandth of a second; and if we raise the temperature but a little more, say to 200° C. (400° F.), the time required for the change will now be only about one-millionth of a second. On the other hand, a change which would require one second to take place at 200° C., would need, at 0° C., a period of a million seconds, that is, about eleven and a half days. This influence of temperature is of the greatest importance, and on its recognition may depend the success of an industrial process.

A further very important result which has followed from the dynamical study of chemical reactions is the recognition of the fact that chemical changes are reversible, and that the

direction in which reaction between different substances takes place depends not merely on chemical affinity but on the relative concentrations of the different substances. When steam (oxide of hydrogen) is passed over heated iron, oxide of iron and hydrogen are produced. On the other hand, when hydrogen is passed over heated oxide of iron, steam (oxide of hydrogen) and metallic iron are formed.

$$\left.\begin{matrix}\text{Iron} \\ \text{Oxide of hydrogen}\end{matrix}\right\} \rightleftharpoons \left\{\begin{matrix}\text{Iron oxide} \\ \text{Hydrogen}\end{matrix}\right.$$

In the former case, the steam is present in large abundance, whereas the hydrogen which is formed is swept away and cannot, therefore, react with the oxide of iron. In the latter case, the hydrogen is present in abundance, and the water vapour is carried away in the stream of gas and so is prevented from reacting with the metallic iron. By altering the relative concentrations of the steam and the hydrogen, therefore, one can cause reaction to take place in whichever direction one pleases. Suppose, now, that the experiment is arranged in such a way as to prevent the removal of the hydrogen or of the steam, as can be done by heating all four substances together in a closed vessel, then it will be found that both reactions will take place; steam will react with iron, and hydrogen will react with oxide of iron, so that finally a state of balance or *equilibrium* will be produced, at which there will be a certain definite relationship between the concentration of the steam and the concentration of the hydrogen.

So long as the temperature is kept constant, the same state of balance or equilibrium will be reached, no matter what may be the initial amounts of hydrogen and of steam, but if the temperature is altered, the state of equilibrium will, in general, also be altered. By raising or lowering the temperature the one or the other reaction can be caused to

take place to a greater and greater extent, and the direction in which the equilibrium is thereby altered is found to be intimately associated with the heat effects which accompany the chemical change.[1]

The discovery of the laws of chemical change, and the recognition that, theoretically at least, all reactions are reversible, mark one of the most important advances in our knowledge of chemical processes and of the action of chemical affinity. Some of the consequences which flow from this will be discussed in the sequel.

Although, as has been said, the progress of a chemical reaction and the rate at which a chemical change proceeds are influenced both by the concentration of the substances and by the temperature, it is found that the velocity of a chemical reaction may also be profoundly affected in another way which, on account of its very great importance both in the laboratory and in the factory, demands a fuller consideration.

In the early decades of last century a number of phenomena were observed, which, although isolated and apparently unconnected, all possessed one common characteristic, namely, that the rate at which a chemical change took place was markedly increased by the addition of certain substances in minute, sometimes in almost infinitely minute, amount. Owing to such additions, it was found, substances which seemed under the particular conditions to be without action on each other, reacted with appreciable, sometimes even with great, readiness. From the magnitude of the result produced, it was evident that the foreign substance could not enter into the reaction in the ordinary way; but, as the

[1] The law which is found to obtain here can be stated in a simple form. It will be clear that if one reaction is accompanied by an evolution of heat, then the reverse reaction must be accompanied by an absorption of heat. *When the temperature is raised, the latter reaction, the reaction accompanied by absorption of heat, is favoured, whereas lowering the temperature favours the reaction which takes place with evolution of heat.* Only when no heat effect accompanies chemical change is the equilibrium unaffected by change of temperature.

Swedish chemist, BERZELIUS, pointed out, the substance which was added appeared to act merely by its presence and by " arousing the slumbering affinities of the substances," and so allowing them to react. How these slumbering affinities were aroused, Berzelius did not hazard a guess, but in order to give a name under which such phenomena could be classed, he introduced, in 1838, the term *catalysis* (a word which signifies a loosening) ; and a substance which brings about catalysis is called a " catalytic agent " or a " catalyst." For long the phenomenon of catalysis, of which the number of cases observed rapidly increased during the nineteenth century, was regarded by chemists, as Gulliver was regarded by the learned men of Brobdingnag, as a *lusus naturæ* ; it was relegated to the realms of the mysterious, and chemists became only too prone to think that the label of catalysis was at the same time an explanation of the phenomenon. It was, indeed, only towards the end of last century and owing to the development of the experimental methods of measuring the rate of chemical change, that the phenomenon of catalysis and the behaviour of catalysts began to form the subject of systematic investigation. For a long time now, the energy of many workers has been directed along this line of investigation, and much valuable information has been accumulated regarding the main characteristics of catalysis and the behaviour of different catalysts. With some of these we must now become acquainted.

As has already been indicated, one of the most striking features of catalysis is the magnitude of the effect produced, compared with the small amount of the substance producing it. An excellent illustration of this is seen in the influence which moisture exercises on the rate of combination of gaseous substances. When hydrogen and oxygen, the two gaseous substances by whose combination water is formed, are heated together, they combine, and if the temperature is sufficiently high, say about 600° C. (1112° F.), the combination takes place with explosive violence. But this occurs

only when a trace of moisture is present in the gases. If the last traces of moisture are removed from the gases by prolonged contact with the substance known as phosphorus pentoxide (obtained by burning phosphorus in air), a substance which combines with the greatest avidity with water, the mixture of hydrogen and oxygen can then be heated even to a temperature of nearly 1000° C. (1832° F.) without explosion occurring. Not only in the case of hydrogen and oxygen, but in the case also of many other gases, combination is found to depend on the presence of moisture, of which, however, the merest trace suffices.

This action of moisture, and, indeed, the action of catalysts generally, have been likened to the action of oil in the bearings of a machine; a catalyst diminishes, as it were, the hindrances to change of whatever nature these may be without itself being used up in the process.

In astronomy one deals with magnitudes so vast as to be beyond the grasp of our minds; in the domain of catalysis the magnitudes are, in some cases, so small that it becomes almost equally impossible to form a true conception of them. In order, however, that the reader may have some knowledge of the very minute amounts of substance which will yet suffice to affect appreciably the speed of a reaction, let me give one example out of the many which might be chosen. When one dissolves sodium sulphite or sulphite of soda (Na_2SO_3) in water, the oxygen of the air slowly oxidises the sulphite of soda to sulphate of soda or sodium sulphate (Na_2SO_4). By the addition of certain catalysts, the speed with which this process takes place can be greatly increased, and in this connection copper has been found to be very efficient. In fact, if only one grain of bluestone or copper sulphate is dissolved in 1,400,000 gallons of water, or one grain in about 250,000 cubic feet of water, the presence of the copper can be detected by its action in accelerating the oxidation of the sulphite of soda! Even water which has remained in contact with metallic copper for three-quarters

of a minute, contains sufficient copper to show a noticeable effect. One is, however, so accustomed to judge of the importance of a thing by the amount of space it occupies that in asking the reader to recognise the infinite importance of the infinitely small and to accept the example I have given, sober fact of science as it is, I am almost afraid that I shall be considered as putting too great a strain on his credulity.

Not only may catalysts increase the velocity of a chemical change, they may also decrease it. That is, we may have *negative* as well as *positive* catalysis. The oxidation of a solution of sodium sulphite by oxygen is, as we have learned, accelerated by copper salts, but it is *retarded* by tin salts; and it is retarded also by certain alkaloids, *e.g.* nicotine. Even a puff of tobacco smoke (containing nicotine) through the solution of sodium sulphite produces a detectable retardation of the oxidation. The occurrence of negative catalysis is frequently of great importance because it becomes possible to retard processes of decomposition and so to stabilise a substance by means of suitable catalysts. Thus, certain explosives are stabilised by diphenylamine (p. 132); and the oxidation process which causes rubber and silk to "perish" can be greatly retarded by means of thiourea, $CS(NH_2)_2$, and other substances.

Catalysis may occur not only in homogeneous but also in heterogeneous systems, as when solid substances act as catalysts in gaseous and liquid systems. Thus, if the case of hydrogen and oxygen be again considered, it is found that although combination of the two gases takes place at high temperatures with explosive velocity, at the ordinary temperature no trace of combination can be detected. If, however, a little metallic platinum be brought into contact with the mixture of the two gases, combination proceeds with appreciable velocity; indeed, if the platinum is used in a finely divided form, known as platinum sponge or platinum black, the rate of combination may be so great, and the amount of heat evolved so large, that the platinum is heated

to incandescence and ignites the mixture. An explosion results. This action of platinum, one of the first cases of catalytic action to be observed, brings out very clearly two of the main characteristics of the phenomenon, namely, the great change produced in the speed of the reaction, and the fact that the catalyst remains unchanged in amount. The same piece of platinum can be used to bring about the combination of unlimited quantities of hydrogen and oxygen.

This remarkable behaviour of finely divided platinum, which greatly impressed, as well it might, the minds of the early observers, was not long in receiving a practical application. In 1823 it was observed by a German chemist, DÖBEREINER, that if a jet of hydrogen is allowed to impinge on a piece of spongy platinum exposed to the air, the heat of combination of hydrogen and oxygen raises the platinum to incandescence and the hydrogen becomes ignited. Döbereiner, therefore, constructed an apparatus in which hydrogen was produced by the action of sulphuric acid on zinc ; and when a tap was opened the gas escaped in a fine jet and impinged on a piece of spongy platinum. In this way fire could be obtained, and, as a matter of fact, this Döbereiner lamp was widely used for that purpose before the days of matches.

Although platinum is by no means a universal catalyst for all reactions—no such universal catalyst is known—it has nevertheless been found that platinum acts very generally as a catalytic accelerator of oxidation reactions, or reactions in which gaseous oxygen takes part. Oxide of cerium, which forms a small part of the Welsbach incandescent gas mantle, also acts as a catalyst and accelerates the combustion of the coal-gas.

The attempt made in recent years to apply spongy platinum for the purpose of automatically lighting a jet of coal-gas did not meet with complete success, by reason of the fact that after a time the platinum was found to lose its effectiveness. This destruction of the catalytic activity, this " poisoning " of the catalyst, as it has been called, is a phenomenon of the greatest

importance, the recognition of which has been, as we shall learn more fully presently, not only of scientific interest, but also of the greatest industrial importance.

By chemists the importance of catalysis is now fully recognised, and the systematic search for the most suitable and effective catalyst for a given reaction is a well-established part of chemical investigation ; but it is part of the romance of science that discoveries of value are made not only as the result of consciously directed effort, but also by the aid of " that power which erring men call Chance." And in this connection the following tale may be re-told, for it illustrates not only the special action of a catalyst, but also the important *rôle* which catalysts may play in industry.

For the preparation of a certain dye—it was a dye called sky-blue alizarin, but the name does not matter—the necessary ingredients were heated for some time in a vessel made of iron. In the course of time fresh apparatus had to be installed ; and with this apparatus no sky-blue alizarin was obtained, but something entirely different. What could be the reason of the failure ? The process was carried out in the same way as before, and the workmen were the same, or were under the same direction. The apparatus, certainly, was new, but it was exactly the same as the old apparatus. And yet, no ; it was not exactly the same. The new apparatus, instead of being entirely of iron, had a copper lid. But surely that could not be the cause of the different behaviour. Yet so it was, for the small trace of copper derived from the lid exerted, it was found, a powerful catalytic influence on the course of the reaction, and instead of the substances reacting so as to form sky-blue alizarin, a further reaction took place which gave rise to a totally different substance.

It might perhaps seem as if the tracing of the trouble to its source would finish the story, but this is by no means the case. Accident had thrown a catalyst for a new reaction in the way of the chemist, who, by careful investigation, found that a trace of copper enabled the ingredients used,

as well as a number of other similar substances, to react a particular manner, and in this way *a new and importa series of dyes was discovered.* It all seems very simple ; a matter of " happy accident." But was it by a hap accident that the cause of the trouble in the first instan was discovered ? Or was it a happy accident that convert a source of trouble in one process into a source of gain another ? How would the matter have stood without t trained intelligence of the chemist with his knowledge of t importance of little things, with his trained faculty of obse vation and his ability to make use of the facts which observed ?

Important as are the phenomena of catalysis in pu science and in industry, they are, literally, of much mc vital importance in the animal and vegetable organism.

The animal organism is like a laboratory in which nume ous reactions and marvellous transformations take pla unceasingly—the transformation of the food consumed in the bone and flesh and blood of the body, and the slc combustion of the tissues to yield the energy and he necessary for vital activity. And so it is also with the pla organism in which there takes place the building up *synthesis*, not only of the complex materials which serve foodstuffs for the animal creation, but also of those swee smelling essences and the compounds which give to flowe their varied odours and colours. Many of these substances, tl products of Nature's laboratory, can also be made in tl laboratory of the chemist, and their synthesis from simp inorganic materials constitutes the crowning achieveme of chemical science. But how different are the methods the chemist from those of Nature. In his laboratory tl chemist makes use of high temperatures and the action powerful and corrosive reagents ; but in the laboratory Nature, the building up of even the most complex con pounds takes place quietly and smoothly at the ordina

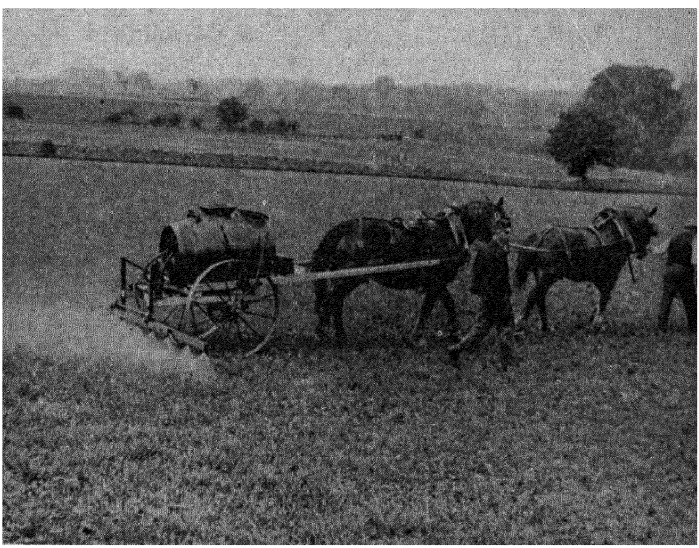
accomplishes by utilising appropriate catalysts, accelerators of reactions, the so-called *enzymes*, which are themselves produced within the living cell of a plant or animal. The ptyalin of the saliva, the pepsin of the gastric juice, the trypsin of the pancreas, the diastase of the sprouting barley-corn, the zymase of the yeast, which has from time immemorial been used by man for the conversion of sugars into alcohol—these are some of the numerous catalytic agents which Nature produces and of which she makes use in her marvellous achievements in chemical synthesis. Not only do enzymes play an indispensable *rôle* in the economy of Nature, but they are also being made to play a part of ever-increasing importance in industry, as we shall learn more fully later (Chap. XVII).

In the manufacturing industries it may truly be said that time is money; and to produce an article of manufacture at a more rapid rate is the same as saving time. And this is just exactly what a catalyst enables one to do. It is, therefore, not surprising that in almost all branches of chemical industry the value of catalysts has become increasingly recognised, and that, by their introduction, new industries of the highest importance have been established, and older industries have been revolutionised. It would, in fact, be no exaggeration to speak of the present as the catalytic age in chemical manufacture. Although reference has already been made to the industrial application of catalysts (*e.g.* in the hydrogenation of coal and production of oils, p. 97), a little space may appropriately be devoted here to the discussion of a few other important reactions in which catalysis has found industrial application. In succeeding chapters, other applications will be discussed.

Manufacture of Sulphuric Acid

Sulphuric acid, or oil of vitriol (H_2SO_4), the discovery of which dates from the fifteenth century, is one of the most

important substances in our modern civilisation, for it finds a use in almost every manufacturing industry, and in agriculture, for the eradication of weeds.[1] Although in a number of industries, such as the manufacture of superphosphates, hydrochloric acid and ammonium sulphate, changes have taken and are taking place which make the use of sulphuric



Courtesy of Imperial Chemical Industries, Ltd.

ERADICATION OF WEEDS BY SPRAYING WITH DILUTE SULPHURIC ACID.

acid less necessary, the production of the acid has gone on increasing, so that the annual production throughout the world now amounts to about 11,000,000 tons.

The reaction on which the production of sulphuric acid

[1] A complex organic compound, *methoxone*, which has been prepared by the chemists of Imperial Chemical Industries, is a weed-killer with marked selective action. It will destroy charlock, pennycress and corn buttercup without damaging the cereal crop. It is put on the market under the name *agroxone*, and may well supersede sulphuric acid as a

depends is the oxidation of the gas sulphur dioxide (SO_2), to form the compound sulphur trioxide (SO_3), which combines readily with water to give the compound known as sulphuric acid. The difficulty is met with, however, that combination between sulphur dioxide and oxygen does not take place appreciably at the ordinary temperature; and when one seeks to hasten the combination by raising the temperature, another difficulty is encountered. As the temperature is raised the rate at which the sulphur dioxide and the oxygen combine certainly increases, as we have already learned to be universally the case, but as the temperature rises the *extent* to which combination takes place becomes less and less, by reason of the fact that at high temperatures the sulphur trioxide decomposes again into sulphur dioxide and oxygen. The result, therefore, is that at a temperature at which the combination of sulphur dioxide and oxygen would take place sufficiently rapidly, the amount of sulphur trioxide formed is too small to allow of the process being commercially successful. We now know, however, the direction in which to look for a way out of the difficulty. We must find a catalyst which will so accelerate the rate of oxidation of the sulphur dioxide that the process may be carried out with sufficient rapidity at a temperature so low that the decomposition of the sulphur trioxide is negligible. Such a catalyst was found at an early date in the oxides of nitrogen, and since the year 1746 the manufacture of sulphuric acid has been carried on by a process depending on the use of these oxides. This method of manufacturing sulphuric acid consists, essentially, in passing sulphur dioxide, together with air, oxides of nitrogen, and steam, into a series of large lead chambers. Here the sulphur dioxide combines with the oxygen of the air under the catalytic influence of the oxides of nitrogen, and the sulphur trioxide formed combines with the steam to form sulphuric acid. The acid produced in this "lead chamber process," as it is called, contains about 65 per cent. of sulphuric acid

(H_2SO_4), and must be subjected to processes of purification and concentration before the pure acid is obtained.

At the beginning of the present century, however, another process began to come into prominence. This was due mainly to the successful development of the process of manufacture of synthetic indigotin (p. 317), which necessitated the use of the very powerful reagent obtained by the addition of sulphur trioxide to pure sulphuric acid, and known as fuming sulphuric acid or " oleum."

As far back as the year 1817, it was suggested by Sir HUMPHRY DAVY that platinum sponge might be employed to accelerate the oxidation of sulphur dioxide by oxygen, just as we have seen that this metal accelerates the combination of hydrogen and oxygen; and in 1831, practical application of this suggestion was made by a vinegar manufacturer of Bristol, PEREGRINE PHILLIPS by name. Great hopes were aroused for the success of this method of manufacturing sulphuric acid, and even in 1835 a well-known French chemist, CLEMENT-DESORMES, gave expression to the conviction that in ten years at most it would be possible to manufacture sulphuric acid directly from its constituents, without the use of lead chambers and nitric acid. But the unwisdom of prophecy is proverbial, and the period of ten years lengthened out to one of nearly seventy, before the ability and persistence of the technical chemists in one of Germany's greatest chemical works succeeded in developing the discovery of Peregrine Phillips into a successful industrial process.[1]

When the attempt was made to utilise the " contact process," as it is called, for the commercial production of sulphuric acid, a difficulty was met with which delayed success and threatened complete failure. The production

[1] On a restricted scale, Squire and Messel, in England, manufactured oleum by the contact process, from 1875 onwards. They obtained the sulphur dioxide by the combustion of sulphur or by the decomposition of sulphuric acid on hot brick surfaces. The oleum so prepared was too costly except for special purposes.

of sulphur trioxide which at first took place with great readiness soon began to diminish, and after some time ceased altogether. The platinum lost its catalytic activity. On investigation, this loss of activity was found to be due to a " poisoning " of the platinum—a phenomenon to which we have already referred—and the substance which was found to be chiefly responsible for this was arsenic. This arsenic was derived from a small amount of impurity contained in the iron pyrites, a naturally occurring sulphide of iron used as the source of the sulphur dioxide, and it was only after much labour that a means was found of ridding the gas of all traces of this poison. When this had been done, the contact process could be carried out with success.

For the production of sulphuric acid by the contact process, the enormous lead chambers, with a capacity sometimes of 150,000 cubic feet, are replaced by comparatively small, cylindrical vessels containing a suitable catalyst. For this purpose, platinum deposited on asbestos (platinised asbestos), or on a porous magnesium sulphate or on silica gel (p. 279), has mainly been used in the past, but compounds of vanadium are now coming into widespread use as catalysts. They are much less costly than platinum and they are not " poisoned " by arsenic or by hydrogen chloride. Through the reaction vessels which are maintained at the proper temperature, about 450° C. (842° F.), by the heat given out in the reaction, the mixture of sulphur dioxide and oxygen (or air) is passed. The oxidation of the sulphur dioxide takes place rapidly and practically completely, and the sulphur trioxide issues from the apparatus as a white mist, which is then passed into a solution of sulphuric acid containing about 98 per cent. of acid. In this way a pure sulphuric acid, as well also as the powerful fuming sulphuric acid (called " oleum "), to which we have referred, can readily be obtained.

Whether the contact process will eventually succeed in entirely superseding the older leaden-chamber process, it

is impossible to say ; for, under the stimulus of competition, improvements have been effected in the latter process which will in any case retard, if they do not altogether prevent, its complete disappearance. Most probably both processes will continue to develop in varying degrees according to circumstances.

The *sulphur dioxide* required for the production of sulphuric acid may be obtained by heating iron pyrites (sulphide of iron, FeS_2) or spent oxide of iron from the gas works (p. 105) in a current of air, or by burning sulphur in air. SULPHUR occurs free over an extensive area in Sicily, and also forms great deposits, 30–40 yards in thickness and situated at a depth of some 700 feet below the surface of the earth, in the State of Texas, U.S.A. These deposits constitute the main source of supply at the present day.

Large amounts of sulphur are now recovered from the sulphur dioxide which is formed as a by-product in the smelting of copper and zinc sulphide ores, and in the manufacture of cement (*see below*) from anhydrite (calcium sulphate) ; but the sulphur dioxide produced in these processes must first be concentrated by freeing it from the other gases (flue gases and air) with which it is mixed. For this purpose it is absorbed in a solution of basic aluminium sulphate (aluminium sulphate with excess of aluminium hydroxide). On warming the solution, the dissolved sulphur dioxide, mixed with water vapour, is evolved, and the gas, after condensation of the water vapour, is passed through coke, at a temperature of about 1000° C. (1832° F.). The coke reduces the sulphur dioxide to sulphur, with formation, mainly, of carbon dioxide ($SO_2+C=S+CO_2$). The sulphur can then be burned for the production of sulphur dioxide in the sulphuric acid plant.

When anhydrite (calcium sulphate, $CaSO_4$) is heated in a furnace with sand (silica), clay (p. 246) and coke, sulphur dioxide is evolved. From this the sulphur can be recovered as described above. The clinker which is left in the furnace

consists of calcium silicate ($CaSiO_3$) and calcium aluminate ($3CaO,Al_2O_3$) and, when ground, forms *cement*.

Considerable quantities of sulphur are now also being recovered from the hydrogen sulphide present in coke-oven gas, formed by the distillation of coal for the production of the coke required for use in blast furnaces and for other metallurgical purposes. In this process, known as the *Thylox process*, the gas is passed through a solution which contains a substance known as ammonium thio-arsenate. This compound exchanges an atom of oxygen for the sulphur in the hydrogen sulphide, as represented by the equation :

$$(NH_4)_3AsO_2S_2+H_2S=(NH_4)_3AsOS_3+H_2O.$$

Air (oxygen) is then passed through the solution, heated to a temperature of about 45° C. (113° F.), whereby the original thioarsenate (" thylox ") is regenerated and sulphur separates out. The sulphur is purified by distillation, and is used not only for the production of sulphur dioxide but also as an insecticide, in the vulcanising of rubber, and for other purposes in chemical industry.

Hydrogenation or Hardening of Oils

Another important industry which depends on the application of catalysis is that of the conversion of liquid oils into solid fats ; a process referred to as the hydrogenation or hardening of oils.

It has already been pointed out (p. 85) that the animal and vegetable fats and oils are, essentially, compounds of glycerine with acids, such as palmitic, stearic and oleic acids. The glycerine compounds of the saturated palmitic and stearic acids (p. 85) are solid, and constitute the main portion of the hard fat, beef suet. The glycerine compound of the unsaturated oleic acid is, however, a liquid, and is the chief constituent of olive oil ; and the other natural

animal and vegetable oils are also mainly compounds of glycerine with unsaturated acids. For these different fats and oils there are, at the present day, two main uses: namely, as foodstuffs, to supply the body with the necessary amounts of carbonaceous matter, and for the purpose of making soap. So far as foodstuffs are concerned, butter, or the fat of milk, constitutes a large part of the fatty material consumed. Owing, however, to the increase of population and to the rising price of butter, the problem of obtaining some substitute for this very important article of diet became of increasing importance. The solution of the problem we owe to French ingenuity, and the industrial production of butter substitutes, *e.g. margarine*, which dates from 1870, has now attained to very great dimensions. Beef-fat or hog's lard, after being melted and clarified, is mixed in churning machines with various vegetable oils, such as cotton-seed oil, soya-bean oil, coco-nut oil, palm-kernel oil, and also with milk. The milk is added in order to emulsify the fats and also to confer flavour, the flavouring properties being developed by the addition to the milk of bacteria which bring about the production of lactic acid. Although the margarine so obtained is an efficient substitute for butter so far as the supply of energy is concerned, it is lacking in certain important food accessories, to which the name of *vitamins* (p. 363) has been given. This defect is now remedied by the addition to the margarine of vitamins A and D, obtained partly by synthesis and partly from fish liver oils; and vitaminised margarines are now put on the market certified to contain these vitamins in as high a proportion as they are contained in the best butter.

Since these butter substitutes are derived mainly from animal fats, the supply of solid fats necessary for the manufacture of soap was seriously diminished; and it became, therefore, a matter of great importance to discover a method by means of which liquid oils could be converted into solid fats. Theoretically, the process is a simple one.

Oleic acid, for example, differs from stearic acid only in the fact that it contains less hydrogen. It is what has been called an unsaturated compound, and if the oleic acid is combined with the proper amount of hydrogen, it is converted into the solid stearic acid ; or, on the other hand, if hydrogen is combined with the liquid glycerine oleate, the solid fat, glycerine stearate, is obtained. Similarly with the other unsaturated compounds present in other oils. Although it was not difficult to carry out such a conversion in the laboratory, no commercially successful process was discovered until it was found that finely divided nickel acts as an efficient catalyst. In the presence of this metal, the liquid oils, olive oil, linseed oil, whale oil, etc., combine with gaseous hydrogen and become converted into solid fats suitable for use in the manufacture of soap and for the preparation of edible fats. This important industrial application of catalysis is based on the purely scientific investigations of the French chemists, PAUL SABATIER and JEAN BAPTISTE SENDERENS, carried out at the beginning of the present century.

Not only does the introduction of this process offer to the soap-boiler a fresh source of the material which he requires, but it also permits of the profitable employment of substances for which formerly comparatively little use could be found. Thus, for example, whale oil, which on account of its unprepossessing taste and smell found formerly but little application, is now converted in large amount, by the process mentioned, into a solid, odourless material suitable for the making of soap.

This result has led to a great expansion of the whaling industry. The introduction of the hydrogenation process, moreover, will, by stimulating the cultivation of oil-producing plants, exercise a profound influence on the economic development of those countries which are suitable for such cultivation. In America, for example, seven million acres are under soya bean cultivation, and in Great Britain the cultivation of soya bean has also been introduced and

will, it is hoped, be rapidly extended. Soya beans contain 18–20 per cent. of oil, which is easily converted into edible fat, and it contains proteins and other substances which make it specially valuable as a feeding stuff for cattle. Of the importance in the service of man of this modern industrial hydrogenation process, founded as so many industrial processes are on investigations of apparently purely scientific interest, it is impossible to form an estimate.

Syntheses from Water-gas

Mention has been made of the fact that the action of catalysts is largely specific, and it is found that by a proper choice of catalyst and regulation of the conditions of reaction, the same substances may be made to react in various ways. No better illustration of these statements could be obtained than what is offered by the numerous products which can be obtained from the mixture of carbon monoxide and hydrogen, known as water-gas (p. 107). This mixture, we have seen (p. 98), is the basis of the Fischer-Tropsch process, and from it hydrocarbons can be produced which are not only of great value as fuels and lubricants, but which, in the hands of chemists, have also been made to yield a great array of materials which are of service to man.

Formerly, practically all the *methyl alcohol* or *methanol*, which is used in large amount as a solvent and in the manufacture of formaldehyde, dyes, perfumes, etc., was produced by the distillation of wood (p. 123); but since 1925, a large and rapidly increasing proportion has been produced by a catalytic process founded on researches carried out mainly by French and German chemists. When a mixture of carbon monoxide and hydrogen is passed over a suitable catalyst (*e.g.* zinc oxide, or a mixture of zinc oxide and copper), under regulated conditions of temperature and pressure, the two gases combine to form methyl alcohol or methanol, CH_3OH, as shown by the equation, $2H_2+CO=CH_3OH$.

From the mixture of carbon monoxide and hydrogen, also, by the use of different catalysts and by suitable variation of the conditions of temperature and pressure, *butyl alcohol*, C_4H_9OH, a valuable solvent for nitro-cellulose lacquers, can be obtained.

Further, very large amounts of water-gas are used at the present day as a source of industrial hydrogen. Although the hydrogen may be separated from the carbon monoxide by a process of liquefaction and distillation, similar to that used in the case of liquid air (p. 58), a catalytic method is mainly employed. Thus, when water-gas and steam, at a temperature of about 500° C. (932° F.), are passed over a catalyst consisting essentially of iron oxide, the carbon monoxide reacts with the steam to form carbon dioxide and hydrogen. The carbon dioxide is then easily removed by dissolving in water under pressure.

A mixture of carbon monoxide and hydrogen is obtained not only when steam is passed over red-hot coke but also when methane and steam are passed over a catalyst of nickel and aluminium at a temperature of about 900° C. (1652° F.): $CH_4+H_2O=CO+3H_2$. This reaction has become of great importance as it can also be used as a means of obtaining cheap hydrogen for the hydrogenation of coal—methane being one of the by-products of the process (p. 97).

CHAPTER X

CHEMISTRY AND AGRICULTURE. POTASH, PHOSPHATE AND NITROGENOUS FERTILISERS

ALTHOUGH agriculture has been practised from time immemorial, it is only in comparatively recent years that a more exact knowledge has been obtained of soil fertility and plant growth. As early as 1563, the view was clearly stated by the French potter, BERNARD PALISSY, that dung was applied to the land in order to replace something which the growing crop had removed, although, early in the following century, the Belgian chemist, JEAN BAPTISTE VAN HELMONT, concluded that water is the sole nutrient of plants. " I took an earthen vessel," records van Helmont, " in which I put 200 pounds of soil dried in an oven, then I moistened with rain water and pressed hard into it a shoot of willow weighing 5 pounds. After exactly five years the tree that had grown up weighed 169 pounds and about 3 ounces. But the vessel had never received anything but rain water or distilled water to moisten the soil when this was necessary, and it remained full of soil, which was still tightly packed, and, lest any dust from outside should get into the soil, it was covered with a sheet of iron coated with tin but perforated with many holes. I did not take the weight of the leaves that fell in the autumn. In the end I dried the soil once more and got the same 200 pounds that I started with, less about two ounces. Therefore the 164 pounds of wood, bark and root arose from the water alone."

The experiment was simple but the conclusion, although it seemed to be convincing, was nevertheless incorrect, for van Helmont had omitted to take account of two factors —the carbon dioxide and water vapour in the air and the salts which had been removed from the soil; for, as we

have already learned, the green leaves of plants take in carbon dioxide and water vapour and, absorbing the radiant energy of sunlight, transmute these substances into sugar, starch and cellulose. In the erroneous conclusion drawn by van Helmont we have a warning of the care which must be exercised in the performance of a scientific experiment and in the interpretation of the results.

Although it had long been known that plants contain inorganic constituents which appear in the ash when the plant is burned, it was the German chemist, JUSTUS VON LIEBIG, who first, in 1840, gained definite acceptance of the view that plants do not subsist merely on the water and carbon dioxide which they abstract from the air and the soil, but that they have also to be fed with the elements necessary for the building up of their structures. No fewer than about thirteen elements are required by plants, and of these, the most important, apart from carbon and hydrogen, are nitrogen, phosphorus and potassium; and these must be present in the soil in the form of salts or soluble compounds which can be taken up by the plants. One ton of wheat, it is stated, abstracts from the soil 47 pounds of nitrogen, 18 pounds of phosphoric acid and 12 pounds of potash. So long as the population of the world was comparatively small, the great tracts of virgin soil contained an ample supply of the necessary mineral salts to secure crops adequate for the feeding of the people; and although the efficacy of dung in increasing the crop was well known, and although such manure was applied, the farmer had little to do but till the soil and sow the seed. Owing to exhaustion of the soil, however, and to the great increase of population which has taken place in modern times, it has become necessary to increase the yield of the soil by the addition in larger and larger amounts of the inorganic salts necessary for the life and growth of food plants. Although some of the fertilisers which are now indispensable for intensive agriculture are found ready-formed in Nature, yet

in the economic exploitation of these natural deposits, in rendering them suitable for absorption by the plant, and in the artificial production of fertilisers in ample amount and at lower cost, we may recognise one of the greatest services which chemists have done for man. Since, moreover, the nature and amount of the different fertilisers to be used depend on the plant, soil and climatic conditions, chemical

Courtesy of Sir John Russell.

EFFECT OF POTASH SALTS ON GROWTH OF MANGOLDS.

The root on the left has been grown in soil to which a potash fertiliser has been added ; that on the right, in a soil containing no potash.

knowledge and investigation are necessary for the production of a properly balanced fertiliser.

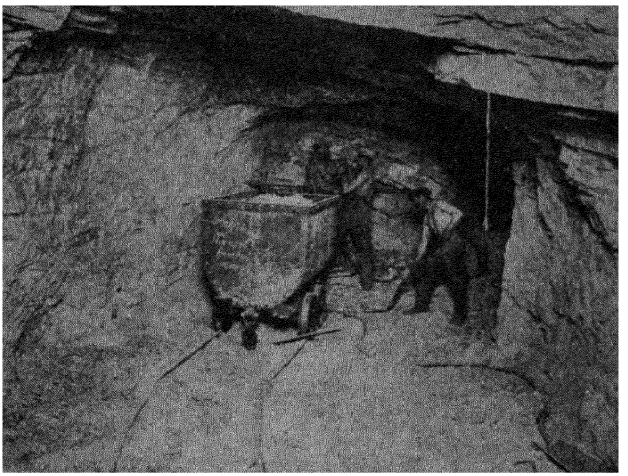
While it is a matter of the highest importance that agriculturists should have at their command adequate supplies of the essential fertilisers, it is also important to bear in mind that a deterioration of the soil may occur if artificial, inorganic fertilisers alone are used, and if attention is not paid to the renewal of the store of organic humus in the soil. This humus can be renewed by the addition to the soil of leaves, vegetable waste, straw, farmyard manure, etc.,

which have been allowed to rot or undergo change under the action of bacteria. Seaweed, also, may profitably be brought into service; and the ploughing up and re-seeding of old grasslands may also be used for the effective renewal of humus. Through the loss of humus, brought about by intensive cultivation and by the sole use of artificial fertilisers, the soil structure is destroyed and soil fertility and quality of the crops may be impaired. Serious erosion, also, may take place owing to the soil becoming less permeable to and being washed away by rain. Artificial fertilisers, therefore, must be made use of with knowledge and understanding.

The addition of POTASSIUM SALTS to the soil is of great importance because such salts give health and vigour to the plant, and make the leaves more efficient in utilising the energy of sunlight and more efficient producers, for example, of sugar and starch. In root crops, therefore, there is a greater storage of food material and the roots become larger. Potassium salts are of importance for the cultivation, more especially, of potatoes, beet and fruit crops, and the banana plant responds in a most surprising fashion when manured with salts of potassium.

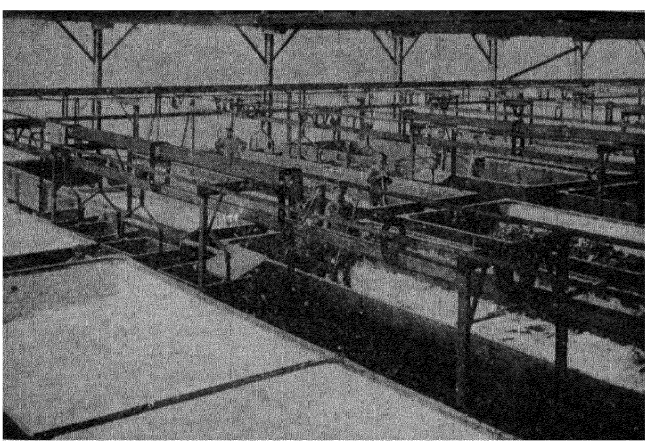
When land vegetation is burned, the potassium which the plants had taken from the soil is recovered in the ash in the form of potassium carbonate (K_2CO_3). This salt was obtained by lixiviation of the ash with water, evaporation of the solution and calcination of the residue in pots. Hence the name *pot-ash* given to potassium carbonate. For long, the potash so obtained constituted the main source of supply of this salt, and in the middle of last century nearly three-quarters of the world's supply came from the wood ashes of the Canadian lumber camps.

At the present time, nearly all the potassium salts used are of mineral origin, and are obtained mainly from the great salt deposits which are found in the neighbourhood of Stassfurt, in Germany, and in the neighbourhood of Mulhouse in Alsace. In the former deposits, which form the



Courtesy of Société Commerciale de Potasses d'Alsace.

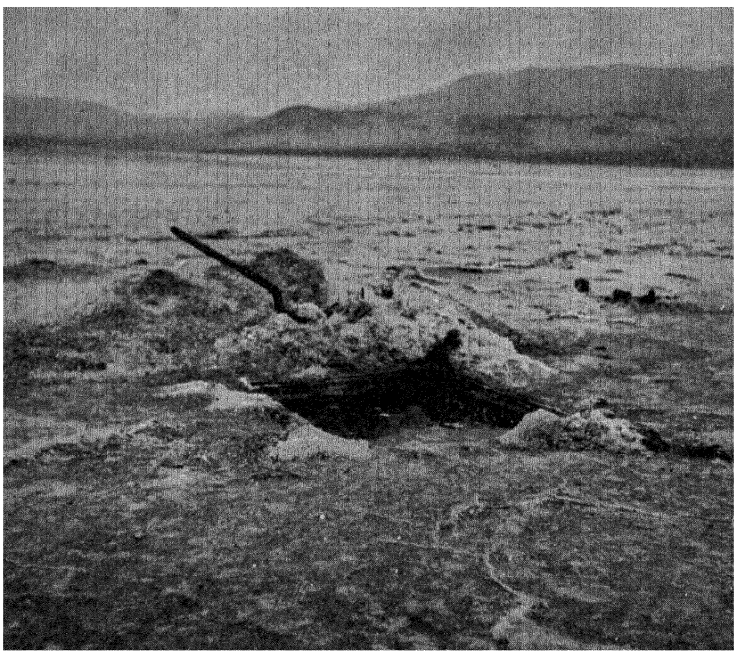
POTASH MINE IN ALSACE.



Courtesy of Société Commerciale de Potasses d'Alsace.

CRYSTALLISING VATS FOR POTASSIUM CHLORIDE.

largest source of potassium compounds, the chief potassium salts are *sylvine* (potassium chloride), *kainite* (a double sulphate containing not only potassium but also magnesium) and *carnallite* (a double chloride of potassium and mag-



SEARLES LAKE, CALIFORNIA.

Below the crust of salts there lies a saturated brine from which potassium chloride, borax and other salts are extracted.

nesium). The crude salts may themselves be used as potash fertilisers, or the potassium salts may be extracted and purified by crystallisation from water; and to learn how this can best be effected very long and laborious investigations had to be carried out. The successful exploitation of these deposits is due mainly to the work of the great Dutch chemist, J. H. VAN'T HOFF.

Deposits of potassium salts are also being worked in Russia, in Spain, and in the U.S.A., especially in Texas and near Carlsbad in New Mexico. Very large amounts of potassium salts are also being extracted from the brine of Searles Lake in the Mojave Desert, California, from the water of the Dead Sea, and from the flue-dust of cement works.

That PHOSPHATES are necessary for healthy plant growth has been known since the end of the eighteenth century, and their importance, more especially for cereals and pasture, became more fully appreciated in later years. In countries with a low rainfall, phosphates are of especial value in increasing and strengthening the crop and also in accelerating the processes of growth and ripening. They are of great value also in improving the feeding value of crops, especially of pastures, so that, by their application, grass land may be greatly improved and may be made to carry more stock.

Before the year 1840, phosphorus was added to the soil chiefly in the form of crushed bones, the phosphorus being present as calcium phosphate, the calcium salt of phosphoric acid. Between 1840 and 1850, however, JOHN BENNET LAWES, founder of the Agricultural Experimental Station at Rothamsted in Hertfordshire, showed that the phosphate could be rendered more readily soluble in the soil and therefore more readily available for the plant, by treating the ground bones with sulphuric acid. The so-called normal calcium phosphate, $Ca_3(PO_4)_2$, is thereby converted into acid calcium phosphate, $CaH_4(PO_4)_2$, with production at the same time of hydrated calcium sulphate or *gypsum*. To the mixture of acid calcium phosphate and gypsum the name *superphosphate* was given. Soon thereafter, deposits of mineral rock (phosphate rock) were discovered, and from this nearly all superphosphate is now produced. About 60 per cent. of the world's supply of mineral phosphate comes from the enormous deposits in French North Africa, and about 30 per cent. from America.

Ground *basic slag* (p. 160) is also used, in large amount,

as a phosphatic fertiliser, more especially for the treatment of grazing land.

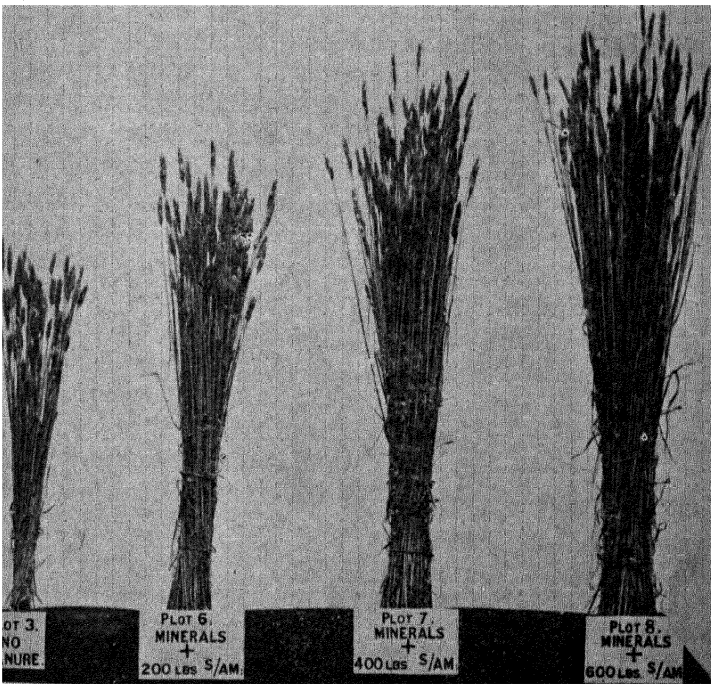
In various countries, the production of another phosphate fertiliser is being developed which may perhaps largely supersede superphosphate. When phosphorus is heated to a high temperature with steam, phosphoric acid is formed and hydrogen is liberated. The hydrogen is used, as we shall learn presently, for the production of ammonia, and the ammonia is then combined with the phosphoric acid to form ammonium phosphate (" di-ammon-phos "), which may be used both as a phosphatic and as a nitrogenous fertiliser.

Of the different fertilisers used in agriculture the most important are those which feed the plant with *nitrogen*, for it is on such fertilisers that increased crop production, in those countries with a not too low rainfall,[1] mainly depends. More especially is this the case with wheat and other cereals. Although it has been found that leguminous plants (peas, beans, lucerne, clover, etc.), through the symbiotic action of colonies of bacteria occurring in nodules on the roots, are able to take up and assimilate elementary nitrogen from the air, most plants are unable to do so ; and combined nitrogen must, therefore, be added to the soil in a form which the plants can assimilate.

Owing to the apparent impossibility of coaxing the enormous store of elementary nitrogen contained in the air into suitable combination with other elements, mankind contented itself, resignedly if not complacently, with the natural sources of supply of useful nitrogen compounds ; and this position was all the easier to adopt as the natural supply was sufficient for the needs of the day. In 1898, however, Sir WILLIAM CROOKES, as President of the British Association, delivered the solemn warning that the years of plenty were quickly passing. The supply of wheat, the staple foodstuff

[1] Where the annual rainfall is less than about 20 inches, nitrogenous fertilisers do not produce large increases in crops. In such countries phosphate fertilisers are specially important.

of Western peoples, from all the land available for cultivation, would soon be insufficient to provide for the needs of the growing population unless the yield of the soil could be greatly increased by intensive cultivation, which in its turn



Courtesy of Sir John Russell.

EFFECT OF NITROGENOUS FERTILISERS (AMMONIUM SULPHATE) ON PLANT GROWTH.

would, in a few years, exhaust all the known sources of combined nitrogen. Famine, therefore, stared them in the face, and there would be no Egypt from whose granaries supplies could be obtained.

Apart from waste animal and vegetable matter, which was quite inadequate in amount and, in some cases, had only

a local importance, agriculture depended for its supply of nitrogenous fertilisers mainly on the ammonia produced as a by-product in the distillation of coal, and on Chile saltpetre or sodium nitrate. In 1898, nearly 300,000 tons of nitrogen, in a combined state, were used for fertiliser purposes, and of this amount about one-third was in the form of by-product ammonium sulphate and two-thirds in the form of Chile saltpetre. Coal, therefore, was a valuable source of supply of combined nitrogen and it became more and more important that as much coal as possible should be distilled and that the ammonia should be recovered. It was, however, economically impracticable to produce by this means an adequate supply of nitrogenous fertiliser. Moreover, although it was possible greatly to increase the production of Chile saltpetre, the nitrate deposits, although enormous, were not inexhaustible.[1] It is clear, therefore, that the situation in 1898 was one which might well cause grave concern to men of foresight and scientific knowledge; and Sir William Crookes was only doing his duty in calling the attention of his countrymen and of the world to the inevitable disaster which threatened unless some fresh means were found of obtaining combined nitrogen.

As the discovery of any considerable new supplies of naturally occurring nitrogen compounds was scarcely to be relied on, there was an imperative demand laid on chemists to discover some means of forcing the inexhaustible store of elementary nitrogen into such a state of combination that its assimilation by plants would be rendered possible. As Sir William Crookes said: "The fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists." And the ingenuity of chemists, assisted by the engineers, has proved itself equal to the task. Since about 1903, not one but several methods have

[1] While it was at one time thought that the Chile saltpetre deposits would be exhausted by 1923, it now seems probable that there will be sufficient to supply world needs for one or two hundred years.

been discovered by means of which the atmospheric nitrogen can, on a large scale and in a commercially successful manner, be forced into useful combination with other elements. Indeed, so far as nitrogenous fertilisers are concerned, the prospect of a wheat famine has now been removed to an indefinitely remote future.

(1) *Direct Combination of Nitrogen and Oxygen.*

Since the atmosphere consists essentially of a mixture of nitrogen and oxygen, it is obviously most natural that attempts should be made to bring about the combination of these two gases, the possibility of which had been proved by the experiments of Cavendish in 1785 (p. 51).

The first successfully to solve the problem of the combination of nitrogen and oxygen on a commercial scale were two Norwegians, BIRKELAND and EYDE, who commenced the industrial production of nitric acid in 1903. For the production of the high temperature required to bring about the combination of nitrogen and oxygen, they made use of the electric arc, the only means whereby a temperature of from 2500° C. to 3000° C. (4532° F. to 5432° F.) can be satisfactorily and economically obtained. By the combustion of the nitrogen there was formed an oxide of nitrogen called *nitric oxide* (NO), which, after being cooled, was passed into chambers lined with acid-proof stone and mixed with air. The nitric oxide combines at once with the oxygen of the air to form a brown-coloured gas, *nitrogen dioxide* (NO_2), which, when absorbed in water, gives nitric acid. For convenience of transport, the nitric acid was neutralised with limestone (carbonate of lime or calcium carbonate), and so converted into nitrate of lime (calcium nitrate). This was then used as a fertiliser under the name of *Norwegian saltpetre.*

The production of nitric acid and nitrates by the direct combination of atmospheric nitrogen and oxygen was carried out mainly in Southern Norway, where the abundant and

very cheap water-power which is necessary for the industrial success of the process was available. But science marches unhaltingly forward, and the Birkeland-Eyde process, the development of which aroused much interest and had important social-economic consequences in Southern Norway, was, in 1928, after a life of twenty-five years, forced to surrender to a more efficient rival. Instead of the electrical energy being used to bring about the combination of nitrogen and oxygen, it is now applied to the electrolysis of water and the production of hydrogen ; and this hydrogen is employed for the production of synthetic ammonia in a manner to be described presently.

(2) *Fixation of Nitrogen by means of Carbides.*

In 1906, another process was introduced for the fixation of atmospheric nitrogen, which depended on the use of calcium carbide, a compound manufactured in large amount for the production of acetylene. When nitrogen is passed over this carbide, suitably heated in retorts, a reaction takes place with formation of a compound known as calcium cyanamide ($CaCN_2$), and the production at the same time of a quantity of carbon. The dark-grey coloured mixture which is thus obtained, and which contains about 60 per cent. of calcium cyanamide, is put on the market under the name of *nitrolim*, or *lime nitrogen*, as it is called in America.

For this compound, calcium cyanamide, quite a number of uses have been developed, but the most important is that as a source of nitrogen in agriculture. When properly applied to the soil, calcium cyanamide has been found to have a fertilising value for cereals nearly equal to that of ammonium salts. The physical qualities of the commercial nitrolim, however, its dustiness and dirtiness, were prejudicial to its use, and although the former defect has been largely removed, much of the cyanamide is used, not directly as a fertiliser but for conversion into ammonium salts,

ammonia being readily obtained by passing superheated steam over the cyanamide.

(3) *Synthetic Production of Ammonia.*

However important may be the processes to which reference has already been made, and however great their contribution towards a solution of the " nitrogen problem," they could scarcely, on account of their greater or less dependence on cheap electric power, furnish a complete solution of the problem. Something more was needed, and the announcement, in 1912, that the direct combination of nitrogen and hydrogen to form ammonia had been developed into a commercially successful process, was recognised as of the highest significance and importance.

The problem of successfully bringing about the direct combination of nitrogen and hydrogen is one which had taxed the ingenuity of chemists for many years. Inert as the two gases are towards each other at the ordinary temperature, it was well known that by the passage of electric sparks through a mixture of the two gases, ammonia is produced, but only in very minute amount. It was, moreover, also known that when electric sparks are passed through gaseous ammonia, decomposition, almost but not quite complete, into nitrogen and hydrogen takes place. In other words, it was known that the reaction between nitrogen and hydrogen is a reversible one, and leads therefore to a state of equilibrium ; but the concentration of ammonia present is exceedingly small, and all attempts to obtain an appreciable amount of the compound by direct combination of nitrogen and hydrogen ended in failure. New weapons, however, were being forged, the weapons of chemical dynamics, and with these the problem was again attacked. In 1912, as the result of ably-directed and painstaking endeavour, the problem was solved.

Experiment has shown that when nitrogen and hydrogen

combine, the volume of the ammonia produced is less than that of the mixed hydrogen and nitrogen; and therefore, according to the laws of chemical dynamics, the relative amount of ammonia produced will be increased by bringing the gases together under a high pressure. Moreover, combination of nitrogen and hydrogen takes place with *evolution* of heat; and therefore (p. 177, footnote) the formation of ammonia will be favoured by keeping the temperature *low*. The following table will show how the predictions of theory were borne out by experiment:

Temperature	Percentage amount of ammonia in the equilibrium mixture when the pressure was	
	1 atmosphere	100 atmospheres
800° C. (1472° F.)	0·011	1·1
700° C. (1292° F.)	0·021	2·1
600° C. (1112° F.)	0·048	4 5
500° C. (932° F)	0·13	10·8

In order, therefore, to attain success in the industrial synthesis of ammonia from its elements, the rule must be borne in mind: Maintain the gases under as high a pressure and at as low a temperature as possible.

But here again we meet with that factor which so sharply distinguishes success in the scientific laboratory from success in the factory, the factor of time. At about 500° C., it is true, quite an appreciable amount of ammonia is formed by the direct combination of hydrogen and nitrogen, but the *rate* at which this amount is produced is so slow that the process would be industrially useless. Again, therefore, the first immediate requirement is the discovery of a suitable catalyst, and such a catalyst was found in osmium, in uranium, in iron, and in certain other substances, some of which previous investigators had also employed, but without achieving success. And here again, as in other cases to which reference has been made, failure was due to a non-recognition of the fact that catalysts can be "poisoned." Through the presence of minute traces of different impurities in the nitrogen or hydrogen, the efficiency of the catalyst can be

destroyed, and it was only by laborious and careful investigation of the behaviour of different catalysts, and of the behaviour of other substances towards these catalysts, that success was made possible. Nor indeed were the engineering difficulties much less than the chemical, but they were all overcome, and the synthetic production of ammonia was added to the industries of the world. In the economic utilisation of Nature's boundless store of nitrogen, therefore, catalysts play an all-important part.

In the manufacturing process, first successfully achieved by the German chemist, FRITZ HABER, and often spoken of as the Haber process, a mixture of nitrogen and hydrogen, under a pressure of 150–200 atmospheres, is circulated, by means of a pump, over the catalyst[1] heated to a temperature of about 500° C. (932° F.). After passing over the catalyst, the gases, which now contain a certain proportion of ammonia, are washed with water, so as to dissolve the ammonia, while the unchanged nitrogen and hydrogen are made to circulate again over the catalyst.

A number of modifications of the original Haber process have been introduced, of which the two most important are the Claude (French) and the Casale (Italian) processes. These differ from the Haber process mainly in the fact that they operate under very much higher pressures. As has already been mentioned (p. 208), the production of ammonia is favoured by high pressures, and in the Claude and the Casale processes, pressures up to 800 or 1000 atmospheres are employed. In these processes, the percentage of ammonia in the gas after passage over the catalyst is much higher than in the Haber process; and under the high pressures employed, also, the ammonia is readily liquefied merely by cooling with water, and is thus easily separated from the residual mixture of hydrogen and nitrogen.

[1] While the exact nature of the catalyst is kept secret, it may be regarded as oxide of iron to which potassium oxide, molybdenum, aluminium oxide or other substances are added to increase the efficiency.

For use as a nitrogenous fertiliser, ammonia is converted into ammonium sulphate. Formerly, this salt was obtained by combining the ammonia with sulphuric acid, but now use is very extensively made of calcium sulphate ($CaSO_4$). If a suspension of finely ground calcium sulphate (anhydrite or gypsum) in water is treated in a closed vessel with ammonia and carbon dioxide,[1] ammonium sulphate and calcium carbonate are formed, as indicated by the equation :

$$CaSO_4 + H_2O + 2NH_3 + CO_2 = CaCO_3 + (NH_4)_2SO_4$$

The calcium carbonate can then be used for the production of cement (p. 248), or as a liming agent in agriculture. Mixed with ammonium nitrate it is used as a fertiliser under the name of *nitro-chalk*.

As a consequence mainly of the development of the synthetic ammonia process, the position of the nitrogen industry has undergone a very remarkable change. Not only has the total production of nitrogen compounds greatly increased in recent years, but the amount produced by the industrial fixation of atmospheric nitrogen (about 60 per cent. of the total) now greatly exceeds the amount contributed by Chile saltpetre and by the distillation of coal. This fact, by itself, will give some indication of the success which has attended the efforts made to utilise the stores of atmospheric nitrogen ; and chemists surely may justifiably feel some pride and satisfaction, and may even look for some sign of appreciation from their fellow-men, by reason of the fact that in the solution of the great problem of the fixation of atmospheric nitrogen, their ingenuity has not altogether been found wanting. To make two ears of corn to grow where only one grew before is an achievement which should surely win for science some larger measure of popular recognition and esteem.

In recent years the substance, *urea*, $CO(NH_2)_2$, first

[1] This carbon dioxide is produced in the process used for obtaining the hydrogen required for the synthesis of ammonia, namely, by passing water-gas (p. 107) and steam over a catalyst. Hydrogen and carbon dioxide are formed (p. 194).

known as a product of animal metabolism, has begun to come into use as a fertiliser and for the production of plastic materials (Chap. XVI). It is produced industrially by the direct union of ammonia and carbon dioxide, under the influence of a catalyst, at a temperature of about 150° C. (302° F.), and under a pressure of about 70 atmospheres. The reaction is represented by the equation, $CO_2+2NH_3=CO(NH_2)_2+H_2O$.

Besides potassium, phosphorus and nitrogen, a number of other elements are required to act either as plant nutrients or to improve the fertility of the soil. Of these, perhaps the most important is calcium in the form chiefly of calcium carbonate (limestone, chalk) or of slaked lime (calcium hydroxide). The addition of lime to the soil is of importance, in the first place, in order to prevent undue acidity; but it has also a specific action not possessed, say, by magnesium. The fertility of a soil, also, depends in great measure on the amount and nature of the colloidal material (p. 273) present; and the compounds of calcium are of great value in bringing about such a degree of flocculation and deflocculation of the colloids in the soil as to secure adequate aeration of the soil and the retention of the soluble salts.

Magnesium, also, is an element which must be present in the soil, for it is an essential constituent of chlorophyll, the green colouring matter of leaves, etc. Usually there is an adequate supply of magnesium salts in the soil, but, if not, they must be added.

Whereas the elements already referred to are to be regarded as plant nutrients and must be present in the soil in adequate amount in a form which the plant can assimilate, recent investigation has shown that the health of a plant may depend on the presence in the soil of other elements in minute quantities. These *trace elements*, as they are called, seem in their action to partake somewhat of the character of catalysts, and to resemble the hormones (p. 369) in the animal organism. Small quantities of iron, for example,

seem to facilitate the formation of chlorophyll, although chlorophyll itself contains no iron; and other elements, although they may be harmful when present in large amount, may have a beneficial action on the health of the plant when present in minute quantities.

During the present century it has come to be realised that two elements especially, boron and manganese, are necessary for the health of higher plants, although the amounts required may be very small. Manganese seems to be an essential factor in plant metabolism and growth, and acts, apparently, as a catalyst of the enzymic reactions of the organism. Boron, also, has been found to be essential for the normal growth of a number of plants, but the addition of 1 part of boric acid in 12,500,000 parts of water has been found sufficient to prevent signs of malnutrition. Various plant diseases, also, such as internal cork of apples, heart rot of sugar-beet and brown heart of swedes, have been found to be due to a boron deficiency and may be prevented by applications of borax (sodium borate) to the soil. Similarly, the disease known as mottle-leaf of citrus has been shown to be induced by a deficiency of available zinc in the soil. The effect of even minute quantities of different elements in the soil is now being energetically investigated.

Although the fixation of atmospheric nitrogen has been considered only as a means of obtaining nitrogenous fertilisers, a brief reference to the industrial importance of nitrogen should not be omitted. Owing to the large amount of heat which becomes latent, and the consequent lowering of temperature which takes place, when liquid ammonia is converted into vapour, this substance is widely used at the present day in refrigeration. It is now also being used to an increasing extent for the production of *nitric acid*, which, as we have learned, is an essential reagent in the manufacture of explosives and is also required in the dye industry, as well as for the production of the oxides of nitrogen used in

the manufacture of sulphuric acid by the lead chamber process (p. 186). Previous to 1913, Chile saltpetre was the only practicable source of nitric acid,[1] and it is therefore clear that a country whose supplies of this salt might be cut off would, in time of war, be rendered powerless. It was, indeed, under the stimulus of the apprehension that such might be the fate of his country, that the German chemist, WILHELM OSTWALD, in the early years of this century, addressed himself to the successful development of a process of obtaining nitric acid from ammonia. Just as platinum acts as a catalyst for the combustion of hydrogen (p. 180), so also it acts as a catalyst for the combustion of ammonia; and when a mixture of ammonia and air is passed over platinum, or platinum-rhodium alloy, in the form of wire gauze heated to a temperature of about 800° C. (1472° F.), the ammonia reacts with the oxygen of the air to form oxides of nitrogen which, dissolved in water, yield nitric acid. By suitably regulating the process of oxidation, one can also obtain *ammonium nitrate*, NH_4NO_3, which is used as a fertiliser (p. 210) and as a constituent of high explosives (p. 135).

The social-economic consequences of these developments in chemical industry have been stupendous. It was in 1913 (a noteworthy and ominous date) that Germany established the synthetic production of ammonia on an industrial scale; and since the later years of the war of 1914–18 she has obtained, through that process and through the catalytic oxidation of ammonia, all the ammonium nitrate and nitric acid which she has required for use in explosives and in the manufacture of explosives and nitrogenous fertilisers.

[1] Obtained by heating Chile saltpetre with sulphuric acid: $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$ (nitric acid).

CHAPTER XI

GLASS, SODA, SOAP, LIME AND CLAY

IN the previous chapter there was discussed one of the younger of the chemical industries, the production of synthetic ammonia, an industry which was developed at the call of necessity to contribute to the well-being of man and the advance of civilisation. In the present chapter we shall turn our attention, in the first place, to one of the oldest industries, which, by reason of the unique and valuable properties of the product, is still one of the foremost industries of civilised countries, the industry of glass-making.

Many, doubtless, are familiar with the legend reported by the Roman writer Pliny in the first century of our era, which ascribed the discovery of glass to a party of Phœnician sailors who were forced by stress of weather to land on the sandy shore under Mount Carmel. Here, standing their cooking-pots on lumps of soda, with which their ship was laden, they observed the soda and the sand to fuse together under the heat of the fire, and so to form a glass. Although it may be that it was by some such accident that glass was discovered, and although the Phœnician towns of Tyre and Sidon were, at an early period, almost as celebrated for their glass as for the famous purple dye which coloured the robes of kings, it is to Egypt that one must look for the first knowledge of glass or glass-like material; to that country which, as Herodotus wrote, "contains more wonders than any other land, and is pre-eminent above all countries of the world for works which almost baffle description." The representation of the art of glass-blowing on the walls of the tomb of Tih (about 3800 B.C.), with which every visitor to Egypt is familiar, and the discovery of glass beads and ornaments

among the ruins of the ancient city of Memphis, bear testimony to a knowledge of this material at a very early period in Egyptian civilisation. What mankind owes to the first discoverer of the process of making glass, it is scarcely possible to describe. That first artificer in glass, as Dr. Johnson wrote, " was facilitating and prolonging the enjoyment of light, enlarging the avenues of science, and conferring the highest and most lasting pleasures; he was enabling the student to contemplate nature and the beauty to behold herself." And in modern times glass has undergone a wonderful evolution through the work and labours of chemists, who have shown how, by variation of the composition, the properties of glass may be altered in a most marvellous degree. Through the production of different kinds of glass there has been made possible the construction of apparatus for the most diverse uses, prisms and lenses for lighthouses, microscopes, telescopes and other instruments, which have contributed to the service of man and a knowledge of the universe.

Before considering more fully the nature and properties of glass, however, there are one or two points of general importance to which it is necessary to direct attention.

Everyone is familiar with the statement that matter can exist in three states—solid, liquid and gaseous; and this statement is familiarly illustrated by the substance water, which is well known in the three forms of ice, water and steam. By elevation of the temperature, solid is made to pass into liquid, and liquid into gas, whereas by lowering the temperature the reverse series of changes is brought about.

At the present moment it is the change from solid to liquid, and more especially from liquid to solid, that claims our interest; and in using the term solid, I mean crystalline solid, and not amorphous solid. In a crystalline solid the particles are arranged in a definite geometrical form and give rise to a structure bounded by plane faces or surfaces,

such as we see in the naturally occurring rock crystal, amethyst, etc. ; whereas an amorphous solid does not naturally assume any definite shape, although it may, of course, be cut into definite forms in imitation of crystals. When a crystalline solid is heated it is found that it passes, *at a definite temperature*, known as its melting-point, from the solid to the liquid state, whereas an amorphous solid, like sealing-wax for example, gradually loses its rigidity and possesses, therefore, no definite melting-point.

When a crystalline solid substance is heated, it is found that melting or liquefaction occurs as soon as the melting-point is reached, and it has never yet been found possible to heat a crystalline solid to a temperature above its melting-point without such a change occurring. If, however, a liquid is cooled down, it is found quite generally that the temperature can be lowered below the normal freezing-point, or below the melting-point of the solid, without any of the solid form being produced. One can, for example, with care, cool water to a temperature much below 0° C. (32° F.) without any ice being formed, and liquids which are in this way cooled to below the normal freezing-point are said to be *supercooled*. Such supercooled liquids appear to be quite stable—they can, apparently, be kept for any length of time unchanged—provided that all traces of the solid form are rigidly excluded. If, however, even a minute trace, even the ten thousand millionth part of a grain, of the solid substance —a particle which might dance as a mote in the sunbeam— is brought into contact with the supercooled liquid, the state of apparent equilibrium is upset, separation of the crystalline solid form begins, and the process goes on until all the liquid has passed into solid.[1] The process of crystal-

[1] When the cooling is carried out slowly, it is found that substances differ greatly in the readiness with which they remain supercooled, but, in general, when a substance has been supercooled to a certain extent, crystallisation or separation of the solid in the crystalline form takes place spontaneously, that is, without the previous addition of the solid form.

lisation, however, does not take place at once throughout the whole mass of the liquid, but only those portions of liquid which are in contact with the solid crystallise out, and the rate at which crystallisation proceeds depends also on the degree of supercooling. The farther a liquid is cooled below the normal freezing-point, the faster will solidification occur once it has been started. This law, however, is subject to modification through the operation of another factor. It has already been pointed out that the speed with which a chemical change takes place depends on the temperature, the speed being all the greater the higher the temperature, and becoming less as the temperature is lowered. Similarly with the process of crystallisation. When crystallisation is started in a supercooled liquid, two opposing factors operate to influence the speed of crystallisation. At first the effect of supercooling is predominant, and so as the degree of supercooling is increased, the rate of crystallisation also increases; but after a point, the effect of the lowering of temperature counterbalances the effect of the supercooling, the rate of crystallisation ceases to increase as the temperature is lowered, and in fact begins now to decrease. There is, therefore, a certain temperature, a certain degree of supercooling, at which the velocity of crystallisation is a maximum, and below which it becomes less and less; and, ultimately, it becomes practically equal to zero. The supercooled liquid no longer crystallises even when brought into contact with the crystalline solid.

We know, however, that as a liquid is cooled down, it becomes more and more viscous, and at last it becomes so viscous that it does not "run" at all so far as ordinary observation can detect, and so we call it a solid. An *amorphous* solid is just such a supercooled liquid, a liquid cooled so far below its crystallisation point that the rate of crystallisation is infinitely slow. In this way are formed, for example, the glassy lavas, or obsidians, by the rapid cooling of molten lava, as well as ordinary glass with which we are so familiar.

When a supercooled liquid or " glass " is maintained at a temperature in the neighbourhood of the softening point, spontaneous crystallisation may set in, and thereby cause the glass to lose its transparent, vitreous character; the glass, it is said, *devitrifies*. Under certain circumstances, this may prove a source of much annoyance.

Silica and Glass

A substance which affords an excellent illustration of the behaviour which has just been discussed is quartz or silica (an oxide of the element silicon), a substance which is very familiar to everyone. It occurs as the clear, glassy particles which form sea-sand, and which can also be readily distinguished in granite; coloured by certain impurities it forms the well-known ornamental stones, the cairngorm and the amethyst, while in the pure colourless form it is known as rock crystal, which ordinarily crystallises in six-sided prisms ending in six-sided pyramids. It is largely employed for making spectacle glasses and optical instruments.

When this crystalline quartz is heated in the oxyhydrogen blowpipe flame, or in a specially constructed electric furnace, to a temperature of about 1650° C. (3000° F.), it melts to a colourless liquid; and when this liquid is cooled fairly rapidly, the quartz can be obtained as a clear, colourless, glassy mass—a supercooled liquid—which looks just like ordinary glass, but is much more transparent. It is, in fact, the most transparent solid material known. This fused quartz, or quartz glass, possesses the exceedingly valuable property that it expands and contracts only very slightly with alteration of the temperature (its coefficient of expansion is less than one-tenth that of glass), and for this reason it can, unlike ordinary glass, be rapidly heated or rapidly cooled without cracking. It can, for example, be heated red hot and then plunged into cold water, or when cold it can

be suddenly introduced into the blowpipe flame, or a wire enclosed within a tube of quartz glass may be heated to a bright red heat by means of an electric current while the tube is immersed in cold water, and the quartz glass remains in all cases uncracked. By reason of this property, quartz glass, formed into apparatus of various kinds, has come increasingly into use in recent years, more especially in cases where rapid changes of temperature are encountered. Although readily attacked by alkalies, it is very resistant to acids, except hydrofluoric acid. Apart from its scientific and industrial uses, fused silica is now largely used in the manufacture of globes for incandescent gas burners and in electric radiators.

When heated for some time to a temperature of about 1150° C. (2102° F.), a temperature considerably below the point at which it becomes fluid, the glassy quartz passes into crystalline form; it "devitrifies," and can then no longer withstand, as before, sudden changes of temperature.

Unlike fused quartz or silica glass, ordinary glass is not a single substance but a homogeneous mixture of substances. When quartz or silica, which occurs in great abundance as sea-sand, is heated together with soda (sodium carbonate), the silica, being an acid oxide, displaces the carbonic acid from the carbonate and a compound is obtained known as sodium silicate. When this is allowed to cool, it solidifies to a glassy material known as *water-glass*, so called because of its solubility in water. Commercial water-glass is an aqueous solution of sodium silicate with excess of silica dissolved in it, and is used as an adhesive for glass and porcelain, as a preservative for eggs and for numerous other purposes. Its use depends on the fact that it readily forms a gelatinous film on objects. If, instead of heating sand or quartz with soda (or potash) only, one also adds other metal oxides or carbonates, such as lime, or alumina (oxide of aluminium), or oxide of lead, mixtures of silicates are obtained which

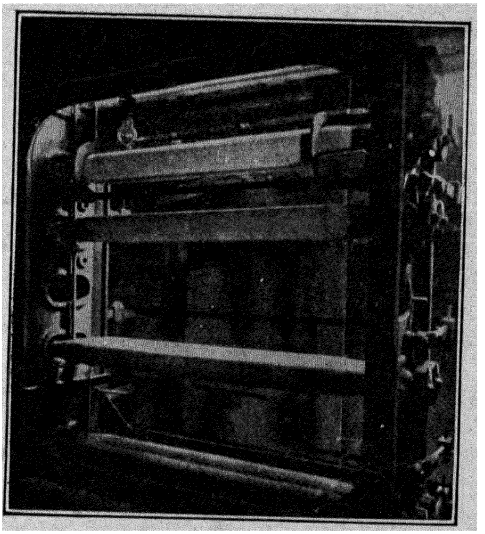
solidify to glasses that do not dissolve in water, and which constitute what one ordinarily calls glass. Glass has, therefore, no definite composition, and by varying not only the constituents but also their relative amounts, glasses of various kinds and possessing very different properties can be prepared. All glasses, however, contain sodium or potassium silicate. Glass for table-ware and for general use consists essentially of a mixture of the silicates of sodium and of calcium, but potassium and aluminium are also frequently present. The quality and appearance of the glass depend largely on the purity of the materials employed in its manufacture. The principal source of the silica is a fine white sand found in various parts of England, but the purer sands of France and of Belgium are also laid under contribution.[1] Such sand, mixed thoroughly with sodium carbonate and sulphate,[2] potassium carbonate, pure white chalk or limestone, and felspar (to supply the aluminium), is melted in large fire-clay pots, placed in furnaces which are now generally heated by means of gas. At first the molten mass is almost opaque owing to the multitude of bubbles of carbon dioxide which permeate it, but these bubbles gradually escape, and a clear liquid is obtained. The desired articles can then be formed either by pouring the molten glass into moulds or by blowing. In the latter case, a quantity of molten glass is taken up on the end of a long metal tube, and by blowing through the tube, hollow articles of varied shape can, by the expert skill of the glass blower, be obtained.

The blowing of electric light bulbs and of bottles, and the production of sheet glass for glazing, etc., are now carried out in automatic or semi-automatic machines; and the introduction of these machines has made necessary various

[1] An abundant deposit of sand at Lochaline on the Sound of Mull, in Scotland, has now been developed for glass manufacture. Its purity exceeds that of the best continental quartz sand imported before 1940 from Belgium, Holland and France.

[2] The addition of sodium sulphate has the effect of strengthening the finished glass.

alterations in the composition of the glass mixture. For the successful working of these machines the molten glass must set or solidify more slowly than the glasses worked by hand. This could be secured by reducing the amount of calcium oxide and increasing the amount of soda, but the resulting glass would then be too readily corroded by water. It was found, however, that if a small amount of magnesia and

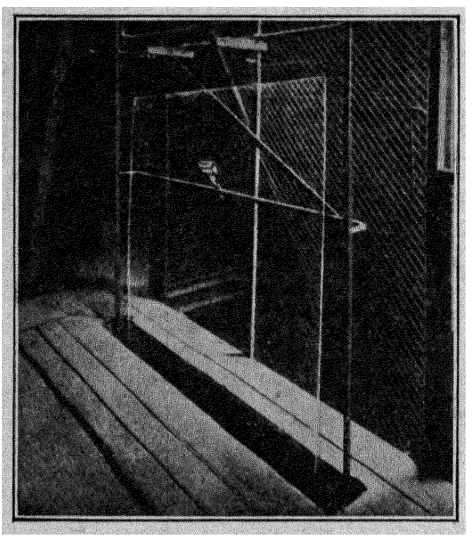


SHEET GLASS, PRODUCED BY THE FOURCAULT PROCESS, PASSING BETWEEN ROLLERS.
(From *Glastechnische Berichte*, 1928.)

alumina was added to the glass mixture, a sufficiently slow setting glass could be obtained which could be worked in the machine without showing devitrification (p. 218) and which was not corroded on exposure to the air. Such a glass has the percentage composition : SiO_2, 72·5 ; Na_2O, 13·5 ; CaO, 10·5 ; MgO, 2·0 ; Al_2O_3, 1·0.

By the process, developed more especially in Belgium by EMILE FOURCAULT, and in America by J. W. COLBURN, sheet glass is produced directly by lowering a metal bar into

the molten glass which is caused to well-up through a slit in a fire-clay plate. As the bar is raised, the glass adheres to it and solidifies, and in this way a sheet of glass is formed. This sheet is drawn slowly upwards between asbestos-covered rollers enclosed in a tall metal box, and is thus slowly cooled. As it passes out at the top of the box it can be cut into lengths as desired. In the Libbey-Owens process



SHEET GLASS, PRODUCED BY THE FOURCAULT PROCESS. GLASS AT TOP OF COOLING CHAMBER READY TO BE CUT.

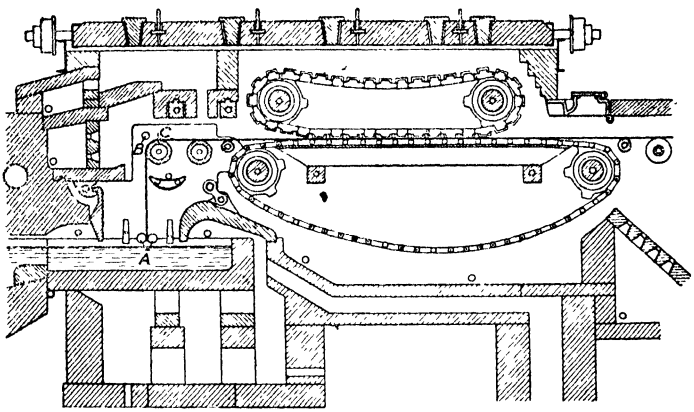
(From *Glastechnische Berichte*, 1928.)

which is now superseding the Fourcault process, the sheet of glass, after rising out of the tank, passes over a roller and is drawn along in a horizontal position (Fig. 17).

The surface of sheet glass is not quite plane, but is covered with slight depressions and ridges, and in consequence of this, objects viewed through such glass are more or less distorted. To get rid of this defect, the sheet glass is ground finish polished, as in the case of plate glass, and in this way

one obtains what is known as " patent plate." Such glass is largely used for the framing of pictures.

Glass articles which have been formed by blowing or moulding must be again heated to near the softening point and then placed in an " annealing " chamber where they can cool very slowly. The purpose of this is to get rid of the stresses which are set up in the rapidly cooled glass and which render the glass very liable to fall to pieces when



Courtesy of Prof. A. Silverman.

FIG. 17.—PRODUCTION OF SHEET GLASS BY THE LIBBEY-OWENS PROCESS.

The sheet of glass which is drawn from the tank of molten glass at point A, passes over the rollers at BC and then passes between moving endless bands.

scratched. This can be illustrated by what are known as Rupert's drops,[1] obtained by dropping molten glass into hot oil, so that the glass is suddenly cooled. This glass is very hard, and can withstand even heavy blows with a hammer, but if the " tail " attached to the drop is broken, or if the glass be scratched with a file, the whole drop falls to a powder.

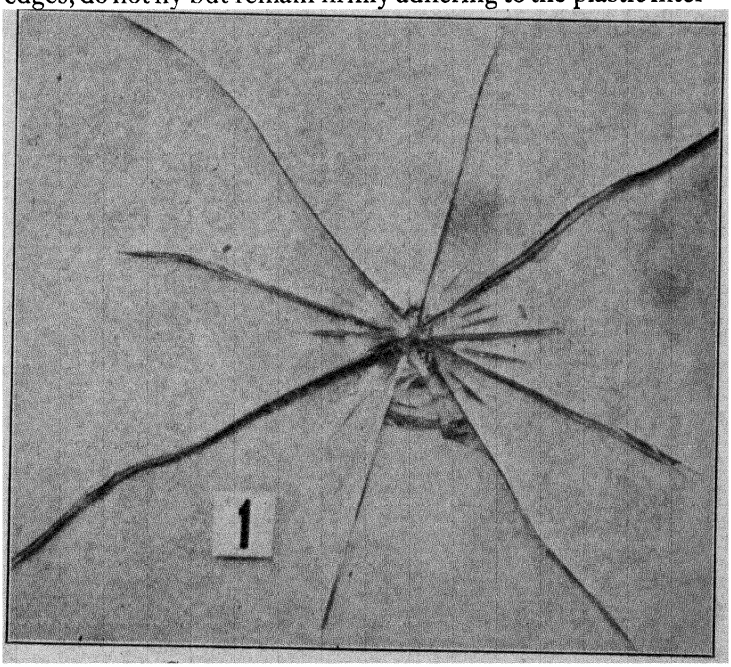
Such hardened or toughened glass, produced by cooling

[1] So called because introduced as a toy by Prince Rupert in the seventeenth century.

the hot glass in oil, appears to have been known at least as early as the first century A.D., as the following incident, related by Petronius in that excellent satire, " Cena Trimalchionis," shows : " There was an artist who made glass vessels so tough and hard that they were no more to be broken than gold and silver ones : It so happen'd that the same person having made a very fine glass mug, fit for no man, as he thought, less than Cæsar himself, he went with his present to the Emperor, and had admittance ; both the gift and the hand of the workman were commended, and the design of the giver accepted. This artist, that he might turn the admiration of the beholders into astonishment, and work himself the more into the Emperor's favour, begged the glass out of Cæsar's hand ; and having received it, threw it with such a force against a paved floor, that the most solid and most firmest metal could not but have received some hurt thereby. Cæsar also was equally amazed and troubled at the action ; but the other took up the mug from the ground, not broken but only a little bulg'd, as if the substance of metal had put on the likeness of glass ; and therewith taking a hammer out of his pocket he hammer'd it as if it had been a brass kettle, and beat out the bruise : and now the fellow thought himself in heaven, in having, as he fancied, gotten the acquaintance of Cæsar, and the admiration of all mankind ; but it fell out quite contrary to his expectation : Cæsar asking him if anyone knew how to make this malleable glass but himself, and he answering in the negative, the Emperor commanded his head to be struck off ; ' For,' said he, ' if this art were once known, gold and silver will be of no more esteem than dirt.' " In such fashion did Nero encourage and foster science.

To obviate the danger of personal hurt by sharp splinters of glass, it is required by law that the windscreens of motor cars shall be made of safety glass. Such safety glass was first produced, under the name of " Triplex Glass," by pressing together, in a hydraulic press heated by hot water, two sheets

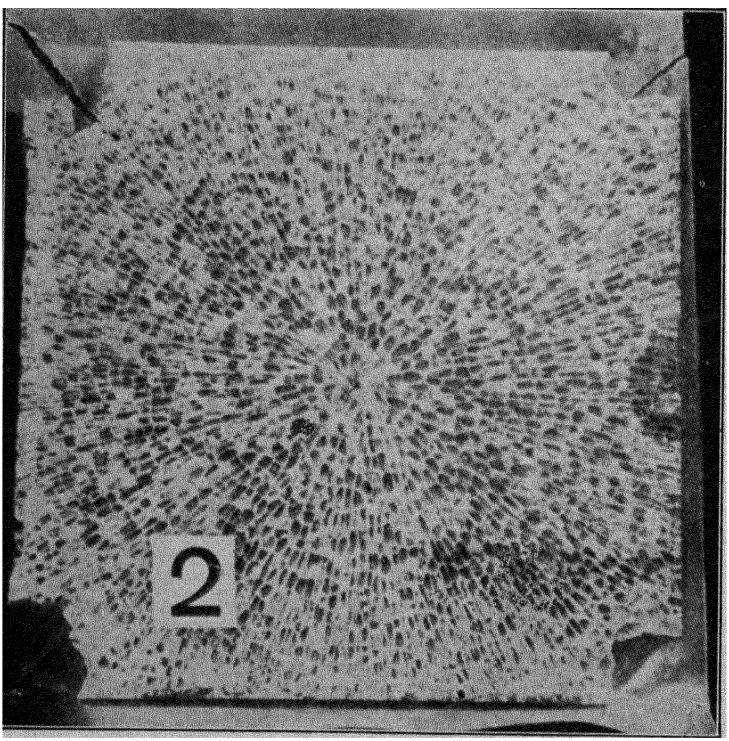
of plate glass with a sheet of transparent celluloid or cellulose acetate between. In England, *vinal*, a polyvinyl plastic (Chap. XVI), is now used as interlayer. When such glass is struck a blow sufficiently hard to shatter it, the broken pieces of glass, often dangerously large and with sharp points or edges, do not fly but remain firmly adhering to the plastic inter-



CRACKING OF ORDINARY PLATE GLASS.

layer. Still more recently, "Armourplate" glass, or "Triplex Toughened" glass, has been introduced, and, in Great Britain, has largely displaced the laminated glass. This is not, in spite of its name, a triplex glass at all, but a single sheet of plate glass which is toughened or hardened, like Rupert's drops, by being heated to the softening point and then cooled rapidly, but in a carefully regulated manner, by

blasts of cold air. By this treatment the glass acquires a much greater strength and flexibility, and a greater resistance not only to breakage by bending but also to fracture by impact. Thus, while untreated plate glass, one quarter of an inch in thickness, was fractured by a weight of 1·68 lb.



CRACKING OF "ARMOURPLATE" GLASS.

falling from a height of 12·7 inches, the toughened "Armourplate" glass was broken only when the same weight was dropped from a height of 122 inches. Moreover, when this toughened glass is broken it does not splinter into dangerously large and sharp pieces which may inflict severe or even fatal wounds, as does ordinary plate glass, but

breaks up into a mass of small and comparatively harmless fragments. Since " Armourplate " glass cannot be cut or chipped without falling to pieces, the plate glass must be cut to shape before being subjected to the hardening process.

In the U.S.A., toughened glass was never widely used, and a laminated " triplex " glass has received official approval. In the production of this " safety glass," a sheet of *butvar*, a polyvinyl butyraldehyde plastic (p. 337), is used as interlayer. The unusual strength and resistance to shock of this glass is shown by the fact that, at the ordinary temperature, it withstands the impact of a steel ball half a pound in weight, dropped from a height of 100 feet.

A reinforced glass, much used for constructional purposes (*e.g.* roofing), can be obtained by embedding in the still molten glass a network of steel or nickel-steel wire.

By a systematic study of the influence of a large number of substances on the properties of glass, hundreds of different glasses have been produced and their physical and optical properties examined. Some of these special optical glasses have proved themselves to be of the highest value and have made possible the construction of apparatus by which scientific knowledge and material well-being have been greatly promoted. Moreover, glasses possessing very different expansibilities with heat have also been produced, and by welding together combinations of these, glasses have been obtained which undergo little change of volume on heating and can withstand even considerable and sudden alterations of temperature without cracking.

Heat-resisting glass with low coefficient of expansion is now widely used for cooking utensils (*e.g.* pyrex ware). Such glass is obtained by reducing the proportion of soda and increasing the proportion of silica, and boric oxide, which greatly reduces the coefficient of expansion of glass, is also added. Thus, pyrex glass contains about 80 per cent. of silica, 12 per cent. of boric oxide, with smaller amounts

(3–4 per cent.) of soda and alumina (aluminium oxide). The value of glass as compared with metal ware for cooking purposes depends on the fact that glass reflects a comparatively very small proportion of the radiant heat which reaches it, so that baking takes place more rapidly in glass than in metal dishes.

To avoid distortion with change of temperature, a glass of the pyrex type, with low coefficient of expansion, has been adopted for the reflector of a large 200-inch telescope which is being constructed for the observatory at Pasadena, California.

By fusing silica with a mixture of potash and red lead (oxide of lead, Pb_3O_4), a lustrous glass with a high refractivity is obtained, and is known as " crystal." When cast in suitable moulds, or, preferably, cut with a wheel and polished, it is much prized for vases and ornamental dishes of different kinds. A still more lustrous glass can be obtained by replacing part of the silica in the crystal glass mixture by boric acid, and so giving rise to what is called generally a borosilicate glass. By reason of its brilliant lustre and high refractive power, such a glass, when suitably cut, sparkles and flashes in a myriad colours. It is, therefore, largely employed under the name of " strass," or " paste," for counterfeiting diamonds, and, when suitably coloured, other gems as well.

The production of coloured or stained glass is easily effected by adding small quantities of suitable substances to the molten mixture of silicates. Thus, addition of iron imparts a green colour to the glass, whereas the addition of manganese oxide colours the glass of an amethyst or purple shade. Salts of the metal uranium give to glass a yellowish green fluorescence, and are much used in the production of fancy glass. With cobalt oxide the colour is deep blue, while with gold, a ruby red is obtained. Paste coloured blue with cobalt, or red with gold, is used to counterfeit the sapphire and the ruby. These counterfeit gems must not be con-

fused with the artificially prepared sapphires and rubies to which reference has already been made (p. 110). They can readily be distinguished from the latter or from the naturally occurring gems by their much greater softness.

In most cases the colour in glass is due to the formation of coloured silicates, silicate of manganese, silicate of cobalt, etc.; but in the case of ruby glass, the colour is due to the presence of gold in what is called the *colloidal state* (Chap. XIII). That is, the gold is present in particles so minute that they are invisible even under a powerful microscope. If, however, too much gold is added, the metal may separate out in visible particles and so render the glass opaque. If one adds selenium to a glass in which the place of lime has been taken by zinc oxide, a highly transparent red glass, much used for signal lamps, tail-lights of automobiles, etc., is obtained.

The transparency of glass, not only for the rays of visible light but also for the invisible rays of longer wave length (infra-red) and of shorter wave length (ultra-violet), can be greatly increased by the use of very highly purified materials. Thus, glass of the " Vita glass " type, which has a considerable degree of transparency to ultra-violet light, must be as free as possible from iron. On the other hand, glass containing a considerable proportion of iron, in what is known as the ferrous state,[1] is used for making goggles to protect the eyes from infra-red rays (heat rays) and ultra-violet rays.

Glasses can also be obtained which are opaque to visible radiations but transparent to ultra-violet rays (*e.g.* Wood's glass, which contains nickel oxide), or to infra-red rays.

Glass is also used in large quantities for the production of mirrors, which are greatly superior to the polished metal mirrors of our forefathers. In order to avoid distortion,

[1] Iron forms two oxides, FeO and Fe_2O_3, known respectively as ferrous oxide and ferric oxide. From these oxides are derived two series of salts, ferrous salts and ferric salts.

plate glass, the surface of which has been polished quite plane and smooth, must be used, and one side of this is "silvered." Formerly, this was effected by coating the glass with an amalgam of tin and mercury, but mercury is a very expensive metal and its use also involves the danger to the workman of mercurial poisoning. For the production of mirrors, therefore, this metal has been superseded by silver, the use of which is not only free from danger, but allows also of a whiter reflecting surface being obtained. By adding caustic soda and ammonia to the solution of a silver salt, *e.g.* silver nitrate, a solution is obtained from which metallic silver can readily be caused to separate out by the addition of certain substances, such as glucose. The surface of the mirror glass, previously well cleaned, is laid on the silver solution, and if the conditions are properly arranged, the silver separates out very slowly and forms a coherent and highly reflecting coating on the surface of the glass. Aluminium, deposited on glass, is now also being used in place of silver for the production of mirrors.

When glass is heated for some time to a temperature just below the softening point, it devitrifies and becomes opaque owing to the crystallisation of the silicates present in the glass.

Soda

The use of carbonate of soda in the manufacture of glass brings that industry into the closest relations with an important series of chemical industries, namely, the manufacture not only of soda itself but also of sulphuric acid, hydrochloric acid, chlorine and bleaching powder.

Sodium carbonate or soda has been known from remotest ages as forming a deposit on the floor and shores of the soda-lakes of Egypt, and this was probably the chief source from which the early Phœnician traders obtained the salt. At the present day, these natural deposits are again being worked (*e.g.* at Lake Magadi in East Africa, and at Owens Lake,

California). Formerly, soda was called " nitre," and by this name it is referred to in the Bible.[1]

Previous to the nineteenth century, the carbonate of soda required, more especially, for the manufacture of glass and of soap, to which we shall refer presently, was obtained mainly from the ash of the saltwort (*Salsola kali* L.). This was grown on large areas reclaimed from the sea along the coast of Spain, and more especially along the coast of Alicante, and was reduced to ash by ignition. This ash, containing up to 15–20 per cent. of sodium carbonate, was sold under the name of *barilla*.[2] The supply, however, was scanty, and barely sufficient to meet the demand. There was, therefore, great need for an abundant source of cheap soda, and the Academy of Paris offered a prize for a process of converting common salt, or chloride of sodium, of which there are such abundant supplies occurring naturally, into the carbonate of sodium or soda. This problem was solved by the French chemist, NICOLAS LEBLANC, and in 1791 a factory for the manufacture of soda by the Leblanc process was established at St. Denis. In 1793, however, this was confiscated by the Committee of Public Safety, and in 1806, filled with despair, the inventor of a process which has contributed so much to the comfort and well-being of the people by giving to them cheap glass and cheap soap, ended his days by his own hand.

Important and successful as was the Leblanc process during the first half and more of the nineteenth century, it had by the end of the century practically succumbed before an economically more successful rival, the so-called ammonia-soda or Solvay process. The reaction underlying this

[1] " As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to an heavy heart " (Proverbs xxv. 20). Soda, when acted on by vinegar (acetic acid), is decomposed with brisk effervescence due to the production of carbonic acid gas.

[2] The barilla industry was introduced into Spain by the Saracens, who called the saltwort, or the ash of saltwort, *al qali* or *al kali*. From this the term alkali is derived. On the salt steppes of the Argentine the saltwort is still grown, and burned for the production of soda.

process, a reaction between sodium chloride and ammonium bicarbonate giving rise to sodium bicarbonate and ammonium chloride, had been placed before the French Academy in competition with the Leblanc process; but the Academy, fearing the loss of ammonia, rejected the process in favour of that proposed by Leblanc. In 1838, DYAR and HEMMING, in England, took out a patent for the working of the ammonia-soda process, but production on an industrial scale was unsuccessful. In 1863, however, after many others had failed, the Belgian chemist, ERNEST SOLVAY, successfully developed the process whereby soda can be produced more economically and in a purer form than by the method of Leblanc. The process depends on the fact that when carbon dioxide is passed into a solution of common salt saturated with ammonia, bicarbonate of soda (*baking soda*) is deposited. By heating the bicarbonate, $NaHCO_3$, carbon dioxide and water are driven off and the ordinary carbonate of soda, Na_2CO_3, is obtained ;[1] and when this is crystallised from water it forms clear, colourless crystals, Na_2CO_3, $10H_2O$, known as *washing soda*. *Bath salts* consist, as a rule, of sodium carbonate, mixed with borax or other salts, tinted and perfumed. *Baking powders* contain the bicarbonate and a solid organic acid, such as citric or tartaric acid or cream of tartar (p. 352). So long as this mixture is kept dry, no action occurs; but when it is brought in contact with water, as in the preparation of dough, the acid reacts with the bicarbonate and carbon dioxide is evolved. The dough is thereby caused to rise.

Although the Leblanc process is no longer used for the manufacture of soda, the first stage of the process, which consists in heating sodium chloride (common salt) with sulphuric acid, is still carried out for the production of hydrochloric acid (muriatic acid or spirit of salt). In this reaction, a knowledge of which goes back to before the seventeenth century, the sodium chloride is converted into

[1] According to the equation : $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.

sodium sulphate or " salt-cake," which is used in the manufacture of glass, and at the same time large quantities of *hydrogen chloride* or hydrochloric acid gas, HCl, are produced. When this gas is passed into water, in which it is exceedingly soluble, the acid, *hydrochloric acid*, is obtained. This is one of the most important of the so-called mineral acids.

Hydrogen chloride, moreover, is a source of the very important substance, *chlorine*; for, when hydrogen chloride mixed with air is passed over heated pumice, impregnated with copper chloride, the copper chloride acts as a catalyst and accelerates the oxidation of the hydrogen chloride by the oxygen of the air, with formation of chlorine—a process known as *Deacon's process*. Chlorine is a gaseous element and a most valuable bleaching and disinfecting agent (*see also* p. 323). It is used in the manufacture of dyes, insecticides, etc. For convenience of transport and use, the chlorine may be passed over slaked lime (p. 245), which reacts with it and gives rise to *bleaching powder*, or chloride of lime as it is popularly called. For this bleaching powder a great demand sprang up in the middle of last century, due to the development not only of the cotton but also of the paper industry, the raw materials for which require to be bleached before use. It is still extensively employed at the present day.

Owing to the development of the electrolytic production of chlorine (p. 262), the Deacon process is becoming of less importance.

Soap

Another very large industry which is dependent on the use of soda is that of soap-making. Even at an early period, about the beginning of the Christian era, a material resembling what is now known as soft soap, and used largely as an ointment, was prepared by boiling fat with potashes; and although in later times the manufacture of soap developed

considerably, it was not till early last century that it passed from being a handicraft carried on by rule of thumb, to an industry controlled by an exact knowledge of the properties of the materials used.

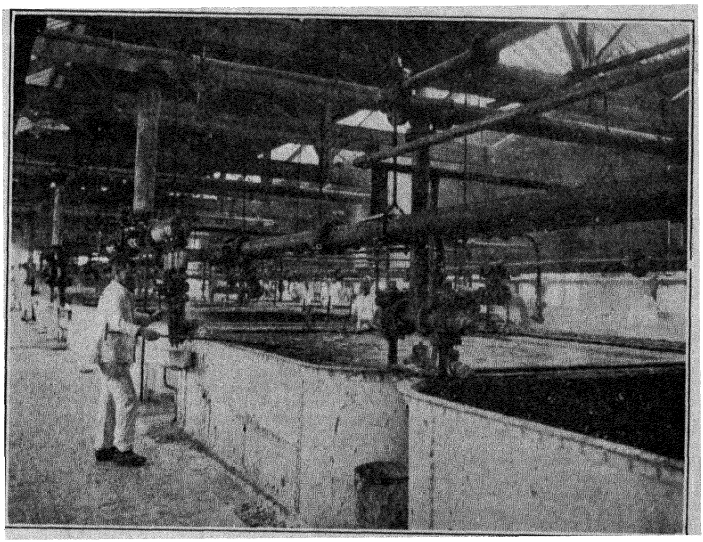
It has already been pointed out that the animal and vegetable fats and oils were shown by the French chemist, Chevreul, to be compounds of glycerine with different acids, which could be obtained by boiling the fats and oils with dilute sulphuric acid, or by treating them with superheated steam. This process of *hydrolysis*, as it is called, or decomposition by water, which is catalytically accelerated by acids, can also be facilitated by caustic soda (sodium hydroxide), or caustic potash (potassium hydroxide), and the acid of the fat or oil then combines with the soda or the potash to form a sodium or potassium salt of the acid. This sodium or potassium salt of the fat or oil acid constitutes soap ; and hence the process of decomposing a fat or oil by means of alkali is known as *saponification.*

Caustic soda (NaOH) and caustic potash (KOH) are obtained by boiling solutions of sodium carbonate or potassium carbonate with slaked lime or calcium hydroxide, $Ca(OH)_2$. Mutual decomposition takes place with formation of sodium or potassium hydroxide and calcium carbonate, and the latter, being insoluble, separates out. Nowadays an electrolytic process (p. 262) in which not only caustic soda or caustic potash is formed, but also chlorine and hydrogen, is assuming ever greater proportions, and may one day largely supersede the method which has just been described.

Although soap can be obtained by using either caustic soda or caustic potash, the nature of the product obtained in the two cases is different, the potash soaps being soft, the soda soaps hard.

The fats and oils used in soap-making are very varied in character. Formerly, animal tallow and olive oil were the chief raw materials employed, but, as has already been

pointed out (p. 191), the increased demand for margarine and other butter substitutes has driven the soap-maker to seek other sources of supply, and a number of different animal and vegetable oils have now been forced into his service. These are either used as such, for the manufacture of soft soap, or are first " hardened " by the catalytic process referred to previously (p. 190), for use in the manufacture of



Courtesy of Lever Brothers, Ltd.

MANUFACTURE OF SOAP.
Pans in which the saponification is carried out.

hard soap. By the admixture of different raw materials in varying proportions, soaps of different kinds and qualities can be obtained; and in the proper blending of the raw materials lies the art of the soap-maker, an art which is now guided by careful scientific investigation.

In the manufacture of soft soap or potash soap, different animal or vegetable oils, *e.g.* linseed oil, cotton-seed oil, soya-bean oil, are boiled with caustic potash. The oils are

thereby decomposed with formation of glycerine and the oil acid, which combines with the potash to form soap. A thick paste is thus obtained which, owing to the presence of glycerine derived from the oil, does not dry up. Additions of water-glass and other " loading " materials are frequently made.

In the manufacture of hard soaps or soda soaps, caustic soda is gradually added to the fat or hardened oil, which is melted and kept stirred by means of steam. After the fat has become saponified, common salt is added, and this causes the paste of soap to separate out as a curdy mass on the surface of the liquid, which contains not only the added salt and excess of alkali and various impurities but also the glycerine of the fat. Although, at one time, this liquid used to be run to waste, it is now subjected to a process of distillation in special vacuum stills in order to recover the *glycerine*, for which there exists a large demand for the manufacture of dynamite and other explosives. It is also used in the manufacture of synthetic resins known as " Glyptals " (*e.g.* glyceryl phthalate), as a humidifying agent in rayon, cellophane and other industries, and as an " anti-freeze " in the radiators of motor cars and in gas meters.

Although glycerine is obtained mainly by the hydrolysis or saponification of fats and vegetable oils, its synthesis from propylene, $CH_2 : CH \cdot CH_3$, one of the gases formed in the cracking of mineral oils (p. 95), promises to become of increasing importance. Under normal conditions, however, it is too costly.

The soap curd, after being boiled up with water to remove impurities, and again " salted out," is hardened by cooling, dried, cut into flakes, mixed with colouring matter or perfumes, and formed into bars. The bars are then cut into lengths and moulded into tablets.

Not infrequently this " genuine soap " is " filled " by the addition of other substances, such as carbonate of soda and water-glass. The soap is thereby hardened, and since the

added salts act as water softeners, its detergent power is increased.

The familiar transparent soaps are obtained by dissolving pure soap in alcohol and then evaporating off the alcohol.

In the case of the cheaper varieties of soap, such as common yellow soap, the fat used is mixed with a quantity of rosin, which also undergoes a process of saponification to form a soap ; and in this way a mixed fat and rosin soap is obtained. This soap is generally cut into bars, as shown in the illustration.

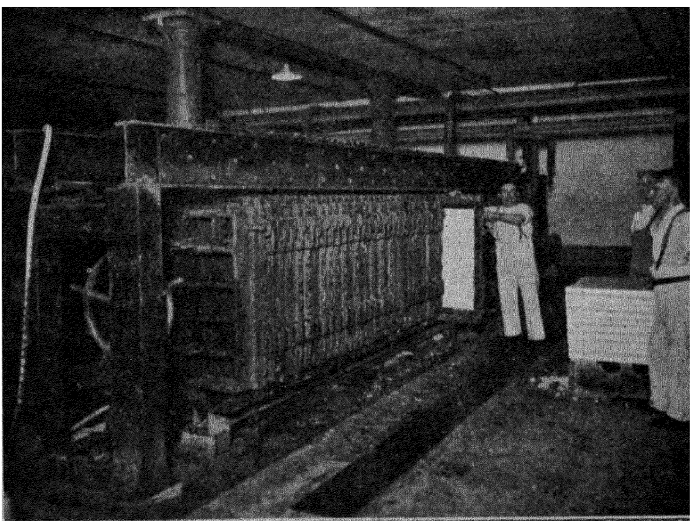
Almost endless is the list of modern commercial soaps now offered for sale for special purposes, in which, with the genuine soap, there are incorporated disinfectants, medicaments of various kinds, scouring materials such as infusorial earth, bleaching materials such as perborates (" persil "), etc.

The cleansing power of soap depends on its physical as well as on its chemical properties ; and in this connection its most important property is that it lowers the *surface tension* of water. What do we mean by this ? Everyone knows that when water is brushed over a greasy surface, it does not form a continuous film wetting the surface, but breaks up into a number of separate drops, for all the world as if each little drop were surrounded by a thin elastic skin ; and the force which keeps the water in the form of a drop is called the surface tension. It is to the action of surface tension that is due the proverbial ease with which water runs off a duck's back. If the surface tension is reduced sufficiently, if, as it were, one reduces the strength of the imaginary elastic skin surrounding the drop, then the water will spread out over the greasy surface and wet it ; and this lowering of the surface tension can be effected by dissolving soap in the water.[1] This property of soap of lowering the surface

[1] The effect described here will be familiar to everyone who has interested himself in water-colour painting. To make the water-colour " take," a little ox-gall is added, when necessary, in order to reduce the surface tension of the water.

Courtesy of Lever Brothers, Ltd.

Soap cut into bars, piled for drying.



Courtesy of Lever Brothers, Ltd.

MANUFACTURE OF SOAP.

Jacobi Rapid Cooling Press in which the liquid soap is cooled in frames clamped between plates round which cold water circulates.

tension of water is an important factor in its cleansing power, because it enables the water to wet and so to come into close contact with even a greasy surface. But there is another property of soap solutions which plays perhaps the most important part of all in the cleansing process. This is the property of emulsifying oils and fats. On shaking up any oil (pure olive oil, paraffin oil, etc.) vigorously with water, it is found that a milky liquid is obtained owing to the oil being broken up into a large number of droplets. But this milky appearance is not permanent; in the course of a few minutes the droplets of oil run together to form larger drops, which then collect as a separate layer on the surface of the water. The milkiness thus disappears. If, however, the oil is shaken not with pure water but with water containing a little soap, the droplets into which the oil breaks up are much smaller (the emulsion appearing, in consequence, much whiter than before), and they do not run together and form a separate layer on standing. The oil is permanently emulsified. And this is what happens when soap is used in cleansing a greasy surface to which dust and other dirt so readily adhere; the film of grease is broken up owing to the emulsifying action of the soap solution, and the grease and dirt are then readily washed away. The removal of dirt is also facilitated in a purely mechanical way by the lather or foam which the soap-water forms, the production of lather being another result of the lowering of the surface tension of water.

In the light of the explanation, just given, of the cleansing power of soap, attempts have been made to produce other detergents very different in chemical nature from an ordinary soap or salt of a fat acid. Thus, by the action of sulphuric acid on higher unsaturated hydrocarbons of the ethylene type (p. 91), containing between ten and eighteen carbon atoms, acids are formed; and the sodium salts of these, placed on the market under various names, such as *Lissapol*, *Teepol*, etc., are found greatly to reduce the surface

tension of water and to have valuable detergent properties. Some of them, *e.g.* sodium lauryl sulphate, find use in shampoo powders. Since these substances do not form insoluble compounds with lime or magnesia, they readily form a lather, and can therefore be advantageously used, even with hard water. They are being increasingly used as substitutes for soap.

Although the salts of the fat acids with sodium and potassium, the ordinary soaps, are soluble in water, the salts with calcium and magnesium are insoluble. Consequently, when soap is brought into water containing salts of calcium or magnesium in solution, the soap is decomposed with production of the insoluble calcium or magnesium salt of the fat acid, which separates out as a scum. Thus—

Soluble soap (sodium stearate, etc.) and Calcium bicarbonate (sulphate, etc.) **give** Sodium bicarbonate (sulphate, etc.) and Insoluble soap (calcium stearate, etc.).

From its " feel " in washing, water containing calcium or magnesium salts is called " hard," and, since the soap is decomposed, no lather can be obtained until sufficient soap has been added to combine with all the calcium and magnesium salts present. Moreover, since the bicarbonate or other salt of sodium which is formed does not lower the surface tension of water and has no power of emulsifying oils, the soap cannot exercise its proper cleansing function until after the removal of the calcium and magnesium salts.

Not only is hard water most wasteful of soap, but it may also be a source of annoyance, both domestic and industrial, owing to the separation out, in hot-water and steam boilers, of the salts of calcium and magnesium (the so-called " fur "), which insulates the kettle or boiler and so causes a loss of heat. Explosions, moreover, may be caused in boiler tubes owing to the " scale " cracking and so allowing water to come in contact with the overheated tubes. It is of importance, therefore, to get rid of or to reduce the hardness.

The formation of " fur " or " scale " may be prevented not only by softening the water, as explained in the following paragraphs, but also by the addition to the water of a small quantity of sodium hexametaphosphate $(NaPO_3)_6$, obtained by fusing the ordinary sodium phosphate, NaH_2PO_4. This hexametaphosphate is produced commercially in the United States under the trade name of " Calgon " and prevents the formation of " fur " by forming with the calcium salts soluble complex phosphates.

When the hardness of water is due to the presence of calcium bicarbonate (formed by the action on limestone, or calcium carbonate, of the carbonic acid gas dissolved in rain water),[1] it can be got rid of by boiling, and is therefore known as *temporary hardness*. On a large scale, the " softening " of the water can be effected by the addition of slaked lime in proper amount (Clark's process). The soluble bicarbonate is thereby converted into the carbonate which, being insoluble, separates out and is removed by filtration : $Ca(HCO_3)_2+Ca(OH)_2=2CaCO_3+2H_2O$.

Hardness which is due to the presence of sulphate of calcium or magnesium cannot be removed by boiling, and is known as *permanent hardness*. It can be got rid of by the addition of carbonate of soda, or " washing soda," the calcium or magnesium being thereby thrown out of solution as insoluble carbonates. Hence the use of washing soda in the laundry.

For industrial and domestic purposes, another process for softening hard water has been introduced, known as the *permutit* process. Permutit is an artificially prepared *zeolite*, sodium aluminium silicate, formed by fusing together quartz, alumina and sodium carbonate. When hard water is filtered through a layer of this material, the calcium and

[1] $CaCO_3+H_2O+CO_2=Ca(HCO_3)_2$
Calcium carbonate. Calcium bicarbonate.
When calcium bicarbonate is heated, it decomposes into calcium carbonate, water and carbon dioxide.

magnesium replace the sodium in the silicate, forming calcium or magnesium aluminium silicate, and are thus removed from the solution. The water is thereby rendered soft. When all the sodium has been replaced, the permutit ceases to be effective, but its activity can be restored by flushing with a solution of common salt (sodium chloride). By this means the sodium aluminium silicate is regenerated.

More recently, great advances in water purification have been made owing to the discovery, in 1935, by chemists working at the National Chemical Laboratory at Teddington, that certain synthetic resins and other products (obtained by treating coal with fuming sulphuric acid) can remove from solution not only calcium and magnesium, but also sodium and other metals (*cations*, p. 256), present in salts, while synthetic resins of another type can remove the acid ions (*anions*, p. 256), such as sulphate and chloride. Thus, by passing water containing, say, calcium, magnesium and sodium salts in solution through resins of the first type, the metal ions are removed and replaced by hydrogen ions, and the effluent contains only free acids. On passing this acid water through resins of the second type, the acids present are removed and replaced by carbonic acid. Water free from dissolved salts is thereby obtained. By passing a current of air through this water, the carbonic acid (CO_2) is removed and the water then resembles distilled water in purity.

The activity of the resins can be restored by treatment with dilute sulphuric acid, in the former case, and with a solution of sodium carbonate, in the latter. By means of these ion-exchange resins, as they are called, industries can now obtain, much more cheaply than by distillation, water equal in purity to distilled water, or, also, water containing any concentration of salts that may be desired (*e.g.* for use as a potable water).

The methods just described for removing dissolved salts from water found, during the war, an application of the highest importance in placing in the hands of airmen,

compelled to " bale out " over the sea, a means of obtaining a potable water from sea-water. For this purpose, a mixed barium and silver zeolite (barium and silver aluminium silicates), containing also a small amount of silver oxide, was employed. When this was shaken up with sea water, the salts were removed by conversion into insoluble barium sulphate, silver chloride, magnesium hydroxide, sodium zeolite, etc., and, by straining through a filtering cloth, a water, almost like distilled water, was obtained. In order to remove from the water any colour imparted to it, by the zeolite, a quantity of charcoal (p. 123) was incorporated in the mixture.

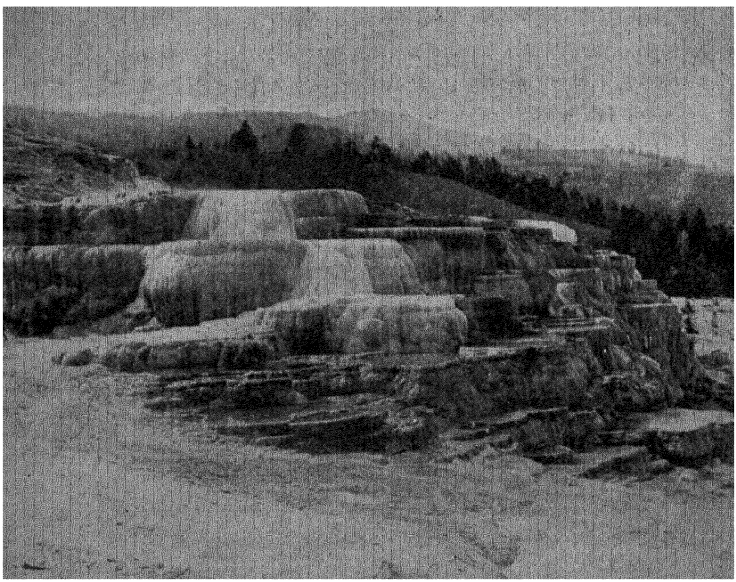
Lime

The solvent action on limestone of water containing carbon dioxide in solution, to which reference has been made, is of great economic and geological importance. Not only is the process mainly responsible for the production of hard water, which is met with in all limestone and chalk districts, but it is the chief agent by which lime is transported through the soil and rendered available for plants.

How great may be the effect of this solvent action of carbonic acid, acting through the ages, is seen from the great limestone caves, like the Mammoth Cave, Kentucky, which have been gradually eaten out of the solid rock by water containing carbonic acid in solution. No sooner, however, are these caves formed than Nature begins to fill them up again, for the rain water, bearing carbonic acid in solution, percolates through the rock and dissolves it. On reaching the roof of the cave the water evaporates and leaves behind a minute grain of limestone ; and as drop follows drop through endless years, grain is added to grain and an icicle-like *stalactite* hangs pendent from the roof. As Shelley has so beautifully written :

> From the curved roof the mountain's frozen tears,
> Like snow or silver or long diamond spires,
> Hang downward, raining forth a doubtful light.

If the drops of water come faster, some may fall to the floor of the cave and, evaporating there, build up a mighty column or *stalagmite*. Many and varied, graceful and grotesque, delicate and massive, are the forms which may thus be produced, and the sight presented by such a cave,



Courtesy of Union Pacific System. *Copyright, J. E. Haynes, St. Paul.*

LIMESTONE TERRACES, MAMMOTH HOT SPRINGS, YELLOWSTONE PARK.

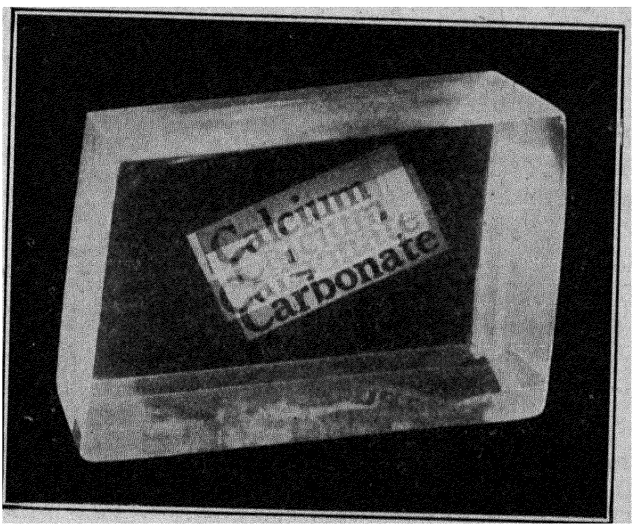
suitably illuminated, is one of the most impressive that can be experienced.

Spring water carrying calcium bicarbonate in solution will deposit calcium carbonate as the carbon dioxide escapes and the water evaporates. In this way there have been and are being formed the great terraced basins of limestone deposited, for example, at Mammoth Hot Springs, Yellowstone Park, U.S.A.

Limestone, or calcium carbonate, when strongly heated,

decomposes into *quicklime* (calcium oxide) and carbon dioxide. This process, which is known as the burning of lime, is carried out on a very large scale in rotary kilns as a step, more especially, in the production of slaked lime and mortar.

When water is poured on quicklime, combination takes



ICELAND SPAR, SHOWING DOUBLE REFRACTION.

place and the quicklime is converted into *slaked lime* (calcium hydroxide). So great is the heat evolved in this process that large volumes of steam are produced, and the water may even be made to boil. In the making of *mortar*, the slaked lime is mixed with a certain amount of sand, in order to prevent too great a contraction taking place when the mortar sets ; and the setting of mortar depends on the fact that on exposure to the air the slaked lime reacts with the carbon dioxide to form a coherent mass of interlocking crystals of calcium carbonate (limestone).

Slaked lime or calcium hydroxide dissolves sparingly in

water, the solution being known as *lime water*. It is used medicinally as a mild alkali.

Calcium carbonate occurs in various forms. *Chalk* and *limestone* have been formed from the shells or skeletons of marine organisms, deposits of which have become compacted under pressure ;[1] and *coral* is built up by the minute coral polyp. *Marble* represents a limestone which has been transformed by heat and pressure into a mass of small crystals. Large transparent crystals of calcium carbonate are also found as *calcite* or *Iceland spar*. This material has the property of double refraction, as it is called, so that an object, printed matter for example, appears double when viewed through a crystal of Iceland spar.

Pearls, also, consist essentially of calcium carbonate deposited, layer on layer, by the oyster on a particle of sand, or other foreign body. Since all carbonates are decomposed by acids, with evolution of carbon dioxide, pearls will be destroyed if allowed to come in contact with acid liquids, *e.g.* vinegar. In this connection one may recall the story told by Plutarch of how Cleopatra, wishing to impress Antony with her wealth and magnificence, wagered that she could spend the equivalent of £150,000 on a single meal. The wager having been accepted, Cleopatra, who was wearing two pearls each equal to half the sum, detached one and dropped it into a cup of vinegar. The pearl quickly disappeared and she then drank the liquid. She was proceeding to do likewise with the second pearl when she was restrained, it being decided that the wager had already been won.

Clay

Among the most important of the naturally occurring minerals are those double silicates of an alkali metal (sodium or potassium) and aluminium which are known as *felspars*. These compounds, present so abundantly in granites, while insoluble in water, are attacked by the atmospheric carbonic

acid and undergo decomposition with formation of alkali carbonate and aluminium silicate; and this aluminium silicate, in a hydrated state and known as *kaolinite*, is the main constituent of kaolin or white china clay. To this material also is mainly due the plastic properties of the common clays in which the kaolinite is mixed with various impurities.

Clay is, in our modern no less than in the ancient civilisations, a material of great importance, and is used for the production not only of building materials but also of porcelain, stoneware and earthenware. This importance it owes mainly to the fact that it forms a plastic mass with water and becomes hard and stone-like when heated to a high temperature. Clay is also used in the manufacture of cement.

In the manufacture of *porcelain* or *china*, pure white clay is mixed with the requisite amount of ground felspar and quartz, known as " frit," and the soft, plastic mass is then formed into the desired shape. On being heated in a kiln to a temperature of about 1200° C. (2192° F.), the clay loses water and passes into an anhydrous silicate, $3Al_2O_3$, $2SiO_2$, and the felspar fuses and dissolves the quartz. A glass is thus formed which binds the mass together and renders it non-porous and non-absorbent of water. The mass also becomes translucent, in proportion to the amount of glassy material present.

In the production of *stoneware*, the fusion of the " frit " is not so complete, so that the body of the ware, although non-porous, is not translucent.

In the manufacture of *earthenware*, the ware is fired at a lower temperature and very little vitreous material is formed. The body of the ware, therefore, is porous. This is known as *bisque* or " biscuit " ware. When pure materials are employed, such earthenware is largely used as table-ware. After the ware has been fired, it is coated with ground felspar, or other fusible silicate, and again heated. A glassy film or glaze is thereby formed on the surface of the ware.

Clay also finds a very important application at the present day for the production of *Portland cement*, a material which owes its name to its resemblance to Portland stone. Clay and limestone (or other form of calcium carbonate) are mixed together so as to give the proper proportions of lime, alumina and silica, and the mixture is then ground to a fine powder and heated in long, rotary kilns to the point of incipient fusion. The partially fused mass, which consists essentially of a mixture of calcium silicate and calcium aluminate ($3CaO, Al_2O_3$), is ground and constitutes the Portland cement of commerce. This has the property of setting even under water.

Concrete, now so largely employed for building purposes and for road making, is a mixture of cement with sand or gravel.

CHAPTER XII

ELECTRICITY AND CHEMISTRY

IN a previous chapter it was sought to point out and to emphasise that a chemical reaction must no longer be considered as involving merely a transformation of material but also a flow of energy; and it was also claimed that one of the chief characteristics of the scientific advance during the past hundred years has been the manner in which and the extent to which the different forms of energy have been transformed and utilised. In our study of the subject of combustion we had a glimpse into that branch of science, thermo-chemistry, which deals with the relations which exist between chemical energy and heat energy; and from the present chapter, it is hoped, the reader will gain some insight into the relationships which obtain between chemical energy and that other form of energy, electrical energy, the utilisation of which is so notable a feature of modern times.

The birth of electro-chemistry, as this twin branch of science which deals with the relations between electricity and chemistry is called, may be dated from the time when, in 1791, the Italian anatomist, LUIGI GALVANI, observed the convulsive twitching of the muscle of a freshly dissected frog, each time the muscle and nerve were connected by two different metals. It was a humble birth, surely, for a science which has revolutionised the world, which has made practicable the telegraph, telephone and " radio," and has supplied mankind with many materials both of ornament and of use.

If it is to Galvani that we owe the observation in which electro-chemistry found its birth, it is to his fellow-countryman, ALESSANDRO VOLTA,[1] Professor of Physics in the

[1] The intimate connection of Volta with electricity is held in remembrance by the use of the term *volt* as the unit of pressure (or *voltage*) of an electric current.

University of Pavia, that the science owes its further development. Rightly interpreting the muscular contraction of the frog's leg as being due to the current of electricity which is produced whenever contact is made between two different metals separated from each other by a liquid conductor, Volta constructed an apparatus whereby a continuous current of electricity could be obtained through the transformation of chemical energy into electrical energy. When a strip of copper and a strip of zinc are partially immersed in a solution of sulphuric acid, Volta found that on connecting the free ends of the metals by means of a conducting wire, a current of electricity is obtained. By connecting a number of such cells together, so that the copper plate of one was joined to the zinc plate of the next, Volta built up a battery—the famous *couronne de tasses*, or crown of cups—with which effects of the most notable character were obtained; and the voltaic cell, as it was called, was the scientific sensation and curiosity of the end of the eighteenth and the beginning of the nineteenth century. Cells of a similar but more efficient character were constructed by others, and the effect of the electric current was tried on a great variety of substances, with the result that, under the guiding genius of Sir HUMPHRY DAVY, the alkali metals, sodium and potassium, were isolated for the first time in 1807, by passing a current of electricity through molten caustic soda and molten caustic potash.

These two metals, *sodium* and *potassium*, which are doubtless unfamiliar to most people, are silvery-white in colour, and very lustrous. When exposed to the air, however, they tarnish immediately, owing to the readiness with which they react with the water vapour in the air. They are soft and of a cheese-like consistency, so that they can be readily cut with a knife. When brought into contact with water they decompose it with great vigour, with production of hydrogen and formation of caustic soda and caustic potash. Such, in fact, is the vigour of the reaction that the hydrogen

which is liberated may become ignited and burn, with a yellow flame in the case of sodium, and a violet flame in the case of potassium. These metals find no application in ordinary life, but are used in considerable quantities in chemical manufactures.

Sodium cyanide, NaCN, which is extensively used in the extraction of gold (p. 154) is produced industrially by passing ammonia over a heated mixture of sodium and carbon :

$$2Na+2C+2NH_3=2NaCN+3H_2.$$

The hydrogen formed in the process can be used in the synthesis of ammonia (p. 207) or for other purposes.

Such was the beginning of man's triumphant success in transforming chemical into electrical and electrical into chemical energy. Important as were the results obtained by the use of the voltaic cells, when regarded from the purely scientific point of view, the cost of working the cells was very considerable, and it was not, therefore, until the introduction of the dynamo (made possible by the scientific researches of Faraday), that the industrial application of electricity became practicable. With the aid of the engineer and by means of the dynamo it has now become possible to obtain a cheap supply of electrical energy, more especially by harnessing the great waterfalls of the world. The *couronne de tasses* of Volta has been replaced by multitudes of humming dynamos ; and in place of the few globules of metallic sodium which Sir Humphry Davy succeeded, with much difficulty, in isolating, that and many other substances are now produced by hundreds and thousands of tons in the electro-chemical factories of the world.

One of the earliest industrial uses to which electricity was put, was to the coating of cheaper with more expensive or more resistant metals, by a process known as *electroplating*, a process which has been widely used from before the middle of last century. At the present day the process is largely applied to the plating of metals not only with silver

and gold, but also with nickel and with chromium, metals which are much used on account of their white colour and power of resisting atmospheric conditions without tarnishing.

In principle the process is comparatively simple, and consists in passing a current of electricity through a solution of a salt of the metal with which the article is to be plated; but in order that we may understand the process better, I

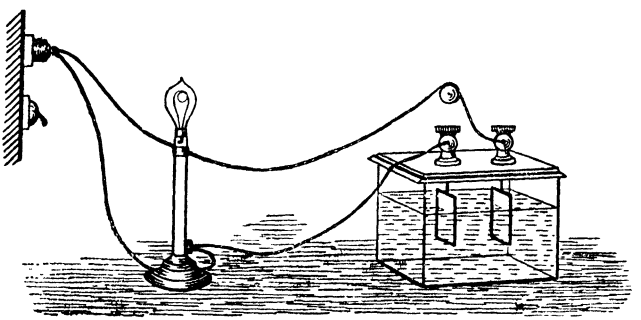


FIG. 18.—CONDUCTIVITY OF SOLUTIONS FOR ELECTRICITY.

would ask the reader to consider with me for a short time what is the nature of the liquids which conduct the electric current.

When one places in a vessel containing pure distilled water the ends of two wires which are connected with an electric-lighting circuit and lamp (Fig. 18), the lamp remains dark. The electrical circuit is broken by the water which is a non-conductor of electricity. If to the water one adds cane sugar, glycerine, or alcohol, the lamp still gives forth no light, for the solutions of these substances do not conduct the electric current. But if one dissolves in the water even a very little common salt, or washing-soda, or hydrochloric acid (spirit of salt as it is frequently called), the lamp at once lights up, showing that the flow of electricity is no longer interrupted by the liquid. In the same way other substances soluble in water may be tested, and it will be found that

substances can be divided into two classes, those that yield solutions which conduct electricity, and those that yield solutions which do not conduct electricity. Substances belonging to the former class are called *electrolytes*, substances belonging to the latter class, *non-electrolytes*. Sugar is a non-electrolyte; salt is an electrolyte. Similarly, all the substances known as *acids*, which have a sour taste and the property of turning red a blue solution of the vegetable colouring matter called litmus, are electrolytes; all the substances, also, known as *alkalies*, which have the opposite property of restoring the blue colour to solutions of litmus which have been reddened by acids, and all the substances known as *salts*, which are formed by the combination of acids and alkalies—all these substances, acids, alkalies and salts, are electrolytes, and yield solutions which conduct the electric current.

When an electric current passes through the solution of an electrolyte, even the most superficial observation will teach us that a liquid conductor differs from a metallic one. In the latter case, no apparent change may take place, but in the former there is a very obvious decomposition of the conducting solution. This process of decomposition by an electric current is known as *electrolysis*. If one dips into a solution of copper sulphate, for example, two bright wires or plates of platinum which are connected to the poles of a battery, the solution of copper sulphate is decomposed and one sees that the surface of one of the *electrodes* (as the portions of the metallic conductor dipping into the solution are called) immediately becomes coated with a bright rose-coloured deposit of copper. This is the process used in electroplating. In the case of solutions of sodium chloride, hydrogen is liberated at one of the electrodes and can be seen rising in bubbles from the electrode. The solution also acquires an alkaline reaction, as is shown by the fact that it turns reddened litmus blue. At the other electrode, chlorine is set free and, dissolving in the water, yields a solution

having bleaching properties, as is shown by the fact that it discharges the colour of a litmus solution. Whenever, therefore, an electric current passes through a conducting solution, there is a movement of electrically charged matter through the liquid—charged particles of copper, or hydrogen, or chlorine, for example—and some of these particles move towards the one electrode, others towards the other electrode.

This conclusion was reached early last century by that great natural philosopher, MICHAEL FARADAY, who called the electrically charged moving particles which thus conveyed the electricity through the solution, by the happily chosen Greek term *ions* (*i.e.* wanderers); and this term is still retained.

During a great part of last century, the conductivity of electrolytes in solution was the subject of much discussion. Faraday, and many others after him, assumed that the molecules of an electrolyte are decomposed *by the electric current* into positively and negatively charged particles—the ions—which then move in opposite directions through the solution. This view was later shown to be incorrect, and in 1886 the Swedish physicist, SVANTE ARRHENIUS, put forward the very revolutionary view that some of the molecules of an electrolyte, when dissolved in water, break up *spontaneously* into ions, and that the fraction of the molecules which undergoes this process of ionisation increases as the solution is made more and more dilute. Thus, the molecules of common salt, or sodium chloride, for example, were supposed to break up in solution into positively charged sodium atoms or sodium ions, Na^+, and negatively charged chloride ions, Cl^-; and these ions were regarded as leading a free and independent existence in the solution, each exhibiting its own properties and showing its own chemical reactions. This *theory of electrolytic dissociation*, as it was called, proved to be, in many respects, exceedingly satisfactory, and was very generally accepted.

In one important respect, however, the theory of Arrhenius,

when applied to solutions of salts, was found to be defective. It has already been pointed out (p. 39) that the molecule of sodium chloride is formed by the electrostatic attraction between a sodium atom which has acquired a positive charge through the loss of an electron and a chlorine atom which has become negatively charged through taking up this electron. In the molecule of sodium chloride, therefore, the sodium and chlorine are already present as electrically charged particles, *i.e.* as *ions*. Solution of salt in water, therefore, does not, as Arrhenius thought, bring about the formation of ions ; solution merely brings about a diminution of the force of attraction between the electrically charged sodium and chlorine atoms (ions), and makes it possible for them to move about freely in the solution. A similar freedom of movement is made possible by melting the salt, and fused sodium chloride or fused sodium hydroxide is also found to conduct the electric current (p. 250), owing to the presence of ions.

As in the case of sodium chloride, so also in the case of other salts, the ions are pre-existent in the molecules, and solution in water merely makes freedom of movement possible.

The same explanation is valid also in the case of the metal hydroxides, such as sodium or potassium hydroxide. These all contain the hydroxide ion, OH^-, and solutions of these hydroxides, therefore, all contain this ion. It is, in fact, to the presence of these ions in solution that the general properties of alkalies are due.

The theory of Arrhenius, however, applies to acids, such as hydrochloric acid, which do not conduct the electric current in the liquid state. Ion formation takes place only on solution, and one may assume the occurrence of a reaction such as $HCl+H_2O=H_3O^+ + Cl^-$, the ion H_3O^+ being a hydrated hydrogen ion $H^+.H_2O$. All acids in solution give rise to this ion, and the so-called acid properties of a solution are really due to the presence of hydrogen ion.

In the light of what has just been stated, the fact that the solution of a salt, an acid or an alkali in water conducts the electric current, becomes readily intelligible. These solutions contain free, positively charged *cations* (hydrogen or metal ion), and free, negatively charged *anions* (hydroxide ion, OH^-, or acid ion, Cl^-, NO_3^-, etc.). When, therefore, two electrodes are placed in the solution of an electrolyte and connected with an electric battery, the positively charged electrode (the *anode*) attracts the negatively charged ions, the anions; and the negatively charged electrode (the *cathode*) attracts the positively charged ions, the cations. These anions and cations move in opposite directions through the solution, and give up their charges at the electrodes; they transport or convey the electricity through the solution, and it is this movement or procession of electrically charged particles that constitutes what is called the electric current in the solution.

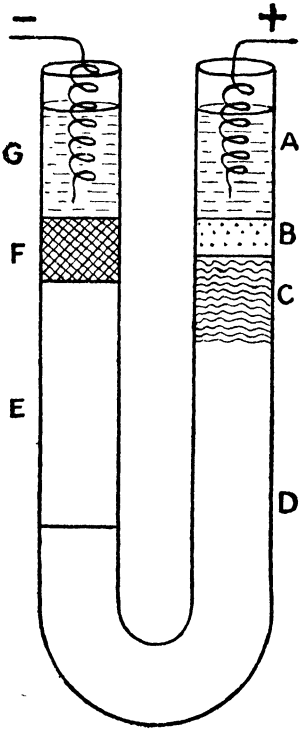


FIG. 19.—MIGRATION OF IONS.

This explanation of the passage of a current through a solution is not a mere speculation, not a mere phantasy, for it is easy to demonstrate not only that there is a movement of the ions through the solution, but also that the ions move with different velocities. There is a pretty experiment by which one can make this clear. Into the bend of a tube bent into the form of the letter U (Fig. 19) is poured a solution of potassium chloride to which sufficient gelatin has been

added to make the liquid set to a jelly; and the solution is also coloured red by the addition of a substance called phenolphthalein and a drop or two of alkali. (Phenolphthalein is a colourless substance which yields a deep-red colour with alkalies, or solutions containing hydroxide ions; and the red colour is again destroyed by addition of acids, or solutions containing hydrogen ions.) After the solution in the bend of the tube has set, a further quantity of the same coloured solution is poured into one limb of the tube (D), while into the other limb (E) is poured the same solution after it has been decolorised by the addition of the requisite amount of acid.

Above this colourless layer of gelatin is placed a quantity of a mixed solution of caustic potash (potassium hydroxide) and potassium chloride (G), while in the other limb of the tube is placed a mixed solution of hydrochloric acid and copper chloride (A). An electric current is now passed through the solutions in the tube, by placing a platinum wire connected with the positive pole of a battery in the solution of hydrochloric acid and copper chloride; and a platinum wire connected with the negative pole of the battery in the solution of caustic potash and potassium chloride. After the current has passed for some time it is found that the hydrogen ions (from the hydrochloric acid), moving from the positive towards the negative electrode, have decolorised the reddened phenolphthalein, and have produced, therefore, a colourless band (C) of a certain depth. The blue-coloured copper ions (from the copper chloride), which move in the same direction as the hydrogen ions but with a slower speed, follow on into the colourless band produced by the hydrogen ions, and give a blue colour to the gelatin (B). In the other limb of the tube, the hydroxide ions (from the caustic potash), moving from the negative to the positive electrode, pass into the colourless gelatin and produce with the phenolphthalein there a band of red (F). This band is deeper than the blue band produced by the

copper ions, but not so deep as the colourless band produced by the hydrogen ions, from which one concludes that the hydrogen ions move faster than the hydroxide ions, and the latter faster than the copper ions.

As has been pointed out, it is not only when in a state of solution that a salt conducts the electric current ; it conducts also when fused, or converted into the liquid state by heat. This fact, as we shall see presently, is of the greatest importance for the practical applications of electricity to preparative chemistry.

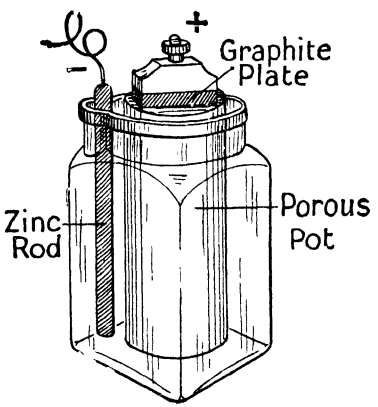


FIG. 20.—LECLANCHÉ CELL.

Not only does the theory of ionisation afford an explanation of the process of electrolysis, whereby electrical energy is transformed into chemical energy, or the potential energy of chemically reactive substances, but it helps us also to understand the reverse process of the transformation of chemical energy into electrical energy, as it occurs in the different voltaic cells.

One of the best known cells, widely used for working telephones and electric bells, is the Leclanché cell (Fig. 20). This very simple cell consists of a jar containing a solution of sal-ammoniac (ammonium chloride), in which are immersed a plate of graphite packed in a porous pot with granules of graphite and black oxide of manganese (manganese dioxide), and a zinc rod. The porous pot also contains a solution of sal-ammoniac. When the cell is in use, zinc readily gives up electrons (negative charges of electricity) and passes into solution as positively charged zinc ions. The electrons given up by the zinc atoms pass through the metallic conductor to the graphite

plate where they neutralise the positive charge on the ammonium ions (NH_4^+) formed by the ionisation of ammonium chloride, and so give rise to the uncharged group of atoms, ammonium (NH_4). This group cannot exist as such and immediately reacts with the water (just as sodium does), with production of ammonium hydroxide (NH_4OH) and hydrogen. This hydrogen, however, is oxidised to water by the oxide of manganese, and so is prevented from forming a non-conducting layer on the electrode, and thereby stopping the current. The electrode is thereby "depolarised" as it is said. When the cell becomes exhausted, its activity can be renewed by replacing the spent liquid by a fresh solution of ammonium chloride. The Leclanché cell has an electro-motive force of 1·5 volt.

The Leclanché type of cell has, in recent years, passed into very widespread use owing to its modification to form the common dry cell. In this cell there is a zinc container which also acts as the negative pole of the cell, and inside this is placed the graphite plate or rod with its depolarising packing. The latter is separated from the zinc container by a layer of paper which, like the whole contents of the cell, is soaked with a solution of sal-ammoniac (Fig. 21). Such dry cells are now in use for flash-light lamps, bells, telephones, radio-batteries, etc.

Although, as has been said, the much more efficient dynamo has superseded the voltaic cell as a source of electricity for industrial purposes, there is one cell which occupies an important place as an auxiliary to the dynamo. This is the lead accumulator, or storage cell. This cell consists of plates of lead and of brown oxide of lead, lead dioxide as it is called, immersed in a solution of sulphuric acid of specific gravity about 1·30. On joining these two plates by means of a conductor, a current of electricity flows through the conductor from the lead dioxide plate to the lead plate. The chemical reaction which yields the energy which

is transformed into electricity, is the conversion of the lead and lead dioxide into lead sulphate : $Pb+PbO_2+2H_2SO_4=2PbSO_4+2H_2O$. When this change has taken place, no more electricity is given out ; the cell is " run down " or " discharged." But this cell has the great advantage that it can be readily brought back to its former condition, can be readily recharged, by sending a current of electricity—obtained, say, from a dynamo—through the cell in the opposite direction to that of the current which the cell itself gives. In the process of charging, the lead sulphate is converted to lead at the negative pole, and to lead dioxide at the positive pole. In this way, electrical energy is converted into potential, chemical energy ; and in this form the energy is stored, and is available for use just when and where it is required.

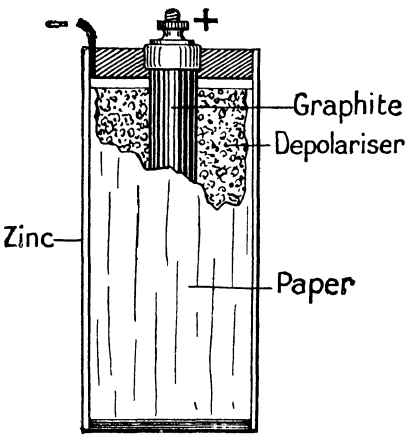


FIG. 21.—DRY CELL.

The process of charge and discharge can be followed by means of a *hydrometer* which enables the specific gravity of the acid to be determined. When the cell is being discharged, sulphuric acid is used up to form lead sulphate, and the specific gravity of the solution falls ; but when the cell is being charged, sulphuric acid is returned to the solution and the specific gravity increases. In the fully charged cell the specific gravity should be about 1·30 ; when the cell is discharged, the specific gravity falls to 1·15.

The lead storage cell is one which has now a multitude of uses, such as giving current for electric lighting on a large scale (as an auxiliary to the dynamo), or in portable hand-lamps ; for energising the self-starters of motor cars ; for

use in portable " wireless " sets ; and in many other cases where a readily transported supply of energy is desired.

Another storage cell, possessing a number of advantages over the ordinary lead accumulator, is the nickel-iron cell which is sometimes known as the Edison cell. In this cell the active mass of the positive plates consists essentially of nickelic hydroxide, $Ni(OH)_3$, or nickelic oxide, Ni_2O_3, in a hydrated form, and this is mixed with powdered graphite to give increased conductivity. The active mass of the negative plates is finely divided iron. The electrolyte is a solution of potassium hydroxide of specific gravity 1·190. The active materials are contained in pockets in the nickelled steel plates and are formed under a pressure of 200 tons.

When this cell is yielding current, the nickelic oxide on the positive plate is reduced to the lower oxide, nickelous oxide (NiO), in a hydrated form, or to nickelous hydroxide, $Ni(OH)_2$; and the iron on the negative plate is oxidised to the oxide (FeO), or hydroxide, $Fe(OH)_2$. The chemical change which takes place, therefore, may be represented by the equation : $Fe+2Ni(OH)_3=Fe(OH)_2+2Ni(OH)_2$. The charged cell has a voltage of 1·35 volts.

When the cell has become discharged, it can be recharged by passing a current through the cell in a direction opposite to that of the current given by the cell. Thereby, the nickelous hydroxide is oxidised to nickelic hydroxide, and the iron hydroxide is reduced to metallic iron.

The nickel-iron accumulator has a lighter weight and greater robustness than the lead accumulator, and it does not undergo deterioration, as the lead accumulator does, when left in a discharged state. It is, in fact, much less liable to damage by careless treatment, and has a longer life.

The nickel-cadmium cell is similar to the one just described. Its electromotive force is 1·25 volts.

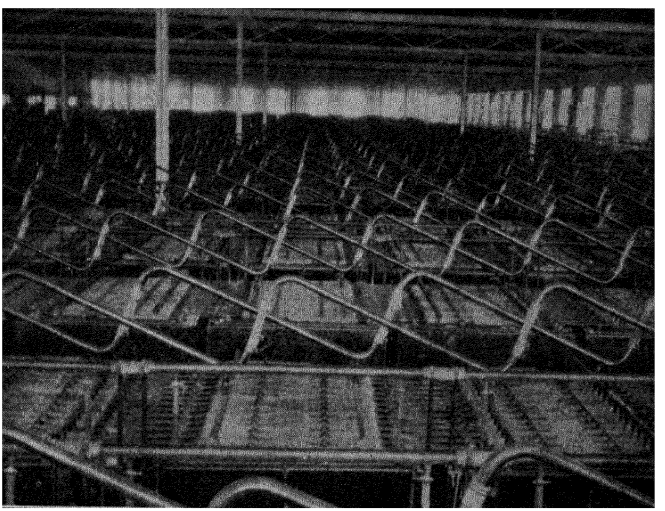
The application of electricity to chemical manufactures has produced an industrial revolution. Not only have electro-

chemical processes more or less completely displaced the older chemical methods employed for the manufacture of such substances as caustic soda and of chlorine, or for the isolation of such metals as sodium, potassium, calcium, magnesium and aluminium, but they have made possible also the discovery and economic production of many new substances of great value. One of the earliest applications of electricity, we have seen, was to the electroplating of metals by a process of electrolysis. By this process metals can be obtained in a state of great purity, and the method is now used for the refining of certain metals, more especially of copper. The crude copper, obtained by smelting its ores, contains a number of impurities, among which are silver and gold, sometimes in not inconsiderable quantities. This crude copper, cast into plates, is made the anode in a bath of copper sulphate solution, while a thin plate of pure copper is made the cathode. When the electric current is passed, copper is deposited in a pure state on the cathode, from which it can afterwards be readily stripped, whereas the copper of the anode passes into solution by combining with the sulphate ions which are discharged at the anode. Some of the impurities present in the copper may also dissolve and accumulate in the solution ; other impurities, however, such as silver and gold, do not dissolve, but fall to the bottom of the bath as a slime or mud, known as the " anode mud," from which the valuable metals are extracted by suitable methods.

By this simple process, the purest commercial copper, so-called " electrolytic copper," is obtained, and is used mainly for electrical purposes. The importance of pure copper in this connection is due to the fact that the conductivity of copper for electricity is greatly diminished even by small amounts of impurity.

The electrolytic preparation of sodium hydroxide or caustic soda and of chlorine, to which reference has already been made (p. 234), depends on the electrolysis of a solution

of sodium chloride or common salt. When a pure caustic soda is desired, the electrolysis is carried out in a large covered-in tank filled with a solution of sodium chloride into which dip graphite electrodes. These serve as anodes. At these electrodes, when the cell is in action, chlorine is evolved and passes away through a pipe in the roof of the



Courtesy of The International Electrolytic Plant Co.

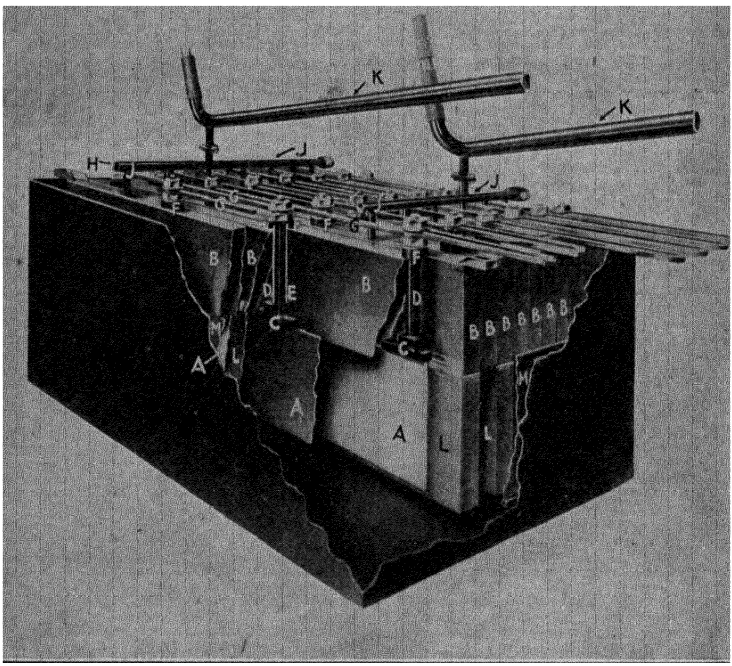
PRODUCTION OF HYDROGEN AND OXYGEN BY ELECTROLYSIS.

tank. Along the floor of the cell mercury is allowed to flow in a slowly moving stream. This forms the cathode, and the sodium which is here set free dissolves in the mercury. The solution of sodium in mercury flows out at the end of the tank and is treated with pure water. The sodium reacts with the water, giving rise to hydrogen and a solution of caustic soda, and the mercury is passed through the cell again.

When the electrolysis is carried out mainly for the production of chlorine, other types of cell are frequently used.

Solid caustic soda is obtained from the solution by

evaporating off the water. It forms a white very hygroscopic solid which undergoes deliquescence or becomes moist when exposed to the air. It is readily soluble in water, and the solution has the soapy feeling characteristic of alkalies.



KNOWLES' CELL FOR THE ELECTROLYTIC PRODUCTION OF HYDROGEN AND OXYGEN.

The electrodes, A, are separated by diaphragms of asbestos cloth, L, and are surmounted by metal boxes, B, in which the gases collect. From these boxes the gases pass by the pipes, J, to the off-take pipes, K.

Large quantities of caustic soda are used in the manufacture of soap.

For the chlorine which is produced in the above electrolytic process, there has developed an ever-widening range of application, both for bleaching and as a reagent in chemical

industry. Owing to its very powerful germicidal action, chlorine is now very widely used for the sterilisation of the water supply of towns, as well as for the sterilisation of the water of public swimming pools, etc.

In the electrolysis of solutions of sodium chloride for the production of sodium hydroxide, the hydrogen which is produced must be considered as a by-product and is sometimes neglected. To an increasing extent, however, the hydrogen and chlorine are now caused to combine together—hydrogen burns in chlorine—so as to form hydrogen chloride. On dissolving this gas in water, a pure hydrochloric acid is obtained.

The electrolytic process is also extensively used for the production, on a large scale, of pure hydrogen and oxygen. In this case, a solution of caustic soda is generally employed as the electrolyte. When the current is passed through the solution, hydrogen is liberated at the cathode, and oxygen is liberated at the anode.

It has already been pointed out that electrolysis may be applied not only to substances dissolved in liquids but also to substances in the fused state, as in the production of the metals sodium and potassium. One of the most important examples of this is found in the electrolytic production of the metal *aluminium*. This is the most abundant of all the metallic elements in the world, but it occurs naturally only in the form of compounds, in combination with other elements. So difficult is it to isolate the metal from its compounds by purely chemical methods, that it was not till 1845 that the metal was obtained in the compact form. And it was then merely a chemical curiosity; for any general or industrial application its cost was prohibitive. It is, in fact, only since 1886 that it has become possible, by the application of an electrolytic method, to produce the metal at a reasonable price. The isolation of the metal is effected by the electrolysis of a solution of purified bauxite or oxide of aluminium in molten cryolite (a naturally occurring com-

pound of aluminium with fluorine and sodium, mainly obtained from Greenland), and the entire world's production of the metal is now obtained by this means. For the electrolysis, an iron bath, lined with graphite, is used, and this forms the cathode, while large graphite rods dipping into the molten mixture form the anode. As the current of electricity passes through the molten mass, aluminium separates out at the cathode and collects in the liquid form at the bottom of the bath, whence it can be run off from time to time. At the anode, the oxygen which is liberated combines with the carbon electrode, producing the poisonous gas carbon monoxide, which may either escape as such or burn to form carbon dioxide.

Aluminium now occupies a permanent and ever-growing place in our modern life. Not only is it largely employed for articles of ornament and of domestic use where lightness and portability are of importance,[1] but it is also used as a conductor of electricity, and, as we have seen, for the production, by the thermit process, of high temperatures and for the isolation of certain metals. Moreover, some of the defects which militated against a more widespread use of the metal, its low tensile strength and softness for example, can be removed to a large extent by admixture with other metals, some of the alloys formed possessing properties of great value. With copper, aluminium yields a bronze, *aluminium bronze*, of great hardness and high tensile strength; and when added to brass, aluminium greatly increases the tenacity of that alloy. With the metal magnesium, aluminium forms a valuable alloy called *magnalium* (containing from 1 to 2 per cent. of magnesium), which is even lighter than aluminium itself and is equal to brass in strength; and the construction of aeroplanes has been revolutionised by the discovery of the alloy *duralumin*, an alloy of aluminium with copper (4 per cent.), magnesium (0·5 per cent.), and manganese (0·5 per cent.). This alloy, while having a tensile

[1] The specific gravity of aluminium is only 2·7, that of steel about 7·8.

stress equal to or greater than steel, has only one-third of its weight.

The metal *magnesium*, to which reference has just been made, is a grey-coloured metal which burns with a very bright and photographically active light. Hitherto, it had been generally known through its use in the preparation of " flash-light " powders, or in the form of ribbon for use in photography. In recent years, however, magnesium has come into rapidly expanding use as an industrial metal, the lightest of all the industrial metals, with a specific gravity of only 1·74. Its main use now is for the production of " ultra light " alloys, containing 90 per cent. or more of magnesium, as structural materials in aircraft and other vehicles and for castings of various kinds. It is also used in the upper structures of ships.

By alloying magnesium with other metals, especially aluminium and zinc, together sometimes with small amounts of manganese or other metals, increased mechanical strength is obtained.

The metal occurs in nature only in the form of compounds. Magnesium chloride, combined with potassium chloride to form the mineral *carnallite*, occurs in the great salt deposits near Stassfurt, and the metal is obtained by the electrolysis of fused carnallite or of magnesium chloride to which potassium chloride is added in order to lower the temperature of fusion.

Magnesium occurs also as the carbonate, known as *magnesite*, in various countries of the world ; and the double carbonate of magnesium and calcium, known as *dolomite*, is abundant and widespread. From these carbonates, the oxide, *magnesia*, can be obtained by calcination ; and processes have been devised for obtaining the metal by the reduction of the oxide by means of various reducing agents, such as calcium carbide, aluminium and silicon. Salts of magnesium occur in very dilute solution in sea-water, and from this the hydroxide is being successfully produced both

in Great Britain and in the United States, by precipitation with slaked lime.

From the everyday use of electricity for heating and lighting purposes, all are familiar with the fact that heat is produced by the passage of electricity through a conductor which offers a certain amount of resistance to the current; and by increasing the strength of the current, the temperature may be raised to any point we please, limited only by the melting or vaporising of the conducting material. We have already

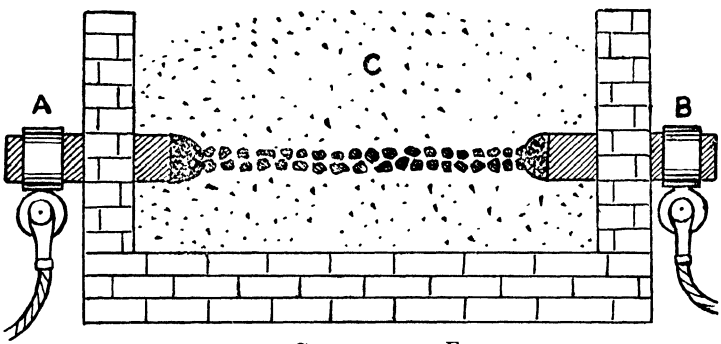


FIG. 22.—CARBORUNDUM FURNACE.

A core of granular graphite is raised to a white heat by a powerful current of electricity which passes between the graphite terminals A and B. At the high temperature which is thereby produced, the carbon and sand of the surrounding mixture, C, react with formation of carborundum.

seen, also, that by means of the electric arc, electrical energy is transformed into heat energy, and that the very high temperature of about 3000° C. (5432° F.) can in that way be obtained. A most powerful instrument has, therefore, been put into the hands of the chemist, and by its means he has been enabled not only to advance to a fuller knowledge of substances and materials already known, but also to prepare others which were hitherto unknown.

Of the utility of electricity applied to the production of high temperatures, we have already had some examples in the direct combination of atmospheric nitrogen and

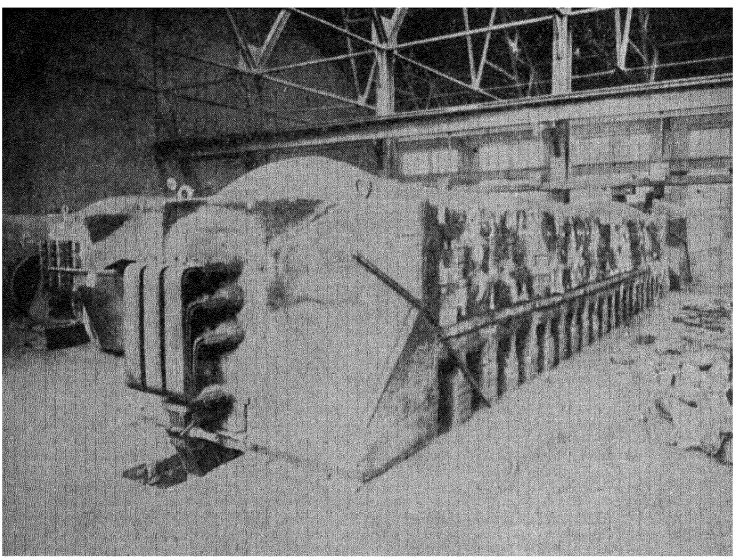
oxygen, and in the manufacture of calcium carbide. Fused quartz or silica glass, with the valuable properties of which we have become acquainted, is also produced by the fusion of quartz sand in specially constructed, electrically heated furnaces; and the high temperatures which can now be produced economically by means of electricity are made use of in the preparation of the substance phosphorus from a mixture of calcium phosphate, quartz sand (silica) and coke (carbon).

As a direct result of the successful application of electricity to the production of high temperatures, we owe the very valuable material known as *carborundum*, a compound of carbon and silicon, discovered by the American chemist, EDWARD G. ACHESON, in 1891. By heating a mixture of coke (carbon) and sand (oxide of silicon) to a high temperature in an electric furnace (Fig. 22), oxygen is removed by the carbon from its combination with silicon, and the latter then combines with the excess carbon to form the crystalline substance, carborundum, the hardness of which approaches that of the diamond. This material is now produced in large quantities and used as a grinding or abrasive material, as well as for incorporating in the surface layer of concrete pavements, stairs, etc. By reason of its very refractory character (it will withstand a temperature of 2200° C., or 4000° F., without undergoing change), it is also used for the protection of furnace walls, and for other heat-resisting purposes.

Another very valuable abrasive and refractory material, of which mention may be made, is *alundum* (alumina or aluminium oxide), obtained by fusing purified bauxite in an electric furnace.

From the manufacture of carborundum there resulted still another discovery of much importance, the discovery, by Dr. Acheson, of a method of making *artificial graphite*. Until 1896, graphite, a crystalline form of carbon familiar under the names of plumbago and black lead (although

it contains no lead at all), was known only as a naturally occurring mineral (p. 120). During the process of manufacture of carborundum, however, it was found that the ends of the rods of gas carbon (a very dense amorphous variety of carbon formed in gas retorts), by which the electric



Courtesy of Acheson Graphite Corporation.

GRAPHITE FURNACE IN ACTION.

current was carried into the furnace, were converted, by the high temperature to which they were exposed, into graphite ; and, moreover, carborundum itself, when heated to a sufficiently high temperature, decomposes with production of graphite. In this way there was initiated a new industry, the manufacture of artificial graphite, which has undergone a great development in recent years.

For the production of Acheson graphite, amorphous carbon (anthracite coal, coke, etc.), mixed with a small

amount of oxide of iron, alumina, or silica, is heated to a high temperature, about 3000° C., in an electric furnace of the same type as the carborundum furnace. At this high temperature the iron, alumina, or silica which was added, is converted into vapour, and the amorphous carbon passes into graphite. The silica and metal oxides added to the coke act as catalysts and accelerate the conversion of amorphous carbon into crystalline graphite; in their absence the change takes place only with difficulty. The graphite so obtained is superior to the natural mineral by reason of its greater purity and uniformity.

To obtain graphite rods, plates, etc., finely-ground anthracite, to which a small quantity of oxide of iron is added, is mixed into a thick paste with pitch or tar. After this paste has been moulded under high pressure it is heated in the electric furnace, and the amorphous carbon thereby converted into graphite.

Someone has said, "Nature's storehouse is man's benefactor, and no gift from it renders greater service than the waters of the earth"; and in the recent developments of electro-chemistry we have seen how Nature's gift has proved of service to man. Although the harnessing of the great rivers and waterfalls of the world is due to the engineer, and was made possible only by the advances in mechanical and electrical engineering of last century, the *utilisation* of the enormous amounts of energy contained in the flowing waters of the earth, the rendering available of which represents so much real gain, so much real progress for the benefit of mankind, is due chiefly to the labours of the chemist. The combined achievement is one that may well fill the mind with wonder; and even the most careless tourist cannot but be profoundly impressed if, after gazing, shall we say, on the majestic down-leaping of the mighty waters of Niagara, he passes into the power stations near by, where the turbines and humming dynamos, working in obedience to the will of

man, without the smoke and dirt and clatter of the ordinary factory, are transforming the energy of the rushing river into the energy of electricity which, in the adjacent factories, is then made to contribute to the material well-being of man and the advance of civilisation.

CHAPTER XIII

THE COLLOIDAL STATE

WHEN one brings sugar, salt, washing-soda and many other common and familiar substances into contact with water, the solid substance, if present in not too large amount, disappears ; it *dissolves*, and a clear liquid is obtained which is called a *solution*. A solution, however, must not be regarded as a compound of the dissolved substance, or *solute*, and the solvent, for the composition of a solution may be varied, whereas the composition of a compound is definite and constant. A solution, rather, is to be regarded merely as a *homogeneous mixture* in which the molecules of the solute, combined it may be with a limited number of solvent molecules, are uniformly distributed throughout and among the molecules of the water, or other liquid, which acts as a solvent. It is a homogeneous mixture of variable composition.

Whatever the nature of the solution process may be, one of the most remarkable facts established by the modern investigation of solutions is the very close analogy which exists between a substance in solution and a gas, an analogy which is illustrated by the property more especially of *diffusion*.

To account for the properties of gases there was developed, about the middle of last century, a theory known as the *kinetic theory of gases*, which was based on the hypothesis that the molecules of a gas are in perpetual and rapid motion, darting about in straight lines with the speed of something like a mile a second, colliding ever and anon, some eighteen thousand million times a second, with other molecules, and pursuing, therefore, as the result of these collisions, a very zigzag course. It is by virtue of this motion inherent in the molecules that a gas can distribute itself or diffuse throughout

a room, or can fill completely the space, however large that space may be, which is offered to it. In the case of liquids the same inherent motion of the molecules, and therefore the same power of diffusion, exists; but the process now takes place more slowly, for the molecules of the liquid are packed more closely together, and the mutual collisions are therefore more frequent. The forward progress of a molecule is therefore very slow, like that of a man who might try to pass through a dense and jostling crowd. That diffusion does take place can be easily demonstrated by gently pouring a layer of pure water on to a solution of some strongly coloured substance, such as bluestone (copper sulphate) or dichromate of potash. After some time it will be found that the coloured substance has diffused upwards some distance into the water. The experiment may be made more easily by dissolving in the water sufficient gelatin to make a firm jelly, and then placing a piece of this jelly in the coloured solution. After a few hours it will be found that the coloured substance has penetrated some distance into the jelly.

Even when the solution is separated from the pure water by a membrane of parchment paper or by an animal membrane (*e.g.* pig's bladder), diffusion takes place just the same, as can be shown by enclosing the solution of copper sulphate in a tube of parchment paper which is then immersed in water. Very soon the presence of the copper sulphate in the water outside the membrane will be detected.

During the sixties of last century this diffusion of dissolved substances through a parchment paper or animal membrane was studied by THOMAS GRAHAM, a native of Glasgow, who later became Professor of Chemistry in University College, London, and Master of the Mint. As a result of his investigations, Graham found that although certain substances pass through a membrane of parchment paper, other substances do not do so. Since the substances, *e.g.* sugar or salt, which could pass through this membrane, were such as generally crystallise well, whereas those which

would not pass through, *e.g.* starch, gelatin, glue, were believed to be amorphous and non-crystallisable, Graham divided substances into the two classes, *crystalloids* and *colloids* (from the Greek *kolla*, glue); and this distinction was one which was long maintained. From a practical point of view, in any case, this distinction was of importance, for, as Graham showed, if a mixture of crystalloids and colloids is placed in a parchment cell and immersed in water, the crystalloids, but not the colloids, diffuse out into the water. In this way a separation of crystalloid from colloid can be effected by a process to which Graham gave the name of *dialysis*, a process used universally at the present day for the preparation of colloids free from crystalloids.

Appropriate as Graham's classification of substances appeared at the time, investigation has shown that it cannot be retained. The terms colloid and crystalloid can now no longer be employed to connote definite and different *kinds* of substances, but only different *states* of matter; for it is now recognised that the distinction between crystalloids and colloids is to be found in the degree of dispersion or sub-division. The term "colloidal state" of matter is now applied to that range of sub-division of matter which lies between the limits of the microscopically visible and the molecular state.

That this particular range of sub-division of matter should be singled out for special study is justified by the fact that matter in the colloidal state possesses properties which are not exhibited, or are not exhibited so markedly, either by molecular matter or by the grosser microscopic particles. Matter in the colloidal state, moreover, plays a very important part in almost every field of human activity—in agriculture and in the tanning of leather, in the working of clay, in the production of rayon, in the dyeing of textile fibres, etc. It is also responsible for the blue of the sky and the blue of the eye, and matter in the colloidal state has been chosen by Nature as the vehicle of life.

Since the term colloidal refers only to a certain degree of dispersion or sub-division, colloidally dispersed matter may exist in the solid, the liquid or the gaseous state, and the medium in which the particles are dispersed (the so-called dispersion medium) may also be solid, liquid or gaseous. In this way one obtains colloidal suspensions, emulsions, smokes, mists, etc. In the present discussion we shall be concerned mainly with those systems in which water is the dispersion medium.

While it could be inferred from the experiments of Graham that the apparently homogeneous colloidal solutions or colloidal *sols*, as they are called in order to distinguish them from true solutions, are in reality heterogeneous, the question arises how this can be proved. The answer is that even if one cannot see the particles themselves their presence can be detected by what is known as the *Tyndall Phenomenon.*

When the air of a room is bathed in a uniform light no particles are seen, but if the sunlight be allowed to pass through a hole in the shutters of a darkened room one sees a diffused light, the sunbeam made visible, in which the larger dust particles are seen to

> " Glitter like a swarm of fireflies, tangled in a silver braid."

The diffused light also is due to particles which are large enough to reflect and scatter the waves of light, although too small to be seen as separate individuals by the eye. So also, by means of this " Tyndall phenomenon," the presence of particles in a colloidal sol can be detected. If a beam of light is passed through pure water or through a solution of salt, the path of the beam is invisible ; the liquid is " optically empty."[1] But if the beam is passed through a colloidal sol the path of the beam is traced by a diffused light, like the sunbeam in a darkened room.

[1] Owing to the presence of floating particles even in filtered water, the " Tyndall phenomenon " will be observed with ordinary pure water. Special precautions must be adopted to free the water from all suspended particles.

From this " Tyndall phenomenon," then, one learns that particles which may be too small to be seen in the ordinary way, may be detected if only the light reflected or dispersed by the particles, and not the direct rays from the source of light, are allowed to enter the eye. And it is clear that if, instead of the unaided eye, one employs a microscope to examine the scattered light, the range of vision will be extended, and it will be possible to detect, although not actually

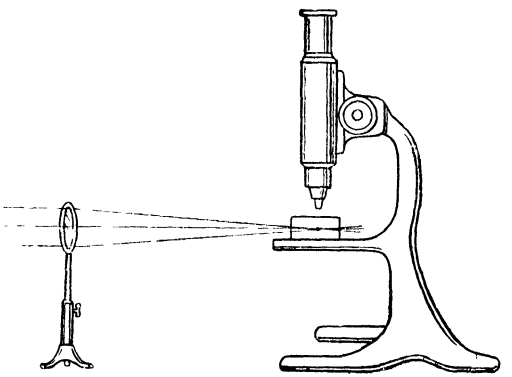


FIG. 23.—ULTRA-MICROSCOPE.

to see in their own shape and colour, particles which are much smaller than can be seen when the microscope is used in the ordinary way. On the basis of this principle there has been devised an arrangement known as the *ultra-microscope*, by means of which not only the heterogeneity of colloid sols can be detected, but also the number of particles in a given volume of the sol can be determined. The arrangement is shown diagrammatically in Fig. 23. A powerful beam of light, instead of being directed into the microscope through the liquid to be examined,. is sent horizontally into the liquid, at right angles to the line of vision through the microscope. If the liquid under examination is optically empty, the field of view in the microscope will appear quite dark ; but if particles are present in the liquid, the light will

be reflected and dispersed, and the minute points of light thus produced will stand out as bright specks against a dark background, in the field of view of the microscope.

A very suitable liquid for examination with the ultra-microscope is colloidal gold sol which formed the basis of the " potable gold " of the alchemists, and was rediscovered in 1856 by Faraday, who obtained it by the reduction of gold chloride with phosphorus. The sol can readily be prepared by adding to a very dilute solution of gold chloride, freed from acid by the careful addition of sodium carbonate, a dilute solution of tannin (tannic acid). In the cold, no change occurs, but when the liquid is heated, a pink colour soon begins to develop ; and by making further additions of the gold and tannin solutions a clear, deep ruby-red coloured liquid is obtained. This contains the gold in a colloidal state, and is similar, in fact, to ruby glass (p. 229).

A similar colloidal sol can be obtained by passing hydrogen sulphide (sulphuretted hydrogen, H_2S) through a solution of white arsenic (oxide of arsenic). A clear yellow liquid is formed which passes unchanged through filter paper (a finely porous, unglazed paper), and is a colloidal sol of arsenious sulphide.

And how large are those particles which are thus detected in the apparently homogeneous colloidal sols ? With the aid of even the most powerful microscope, the smallest particle that can be seen by the ordinary method must have a diameter of not less than about one ten-thousandth part of a millimetre or one two-hundred-and-fifty-thousandth part of an inch ; but by means of the ultra-microscope, particles about one-twentieth of this size, with a diameter of about six-millionths of a millimetre ($\frac{6}{1000000}$ mm.) or one four-millionth of an inch, can be detected. This, however, is still about sixty times greater than the diameter of the hydrogen molecule.

From the investigations carried out by means of the ultra-microscope, it is found that colloidal sols may contain

particles of very different size, even in the case of the same substance, and there is every reason to believe that there exist, in some at least of the sols, particles which are smaller than can be detected by the ultra-microscope, although they are of greater than molecular dimensions. In short, there appears to be no sharp division between colloidal sols and true solutions, and it is possible to pass gradually and without break from one to the other.

Since matter in the colloidal state is very finely subdivided, the extent of surface exposed is very large relatively to the total volume of the matter. Surface forces, therefore, play an important part and bring about what is known as *adsorption*, or changes of concentration at the surface. Charcoal, a finely porous material with a large surface, has the property (p. 123) of removing noxious gases (*e.g.* sulphuretted hydrogen) from the air and colouring matters from solution. This is due to the fact that under the action of surface forces, the noxious gases or colouring matters are adsorbed or concentrated on the surface of the charcoal. Similarly, gelatinous silicic acid—obtained by adding hydrochloric acid to a solution of water-glass (p. 219) and separating the silicic acid from the sodium chloride by dialysis—when partially dehydrated, forms a porous material, *silica gel*. This also shows the property of adsorption in a very marked degree, and is extensively employed in industry for the recovery of volatile solvents, the removal of gasoline vapour from natural gas, etc. Thus, when air containing the vapour of a solvent such as acetone is passed through a layer of silica gel, the acetone is condensed on the surface of the gel and so removed from the air. The solvent can be recovered by heating the gel.

Adsorption plays a very important part in the production and character of colloids. By the adsorption of ions from the dispersion medium or from electrolytes present in solution, the colloid particles acquire an electric charge ; and adsorption of the medium as a whole may also take place. In the

case of the so-called *suspensoid* colloids, *e.g.* colloidal gold and colloidal arsenious sulphide, the dispersed particles adsorb practically none of the dispersion medium, and their stability is due to their motion (Brownian movement, p. 288), and to the electric charge which they carry. The particles, being charged, mutually repel one another and so agglomeration and precipitation are prevented. In the case of the *emulsoid* colloids, however, *e.g.* gelatin, silicic acid, etc., the dispersion medium itself is adsorbed to a greater or less extent. The greater the adsorption of the medium, the more will the stability and properties of the colloidal sol be dependent on this adsorbed medium, and the less will they depend on the electric charge. Owing to the adsorption of the dispersion medium, emulsoid colloids show certain marked differences in behaviour from that of suspensoid colloids.

That the particles of a suspensoid colloid are electrically charged can readily be demonstrated with a colloidal solution of sulphide of arsenic. If this is placed in a U-shaped tube, and if wires connected with the terminals of a high voltage battery or dynamo[1] are inserted in the liquid, one in either limb of the tube, it will be found that the sulphide of arsenic migrates towards and collects around the positive terminal. The particles of arsenic sulphide are thus shown to carry a negative charge of electricity. Even with fine suspensions, such as a suspension of fine clay or a slime of peat, the same phenomenon is observed ; the clay particles or the peat fibres collect around the positive terminal in a firm mass. Since the effect depends primarily on the voltage of the current, while only an insignificant amount of electricity is used, this process of *electrophoresis*, or electric transport of suspended particles, may be applied for the purpose of freeing a fine suspension from water, and has, in fact, been applied to the drying and purification of clay.

[1] The ordinary electric-lighting circuit can conveniently be employed, provided it supplies direct current.

The process of electrophoresis is also applied to the manufacture of articles of rubber. The juice or latex of the rubber plant consists of a liquid in which negatively charged particles of rubber are suspended, and these particles will therefore be carried to the positively charged electrode or anode. Moulds of any desired form, or fabric or wire, may thus be coated with a layer of rubber, and in this way hot-water bottles, bathing caps, etc., may be produced, or wire may be insulated.

Since the stability of the suspensoid colloids is mainly due to the electric charge carried by the particles, precipitation of the colloid is brought about by neutralising the electric charge. This can be effected by the addition of an electrolyte (p. 254). Negatively charged colloid particles will preferentially take up or adsorb positive ions, and positively charged colloids will adsorb negative ions, and the charge on the colloid will thereby be neutralised. The colloid particles will then no longer repel one another but will agglomerate into larger particles and settle out of the liquid. Thus, when a small quantity of hydrochloric acid (hydrogen ion) or of calcium chloride (calcium ion) or of some other electrolyte is added to a colloidal sol of arsenious sulphide or of gold, precipitation of the colloid takes place.

A similar behaviour is found in the case of ordinary fine suspensions (*e.g.* of clay in water), the particles of which are also electrically charged; and this fact is sometimes of considerable geological or geographical importance. Thus, the sedimentation of finely divided, water-borne clay is markedly influenced by the purity of the water transporting it, and takes place more rapidly when salts are present than when they are absent. This, indeed, is one reason for the rapid deposition of river mud on mixing with sea-water, and for the consequent silting up of river mouths and the formation of deltas, such as has taken place at the mouth of the Nile and of the Mississippi.

The electrical charge on a colloid particle may be

neutralised not only by the ion of an electrolyte but also by another colloid carrying an electric charge of opposite sign. Thus, when a positively charged and a negatively charged colloid, such as ferric hydroxide and arsenic sulphide, are brought together, the oppositely charged particles attract one another, and this leads to a mutual flocculation and precipitation of the colloids.

The process of adsorption plays an important part in the dyeing of textiles. In the case of what are called substantive dyes, the dye itself is in a colloidal state, and may be precipitated and fixed on the fibre by the addition of salts, just as arsenious sulphide is precipitated by electrolytes. In the case of acid and basic dyes one is dealing with coloured ions. Since, in an acid bath the textile fibre becomes positively charged, owing to adsorption of hydrogen ion, the fibre will attract and retain negatively charged or acid dyes; but in an alkaline bath the fibre becomes negatively charged and so will attract and retain positive or basic dyes.

Whilst it is found that, in very many cases, silk and wool have the power of taking up and fixing the dye stuff directly, it is frequently found that in the case of cotton the fixation of the dye has to be assisted by a *mordant*, which is either a colloid itself or can give rise to a colloid. The colloid so formed is deposited on and within the fibre to be dyed, and attracts and fixes oppositely charged colloidal dyes. According to the nature of the dye, so must be the nature of the mordant employed, salts of aluminium, chromium, etc., which give rise to the hydroxides of the metals being used when the dye has a negative charge or has acid properties (*e.g.* alizarin); while tannic acid and similar substances are employed for dyes with a positive charge or with basic properties. After the dye has been adsorbed, secondary changes may take place which render the dye less easily removed.

In agriculture, also, the colloidal state is of the greatest importance. In the soil there exist various colloidal sub-

stances, such as the humus, colloidal ferric hydroxide and aluminium hydroxide, clay, etc. Owing to the presence of these, soluble substances, such as the salts of potassium, phosphates and other substances necessary for the life of the plant, are adsorbed and retained in the soil, and so kept available for the support and nourishment of vegetation instead of being washed away into the rivers and sea. The humus, moreover, being a colloid similar to albumin and gelatin, has the property of imbibing water and so helps to maintain the soil in a moist condition, while it also acts as a substrate for the bacteria concerned in the conversion of nitrogenous organic matter into a form which can be taken up by the plants, as well as for the other bacteria always present in the soil. The water-holding power of the soil colloids may be considerably modified by the addition of various substances, *e.g.* lime ; and the addition of lime may have an effect on the fertility of the soil, not only by neutralising excess of acid but also by altering the structure of the soil colloids (p. 211).

Owing to the presence of such colloids as ferric hydroxide and aluminium hydroxide, filtration through soil acts as a very efficient means of purifying sewage and other waste water from organic impurities. These impurities in sewage, for example, have been found to be, to a large extent, negatively charged colloids which are therefore precipitated and retained by the positively charged colloids, ferric hydroxide and aluminium hydroxide. By such filtration through the soil, therefore, even the highly impure water which drains from cultivated and manured land is rendered comparatively sweet and harmless. In the same way, the purification of drinking-water by filtration through beds of sand or through charcoal, depends on the removal of impurities by adsorption on the large filtering surface exposed and on the retention of positively charged colloidal matter, bacteria, etc., by the negatively charged sand or charcoal particles.

An important application of the behaviour just described

is found in sewage farms, where the drainage of towns is pumped on to the land and the liquid allowed to drain through the porous soil. Here, the waste organic matter as well as phosphates and other salts are retained and afford a rich nutriment for the growing crops, while the liquid effluent which drains away is free from objectionable impurities. By such means can, in suitable surroundings, a source of annoyance and loss be turned to profit.

In the case of emulsoid colloids, such as gelatin, albumin, etc., the stability of the colloid is due not so much to the electric charge on the particles as to the adsorbed water. Such colloids, therefore, are not so sensitive to added electrolytes, and actual precipitation does not take place until the concentration of electrolyte is relatively large, although changes may be brought about in the water-content of the colloid. This comparatively great insensitiveness to electrolytes, further, may be transferred to suspensoids. Thus when gelatin, for example, is added to a colloidal gold sol, the gold is adsorbed by the gelatin and a much greater concentration of electrolyte is required in order to precipitate the gold than is necessary in the absence of the gelatin. The gelatin is said to " protect " the gold, and owing to this so-called *protective action*, a suspension or suspensoid colloid is rendered much more stable. Indeed, so stable may the colloid become that the colloidal sol may even be evaporated to dryness without destroying the colloidal state ; on treating the dried solid with water, it passes back again into the state of a colloidal sol. A number of colloidal sols find application as therapeutic agents. Thus, colloidal silver is administered for influenza, colitis, and bacillary dysentery ; injections of colloidal manganese are given in cases of acne ; colloidal sulphur and colloidal iodine have been recommended for rheumatism and neuritis.

In the manufacture of photographic plates, prepared by coating plates with gelatin containing a fine suspension of silver bromide, one finds an important industrial application

of the protective action of emulsoid colloids. If a solution of potassium bromide is added to a solution of silver nitrate silver bromide is formed and separates out as an insoluble curd, quite unsuitable, on account of its coarseness, for photographic purposes. But if gelatin is first dissolved in the solutions of potassium bromide and of silver nitrate, no curdy precipitate but only a uniform colloidal suspension of very fine particles of silver bromide is obtained on mixing the solutions.

The protective action of emulsoid colloids is also clearly seen in the nature of the curd which is formed from milk, and in the readiness with which it is formed on addition of acid or of rennet. In cow's milk there is a relatively large amount of casein and a relatively small amount of the protective colloid, lact-albumin. Cow's milk, therefore, readily curdles. In human milk, there is a smaller proportion of casein and a larger proportion of lact-albumin. The casein is therefore more effectively "protected" and curdling takes place less readily. Human milk is, therefore, more readily digested than cow's milk. In ass's milk, the proportion of protective colloid to casein is highest of all, and curdling, therefore, takes place still less readily. The digestibility of ass's milk is greatest of all. By increasing the proportion of protective colloid in cow's milk by the addition, for example, of gelatin, white of egg, or barley water (containing starch), the formation of a curd in the stomach may be more or less completely prevented; and the curd, when formed, is less compact. The digestibility of the milk is thereby increased.

In the manufacture of ice cream, likewise, the addition of protective colloids, like albumin (white of egg) and gelatin, to the milk ensures a smoother product, because the casein is prevented from coagulating and the ice particles are kept very small.

The protective action of emulsoid colloids and the precipitating action of salts are excellently illustrated, also, on

a large scale in Nature. Some of the great rivers of the world, like the Mississippi and the storied Nile, whose turbid waters have from time immemorial carried in their bosom the promise of bountiful harvests, are always muddy, owing to the presence of a large amount of colloidal organic matter, which stabilises the fine suspension of clay and soil; and it is only when the rivers reach the salt waters of the sea with its high concentration of salts, that the suspended matter is precipitated with the production of river bars and deltas.

Many colloidal sols, *e.g.* gelatin, starch, etc., when cooled or coagulated, pass into a jelly, owing to the coalescence of the hydrated colloid particles. The jelly so formed may be regarded as constituted by a honeycomb or network of hydrated colloid, the meshes or cells of which are filled with a dilute solution of the colloid. The water-holding or liquid-holding power of such jellies is sometimes very great, as is seen from the fact that jellies have been obtained which contain less than 0·5 per cent. of the colloid. "Solidified alcohol," used as a fuel for spirit lamps, is a jelly formed by colloidal calcium acetate in alcohol.

Although electrolytes, as we have seen, may bring about the precipitation of colloids, they may also, when present in only very small amount, facilitate the dispersion of a solid substance by giving to the particles, by adsorption, the electric charge necessary for the stability of the colloidal sol (p. 279). This process of deflocculation or breaking up of large particles is spoken of as *peptisation*, on account of its superficial resemblance to the process of conversion of insoluble protein into soluble or colloidally dispersed peptone.

Even when adsorbed substances may not, by themselves, be able to peptise solids, they may, by acting as stabilisers and as protective colloids, assist mechanical or other processes in the production of the colloidal state. Thus, Dr. E. G. Acheson, to whom we owe the discovery of carborundum and the process of making artificial graphite, found

that when graphite is ground with a solution of tannin (tannic acid), a colloidal sol of graphite can be obtained. This so-called *deflocculated Acheson graphite* (" Dag "), when mixed with oil, is largely used as a lubricant.

The production of colloidally dispersed or deflocculated materials by grinding in special mills in presence of protective colloids or " dispersators " is now a considerable industry. Such very finely divided materials find application in the paint industry and as " fillers " in paper, rubber, etc.

Although, in recent years, the importance of the colloidal state in its bearing on many of the activities of daily life has become more clearly recognised and more fully appreciated, it is in connection with our conceptions of the constitution of matter that the investigations of microscopic and ultramicroscopic suspensions have gained some of their most brilliant triumphs. For more than two thousand years there has existed in men's minds the idea of matter as made up of separate, discrete particles ; and in the nineteenth century, as we have seen, this idea was given a more definite form at the hands of Dalton and of Avogadro. But the particles, the molecules, which make up matter as our eyes reveal it to us, are not in a state of rest. In the case of a gas, these molecules are in a state of almost inconceivable tumult and commotion, which even the restraint imposed by the condensation and the congealing of the gas to the liquid and the solid state is not able wholly to subdue. Such, at least, is the picture of matter which the genius of a Clerk Maxwell and a Clausius revealed to us in what is known as the kinetic theory of matter. But although this theory has been found to give a satisfactory explanation of the behaviour more especially of gases, and has made it possible to calculate not only the absolute mass of the molecule—the hydrogen molecule weighs about three quadrillionths (or three million million million millionths) of a gram[1]—but also its dimensions

[1] This number is more conveniently represented by 3×10^{-24} gram, which is the same as dividing 3 by 10 twenty-four times in succession.

(rather less than a three hundred millionth of a centimetre in diameter),[1] and the speed of its flight (say, a mile per second), there were not wanting some who refused to believe in the objective reality of molecules and of the picture presented by the kinetic theory. And yet, even as early as 1827, these molecules, although by their minute size removed far beyond the range of human vision, had, all unknown to their observers, made their presence manifest by the effects which they produced. In that year, the botanist, ROBERT BROWN, while examining suspensions of pollen grains under the microscope, observed that the particles were never at rest, but were in rapid motion, vibrating, rotating, moving irregularly along a zigzag path, sinking, rising—*perpetually* in motion. In this *Brownian movement*, as it is called, the full significance of which has only recently been grasped—it had, indeed, been observed long ago by the French naturalist, Buffon, who saw in it a manifestation of life—we have an actual picture of that tumult and commotion of the molecules which were revealed to the mental vision of mathematical physicists. But it is not, of course, the motions of the molecules themselves that one sees in the Brownian movement, but only the effect of the incessant bombardment of the coarser, visible particles of the suspension, by the molecules of the liquid.

Over a lengthened period of time, the number of blows which a suspended particle of sufficient size, say such as is visible to the naked eye, would receive from the molecules of the liquid in which it is suspended, would be the same in the different directions. The suspended particle, therefore, would show no sign of motion. But if the period of time is made sufficiently short, the number of impacts of the liquid molecules will no longer be equal in different directions, the impacts will no longer balance one another, and if the suspended particle is small enough it will, at each blow, be caused to move, first in one direction and then in another,

[1] The diameter of a hydrogen molecule is $2{\cdot}68 \times 10^{-8}$ cm.

and all the faster the smaller the particle; and it is this motion of a particle of a suspension under the blows which are rained upon it by the molecules of the liquid, that constitutes the Brownian movement. With particles of ultra-microscopic dimensions the phenomenon is exhibited with extraordinary vividness, and it is an impressive sight to observe the rapid darting motions of a colloid particle by means of the ultra-microscope. As Zsigmondy, who first observed it, wrote: "A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold. They hop, dance, spring, dash together and fly apart so rapidly that the eye can scarcely make out their movements. . . . These motions show that there is a continual mixing together of the interior parts of every liquid going on unceasingly, year in year out." It is to this Brownian movement that the stability of colloidal sols is largely due. From the careful quantitative investigations of this phenomenon, carried out during the present century, the various molecular magnitudes—the kinetic energy of the particles and their velocity of diffusion, for example—have been computed; and such is the closeness of agreement between the results so obtained and the values which the kinetic theory would lead one to expect, that one cannot any longer hesitate to believe that in the rapid, darting motions of the ultra-microscopic particles there is made manifest to us something of the turbulent stir and bustle which is going on unceasingly in that under-world of molecules which lies beyond the reach of our senses.

CHAPTER XIV

MOLECULAR ARCHITECTURE

Of all the known elements, the element carbon, familiar to all in the three physically distinct forms, charcoal, graphite, diamond, stands out pre-eminent in its power of forming compounds with other elements. So numerous, indeed, are its compounds—their number at the present day exceeding 250,000—that their study has developed into a special branch of chemistry, *organic chemistry*. This name is a survival from an older period when chemists drew a distinction between the compounds occurring in the non-living, mineral world, and those occurring in the living animal and vegetable organisms, and which were thought to be producible only with the help of a special form of energy, the so-called vital force, inherent in the living cell. That any essential difference exists between the two classes of compounds, that the chemical laws which obtain within the domain of living nature are different from those which are found in inanimate nature, can no longer be held. For not only can many, very many, of the compounds which were formerly regarded as typical products of animal and vegetable metabolism, typical organic compounds in the older sense, be prepared in the laboratory from purely mineral materials, but the synthetic production of not a few of these compounds has even developed into industries of enormous magnitude. The term " organic chemistry " is still retained, not with its old signification, but merely as denoting the chemistry of carbon and its compounds ; for, indeed, the vast majority of these " organic " compounds are found in no animal or vegetable organism, but have been prepared by the intelligent combining together of substances by the chemist.

But if I have referred here particularly to the compounds of carbon, it is not for the purpose of describing either the methods of preparation or the specific properties of any of these substances, but rather for the purpose of discussing very briefly a phenomenon which, although met with in the case of the compounds of other elements, is found with extraordinary frequency in the case of the compounds of carbon. This is the phenomenon to which the name of *isomerism* has been given.

When Dalton introduced his atomic theory, the basis on which all modern chemistry has been built, he showed, as we have seen, that a compound could be regarded as being formed by the combination or uniting of the atoms of the constituent elements in certain constant and definite proportions. But while the law, " One compound, one composition," has remained unshaken, the progress, more especially of organic chemistry, soon showed that the converse statement, " One composition, one compound," which, to the earlier chemists, was equally an article of faith with the former, is very far removed from the truth. As the number of compounds became multiplied, it began to be more and more frequently observed that the same elements may be united in the same proportions and yet yield compounds with entirely different properties. More than a hundred different compounds, for example, can be produced by combining together nine atoms of carbon, ten atoms of hydrogen, and three atoms of oxygen. To this phenomenon, that different compounds may have the same composition, the term *isomerism* has been applied. Just as the same set of bricks can, by varying their arrangement, be formed into structures of totally different kinds, so also the same atoms can, by varying their arrangement within the molecule, give rise to different molecular structures, or different compounds. In other words, the discovery of isomerism, so entirely unforeseen by Dalton and by the

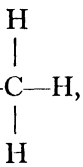
earlier organic chemists, led to the recognition of the fact that the properties of a compound depend not merely on its composition, but also on its internal structure or the arrangement of the atoms within the molecule; and our knowledge of a substance is not complete until we know what is this internal structure or *constitution* of the molecule. We must gain a knowledge of the molecular architecture.

A knowledge of the molecular constitution is, moreover, essential for the successful building up or synthesis of a compound from simpler materials, which will be discussed more fully in the following chapters. To elucidate the constitution of the different compounds is one of the main aims of the organic chemist, and in the case of the more complex compounds, the problem becomes one of the greatest difficulty. As to how this problem is solved, only this much can be said here. Through the laborious efforts of numberless chemists, a knowledge has been gradually built up of the internal structure or constitution of a very large number of substances, and also of the relations between these different structures and the physical and chemical properties of the compound. In order to determine the constitution of an unknown compound, therefore, the properties and reactions of the substance are studied, and the compound is also, by the action of various chemical reagents, decomposed into simpler compounds. It is broken down into bits, as it were, and one then seeks to identify the fragments, the simpler substances, so obtained, with substances of which the constitution is already known. From the knowledge gained in this way, the chemist, with his imaginative insight and wide knowledge of how substances react with one another, then attempts to piece the fragments together again, and so to build up or synthesise the original substance.

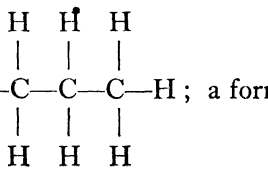
But the task of elucidating the constitution of organic compounds would be a hopeless one without the aid of some guiding principle and some method by which the

molecular constitution can be represented. It was, therefore, a great step in advance when the Scottish chemist, ARCHIBALD SCOTT COUPER, and the German chemist, FRIEDRICH AUGUST KEKULÉ, in 1858, showed how molecular constitutions could be represented diagrammatically, using as a guiding principle what is known as the doctrine of *valency* (p. 17).

Although there is, of course, no material link or bond between the atoms, one can nevertheless represent union between atoms as if it were material by means of a line, or lines, according to the valency of the atom. Thus, as we have already seen, we can represent the compound marsh gas by the diagrammatic formula



hydrocarbons of that series by such a chain of carbon and hydrogen atoms as



; a formula which can also be written in the simpler form, CH_3—CH_2—CH_3. By the extension of this idea, it became possible not only to represent the molecular constitution of known compounds, but also to foresee the possible existence of isomeric compounds. Thus, for example, in the case of the compound $CH_3 \cdot CH_2 \cdot CH_3$ (the bond between the carbon atoms being now represented by a dot), it is clear that one atom of hydrogen in this compound can be replaced by an atom, say, of chlorine, in two ways, so as to form either the compound $CH_3 \cdot CH_2 \cdot CH_2Cl$, or the compound $CH_3 \cdot CHCl \cdot CH_3$, the

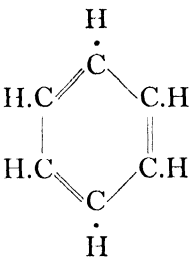
chlorine being in the former case attached to a terminal carbon atom and in the latter case to the intermediate carbon atom. Accordingly, there should exist two and only two different compounds having the composition C_3H_7Cl; and as a matter of fact two compounds and only two are known.

The origin of this theory of chemical structure, as it occurred to Kekulé, has been recounted by Kekulé himself. During a period of residence in London he was returning from a visit paid at Islington to where he was staying at Clapham. "One fine summer evening," he relates,[1] "I was returning by the last omnibus, 'outside' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie, and lo! the atoms were gambolling before my eyes. Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time, I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain." And then he adds: "I spent part of the night putting on paper at least sketches of these dream-forms." From these sketches were developed the constitutional or structural formulæ, of which examples have just been given.

And again he had a dream. Now he was at Ghent, and dozed before his fire. Again he saw the atoms gambolling before his eyes, the chains twining and twisting in snake-like motion. "But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke";

[1] F. R. Japp, "Kekulé Memorial Lecture" (*Transactions of the Chemical Society*, 1898).

but the picture Kekulé had seen of the snake which had seized its own tail gave him the clue to one of the most puzzling molecular structures, the structure of the benzene molecule, a ring of six carbon atoms to each of which one hydrogen atom is attached. Thus we obtain the structural formula[1] of the benzene molecule,



the " ring " of carbon atoms being written in the form of a hexagon[2] instead of in the form of a circle. " Let us learn to dream," said Kekulé, " then perhaps we shall find the truth." " But," he wisely added, " let us beware of publishing our dreams before they have been put to the proof by the waking understanding." The hexagonal form of the benzene molecule has been confirmed by X-ray examination.

By the introduction of the doctrine of valency and of Couper's and Kekulé's diagrammatic method of representing molecular constitution, a satisfactory basis seemed to have been obtained for the future development of organic chemistry. And yet, it was not long before the inadequacy of this theory of chemical structure became only too apparent,

[1] Just as in the study of the architecture of buildings, plans and architectural drawings are necessary for the proper understanding of the subject, so also structural formulæ are required for the understanding of molecular architecture.

[2] The reason why six carbon atoms readily arrange themselves in the form of a hexagon is that the four valencies of a carbon atom are directed in space towards the four corners of a regular tetrahedron (p. 303). The angle between the valencies is 109° 28′, and the angles of a hexagon are 120°. The six carbon atoms can thus join up to form a hexagon with only a small degree of " strain."

owing to the discovery that, in some cases, the number of isomeric compounds is greater than can be represented by the structural formulæ of Couper and Kekulé. A new isomerism was discovered, an isomerism which manifested itself in the property known as *optical activity*. Let me try to explain this.

Early last century it was discovered that when a ray of light is passed through a crystal of Iceland spar, the ethereal vibrations, which propagate the light, and which, ordinarily, take place in all directions at right angles to the path of the ray, are all brought into one plane. The light is said to be *polarised*. When, now, this polarised light is passed through certain substances, quartz, turpentine, a solution of cane sugar, etc., it is found that the plane of polarisation, the plane in which the ethereal vibrations take place, is rotated or twisted, this rotation or twisting taking place sometimes to the right, sometimes to the left; an effect which one can illustrate by the twisting of a strip of stout paper into a right-handed or left-handed spiral, such as is represented in Fig. 24. Substances which possess this property of rotating the plane of polarised light are said to be "optically active."

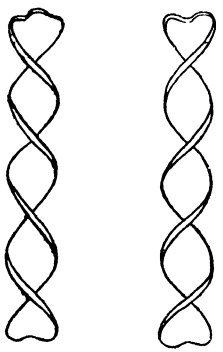


FIG. 24.—RIGHT- AND LEFT-HANDED SPIRALS.

This property of optical activity can also be demonstrated by a modification of a very interesting experiment due to the late Sir George Stokes. When a parallel beam of light from a projection lantern (Fig. 25) is reflected vertically downwards by means of a mirror, through a column of water rendered slightly turbid by the addition of a few drops of an alcoholic solution of rosin, the path of the beam is rendered visible by the fine suspension of rosin particles (Tyndall phenomenon, p. 276); and the beam of light appears equally bright all round. But if the light from the lantern

is first polarised by passage through a so-called Nicol prism formed from Iceland spar or through a disc of *polaroid*,[1] and then reflected downwards through the column of water, the appearance obtained is that of a band which is light *only on two* opposed sides, and dark on the other two opposed sides. On rotating the Nicol prism or polarised disc, the band also rotates and turns alternately its light and dark sides to the eye. The effect produced is as if the beam of light on passing through the Nicol prism or polaroid disc, were given a flat form, like a book, from the two opposite edges of which

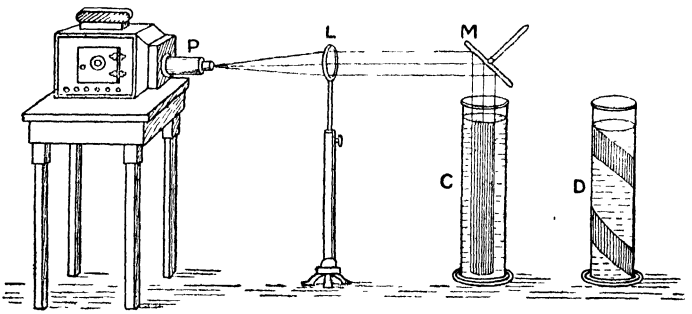


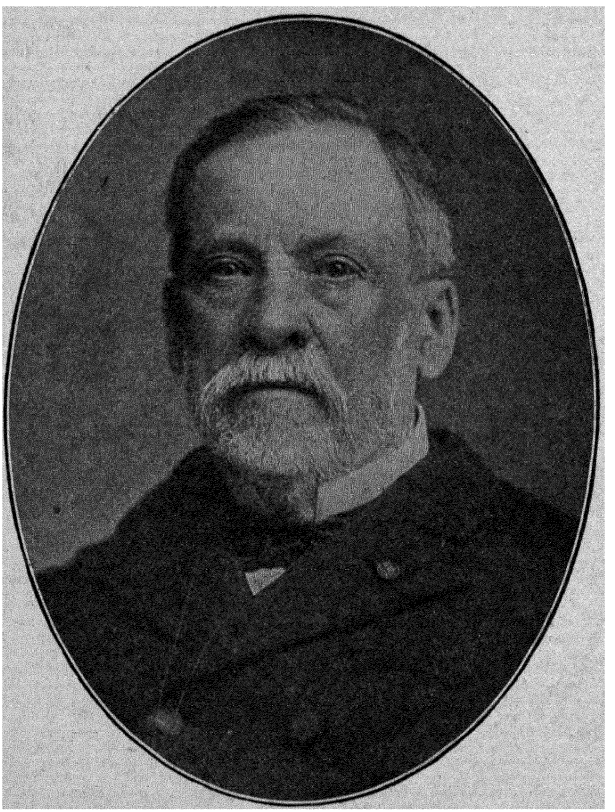
FIG. 25.—DEMONSTRATION OF THE POLARISATION OF LIGHT.

Light from a lantern is polarised by passage through the polarising prism P, and the beam of light is then directed by the lens L on to a mirror M, by which the light is directed vertically downwards through water contained in the cylinder C, and rendered turbid by a fine suspension of rosin. A vertical, polarised band of light is obtained. If the cylinder C is replaced by D, which contains a concentrated solution of cane sugar, the band of light is twisted into the form of a spiral.

light is emitted, while the sides remain dark. Thus we have illustrated the phenomenon of polarisation of light. If, now, the cylinder of water is replaced by a cylinder containing a solution of cane sugar, also containing a suspension of rosin, the band of light is twisted into a spiral form; and on rotating the polarising prism or disc, this spiral band of

[1] Polaroid consists of a film of cellulose acetate mounted between two plane glass plates. The film is a matrix for sub-microscopic dichroic crystals accurately oriented in such a way that the entire film acts as a single polarising crystal.

light will appear to move with a screw-like motion. From the fact that the different rays of coloured light which together constitute white light are twisted or rotated to



LOUIS PASTEUR.

different extents (the blue rays being rotated more than the red), the spiral band of light shows the colours of the rainbow.

What then is the explanation to be given of this remarkable property of substances, the study of which, starting with the

brilliant discoveries of PASTEUR[1] in 1848, has occupied the attention of many of our foremost chemists down to the present day ?

When Pasteur commenced the investigations which were to initiate a revolution in the current ideas regarding the molecular structure of organic compounds, two isomeric acids were known having the same composition, namely, tartaric acid and paratartaric acid (now called racemic acid). The former, which is found occurring in grape juice, is

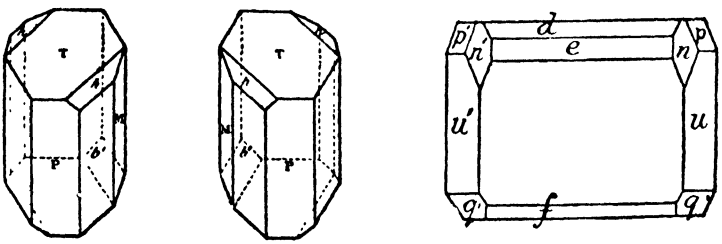


FIG. 26.—HEMIHEDRAL CRYSTALS OF *d*- AND *l*- SODIUM AMMONIUM TARTRATE, AND HOLOHEDRAL CRYSTAL (RIGHT) OF SODIUM AMMONIUM RACEMATE.

optically active ; the latter is inactive. On examining the crystals of these two acids, and of a number of their salts, Pasteur found that whereas the crystalline faces of the inactive racemic acid and its salts were all fully developed, and the crystals symmetrical (Fig. 26), the full development of the crystalline faces of the active tartaric acid was interrupted by the occurrence of so-called hemihedral faces (Fig. 26). The occurrence of these hemihedral faces was regarded by Pasteur as the outward and visible manifestation of the property of optical activity, in accordance with a view which had been suggested by Sir JOHN HERSCHEL in the case of crystalline quartz, which is also optically active.

[1] Louis Pasteur, the son of a tanner, was born in 1822. For a number of years he was Professor of Chemistry at Strasbourg, Lille, and Paris, and carried out a large number of important investigations in biochemistry and bacteriology. On his work, antiseptic surgery was built up and a cure for rabies or hydrophobia obtained. He died in 1895.

But whereas quartz is optically active only in the crystalline state, tartaric acid retains the property even when dissolved. In the former case, the property depends on the crystalline structure ; in the latter, it depends on the internal molecular structure.

A further discovery was made by Pasteur. During his investigation of one of the salts of tartaric and racemic acid (namely, sodium ammonium tartrate and sodium ammonium racemate), Pasteur found, as was to be expected, that the crystals of the tartrate resembled those of the other tartrates he had examined in possessing hemihedral faces, arranged in a similar manner in the different crystals. The crystals obtained by crystallisation from a solution of the racemate, however, instead of being holohedral, with the crystalline faces fully developed, were found also to have hemihedral faces ; but these hemihedral faces, instead of, as in the tartrates, all being turned the same way, were inclined, sometimes to the right and sometimes to the left (Fig. 26). This result was quite unexpected ; and Pasteur, on carefully separating the two sets of crystals and examining their solutions, discovered with no less surprise than pleasure, that one set of crystals rotated the plane of polarised light to the right, while the other set rotated the plane by an equal amount to the left. On dissolving together equal amounts of the two sets of crystals, a solution was obtained which was quite inactive.

Here, then, we have the discovery of that new kind of isomerism to which reference has just been made, and which showed the inadequacy of the structural formulæ of Kekulé. The two salts into which the racemate had been separated were identical in all their chemical and physical properties, save only in the disposition, to the right or to the left, of the small hemihedral faces occurring on their crystals, and in the property of rotating the plane of polarised light to an equal extent but in opposite directions. From these two salts, Pasteur obtained two different tartaric acids ;

one having the power of rotating the plane of polarised light to the right and identical with the acid occurring in grape juice, the other hitherto unknown, and having the power of rotating the plane of polarised light to the left. Moreover, on mixing together in solution equal quantities of these two optically active acids, there separate from the solution crystals of the inactive racemic acid, which is thus shown to be a compound of the two active acids in equal proportion.

The discovery of the two optically active tartaric acids was a momentous one, effecting a revolution in the views of chemists regarding molecular structure; and one can well understand the feeling of happiness and the nervous excitement by which Pasteur was overcome on making the discovery. Rushing from his laboratory and meeting the *préparateur* in physics, he embraced him, exclaiming: "I have just made a great discovery! I have separated the sodium ammonium paratartrate into two salts of opposite action on the plane of polarisation of light. The dextro-salt is in all respects identical with the dextrotartrate. I am so happy and overcome by such nervous excitement that I am unable to place my eye again to the polarisation apparatus." The question, however, now arose as to how the existence of the two optically active tartaric acids could be explained.

All material things belong to one or other of two classes, according as the image which is formed of the object in a mirror is such that it can or can not be superposed on the object. In the case of a cube, for example, the image formed in a mirror is identical with the object, and one can imagine the image superposed on the original cube. A cube is a symmetrical object. But if a right hand is held in front of a mirror, the image which is obtained represents a left hand, and this cannot be superposed on the right hand; a right hand will not fit into a left-hand glove. A hand, therefore, is an asymmetrical object, which can exist in two distinct,

so-called *enantiomorphic* forms, similar in all respects, but not superposable, not identical. And when one examines the crystals of the two optically active tartaric acids (or of their salts), it is seen that they also are related to each other as the right hand is to the left hand ; each represents the non-superposable mirror image of the other (Fig. 26), and the two crystals, although in all points similar, are not identical. If, however, the crystalline form is to be regarded, as Pasteur regarded it, as a visible manifestation of the internal structure, one is led to the conclusion that the *molecular* structures of the two active tartaric acids are asymmetric and enantiomorphously related to each other as object to non-superposable mirror image. " Are the atoms," Pasteur asked, " are the atoms of the dextro-acid grouped in the form of a right-handed helix, or do they stand at the corners of an irregular tetrahedron, or are they arranged in some other asymmetrical manner ? " And he replied, " We are not as yet in a position to answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in an asymmetric order, having a non-superposable image."

Looking back on the experimental investigations of Pasteur, one cannot suppress a feeling of disappointment that it was not vouchsafed to him, with the clear views he possessed, to take but a little step forward and to develop these views into a theory of chemical structure. But the time was not yet ripe, and it was not until after more than twenty years that the study of organic chemistry furnished a sufficient number of examples of optically active compounds to make it possible to give an answer to Pasteur's questions. Nevertheless, Pasteur introduced into chemistry a conception of extraordinary importance and fruitfulness, the conception of *molecular asymmetry*, and he recognised that molecular structure is not a matter of two dimensions only, but of three. The atoms are not arranged in a plane, as the formulæ of Couper and of Kekulé represent them,

but in three-dimensional space. In this way Pasteur inaugurated a new chemistry, a " Chemistry in Space " or " Stereochemistry."

The conception of molecular asymmetry and the idea of the grouping of the atoms at the corners of an irregular tetrahedron were developed, in 1874, into a consistent theory of molecular structure, embracing the optically active isomeric compounds, by a Dutch and a French chemist independently, VAN'T HOFF and LE BEL.

If we imagine a carbon atom at the centre of a tetrahedron, and if the four atoms or groups, with which, as we have

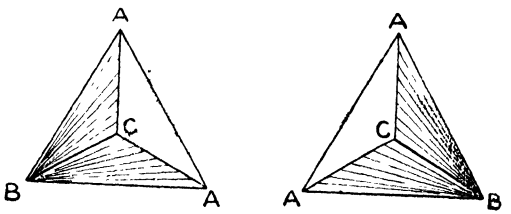


FIG. 27.

seen, a carbon atom can be united, are situated at the four corners of the tetrahedron, it will be found that so long as two, at least, of the atoms or groups are the same, the molecule, represented as a tetrahedron, will be symmetrical and its mirror image will be superposable on and therefore identical with the original. This will be clear from an inspection of Fig. 27, which represents such a tetrahedron and its mirror image. The right-hand tetrahedron, obviously, only requires to be turned through an angle of rather more than 90°, on the corner B as a pivot, to become identical in disposition with the left-hand tetrahedron.

If, however, the four atoms or groups attached to the carbon atom are all different, the molecule, as represented by the tetrahedron, becomes asymmetric, and gives a mirror image which is no longer superposable on the original. Two someric forms are therefore possible. This will be

understood from Fig. 28. Viewing these tetrahedra from a similar position, we see that the groups B C D, in the one case, are arranged from left to right; in the other case, from right to left. If one of these represents a molecule which rotates the plane of polarised light to the right, the other will represent a molecule which rotates the plane of polarised light to the left.

The views of van't Hoff and Le Bel have received the amplest confirmation. Not only has it been found that the molecules of all compounds which are optically active do contain at least one atom of carbon to which four different

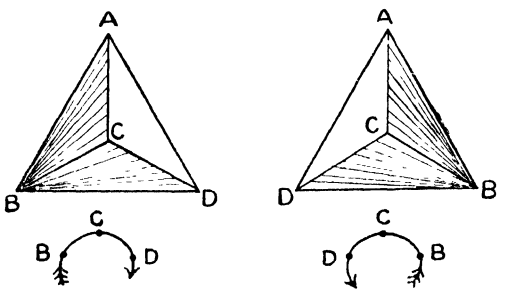


FIG. 28.

atoms or groups are attached—a so-called *asymmetric carbon atom*—or are, for some other reason, asymmetric, but also, no compound has been obtained the possible existence of which could not be predicted by means of the van't Hoff and Le Bel theory. So fruitful has the conception of molecular asymmetry and of the asymmetric carbon atom proved, that it has been extended also to the atoms of elements other than carbon, of which optically active isomers have been prepared.

We have already seen that in the case of tartaric acid—and the same holds for all other optically active substances—there exist, or can exist, not only the two optically active isomers, but also an inactive isomer, produced by the combination of the two oppositely active forms in equal amounts,

and separable again, by suitable means, into the active forms. This inactive form is known as the *racemic* form. In the case of one particular salt, sodium ammonium paratartrate, as we have seen, this breaking up of the racemic form (the paratartrate) takes place on crystallising from water at the ordinary temperature. But this method is capable of only a limited application. Pasteur, however, introduced two other methods for effecting the resolution of the racemic into the active forms or for obtaining one of the active forms separate from the other, namely, by making use of some living organism or of some other asymmetric, optically active material. When, for example, the solution of the racemic paratartaric acid is acted on by blue mould, *Penicillium glaucum*, the fungus feeds on and destroys the dextro-rotatory acid, which occurs naturally in grapes, but leaves unchanged, or acts much more slowly on, the lævo-acid, which is an artificial product of the laboratory. The solution, therefore, becomes lævo-rotatory, and the lævo-acid can be obtained by concentrating the solution and allowing it to crystallise. In the process of fermentation, also, under the action of various enzymes, which are themselves asymmetric agents, produced in living animal and vegetable cells, we find a similar selective action. Thus, whereas the dextro-rotating glucose, the well-known grape sugar, undergoes fermentation, the lævo-rotating glucose, a compound obtained only artificially, remains unchanged in the presence of yeast. An asymmetric agent acts only on materials of similar asymmetry to itself, just as a right-handed screw will fit only into a right-handed thread. *So long as the two optically active isomers are brought into relations with symmetrical agents, they behave identically; but when they react with an asymmetric agent, a different behaviour is exhibited by the two forms.*

This selective action is of great physiological importance, since in all life processes, such as digestion and assimilation, one is dealing with the action of the optically active,

asymmetric materials contained in the cells and tissues. It is found, therefore, that although the naturally occurring albumins and sugars, for example, are capable of being digested, the isomeric compounds of opposite activity pass through the body without being absorbed. And a similar differentiation of action is met with in the case of many of the optically active alkaloids. " Here, then," said Pasteur, " the molecular asymmetry proper to organic substances intervenes in a phenomenon of a physiological kind, and it intervenes in the *rôle* of a modifier of chemical affinity. . . . Thus we find introduced into physiological principles the idea of the influence of the molecular asymmetry of natural organic products, of this great character which establishes, perhaps, the only well-marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry of living matter."

In the investigation of molecular structure, the study of optically active substances has been of supreme importance, and the knowledge which has been gained has exercised an important influence on the understanding and interpretation of biological processes, opening to physiology, as Pasteur said, new horizons, distant but sure. But it is not merely the domain of the material sciences which has been enriched by the investigations of stereochemistry ; the most fundamental problems of life, our very ideas with regard to life itself, and the phenomena of life, receive illumination.

Until 1828, as we have seen, the production of the organic substances occurring in the animal and vegetable organisms was considered to be the prerogative of life ; but the synthetic production in the laboratory of many of the compounds which are typical products of the animal and vegetable organism led to the abandonment of that belief, and science began to look upon the phenomena of life as completely explicable in terms of physics and of chemistry. But the discovery and investigation of optically active compounds introduced a new factor. As Professor F. R. JAPP, in his

Presidential Address to the Chemical Section of the British Association in 1898, so admirably emphasised, " the phenomena of stereochemistry support the doctrine of vitalism as revived by the younger physiologists, and point to the existence of a directive force which enters upon the scene with life itself, and which, whilst in no way violating the laws of the kinetics of atoms, determines the course of their operation within the living organism."

In Nature, most asymmetric compounds are found occurring in *one* of the optically active forms only. Dextro-rotatory tartaric acid, for example, occurs in grape juice, but the lævo-rotatory acid is not found in Nature, and is known only as a laboratory product; grape sugar likewise occurs naturally only as the dextro-rotatory form; while the albumins are lævo-rotatory. When, however, it is attempted to prepare an asymmetric compound in the laboratory from symmetric substances only, from substances, that is to say, which are not themselves optically active, it is always found that the product obtained is *inactive*. As Pasteur said: " Artificial products have no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life and all others."

It is true that the inactive, racemic form, which is obtained as the result of artificial synthesis, can be separated into the two optically active forms, with the help of asymmetric, optically active compounds; or one can even, by the process of fermentation or the action of organisms, destroy one of the active forms and so obtain a single optically active compound. But these processes involve the use either of living organisms or of materials which have been produced by living organisms, and the production of the active form is, therefore, due directly or indirectly to living matter. However, as has been pointed out, Pasteur found that, in some cases, the resolution of the racemic form can be effected simply by crystallisation. By allowing a solution of the

inactive racemic sodium ammonium paratartrate to crystallise, crystals of the dextro- and of the lævo-rotatory sodium ammonium tartrate were deposited separately, and could, owing to the difference in their crystalline forms, be distinguished from one another and be separated by hand. Since the original racemic paratartrate could be prepared synthetically from symmetrical materials by the action of only symmetrically acting reagents, and since this racemic form could be resolved into the active forms by the symmetrically acting process of crystallisation, it was thought that " the barrier which M. Pasteur had placed between natural and artificial products " had been thereby broken down. And this was undoubtedly the view held by the majority of chemists.

But was this view—a view still held by many—correct ? Pasteur certainly did not think so, and he pointed out very pertinently that " to transform one inactive compound into another inactive compound which has the power of resolving itself simultaneously into a right-handed compound and its opposite, is in no way comparable with the possibility of transforming an inactive compound into a *single active* compound. This is what no one has ever done ; it is, on the other hand, what living nature is doing unceasingly before our eyes." The artificial, racemic compound, certainly, had been resolved into the two active forms by the symmetrical process of crystallisation, but these two forms had not been *separated* from each other ; both active forms were present side by side. Their separation " requires the living operator, whose intellect embraces the conception of opposite forms of symmetry." And, as Professor CRUM BROWN asked long ago : " Is not the observation and deliberate choice by which a human being picks out the two kinds of crystals and places each in a vessel by itself, the specific act of a living organism of a kind not altogether dissimilar to the selection made by *Penicillium glaucum* ? " a mould which, as we saw, destroys one optically active form but not the other.

While Pasteur certainly believed that all the attempts which had been made to synthesise a single optically active form, without the intervention, direct or indirect, of life, had been unsuccessful, he appears to have held the view that as science advanced, the inability to effect such a synthesis might be removed; for while he recognised the necessity for the existence of asymmetric forces "at the moment of the elaboration of natural organic products," he conceived the possibility that such asymmetric forces might lie outside the living organism and "reside in light, in electricity, in magnetism, or in heat." In 1894, also, van't Hoff made the suggestion that the formation of optically active compounds might take place under the directive action of right or left circularly polarised light. Many attempts were made to effect the synthesis of such compounds under the action of circularly polarised light, but it was not till 1929 that success was attained. By the action of circularly polarised light on a symmetrical compound, an optically active compound was obtained, the rotatory power of which varied in sign according as the light was dextro- or lævo-circularly polarised. The possibility of an asymmetric synthesis under the directive action of a purely physical force was thereby demonstrated. Moreover, it has been shown that dextro-circularly polarised light predominates at the earth's surface in reflected sunlight, and it would therefore appear that an unsymmetrical form of photochemical energy exists in Nature under the directive action of which an asymmetric synthesis could take place. The possibility that the formation of the first asymmetric molecule (from which other asymmetric molecules might later be formed) took place under such directive influence has thus been established. The proof that it did in fact so take place cannot of course be given.

CHAPTER XV

SYNTHETIC CHEMISTRY—I

It may, perhaps, have seemed to some that however interesting, as an intellectual speculation, the theories of molecular structure discussed in the previous chapter might be, however much they might satisfy a philosophical curiosity regarding the mystery which lies at the heart of things, they could be of very little practical importance and could scarcely come at all into direct touch with the daily life of mankind. Nothing could be farther from the truth, for these theories form the very basis and foundation of some of the greatest industries of the present day! Kekulé's dreams, perhaps, were an interesting psychological phenomenon, but the stuff that his dreams were made of, the theories of molecular structure, were as important for the advance and development of organic chemistry as a chart and compass are for a mariner. For, it must be remembered, the purpose of a scientific theory is not only to explain or co-ordinate knowledge already acquired, but also to be a guide to the exploration of the unknown; and without the theories of molecular structure or constitution put forward by Kekulé, van't Hoff, Le Bel and others, there could not have been built up that vast structure of organic chemistry such as we know it at the present day, nor could we have witnessed that crowning achievement of chemists, the artificial, synthetic preparation of many of Nature's own products, and the industrial production of those innumerable dyes, therapeutic agents, perfumes and other materials, which are regarded as necessaries in our modern civilisation.

While, however, the theories of molecular structure and constitution gave the guidance necessary for the altogether phenomenal development of organic chemistry during the

past hundred years, that development could actually take place only through the genius, scientific insight, energy and persistence of hundreds of zealous workers who devoted themselves to the development of knowledge by experimental investigation, and to the task of elucidating the constitution of and synthesising thousands of organic compounds. And it must not be forgotten that the industries dependent on synthetic organic chemistry can flourish only if the importance of intensive and unremitting experimental investigation is whole-heartedly recognised and its prosecution generously encouraged.

Not only has the chemist prepared numberless compounds hitherto unknown, but he has even entered into competition with Nature herself, and has successfully broken the monopoly which heretofore she had enjoyed in the production of many compounds both of ornament and of utility. In fact, so successful has the chemist been, that not only can the artificial products, in a number of cases, compete with the natural products, but they have even driven these entirely out of the market. In this way great industries have arisen, the social and economic effects of which have been both profound and widespread.

In achieving the successful building up of molecular structures, whether of naturally occurring substances or of substances hitherto unknown, the chemist may start with molecular structures which occur in nature (*e.g.* cellulose) or which can be readily obtained from naturally occurring materials (*e.g.* benzene) ; or he may start from the elements or simple compounds (*e.g.* carbon from coal, oxygen and nitrogen from the air, hydrogen from water, etc.), and from these build up molecular structures of increasing diversity and complexity. In the nineteenth century, important and closely interdependent industries were established, which found their raw materials mainly in coal tar ; but in more recent years synthetic organic chemistry has drawn its raw materials to an increasing extent from petroleum.

By the distillation of coal there is obtained not only the gaseous mixture so largely employed as a fuel and illuminant, but also considerable amounts of ammonia and of a thick, dark-coloured, evil-smelling liquid, coal-tar—one of the most valuable and important materials obtained by man. It is not an attractive-looking material, and yet there have been evolved from it, by the painstaking labours of a multitude of chemists, substances innumerable—dyes by the thousand, which rival in range and beauty of tone the finest products of Nature's imagining; explosives which the strongest works of man are powerless to resist; antiseptics and drugs; the sweet-smelling essences of flowers; photographic chemicals; plastics and rubber-like materials, the manufacture of which has developed into enormous and rapidly expanding industries. This coal-tar is, indeed, an almost inexhaustible storehouse of raw materials for the manufacture of products of manifold variety.

By subjecting the crude coal-tar to a process of distillation, as is done in the refining of crude petroleum, various substances are obtained which distil over at different temperatures. Of these the most important are the following:

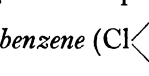
LIQUIDS.

	b.p.
Benzene	80·5° C. (176·9° F.)
Toluene	111° C. (231·8° F.)

SOLIDS.

	m.p.
Phenol (carbolic acid)	41° C. (105·8° F.)
Naphthalene	80° C. (176° F.)
Anthracene	213° C. (415° F.)

Benzene, C_6H_6, or benzole, as it is frequently called in commerce, forms the starting-point in the manufacture of aniline (which can be regarded as benzene in which one of the atoms of hydrogen is replaced by the group NH_2); and this, in turn, is the starting-point in the preparation of a large number of dyes—the aniline dyes. These aniline

dyes, which were the first synthetic dyes to be prepared, constitute, however, only a part of the total number of dyestuffs which are now manufactured from coal-tar products. Benzene is not only an important raw material in chemical industry, but is also mixed with petrol for use as motor fuel (p. 96). When the hydrogen atoms at two opposite corners of the benzene hexagon are replaced by chlorine atoms, one obtains *paradichlorobenzene* (), which is a powerful moth insecticide.

Toluene, $C_6H_5 \cdot CH_3$ (commercially, toluole), is used as a raw material in the manufacture not only of dyes, but also of the powerful high explosive, trinitrotoluene or T.N.T. As the formula indicates, the structure of toluene is that of benzene in which one hydrogen atom is replaced by the methyl group (CH_3). To satisfy the very large war demand for toluene, this hydrocarbon had also to be produced from petroleum.

Phenol or *Carbolic Acid*, $C_6H_5 \cdot OH$, is a well-known antiseptic, and is also the starting-point in the preparation of the explosive, picric acid, lyddite or melinite. It is also used in the manufacture of dyes and of plastics.

Cresols, $CH_3 \cdot C_6H_4 \cdot OH$, of which there are three isomeric forms, also occur in coal-tar and are largely used in the preparation of antiseptics (*Lysol*, *Jeyes' Fluid*, etc.) and for the production of plastic materials (p. 335).

Naphthalene, $C_{10}H_8$, is a valuable constituent of coal-tar. Its molecular structure is represented by two benzene hexagons joined together. It is the raw material chiefly employed in the manufacture of indigotin. When naphthalene is heated with hydrogen under pressure and in presence of nickel as catalyst (cf. p. 190), hydrogenation takes place and the important solvents *tetralin*, $C_{10}H_{12}$, and *decalin*, $C_{10}H_{18}$, are obtained. By the action of chlorine on naphthalene, non-inflammable waxes (*e.g. Seekay*) are formed.

Anthracene, $C_{14}H_{10}$, is the raw material employed in the

manufacture of a large number of important dyes, the most familiar of which is the red dye, alizarin, or Turkey red. Its molecular structure is represented by three benzene hexagons joined together.

Important as these different substances are, they constitute only a small part of coal-tar, the amounts in which they occur being, moreover, dependent not only on the nature of the coal used but also on the temperature at which the coal is distilled. Thus, the benzene and toluene together constitute about 3 per cent., phenol about 1 per cent., naphthalene about 5 per cent., and anthracene about 0·5 per cent. of the coal-tar formed in gas manufacture. By the distillation of one ton of coal, therefore, we should obtain the above constituents in the following quantities, roughly :

Benzene and Toluene	3½ lbs.
Phenol	1¼ lbs.
Naphthalene	6 lbs.
Anthracene	10 oz.

The Coal-tar Dyes

Until the middle of last century, men were dependent for all the dyes with which they coloured their bodies or their garments on colouring matters which were chiefly of animal and vegetable origin : the colouring matter of logwood and of safflower ; the animal dyes, kermes and cochineal ; the blue dye, indigo or woad, with which our ancestors in these islands are said to have stained their bodies ; the red dye, alizarin, obtained from the root of the madder plant, once extensively cultivated in Southern Europe ; and the costliest of all dyes, the most famous dye of the ancient world, Tyrian purple, obtained from a shell-fish (*Murex brandaris*) found on the eastern shores of the Mediterranean.

" Who has not heard how Tyrian shells
Enclosed the blue, that dye of dyes
Whereof one drop worked miracles,
And coloured like Astarte's eyes
Raw silk the merchant sells ? "

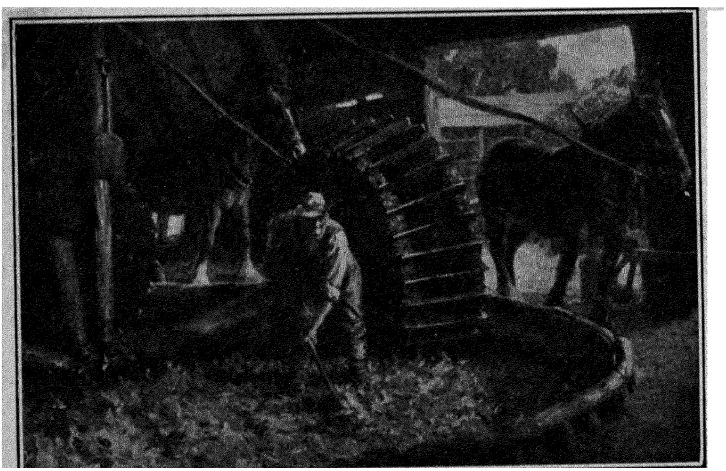
(Browning : *Popularity.*)

These dyes, and a few others, were all that were available until the year 1856. In that year the first synthetic dye, the once favourite mauve, was prepared by W. H. PERKIN, by the oxidation of crude aniline ($C_6H_5NH_2$), and since that time colouring matters to the number of several thousands have been synthesised by the chemist. The natural dyes are mostly of a pronounced, even crude, colour, but the products of the chemist are of an almost infinite variety; and, far outrivalling the natural dyes in range of colour and delicacy of tone, they have ousted these dyes from the dye-works. Starting from benzene, naphthalene and anthracene, constituents of the dark-coloured liquid, coal-tar, which less than a hundred years ago was a useless waste material and a nuisance to the gas manufacturer, dyes and other organic compounds are now prepared in large quantities.

It is quite impossible here to enter into a discussion of the composition and constitution of the coal-tar dyes, some of which are among the most complex of the compounds of carbon; but it may be said that the technique of dye manufacture has become so perfected, and our knowledge of the variation of colour with the constitution of the compound has become so well established, that the synthetic production of new shades is no longer a haphazard process, but one of which the conditions of success are clearly known.

Although thousands of different dyestuffs have been prepared, it is in the artificial production of Nature's own colouring matters, more especially of alizarin and indigotin, that organic chemistry has achieved some of its most striking successes. Through the labours of many chemists the composition of these natural products was determined and their constitution or molecular structure unravelled; and with the knowledge thus obtained chemists have succeeded in preparing these compounds artificially—not merely substitutes for or imitations of the natural products, but the actual products themselves—and that more cheaply than Nature herself can produce them.

Until about 1870, over the whole of Southern Europe, and eastwards to Asia Minor, great tracts of land, some three or four hundred thousand acres, were devoted to the growing of the madder plant; in France alone, 50,000 acres were devoted to its culture. When the roots of this plant were allowed to ferment, a substance, *alizarin*, so called from the name given by the Arabs to the madder



CRUSHING THE LEAVES OF WOAD IN A ROTATING HORSE-MILL.
(Painting of a Lincolnshire Woad-mill by J. Doyle Penrose.)

root, was formed. This substance was capable of dyeing cotton a bright red colour—the so-called Turkey red—and was one of the oldest of dyes and largely used in the dyeing of cotton goods. But these madder fields have now all disappeared; for when the composition and nature of this dye-stuff had once been ascertained, it was not long before chemists discovered a method by which the dye could be manufactured from what was then practically a waste material, anthracene, one of the constituents of coal-tar. By a series of comparatively simple reactions one could pass from the hydrocarbon anthracene ($C_{14}H_{10}$) to anthra-

quinone ($C_{14}H_8O_2$), and from anthraquinone to dihydroxy-anthraquinone or alizarin [$C_{14}H_6O_2(OH)_2$]. More recently, a new and more economical process has been introduced and anthraquinone is now produced by allowing benzene and phthalic anhydride (obtained from the more abundant hydrocarbon naphthalene, p. 313) to react together in presence of aluminium chloride as catalyst. The anthraquinone is then converted into alizarin. In this way the madder dye can be manufactured much more cheaply than Nature can produce it, and the madder fields of Southern Europe exist no more.

Similar social-economic effects have been produced in India, which was for long the chief home of the indigo-bearing plants. Known for over three thousand years, indigo was obtained from various species of *Indigoferæ*, cultivated more especially in India. The woad (*Isatis tinctoria*), from which indigo is obtained, was cultivated in Europe even as late as the seventeenth century, and its cultivation lingered on in the Eastern Counties of England until recent years. In the sixteenth century, with the opening up of trade with the East, the superior Indian indigo began to make its appearance in Europe, and although the use of the " devilish drug " was at first prohibited by law, the ban was removed in the eighteenth century. Down to near the beginning of the present century the Indian indigo plantations controlled the markets of the world. In 1896–7, India produced over eight thousand tons of indigo, the value of which was £4,000,000. It was a valuable prize, therefore, which the German dye-manufacturers set themselves to win, and after seventeen years of effort the genius and resourcefulness of their chemists won the day. In 1897, synthetic indigotin[1] was placed on the market in competition with the

[1] Indigo, the dye material obtained from the indigo plant, is not a single substance but a mixture, the chief constituent of which is the blue dye-stuff indigotin. It is on this difference between indigo and synthetic indigotin that the difference between the dyeing power and quality of (so-called natural) indigo and synthetic indigotin (wrongly called synthetic indigo) depends.

product from the Indian plantations, which it has almost entirely replaced; and more than a million acres of land, formerly devoted to the production of indigo, are now given over to the growing of food. The industrialist, however, has not achieved a complete victory, for the production of the natural indigo has, by the application of scientific knowledge, been improved and cheapened, and the natural dye is still favoured by dyers for certain purposes. In 1938, some 55,000 acres were still under cultivation for indigo.

Since the industrial production of indigotin involves a considerable number of different processes, and requires the use of a number of different substances, of which sulphuric acid, ammonia, chlorine and acetic acid are the chief, the success of the synthesis as a whole depends on the success with which each step of the process can be carried out, and on the cost of the substances employed. The starting-point in the manufacture is the hydrocarbon naphthalene, a constituent of the invaluable coal-tar, and familiar to all on account of its use in preserving furs against the attack of moths; and the first step in the synthesis of indigotin is to convert this naphthalene into a compound called phthalic acid ($C_6H_4<\begin{matrix}COOH\\COOH\end{matrix}$), and then into phthalic anhydride ($C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O$). This, it was known, could be done by heating the naphthalene with strong sulphuric acid; but when the manufacturer attempted to make use of this fact, he found that although the desired conversion did indeed take place, it did not proceed sufficiently readily and the cost of carrying out this first step in the process was so great that it would have rendered the industrial production of indigotin unremunerative. But here a lucky accident came to the assistance of the manufacturer, for, through the accidental breaking of a thermometer, it was discovered that mercury acts as an efficient catalyst in the conversion of naphthalene to phthalic acid, facilitating the process to such a degree as

to allow it to be carried out with commercial success. The method is, however, no longer used, and naphthalene in the state of vapour is now oxidised to phthalic anhydride by the oxygen of the air with the help of a catalyst, vanadium pentoxide.

A broken thermometer sealed the fate of the Indian indigo plantations! Yet, this fate might, perhaps, have been averted if only a fraction of the money and energy and scientific ability which were devoted to the industrial production of the synthetic dye had been devoted to research into the improvement of the production of the natural dye.

The successful industrial production of indigotin depended also on improvements being effected in the manufacture of the various chemicals employed. Thus the demand for a very powerful sulphuric acid — pyrosulphuric acid or "oleum"—and the fact that during the process of heating it with naphthalene large quantities of sulphur dioxide are formed, led to the development of a new method of making the acid, namely, the "contact process" to which reference was made in Chapter IX. For the production of chlorine, also, of which enormous quantities are required, the old method of obtaining the gas from hydrochloric acid was useless, and has been replaced by the electrolysis of a solution of common salt, the chlorine being then obtained in a pure state by liquefaction. The ammonia may be obtained, as we have seen, as a product of the distillation of coal, but is mainly produced by direct synthesis from nitrogen and hydrogen (p. 207); and the acetic acid is obtained by the distillation of wood, and from acetylene (p. 356).

Although it is not possible to enter into a detailed discussion of the practical process of dyeing, it is of interest to note that the process is different in the case of indigo and other so-called vat dyes, from what it is in the case of other dye-stuffs (*see* p. 282). On account of its insolubility, the indigo is first converted into a colourless compound, called indigo-white, which is soluble in alkalies. After the material

to be dyed has been immersed in this solution, it is removed and exposed to the air, whereby the oxygen of the air oxidises the colourless indigo-white to indigo-blue. The dye is, therefore, developed in the fibre after its removal from the bath. The vat dyes, it is interesting to note, have now been obtained in a soluble form and so have become available for dyeing wool and silk which are destroyed by the strongly alkaline solutions formerly required. Important as has been the *rôle* played by indigo in the past, this dye, like other dyes, is always under peril of being replaced by newer and better synthetic dyes.

Closely related, chemically, to indigo, is that other ancient dye, Tyrian purple, which is secreted by certain species of marine snail, the *Murex brandaris* and *Murex trunculus*, found, more especially, on the shores of the Mediterranean. On investigation, it was ascertained that this " dye of dyes, whereof one drop worked miracles," is a compound of indigotin with bromine, a compound which can be prepared synthetically with comparative ease. The costliness of this natural dye was almost proverbial, and the reason for this is not far to seek; for the colouring matter obtained from the glands of twelve thousand shell-fish by the German chemist who investigated the dye, amounted only to about twenty-three grains, and the estimated cost of the dye was nearly £60 an ounce.

During the present century many synthetic dyes with very valuable properties have been produced. Thus, the so-called indanthrene dyes, prepared from anthraquinone, an oxide of the hydrocarbon, anthracene, are distinguished by their great fastness to light and are used for dyeing various " fadeless " fabrics; while another important series of dyes finds application for the dyeing of celanese or acetate rayon (p. 145). Anthracene occurs only in small amounts in coal-tar but anthraquinone can now, as has been pointed out, be prepared from phthalic acid, produced by the oxidation of the relatively abundant naphthalene, and benzene (p. 317).

Anæsthetics, Antiseptics, Drugs and Insecticides

The sixteenth and seventeenth centuries are regarded as marking a distinct era in chemistry, inaugurated by Paracelsus. During that period, chemistry was looked upon as the handmaid of medicine, and the study of the action of substances on the human organism and the preparation of drugs were held to be the true functions of the chemist. That was the period of what was called iatro-chemistry or medical chemistry.

While the modern chemist would resent the restriction of his functions within such narrow limits, the services which chemistry has, in modern times, rendered to medicine are greater beyond comparison than all the iatro-chemists were ever able to perform, or even to imagine. Not only have "Nature's remedies," the juices and extracts of plants, the valuable alkaloids like quinine and morphia, been exhaustively studied and the methods of their extraction improved, but they have been supplemented, in some cases even displaced, by a large array of new drugs and medicinal preparations which owe their origin to the genius and painstaking labours of chemists. The herbalist, in fact, has given place to the scientific chemist, and the manufacture of anæsthetics, hypnotics, antipyretics, and drugs for the treatment of special diseases, has developed into an industry of great importance.

Anæsthetics.—The first of these synthetic products to come into use was *chloroform* ($CHCl_3$), which had been prepared by the German chemist Liebig in 1832, by the action of bleaching powder on alcohol.[1] It was first used as an anæsthetic by Sir James Simpson in 1847, and has not only facilitated the work of the surgeon but has freed mankind from untold misery and suffering. The discovery of the anæsthetic properties of chloroform led to a search for and discovery of other anæsthetics, such as ether and ethyl chloride, substances which are also produced from alcohol.

[1] Chloroform is now prepared from acetone (p. 356).

The introduction as a local anæsthetic of the alkaloid cocaine, which occurs in the leaves of the coca plant, aroused, in 1884, much interest among surgeons, and led chemists to undertake a systematic investigation of substances related structurally to cocaine, the molecular constitution of which had been elucidated in 1898. As a result, it was found that a particular physiological action is due, in many cases, to the presence of certain groupings of atoms in the molecule of a compound, and can be modified or even entirely altered by the introduction of different atoms or groups into the parent molecule, or by eliminating certain groups from it. Guided by this discovery, chemists succeeded in synthesising a number of compounds, all of which possess local anæsthetic action. Of these, one may mention *novocaine* and *amethocaine* (known also by other names), the latter compound being, it is stated, a perfect substitute for cocaine for all purposes. It has, moreover, greater stability, and is not habit-forming.

The introduction of the anæsthetic chloroform marked a new era in surgery, and a further advance was made through the introduction of the substance *adrenaline*, the active principle of the suprarenal glands (p. 370). This substance when injected subcutaneously, even in excessively minute amount, produces so violent a contraction of the arteries that the blood is driven away from the injected tissues and " bloodless " surgery becomes a possibility.

Adrenaline was isolated for the first time in 1901, from the suprarenal glands of sheep and oxen, close on 1000 lbs. of tissue (the glands from 20,000 oxen) being required to yield 1 lb. of adrenaline. It was not long, however, before the molecular structure of the substance had been determined, and a process for preparing it synthetically on an industrial scale had been devised. It is now placed on the market under the name *suprarenine*.

The compound adrenaline formed in the glands of animals is optically active and rotates the plane of polarised light to

the left ; whereas the synthetic product is a racemic compound of the two optically active forms, and is therefore inactive (p. 305). With the help of dextro-tartaric acid, however, this racemic form can be resolved into its two optically active isomers, and the lævo-form isolated.

The difference in the behaviour of an optically active substance towards the asymmetric living tissues was emphasised in the previous chapter, and an excellent illustration of this property is afforded by adrenaline ; for it is found that the physiological action (the increase of the blood pressure) is twelve to fifteen times greater in the case of the naturally occurring lævo-adrenaline than in the case of the synthetic dextro-adrenaline and about twice as great as in the case of the inactive racemic form.

Hypnotics.—Following closely on the discovery of chloroform came the discovery of *chloral* ($CCl_3 \cdot CHO$) and its soluble crystalline hydrate, the first hypnotic to be produced industrially. The dangers attending the use of chloral, however, led to the search for and discovery of other hypnotics which are free from its bad qualities ; and at the present day quite a number of synthetic hypnotics are available. Two of the most familiar are *veronal* and *luminal*, compounds derived from barbituric acid and known as barbiturates.

Antiseptics.—Since the discovery by Pasteur of the bacterial origin of putrefaction and disease, and the introduction by Lord Lister of aseptic surgery, chemists have applied themselves to the synthesis or building up of compounds which should be more and more effective as germicides but should be non-toxic to the leucocytes or white " warrior cells " of the blood, which are the natural defence of the patient against the organisms producing sepsis. Although the germicidal properties of chlorine have long been known, and are widely applied for the destruction of bacteria in water, this element is not suitable for use as an antiseptic in the treatment of wounds. Various compounds, however, of chlorine, such as chloramine T ($CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl\ Na$),

the relation of which to toluene is clear from the formula, and the chlorine derivatives of the cresols (p. 313), have powerful antiseptic properties and are non-toxic and non-corrosive. A number of dyes, *e.g.* acriflavine, prepared from the coal-tar constituent, acridine, also act as powerful antiseptics without interfering with the normal processes of healing.

In 1929, the important discovery was made by Sir ALEXANDER FLEMING, of St. Mary's Hospital, London, that the mould *Penicillium notatum* produces, during its growth, a material which has powerful bacteriostatic properties. He gave to it the name *penicillin*. In 1940, the method of isolating and of producing it in quantity was developed by a team of workers under Sir H. W. FLOREY at Oxford, and there was thus put into the hands of the surgeon and physician a unique antiseptic which, while non-toxic to the patient, is extremely efficacious in rendering harmless the micro-organisms responsible for pus formation, gas gangrene and other wound infections which, in the past, have been the cause of many deaths. Penicillin, it has been found, may also be used beneficially in the treatment of diphtheria, tetanus, carbuncles and impetigo.

As a result of an intensive co-operative effort directed towards the elucidation of the chemical nature of this rather unstable material, it has been found that there are several different natural penicillins, the complex molecular structure of which chemists have succeeded in unravelling. The penicillins, it has been found, are acids with the general formula $C_9H_{11}O_4SN_2R$, where R stands for $C_5H_9\cdot$, $C_6H_5\cdot CH_2\cdot$ or $HO\cdot C_6H_4\cdot CH_2\cdot$. With the knowledge of the chemical nature and molecular structure thus revealed it may be hoped that great as have been the achievements made possible with penicillin, new synthetic compounds may be obtained possessing still greater efficacy and range of application.

Drugs and Therapeutic Agents.—During the last quarter of the nineteenth century, chemists, seeking to obtain drugs

which might supplement or replace the specific anti-malarial alkaloid quinine, prepared a number of compounds which were found to possess valuable antipyretic and analgesic (or pain alleviating) properties. One of the first of these was *antifebrin*, known to chemists as acetanilide ($CH_3 \cdot CO \cdot NH \cdot C_6H_5$), the physiological properties of which were accidentally discovered in 1886 ; and this was followed, in 1887, by the analgesic drug *phenacetin*, obtained by introducing the ethoxy-group (C_2H_5O) into the molecule of acetanilide. The toxic action of this compound is thereby greatly diminished. Similarly, by a modification of the molecular structure of salicylic acid $\left(C_6H_4 \begin{< OH \\ COOH \end{> \right)$ there was prepared acetylsalicylic acid $\left(C_6H_4 \begin{< O \cdot COCH_3 \\ COOH \end{> \right)$, or *aspirin*, which does not produce the gastric disturbances caused by the parent compound. As an anti-rheumatic and anti-neuralgic drug, aspirin is by far the most popular and widely used of all the synthetic drugs, over 130 tons of it being sold annually in Great Britain alone.

Valuable, however, as these compounds were found to be as therapeutic agents, their use merely alleviated the symptoms of disease ; and it was not until early in the present century that the foundations of a true *chemotherapy* were laid, by which the causes of disease were attacked by means of chemical compounds of specially planned molecular structure.[1]

Guided by the observation that various living tissues and organisms show selective absorption for different dyes, the German physiologist and chemist, PAUL EHRLICH, conceived the idea of combating diseases due to protozoal parasites by the use of substances which are poisons for the

[1] The natural alkaloid, quinine, had of course long been in use as a specific against the organism causing malaria.

parasites but which are not absorbed by and are therefore not harmful to the cells of the host. After many trials and many failures, Ehrlich was successful in finding, in 1912, in the complex, arsenic-containing compound which he called *salvarsan*, a cure for syphilis. Since that time, chemists have prepared a number of other compounds which have proved effective in treating many tropical and other diseases (*e.g.* sleeping sickness, kala azar, etc.), of protozoal origin.

Even for the treatment of malaria, quinine[1] has met with rivals in the synthetic drugs *plasmoquin* (or *pamaquin*), a derivative of quinoline, and *mepacrine hydrochloride* (or *atebrin*), a derivative of acridine. These substances are specific poisons for the malarial parasite at two different stages of its life cycle and are widely used for the treatment of malaria. Tablets of atebrin, packed between thin sheets of the plastic polythene (p. 336), to protect them from moisture, were issued to British and Allied troops in Burma and the Far East.

Valuable as mepacrine has proved itself to be as a substitute for quinine, a new drug, *paludrine*, prepared in 1945 by the chemists of Imperial Chemical Industries, has been found to be more effective than quinine and mepacrine as a protective against infection from the bite of mosquitoes and more powerful in destroying the parasites and in controlling the symptoms of malaria.[2]

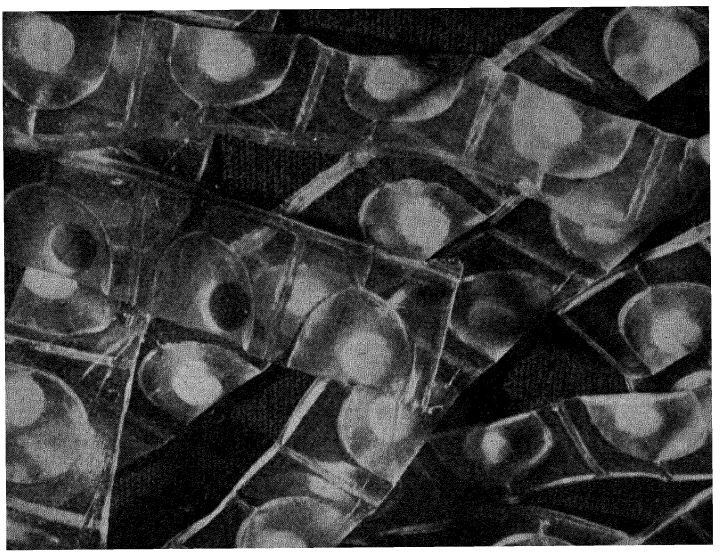
Since 1935, great advances have been made, and one of the most remarkable discoveries in the domain of chemotherapy has been that of the therapeutic value of a number of compounds belonging to what is called the sulphanilamide ($NH_2 \cdot C_6H_4 \cdot SO_2NH_2$) group, and generally spoken of as *sulpha-drugs*. Sulphanilamide itself arrests the action[3] of

[1] Although the synthesis of quinine has been achieved in the laboratory, it has not yet been developed industrially.

[2] It has been announced that over 99 per cent. of malaria cases treated in the State of Victoria, Australia, were cured by paludrine.

[3] The sulpha-drugs are bacteriostatic, not bactericidal, in action ; that is, they prevent the multiplication and arrest the action of the bacteria, which are then destroyed by the leucocytes of the blood.

the streptococci which are the cause of puerperal fever, scarlet fever and erysipelas, and is also of value in preventing sepsis in wounds. It was found, however, as the result of chemical investigation by the research staff of Messrs. May and Baker, that if one of the hydrogen atoms of the $-SO_2NH_2$



[*Courtesy of Imperial Chemical Industries Ltd.*
TABLETS OF ATEBRIN PACKED IN POLYTHENE ENVELOPES.

group is replaced by various molecular structures (pyridine, thiazole, guanidine, etc.), the effectiveness and range of usefulness of the sulpha-drugs could be extended. Thus, *sulphapyridine* (M. and B. 693) and *sulphathiazole* (M. and B. 760) are effective in combating not only streptococci but also pneumococci and meningococci, the organisms responsible for pneumonia and meningitis. Sulpha-guanidine is especially valuable in the treatment of dysentery.

Through the introduction of the sulpha-drugs, regarded, popularly and not without reason, almost as miracle-working

drugs, the treatment of bacterial diseases in man has, since 1935, been completely revolutionised ; and a very notable reduction in the number of deaths due to puerperal fever, pneumonia, pneumococcal meningitis and other diseases has been effected. There even seems good reason for hope that, through the genius of chemists, drugs may be obtained by which also tuberculosis may be combated.

The important contribution which the chemist has made to the alleviation of pain, the maintenance of health and the conquest of disease, is one of the most notable features of the history of medicine. By none has a greater service been rendered to mankind.

Insecticides.—Since it has been found that many protozoal and bacterial diseases are transmitted from man to man by insects, one may combat these diseases not only by means of prophylactic drugs but also by the destruction of the insect carriers. For many years one has used, for the destruction of mosquitoes and other insects, an extract of pyrethrum flowers (containing two active ingredients, the *pyrethrins*), dissolved in kerosine (as in the familiar " flit "), or in the liquid *freon* (dichlorodifluoromethane), as well as an extract of Derris root, the chief active principle of which is *rotenone.* The larvæ of mosquitoes, on the other hand, have been destroyed by spraying the breeding areas with kerosine or with Paris green, an organic compound containing arsenic and copper.

During the war of 1939–45, however, supplies of the above insecticides were largely cut off, owing to the entrance of Japan into the war, and it became necessary to obtain other insecticides to cope not only with mosquitoes but also with other insect carriers of disease. Of these, especially in times of war, the louse, carrier of typhus, which in the past has decimated armies and civilian communities, is one of the most important. During the war, therefore, as the result of research work by the chemists of this country and also of America, there was developed the manufacture

of an insecticide known to chemists by the somewhat formidable name of diparadichlorodiphenyltrichloroethane ($\left(\begin{matrix}Cl\cdot C_6H_4\\ \\ Cl\cdot C_6H_4\end{matrix}\!\!>\!CH\cdot CCl_3\right)$, disguised under the official contraction *D.D.T.* This compound has been found to be an insecticide of remarkable potency and persistence, although it does not possess the rapid " knock-down " property of the pyrethrins. It can be used for the destruction of the insect carriers of malaria, yellow fever, sleeping sickness (tsetse fly), dysentery (house fly), typhus (louse), plague (flea), etc. In 1942 it had one of its greatest triumphs in successfully combating an epidemic of typhus which broke out in Naples. The freedom of the men of the Allied forces from lice infestation was due largely to the impregnation of their clothing with D.D.T.

More recently, chemists of Imperial Chemical Industries have produced a compound which is an even more powerful insecticide than D.D.T. This substance, to which the name *gammexane* has been given, is one of the four isomeric forms of the compound, benzene hexachloride ($C_6H_6Cl_6$). Like D.D.T., gammexane is a solid and can be used either as a dusting powder, mixed, say, with gypsum, or as a spray, when dissolved in a suitable solvent. Like D.D.T., gammexane has a persistent rather than an immediate knock-down action, and is outstanding in its toxicity to locusts.

CHAPTER XVI

SYNTHETIC CHEMISTRY—II

Synthetic Perfumes

For thousands of years the volatile substances to which the different flowers and plants owe their odours have been obtained by distillation or by extraction by means of solvents. In the past sixty or seventy years, however, the secrets of Nature have been largely unravelled, and the chemical laboratory has become odorous as a garden and filled with the perfumes of violet and rose, heliotrope, lilac, hyacinth and orange blossom; and from the stills of the chemist there also flow liquids the flavours of which imitate those of the apple, pear, pineapple and other fruits, and which, in consequence, find application as artificial fruit essences (p. 354). Although in a number of cases the synthetic perfumes and flavouring essences merely imitate the products of Nature, in other cases the chemist has succeeded in preparing the identical substances to which the flavour of the natural fruit or the perfume of the growing flower is due.

One of the first of these natural substances to be prepared by the chemist was the substance coumarin, the odoriferous principle of the sweet woodruff (*Asperula odorata*), a fragrant substance used in the preparation of the perfumes known as Jockey Club and New-mown Hay. This synthetic preparation of a natural odoriferous principle was speedily followed by the preparation of the flavouring material, vanillin, the active principle occurring in the vanilla bean. This substance, formed by the oxidation of eugenol, the chief constituent of clove oil, is now manufactured from toluene, as raw material, and is of great commercial importance. To these earliest synthetic products numerous others have since been added, so that the main odoriferous principles of oil of wintergreen

(*methylsalicylate*), oil of bitter almonds (*benzaldehyde*), hawthorn blossom (*anisic aldehyde*), lily of the valley (*terpineol*), ambergris (*ambrein*), and others, can now be prepared artificially. Other synthetic compounds, while not identical with the natural perfumes, closely resemble them in odour, and are employed in large quantities either as substitutes for the natural perfumes or for blending with them. Of these the most important are ionone, or imitation violet, imitation musk, and imitation oil of bitter almonds, or " oil of mirbane " (*nitro-benzene*).

The synthetic production of sweet-smelling substances, often at only a fraction of the cost of the natural product, has led to a great extension in the use of such substances, more especially for the perfuming of soaps, creams and other toilet materials.

It has been pointed out that the synthetic production of the colouring matters alizarin and indigotin produced vast social and economic changes by the more or less complete supersession of natural by synthetic dyes. In the commercial production of camphor one finds another illustration of the successful synthesis of an important natural product, without, however, the same disastrous consequences to the latter.

Camphor, one of the most familiar of substances, has been produced for many centuries in Japan, Borneo, Formosa, and other regions of the Far East. It is found chiefly in the leaves of a species of the laurel-tree, the *Laurus camphora*, from which it is obtained by distilling the leaves or other parts of the tree in a current of steam. The camphor, being volatile, passes over with the steam and can be condensed in cooled vessels.

Camphor has for long been a highly valued substance on account of its therapeutic, disinfecting and other properties, and the demand for the compound has been very greatly increased in the past fifty or sixty years owing, more especially, to its employment in the manufacture of celluloid for

cinema and photographic films and plastics. Japan had, therefore, a valuable source of revenue in her practical monopoly of the production of camphor through her possession of the plantations of the camphor-tree in Formosa, the extent of which, in the years following the Russo-Japanese War, she very greatly increased; and the monopoly she possessed she sought to exploit to the utmost.

The substance, however, had long attracted the attention of chemists, and in spite of the difficulty of the problem its molecular constitution was at length unravelled and the compound prepared synthetically in 1903. Two years later, synthetic camphor, identical in all respects with the substance produced in the camphor-tree, was placed on the market in competition with the natural product.

The Japanese camphor plantations have hitherto escaped the fate which befell the plantations of madder, and, so far as can be foreseen, they are not likely to suffer great disaster. The reason for this, however, lies outside the control of the chemist, and is to be found in the scarcity and cost of the raw material used in the manufacture. The source of the raw material is oil of turpentine, an essential oil which is produced in trees belonging to different species of pine, and which is not only restricted in quantity, but is also subject to increase in price. The synthetic camphor, therefore, has not been able to displace the natural, but it has prevented an excessive rise in the price of the compound.

The remarkable achievements of the last half century in the synthesis of dyes, drugs, perfumes, etc., give an almost prophetic sound to the words of Lucretius: "I tell you, barbaric robes and radiant Melibœan purple dipped in Thessalian dye of shells (and the hues which are displayed) by the golden brood of peacocks steeped in laughing beauty would be thrown aside surpassed by some new colour of things; the smell of myrrh would be despised and the flavours of honey . . . would in like sort be suppressed . . . for something ever would arise more surpassing than the rest."

Plastics

Among the most important of industrial synthetic products are those numerous materials which are known by the general name of plastics. These materials, although hard and rigid under ordinary conditions, exhibit the property of plasticity, or the property of undergoing deformation under mechanical stress, during some stage of their manufacture. In some cases, they are *thermoplastic* ; in others, *thermosetting*. The former become plastic when heated, and can be repeatedly moulded and remoulded by the application of heat and pressure ; the latter also can be moulded by heat and pressure, but undergo a chemical change under the action of heat and pass into a hard mass which cannot be softened and remoulded by the further application of heat and pressure. To the former group belongs celluloid (p. 148), one of the first plastics to be introduced ; to the latter, bakelite.

To whichever group they belong, plastics are compounds with large molecules, or compounds of high molecular weight. In some cases, the large molecules have been built up by nature and exist in the raw material (*e.g.* cellulose) used in the manufacture of the plastic ; but in most cases, the large molecules are formed during manufacture, either by the combining together of a large number of small molecules, that is, by *polymerisation* (p. 98), or by a chemical reaction in which a molecule of water is eliminated between each pair of simple molecules, that is, by *condensation* (p. 138). The formation of polythene (p. 336) is an example of the former process ; the formation of nylon (p. 337), an example of the latter.

Although, no doubt, plastics were at first introduced as substitutes for naturally occurring materials—bone, ivory, gums and resins—they must no longer be so regarded ; and certainly not as substitutes which are inferior to natural products. Plastics are new materials made available to man,

materials which have their own distinctive and valuable properties. For many purposes, they are superior to and have displaced wood, metal and stoneware, and they have found very widespread and varied use as new constructional materials. The foundation of what has now become a vast and rapidly expanding industry was laid by the American chemist, L. H. BAEKELAND, about the year 1908.

On warming together phenol (carbolic acid) and formaldehyde (p. 135), along with a little ammonia, which hastens the reaction, a thick gummy mass is produced. When freshly prepared this gummy material can be dissolved in alcohol, acetone and other similar solvents, and used as a lacquer or varnish ; but on being heated, under pressure, to a temperature of over 100° C. or 212° F., it undergoes polymerisation and changes into a hard, resin-like solid, to which the commercial name of *bakelite* is given. Bakelite is a thermosetting plastic, is infusible and insoluble in all solvents, and is the most versatile and widely used of all the synthetic resins. It is an excellent insulator for electricity, and finds, in consequence, its most important applications in the electrical industries. Bakelite may be employed for a great variety of purposes—as a substitute for amber in pipe-stems and beads ; and for making buttons, knobs, knife-handles, telephone instruments and many other articles for which bone, celluloid, ebonite, or other material was formerly employed. It is not so flexible as celluloid, but it is more durable, is not inflammable, and is less expensive. In some of their most important applications, the phenol-formaldehyde resins are used along with various fibrous " fillers "—wood-meal, cotton fibre, asbestos, etc.—whereby the strength and resistance to shock are increased and the moulding properties improved. Layers of textile fabric, impregnated with a solution of phenol-formaldehyde resin in volatile organic solvents, and moulded and hardened under heat and pressure, are used not only as insulating materials, but also for noiseless gears, bearings and decorative panelling.

Wood, also, impregnated with the initial liquid material, and then heated, becomes coated with a hard enamel-like layer, equal to the best Japanese lacquer; and metal articles, similarly, can be covered with a hard and resistant coating.

For the production of plastics, use may be made not only of phenol but also of cresol, and besides formaldehyde other aldehydes may be employed. Thus, when phenol is allowed to react with an aldehyde known as furfuraldehyde (obtained by heating bran, corn-cobs, etc., with acid), another series of resins can be obtained, which, like bakelite, can also be used as plastic material.

A notable advance in the production of synthetic resins was made when it was discovered that a clear colourless solid is formed by the reaction between urea (p. 210) and formaldehyde. Attempts, however, to produce in this way an "organic glass," as a substitute for ordinary glass, failed, as it was not found possible to prevent the material from cracking under the strains brought about by shrinkage.

Fortunately it was found by the English chemist, E. C. ROSSITER, that when thiourea (p. 105) is substituted for urea, colourless resins are also produced; and by acting with formaldehyde on a mixture of urea and thiourea, under suitable conditions, a mixed thermosetting resin is obtained which has properties superior to either of the single resins, and which shows no tendency to crack. This mixed resin, produced industrially under the name *beetle ware*, forms a transparent, colourless material, of glass-like clearness. It may also be tinted or coloured and used for domestic ware, electrical switches and fittings, lacquers and many other purposes.

Urea-formaldehyde resins are also made use of for the production of non-creasing cotton goods. The fabric is impregnated with a solution of urea and formaldehyde and the resin formed, by heating, on the fibre.

Of still greater importance as a transparent "organic

glass " is the synthetic resin introduced by Imperial Chemical Industries under the name *perspex*, a material produced from the compound known as methyl methacrylate ($\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>\!C\cdot COOCH_3$). This compound — formed from acetone, hydrocyanic acid and methyl alcohol—is a liquid which, in presence of oxygen or organic peroxides, undergoes polymerisation and is gradually transformed into a colourless glass.

Perspex (also called *lucite* in America) has a transparency second only to that of quartz glass (p. 218) and is the most successful organic substitute for glass so far obtained. It is thermoplastic and can be moulded into spectacle lenses, photographic lenses, and other optical apparatus. The cost involved in grinding glass is thus avoided. As it is non-splinterable, perspex is now also finding extensive use in the construction of the cockpits, turrets, etc., of aeroplanes and in the production of bullet-proof " glass." Its specific gravity is only about one-third that of glass, but a sheet of perspex is about ten times as strong as glass of equal thickness. It is largely used for dentures.

By allowing methyl methacrylate to undergo polymerisation in an emulsified condition, the resin is obtained in a granular form. This is sold for moulding purposes under the name *diakon*.

By means of a trace of oxygen, the unsaturated hydrocarbon ethylene, when under a high pressure, undergoes polymerisation and forms polyethylene or *polythene*, a long chain hydrocarbon consisting of about 1000–2000 CH_2–groups joined together. In this way one obtains a very remarkable plastic, the trade name of which is *alkathene*. It is one of the lightest of all the plastics and will float on water. It is characterised by its toughness and flexibility, its resistance to water, its chemical inertness and its unique electrical properties. Its tensile strength can be increased by cold drawing. It is used as a flexible insulating covering

for electric wires and cables, for making collapsible tubes for creams, cosmetics, etc., and for the production of flexible or rigid piping.

By allowing butyraldehyde, $C_3H_7 \cdot CHO$, to react with polymerised vinyl alcohol

$$(\cdots -CH(OH) \cdot CH_2 \cdot CH(OH) \cdot CH_2 - \cdots),$$

a long chain molecule is formed, one link of which can be represented by the formula

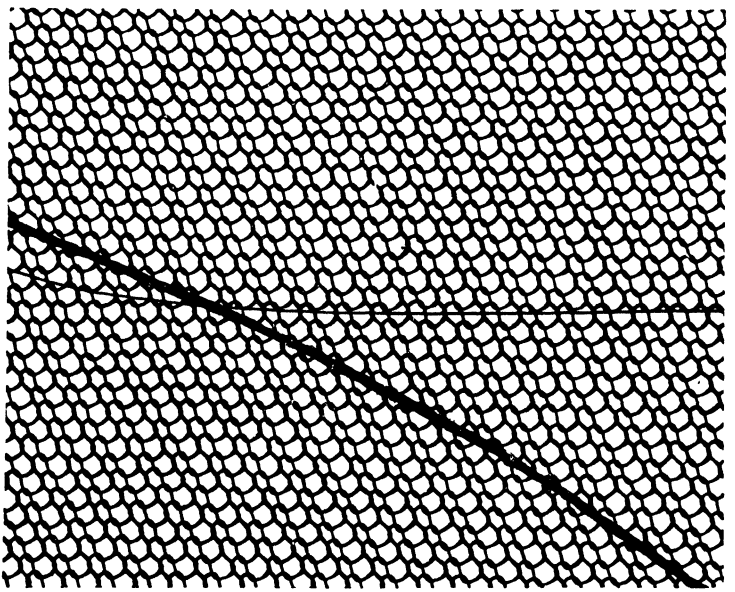
$$\begin{array}{c} -CH_2-CH-CH_2-CH-CH_2- \\ \dot{O}-\!\!-CH-\!\!-\dot{O} \\ \dot{C}_3H_7 \end{array}$$

This forms a strong plastic material, polyvinyl butyral or *butvar*, used in the U.S.A. as an interlayer for triplex safety glass.

As in the case of celluloid, so also in the case of the plastic *erinoid* or *galalith*, the raw material is a natural product of high molecular weight, a protein known as casein (p. 357). Ground casein, mixed with filler and pigment, if desired, is heated and extruded by pressure in the form of a rod, or formed into sheets by pressing between metal plates at a suitable temperature. It is then " cured " or hardened and rendered insoluble and horn-like by being soaked in a solution of formaldehyde (formalin). By suitable working it can be made to resemble bone, ivory, horn, coral, tortoise-shell, amber, etc., and is used for a great variety of articles, *e.g.* buttons, beads, umbrella handles, combs. It is non-inflammable but cannot be obtained in a form suitable for photographic films.

In 1940, there was produced by the firm du Pont de Nemours, in America, a compound to which the trade name *nylon* was given. It is obtained by allowing the compound hexamethylene diamine, $NH_2 \cdot (CH_2)_6 \cdot NH_2$, to react with adipic acid, $COOH \cdot (CH_2)_4 \cdot COOH$. By a process of condensation (p. 138), a highly complex molecule with the

protein-like structure $[-NH\cdot(CH_2)_6\cdot NH\cdot CO\cdot(CH_2)_4\cdot CO-]_n$ is built up, the molecular weight of the compound being greater than 10,000. In the molten state it can be extruded through perforated plates to form strong and elastic filaments with a silky lustre. By drawing out these extruded filaments to about four times their original length, the long chain



[*Courtesy of Science Service, Inc.*

FINE MESH OF NYLON STOCKINGS, CONTRASTED WITH A HUMAN HAIR (FINE HORIZONTAL LINE) AND A PIECE OF NO. 60 SEWING COTTON) (HEAVY DIAGONAL LINE).

molecules are orientated and the tensile strength is greatly increased. Transparency and a high degree of lustre are also developed. On account of its great tensile strength, fabric woven of nylon yarn has found extensive use for parachutes ; and ropes of nylon were used during the war for towing gliders. A nylon rope, half an inch in diameter, will support a weight of three tons. Weight for weight, it has a greater tensile strength than steel.

Nylon can also be obtained in the form of sheets and of bristles, for use in tooth brushes, for example. Bristles for paint brushes, which have to have tapering ends, are also produced. Nylon is also extensively used in the manufacture of ladies' stockings and of strong fabrics for upholstery.

In 1904, Professor F. S. KIPPING, of University College, Nottingham, synthesised a number of compounds of the types $R{\cdot}Si(OH)_3$, $R_2{\cdot}Si(OH)_2$, where R stands for a hydrocarbon radical such as $CH_3{\cdot}$, $C_2H_5{\cdot}$, etc. These compounds, which were called *silicols*, were found readily to undergo condensation with loss of water and production of substances of high molecular weight known as *silicones*. These compounds were for long of theoretical interest only, but since 1945 their production on an industrial scale has been developed. By allowing condensation of different silicols or mixtures of silicols to take place, a great variety of silicones, liquid, semi-liquid and solid, can be obtained which have very remarkable properties. Possessing great heat resistance and high electrical insulating properties, the silicones have been coming into use as heat-resisting varnishes, as insulating liquids in electrical transformers, as lubricants, the viscosity of which varies very little with the temperature, as a rubber-like material which is stable to heat and is not hardened by cold. "Bouncing putty" is a methyl silicone polymer which is extremely elastic to sudden impact but is plastic under gradually imposed pressure. The silicones are highly water-repelling and may be used to impregnate cotton to give a waterproof material. Cost of production still restricts the use of these remarkable substances.

RUBBER-LIKE MATERIALS

One of the most important materials in our present-day civilisation is *rubber*, obtained by the coagulation, by means of acid, of the sap or latex of certain species of trees, more

especially *Hevea Brasiliensis*. Although, formerly, rubber was obtained mainly from the " wild " rubber trees, indigenous to the Amazon Valley, most of it is now derived from the plantations of cultivated trees in Malaya, Ceylon and Dutch East Indies. The production of plantation rubber has been greatly improved and increased by scientific investigation.

The development of the rubber industry dates especially from the discovery, made more than a hundred years ago by Thomas Hancock in London, that when rubber is " masticated " by being disintegrated and worked between rollers, it forms a plastic mass, and from the later discovery that rubber can be vulcanised by means of sulphur or by treatment with certain compounds of sulphur. In this way the stickiness of rubber on being heated is counteracted. When the amount of sulphur taken up by the rubber amounts to about 50 per cent., a hard rubber known as *vulcanite* or *ebonite* is obtained. This is a material which had, at one time, a great vogue for the production of moulded articles.

Most of the rubber used at the present day for motor-car tyres and for rubber articles of all kinds is vulcanised, but the properties of the finished article can be greatly modified and the process of manufacture facilitated by the addition of different substances. In 1915, it was found that the addition of carbon black, for example, increases the tensile strength of the rubber and confers a high degree of resistance to abrasion. By the addition to rubber of about 28 per cent. of carbon black and of certain " anti-oxidants," whereby the tendency to crack on exposure to light and air is counteracted, the life of a motor-car tyre has been trebled or quadrupled.

For many years chemists have sought to produce artificially rubber or a rubber-like material, and in recent times great success has attended their efforts.

It has long been known that when natural rubber is decomposed by heat, the most important product is a hydrocarbon called *isoprene* (CH_2:C(CH_3)·CH:CH_2) ; and

it was found that this compound, on being kept, very slowly undergoes polymerisation to form a rubber-like material, consisting of a large number of isoprene molecules combined together to form a large complex molecule. The process of polymerisation, however, took place so slowly that it was industrially of no value. In 1910, the important discovery was made, first in England and then in Germany, that the polymerisation of isoprene is very greatly accelerated by metallic sodium.

Although the polymerised isoprene was of no practical significance, it was found that the simpler hydrocarbon *butadiene* (CH_2:CH·CH:CH_2) can also be caused to polymerise with the formation of a rubber-like material ; and it is on the development of this process, more especially, that the efforts of chemists, at first in Germany but, in recent years, also in the U.S.A., Canada and Russia, have been concentrated. The artificial rubber produced from butadiene is generally referred to as *Buna.*[1] The butadiene required for this process can be synthesised from acetylene, and it is also obtained by various processes from alcohol and from the gases butane and butylene which are present in or can be obtained from petroleum. To bring about the polymerisation of butadiene, other catalysts than sodium, *e.g.* benzoyl peroxide, are now used.

To improve the qualities of the butadiene rubber, the butadiene is generally mixed with another polymerisable substance, especially with styrene, C_6H_5·CH:CH_2, or with acrylic nitrile, CH_2:CH·CN, and the two substances are polymerised together. The products so obtained are known as *Buna S* and *Buna N.* During the war, the U.S.A. established a synthetic rubber industry, the production of which in 1944 amounted to over 700,000 tons of Buna S (renamed GR·S).

[1] The name Buna is derived from bu (tadiene) and Na, the symbol for sodium. The name has, however, lost its significance as sodium is no longer used as catalyst to accelerate the polymerisation of butadiene.

At an earlier date, the firm of du Pont de Nemours introduced another synthetic rubber-like material, *neoprene*, formed by the polymerisation of chlorinated butadiene or *chloroprene* (CH_2:CCl·CH:CH_2). Although more similar to rubber in its molecular constitution than are other synthetic products, neoprene should not be regarded merely as a rubber substitute. It should rather be regarded as a new material with its own special qualities which make it suitable for a great variety of purposes for which rubber is not so well adapted. Neoprene, while it equals rubber in elasticity, strength and resistance to abrasion, is greatly superior to rubber in its resistance to petrol, oils, fats, solvents, heat and ozone. It is also less pervious to gases. While it can be destroyed by heat, it does not propagate flame. For many purposes, therefore, neoprene should be used in preference to rubber.

By treatment with chlorine, rubber can be chlorinated, and chlorinated rubber is now produced under the name *alloprene*. Mixed with a suitable solvent (*e.g.* xylene), with addition of decalin (decahydronaphthalene) or solvent naphtha, according to the rate of drying required, and with a plasticiser (*e.g. cerechlor* or chlorinated paraffin wax), alloprene is used as a protective paint, highly resistant to acids, alkalies and salts. In a fibrous or spongy form, alloprene is also an excellent heat and sound insulator. It can readily be moulded when hot.

CHAPTER XVII

FERMENTATION AND THE ACTION OF ENZYMES AND MICRO-ORGANISMS

WE have already seen (p. 184) how Nature, in carrying out her wonderful syntheses and decompositions within the animal and vegetable organism, makes use of a number of catalysts, the so-called *enzymes*, produced within the cells of the living plant or animal. Even in the lowliest forms of life, when as yet differentiation of structure and function has not appeared, when life with all its mystery is contained in the microcosm of a single cell, even there also these complex catalysts, without whose presence the great life-processes would slow down to the sluggishness of death, are produced, and exercise their quickening power. Borne on the breeze, carried in water, the earth teeming with their countless myriads, these micro-organisms—the yeasts, bacteria and moulds—through the enzymes which they produce, carry out, unseen, the never-ceasing changes of an ever-changing Nature. Putrefaction and decay, by means of which Nature resolves the body of a life outlived into the elements from which new living structures can be built; the souring and curdling of milk; the production of the dye-stuff indigo from the compound indican contained in the woad; the "puering" of hides and the curing of tobacco; the development of the pungent flavour of mustard and the production of benzaldehyde or oil of bitter almonds from the amygdalin contained in the almond seed; all these and many other processes — so-called fermentation processes — by which complex organic material is broken down into simpler substances, are brought about by the action of living organisms which secrete the enzyme-catalyst appropriate to the process.

This explanation of the fermentation process—a term at first applied to all changes which are accompanied by effervescence due to the escape of gas—is one which has been accepted by science only in comparatively recent years. Prior to 1857, chemists and biologists were divided in their views. Some favoured the physical and chemical explanations put forward by Berzelius and Liebig. The former, who introduced the conception of "catalytic force" (p. 178), likened fermentation to the decomposition of hydrogen peroxide under the influence of platinum; and the latter, with greater apparent definiteness, regarded a ferment as being an unstable substance which, formed by the action of oxygen on the nitrogenous materials of the fermentable liquid, undergoes a decomposition. The internal motion which thereby took place was regarded as being communicated to the fermentable medium. With these mechanical explanations, however, dissatisfaction became more and more widely expressed, and in 1857 it was shown conclusively by Pasteur, to whose genius the advance of science in many directions is due, that all fermentative changes are associated with and produced by living organisms; and this vitalistic explanation, summed up by Pasteur in the well-known phrase, "No fermentation without life," is accepted, in the main, at the present day. The growth of knowledge, however, has rendered necessary a certain modification of the views which were put forward in the middle of last century. For a considerable time the view was held that the fermentation processes are the result of the direct action of the living organism on the fermentable material. Cases, however, began to accumulate of changes brought about by substances, *e.g.* diastase and pepsin, which are the product, certainly, of life, but are not themselves living; and the matter was put beyond dispute in 1897 when E. BUCHNER showed that in the production of alcohol from sugar, the fermentation is brought about not by the direct action of the living organism, but by a substance, which he called *zymase*,

produced by and contained in the cell of the yeast.[1] It is now generally accepted, therefore, that fermentation changes are produced by substances which although produced by living organisms are not themselves living; and to these substances the name *enzyme* (ἐν, in; ζύμη, yeast), introduced in 1878, is applied. In proposing the adoption of this term, the German physiologist, W. KÜHNE, stated: "This is not intended to imply any particular hypothesis, but it merely states that ἐν ζύμῃ (in yeast) something occurs that exerts this or that activity, which is considered to belong to the class called fermentative. The name is . . . intended to imply that more complex organisms, from which the enzymes, pepsin, trypsin, etc., can be obtained, are not so fundamentally different from the unicellular organisms as some people would have us believe."

Not only do the enzymes play an indispensable *rôle* in the economy of Nature, but they play also an essential part in many of the most important industrial processes. Of the processes which depend on fermentation, none is of greater importance than that which has been carried on from the earliest days of man's history, the fermentation of sugar with production of alcohol.

Although in chemistry the term "alcohol" is a generic one, and is applied to a whole series of compounds in which the so-called *hydroxyl* group (OH) is present, the name when used without qualification is applied to the best known and most valuable of the alcohols, *ethyl alcohol* ($C_2H_5 \cdot OH$), or as it is frequently called, *spirits of wine*. In the fermentation industry, it is sometimes also called grain spirit or grain alcohol, or potato spirit, according as the raw material of its manufacture is derived from grain or from potatoes.

Alcohol is produced by the action of a particular enzyme,

[1] Zymase, it has been shown, consists of at least two substances, an enzyme and a co-enzyme, one a colloid, the other a crystalloid (p. 275), and the presence of both is necessary for fermentation.

zymase, on certain sugars, the most important of which is the sugar glucose which, along with the isomeric sugar, fructose, is found in sweet fruits and in honey. Zymase is secreted by the micro-organisms known as yeasts (*Saccharomycetes*), and when yeast is introduced into a solution of glucose, decomposition of the latter with production of alcohol and of carbon dioxide is brought about through the agency of the zymase. Not all sugars, however, can be fermented by zymase. Thus, cane or beetroot sugar (known chemically as *sucrose*), and malt sugar or maltose, are not fermentable with zymase. If, however, yeast is introduced into solutions of these sugars, fermentation does take place, owing to the fact that yeast secretes not only the enzyme zymase, but also the enzymes *invertase* and *maltase*. The former of these converts cane and beetroot sugar into the two simpler isomeric sugars, glucose and fructose, by a process of hydrolysis (p. 150),

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

and maltase, similarly, converts maltose into glucose. The production of alcohol from sugars by means of yeast is, therefore, to be referred, in the last instance, to a fermentation of glucose (sometimes also of fructose) by zymase.

Fermentable sugars can be obtained not only from sucrose (which is largely employed in France in the form of beetroot molasses), but also from starch, which constitutes, as a matter of fact, by far the most important raw material for the manufacture of alcohol. The starch is of varied origin. In England it is derived mainly from maize, rice, wheat and barley, and in the United States, also, maize (corn) is largely used. In the future, cellulose, from wood-waste, may perhaps play a *rôle* of still greater importance (p. 150). In Germany, most of the starch is derived from potatoes.

For the conversion of the starch into fermentable sugar,

use is chiefly made of the enzyme *diastase*, contained in malt; or, the starch can also be converted into glucose by heating with dilute sulphuric acid. In the latter process, the large starch molecule undergoes hydrolysis (p. 150) and breaks up into the smaller molecules of glucose of which, like the cellulose molecule, it is built up. It is of some interest to note here, that the reverse process, the synthesis or building up of the starch molecule by the condensation of molecules of glucose, has also been effected under the influence of enzymes.

For the production of malt, barley grains are steeped for some days in water and then spread out, or "couched" to a depth of two or three feet on the floor of the malt-house. Soon the moist grain begins to sprout and to become hot. As the temperature must not be allowed to rise above 15° C. or 60° F., the "couch" is broken down and the germinating barley spread out in a thin layer, only a few inches in depth, turned over from time to time so as to allow access of air to the grains, and sprinkled with water when necessary. During the germination of the barley, diastase and other enzymes are produced, and when growth has proceeded sufficiently far, it is stopped by allowing the rootlets to wither, and then drying the malt in a kiln. The malt, which contains a considerable amount of starch and a small amount of sugar, together with the enzyme diastase, is crushed and mixed with hot water, and a quantity of raw grain or potato starch is added. By the action of the diastase, which is best carried out at a temperature between 40° and 60° C. or 104° and 140° F., the starch is converted into maltose or malt sugar. When this process of "mashing" is complete, the liquid is boiled to destroy the diastase, and the sweet liquor or "wort" is run into the fermenting vats and yeast is added.[1] By the action of the enzyme maltase, which is contained in the yeast, the maltose is converted into glucose; and this, in turn, is

[1] The necessity for using pure culture yeasts belonging to definite races is now recognised. The result of the fermentation varies with different yeasts.

converted by the yeast-enzyme zymase mainly into alcohol and carbon dioxide, although small quantities of other substances—higher alcohols, succinic acid, etc.—are also produced.

Alcohol may also be produced by the action of yeast on commercial glucose, obtained by heating starch (*e.g.* potato starch), or cellulose (p. 150), with dilute sulphuric acid, or on cane sugar and beetroot sugar molasses (sucrose). In the latter case, conversion of the sucrose to the fermentable sugars, glucose and fructose, is effected by the yeast-enzyme, invertase.

When fermentation is allowed to take place at a temperature of about 15° C. or 60° F., a turbulent effervescence is produced and the evolution of carbon dioxide is so rapid that the yeast cells are carried to the surface of the liquid and there form a thick froth. This is known as " top fermentation," and is the process which is mostly used in England. On the other hand, when the temperature is kept low, say about 6° C. or 43° F., the evolution of carbon dioxide is too slow to buoy up the yeast cells, which therefore remain at the bottom of the vat. This is known as " bottom fermentation," and is made use of in Germany in the production of certain beers.

The fermentation of the sugar solutions does not proceed indefinitely, and when the liquid contains from 10 to 18 per cent. of ethyl alcohol, the fermentation stops. The liquid, or " wash," as it is now called, contains not only ethyl alcohol, but also furfural (or furfuraldehyde) and fusel oil—a mixture of higher-boiling alcohols, such as butyl alcohol, $C_4H_9 \cdot OH$, and amyl alcohol, $C_5H_{11} \cdot OH$, and other substances. From these different substances the ethyl alcohol is separated by distillation in special fractionating stills (*e.g.* the Coffey still), from which a mixture of alcohol and water containing about 96 or 98 per cent. of alcohol by volume is directly obtained. Alcohol so obtained is spoken of as " silent spirit," or " patent still spirit." By allowing this alcohol to

stand over quicklime for some time and then distilling, " absolute alcohol," or pure ethyl alcohol, is obtained.[1]

For industrial and other purposes, alcohol finds abundant and varied use. Not only is it employed as a heating agent, in spirit lamps, but it is also used, to some extent, as an illuminant (with incandescent mantles), and as a motor fuel, when mixed with ether or with benzene. Its relatively high cost, however, militates against any immediate and extensive development in this direction. Alcohol is also used very extensively as a solvent in the preparation of varnishes, lacquers and enamels ;[2] in the manufacture of ether, chloroform, acetic acid, celluloid, collodion, dyes, cordite and similar explosives, and many other substances. Ordinary *methylated spirit*, so largely used in spirit lamps and for other purposes, consists of ethyl alcohol " denatured " by the addition of wood-naphtha (crude wood spirit or methyl alcohol), and mineral naphtha,[3] the presence of which is intended to render the liquid undrinkable. Such methylated spirit is free from the excise duty ordinarily placed on alcohol. For industrial purposes, special *industrial methylated spirit* can also be obtained which consists of alcohol denatured with wood-naphtha only or with other denaturants suitable for particular industries.

[1] For the purposes of taxation in Great Britain the strength or concentration of a spirit is generally expressed in terms of " proof " spirit. Proof spirit is a mixture containing 49·24 per cent. by weight, or 57·1 per cent. by volume, of alcohol. Weaker spirits are said to be so much " under proof " according to the percentage of water and proof spirit which they contain. Thus, a spirit 10° under proof means a liquid which contains, at 60° F., 10 volumes of water and 90 volumes of proof spirit. " Over-proof " spirits are defined by the number of volumes of proof spirit which 100 volumes of the spirit would give when diluted with water to proof strength. If 100 volumes of an over-proof spirit would yield 150 volumes of proof spirit, it is said to be 50° over proof.

[2] For many technical purposes the place of ethyl alcohol is being taken by the cheaper isopropyl alcohol ($CH_3 \cdot CH \cdot OH \cdot CH_3$), which is prepared synthetically by passing acetone vapour and hydrogen over a heated nickel catalyst, or by the action of dilute sulphuric acid, in presence of a catalyst, on propylene obtained by the cracking of mineral oils (p. 95).

[3] In the United States, alcotate, a mineral oil product, is used, and in Germany, methyl alcohol and pyridine bases, derived from coal-tar.

In the process already described, starch is converted into fermentable sugars by means of diastase or by heating with dilute sulphuric acid. About the beginning of this century, however, another process, the so-called " amylo " process, was introduced for the saccharification of starch, and this process has now developed into an industry of considerable magnitude.

Many moulds produce the enzyme diastase and possess, therefore, the power of converting starch into fermentable sugar. This fact has been made use of in the East from very early times, Chinese yeast, which has been largely used for this purpose, containing the mould *Mucor rouxii*. Mixed with various materials, it is sold under the name of " migen " or " men." In the modern process, which has been carried out chiefly in France, and to a less extent in Spain, Italy and the United States, the moulds employed are *Rhizopus Delemar* and *Mucor Boulard*.

Maize, rice, potatoes, or other starchy material is reduced to a state of fine division and then steeped for a short time in water; after this, it is heated by means of steam so as to render the starch gelatinous. The liquid (" mash ") is transferred to the fermenting vessel and after it has cooled down, spores of the mould are added. Growth takes place rapidly, and in twelve or fifteen hours the mass is penetrated by the mycelium of the mould. A few hours after the introduction of the mould, when, therefore, a certain amount of sugar has been formed, yeast is added; the processes of saccharification and of fermentation then go on side by side. Less fusel oil is produced in this process and the yield of alcohol is higher than when the fermentation is carried out in the ordinary way.

Although ethyl alcohol is produced mainly by the fermentation process, large quantities are also produced in Switzerland from acetylene (p. 356), and it can readily be manufactured, also, from the hydrocarbon ethylene, enormous quantities of which are available in natural gas and the gas from the cracking of mineral oils.

In the case of *alcoholic beverages*, although ethyl alcohol is the most important ingredient, the taste, aroma and special character of each depend on the presence of small quantities of other substances, which vary both in amount and in kind with the materials from which the beverage is prepared, and with the method of its preparation. These beverages may be classed into distilled liquors (spirits), wines and beers.

In the case of *whisky*, the process of fermentation is carried out essentially as already described ; malted barley, mainly,

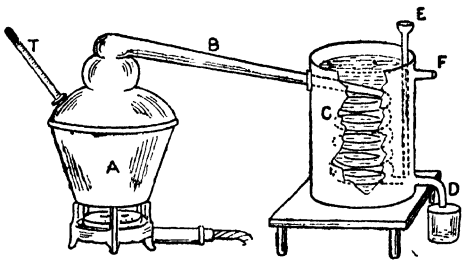


FIG. 29.—APPARATUS USED FOR DISTILLING LIQUIDS.

A, a vessel in which the liquid is boiled and so converted into vapour which passes through the long neck, B, to a spiral " worm," or condenser, C, kept cold by means of flowing water. The condensed vapour issues at D and can be collected. E, tube through which cold water enters ; F, exit for warm condenser water ; T, thermometer to indicate the temperature of the vapour.

is employed, and the wash is distilled from a simple pot-still similar to that shown in Fig. 29. The result, therefore, is not merely a mixture of pure alcohol and water, but one which also contains small quantities of various other substances—fusel oil, aldehydes, esters, etc. This raw whisky is then placed in casks to mature, and during this process the aldehydes become converted into acids which unite with the alcohols present to form esters, which give a special flavour and aroma to the whisky.

In the case of *gin*, the distilled spirit is flavoured by redistilling with juniper berries, coriander, fennel, or other

substances; *brandy* is obtained by distilling wine, and owes its particular flavour to the various esters contained in the wine from which it is prepared; and *rum*, prepared from fermented molasses, owes its flavour chiefly to the esters, ethyl acetate and ethyl butyrate. Sometimes it is also flavoured by placing the leaves of the sugar-cane in the still.

These distilled liquors all contain a high percentage, 40 to 50 per cent., or more, of alcohol.

Wines are prepared by the fermentation of fruit juices—chiefly juice of the grape—in which the two sugars, glucose and fructose, are present. The juice also contains various acids, especially tartaric acid; and the skins of the grape contain tannin, various essential oils, and, it may be, colouring matter. These all pass into the juice when the grapes are pressed, and according to their nature and relative amounts, give wines of different flavours and qualities.

Owing to the presence of a species of *Saccharomyces* on the grape itself, fermentation of grape juice must have been observed in warm, grape-growing countries at a very early period in man's history; and the manufacture of wine must have been developed at a very remote time. Although the grapes are now crushed mainly by wooden rollers, the method of treading with the bare feet—treading the wine press—has not yet ceased to be practised. The juice extracted from the grape is called "must," and by its fermentation, alcohol is produced. After the first "active fermentation" is over, the "new wine" is drawn into casks which are filled full and loosely closed in order to prevent the conversion of the alcohol into acetic acid (p. 355). In the casks, a "still fermentation" proceeds for several months, during which time the yeast settles down, and the tartaric acid, along with various salts and colouring matters, separates out as *argol*. This consists chiefly of potassium hydrogen tartrate, and is the main source of this salt, known familiarly as *cream of tartar*.

After the wine has become clear, it is drawn off into casks

and allowed to ripen for perhaps two or three years. During this process, the tannin and some other impurities are precipitated, and at the same time the alcohol and fusel oil combine with the small quantities of acids present to form esters, which give the peculiar and characteristic flavour and " bouquet " to the wine. After ripening, the wine is bottled.

Since the quality of the grape juice varies with the soil, and also with the climate, some vintages give better wines than others. Wines, also, are subject to " diseases," due to the presence of enzymes, which bring about an alteration of the wine, *e.g.* conversion of alcohol into acetic acid.

For the production of *beers*, malted grain is employed, but in the mashing process the complete conversion of the starch into maltose is not allowed to take place, a portion being converted only into the intermediate product of hydrolysis, dextrin.[1] This dextrin is retained in order to give " body " to the beer. Further, the nitrogenous compounds, the albuminoids and proteins, in the grain, are converted by the malt-enzyme, *peptase*, into peptones and other substances, which also add " body " to and increase the nutritive properties of the beer. All these various substances are classed together under the name " extract."

When mashing is complete, the wort is drawn off and boiled with hops, and, after settling, the clear liquid is fermented with yeast. When the active fermentation has subsided, the new beer is run into casks and slow fermentation allowed to continue, the froth which is formed being allowed to pass out through the bung-hole. At the conclusion of the process, the beer is drawn off into casks or bottles.

The fusel oils obtained as by-products in the manufacture of ethyl alcohol, and formerly regarded as waste material, are now subjected to special distillation in order

[1] Dextrin is also produced industrially by heating starch with dilute sulphuric acid. It is used as an adhesive on stamps, envelopes, etc. It constitutes the so-called " British gum."

to obtain the higher alcohols present. Although the composition of the fusel oil depends on the process in which it is formed, one can obtain from the different fusel oils the alcohols known as propyl alcohol ($C_3H_7 \cdot OH$), butyl and iso-butyl alcohol ($C_4H_9 \cdot OH$), and amyl and iso-amyl alcohol ($C_5H_{11} \cdot OH$). These alcohols find their use not only in the scientific laboratory, but also in industry, for the purpose of preparing artificial fruit-essences, and as solvents. These artificial fruit-essences and flavouring materials are pleasant-smelling compounds of alcohols with acids, known as *esters*. Thus amyl acetate (from amyl alcohol and acetic acid) forms the main constituent of artificial essence of pears; ethyl butyrate (from ethyl alcohol and butyric acid) is used in making artificial essence of pineapples; amyl butyrate is used in making apricot essence; and amyl iso-valerate (from amyl alcohol and iso-valeric acid) is used as a constituent of apple essence.

The introduction and increasing use of nitro-cellulose lacquers (p. 149), and the need for special solvents and plasticisers, have led to a demand for butyl and amyl alcohols which is greater than can be satisfied by fusel oil. Chemists, therefore, have been called upon to develop processes for the large-scale manufacture of these alcohols and of esters derived from them. At the present day, butyl alcohol (or butanol) is produced industrially from a mixture of carbon monoxide and hydrogen (p. 194), from acetylene and by the fermentation of starch (from maize, for example), by means of special bacterial cultures introduced by Professor FERNBACH, of the Pasteur Institute. In this process there are produced butyl alcohol (about 60 per cent.), acetone (about 30 per cent.), and ethyl alcohol (about 10 per cent.), as well as large quantities of carbon dioxide and hydrogen. The carbon dioxide is liquefied and then converted into carbon dioxide snow (p. 50), while the hydrogen is used for the production of ammonia (p. 207). From butyl alcohol there are produced various compounds, *e.g.* the solvent, butyl

acetate, and the plasticiser, butyl phthalate (from butyl alcohol and phthalic acid). Acetone, also, is a valuable solvent and is used in the manufacture of cordite, etc. Amyl alcohol is now produced industrially from the hydrocarbon pentane, C_5H_{12}, large quantities of which are present in natural gas.

Many weak alcoholic beverages, such as light wines, become sour when exposed for some time to the air. This souring is due to the conversion (oxidation) of the alcohol to acetic acid by the oxygen of the air, under the influence of certain fungi and bacteria (*e.g. Mycoderma aceti* and *Bacterium aceti*); and the process is carried out on a large scale for the production of *vinegar*.

In England, vinegar is manufactured mainly from malt, which is mashed and fermented with yeast as in the preparation of alcohol. After fermentation, the alcoholic liquor (in which not more than 10 per cent. of alcohol should be present), containing the nitrogenous matter and salts necessary for the growth of the bacteria, is sprinkled over beechwood shavings or basket work inoculated with the acetic acid bacteria, and contained in a large vat to which air can be admitted. In this way the alcoholic liquor is spread over a large surface while exposed to the action of the air, and oxidation of the alcohol to acetic acid rapidly takes place. The liquid is drawn off from the bottom of the vat and passed repeatedly over the same shavings or basket work, until conversion of the alcohol to acid is nearly complete. A very small amount of alcohol, however, is left in the vinegar because, otherwise, oxidation and destruction of the acetic acid would take place.

Vinegar thus obtained contains about 6 per cent. of acetic acid, but commercial vinegars are frequently weaker. Vinegar is also frequently made, especially in France, from wines, the process being carried out, as a rule, in large casks.

Although vinegar is, essentially, a dilute solution of acetic

acid in water, it receives its special flavour and quality from the presence of small quantities of other substances derived from the materials of its preparation, malt, wine, etc. More especially does it contain esters, like ethyl acetate, which impart their aroma to the vinegar.

Sometimes " vinegars " are prepared artificially by adding to a solution of acetic acid in water, caramel or burnt sugar, and various aromatic substances and esters.

The production of acetic acid on an industrial scale is not carried out by the method just described, since only a dilute solution (up to 10 per cent.) can be obtained in this way, but, as we have seen, by the distillation of wood. The pure acid forms ice-like crystals, which melt at 17° C. (62·6° F.), and is spoken of as *glacial acetic acid.*

Since, owing to the synthetic production of methanol from carbon monoxide and hydrogen, the wood distillation industry has greatly diminished, other methods have come into prominence for the production of acetic acid. When acetylene is passed into a dilute sulphuric acid solution containing mercuric sulphate, which acts as a catalyst, the acetylene combines with water to form a compound known as *acetaldehyde* ($CH_3 \cdot CHO$). Acetaldehyde is also produced industrially by passing the vapour of ethyl alcohol over heated silver-gauze. Under the catalytic action of the silver, hydrogen is removed from the ethyl alcohol and acetaldehyde is formed. By passing air or oxygen into liquid acetaldehyde to which solid manganese acetate has been added, oxidation of the aldehyde to acetic acid ($CH_3 \cdot COOH$) readily takes place. By acting on acetaldehyde with hydrogen in presence of nickel, as catalyst, the aldehyde is reduced to ethyl alcohol, $CH_3 \cdot CH_2 \cdot OH$.

At a low temperature, in presence of acids, acetaldehyde undergoes polymerisation and forms a white solid, known as *metaldehyde.* This is used as a " solid fuel," in place of methylated spirit, under the name " Meta."

The solvent *acetone*, to which repeated reference has been

made, is produced not only by the fermentation process already described, but also by passing the vapour of acetic acid, at a temperature of about 400° C. (752° F.), over a catalyst, *e.g.* oxide of thorium or of manganese. It is also produced by passing ethyl alcohol and steam over a suitable catalyst; by passing the vapour of isopropyl alcohol (p. 349, footnote) over a copper catalyst at 500° C.; or by passing a mixture of acetylene and steam over a heated zinc oxide-iron catalyst. These processes afford further illustration of the importance of catalysis, on which emphasis has already been laid.

When rennet is added to milk, the enzyme *rennin*, which it contains, brings about a curdling of the milk by causing a decomposition of the casein present in the milk into para-casein, which forms the curd, and whey albumin. This process of enzyme action is one of great importance, because it is employed not only for the industrial production of casein, but also as the first step in the manufacture of cheese. In making *cheese*, a " starter," or culture of bacteria capable of producing lactic acid from milk-sugar is added to milk at a controlled temperature, and rennet is then added. By careful control of the temperature and of the acidity, which increases gradually owing to the production of lactic acid, casein separates out as a curd, from which, later, whey is expelled. After allowing the curd to remain for some time in order to mature, it is ground, salted and pressed in a cheese-mould. The cheese is then allowed to " ripen," when a complicated series of changes takes place under the influence of various enzymes, part of the casein undergoing a decomposition with production of a number of different substances, the nature and amount of which vary greatly in the different kinds of cheese. The presence of these decomposition products gives the characteristic flavour to the cheese. The different kinds of cheese vary considerably in composition, but contain about 24 to 40 per cent. of water,

23 to 39 per cent. of fat, 27 to 33 per cent. of casein and other nitrogenous compounds, and 3 to 7 per cent. of salts.

In the industrial production of casein, skimmed milk is used, and the milk may be curdled by means of rennet, as already described, or by the addition of hydrochloric acid with careful control of the acidity. This acid-produced casein has a different composition and different physical properties from that obtained with rennet. It is largely used as a sizing material for paper and cotton ; in calico printing ; and in the manufacture of casein water-paints or *distempers* (casein mixed with alkali and slaked lime, to which mineral colouring matters are added).

Reference has already been made to the production of rayon and to the use of de-lustred rayon as a textile fibre of a wool-like appearance (p. 146). In 1935, another wool substitute or wool-like fibre, the invention of an Italian chemist, ANTONIO FERRETTI, of Milan, was placed on the market by the firm Snia Viscosa. This material, known as *lanital*, is made from casein and, in its molecular structure —that of a protein—approaches much more closely to wool than rayon does to silk.

Casein, made into a paste, is squirted through fine perforations in a steel disc, and the filaments so formed are coagulated in sulphuric acid. After drying, the filaments are treated with formaldehyde and a suitable plasticiser, whereby they are hardened, rendered more elastic and more resistant to water. By treatment with chlorine, the wool-like appearance of the lanital is accentuated. In its strength, lanital is somewhat inferior to wool, but great improvements have recently taken place and a material, not greatly inferior to wool in strength, has been obtained. Casein fibres of a superior quality are produced in America and marketed under the name *aralac*. Lanital and aralac are generally used in admixture with wool or cotton. They are non-creasing and do not shrink.

In 1945, the production in Great Britain of a wool-like

synthetic fibre, the invention of the chemists of Imperial Chemical Industries at Ardeer, was announced. It has been given the name *ardil* and is produced from the protein of ground-nuts or pea-nuts. An alkaline solution of the protein is extruded through spinnerets into a bath of sodium sulphate and sulphuric acid, the filaments stretched in order to increase their tensile strength and hardened in a solution of sodium chloride to which a small quantity of hydrochloric acid and of formaldehyde has been added.

When the fermentation of sugar solutions is brought about by means of yeast, ethyl alcohol, as we have learned, is formed as chief product. As far back as 1858, however, Pasteur had shown that appreciable amounts of glycerine are also produced, about three parts of glycerine being formed from one hundred parts of sugar. Since glycerine is a valuable substance, attempts began to be made to increase the proportion of glycerine by altering the conditions under which the yeast acted, and it was found that by making the fermenting liquid slightly alkaline by the addition of sodium sulphite or of sodium carbonate, the yield of glycerine could be increased up to nearly 40 per cent. of the sugar used. During the Great War of 1914–1918, this fermentation method for the production of glycerine was extensively employed in Germany, where, owing to the scarcity of fats, a dearth of glycerine, used for explosives, was threatened. By the fermentation process as much as 1,000,000 kilograms of glycerine a month are stated to have been produced. The cost of production, however, is higher than by the saponification of fats (p. 236).

During the past quarter of a century, the attention of chemists has been turned to the utilisation of the many thousands of tons of yeast which are produced annually in excess of that required in the fermentation industries. During the process of fermentation, the yeast grows and multiplies with very great rapidity, and builds up its proto-

plasmic cell contents from the organic and inorganic materials present in the fermenting liquid. Since the yeast contains large quantities of proteins and carbohydrates in addition to small amounts of fat and mineral matter, dried yeast has been used to a considerable extent as a food for cattle ; and from it also has been prepared, for human consumption, an extract (*marmite*), similar to extract of meat. This yeast extract is, indeed, claimed to be superior in its nourishing qualities to extract of meat by reason of the presence of the accessory food substances, the so-called vitamins.

The rapid growth and synthesising power of other micro-organisms have also been utilised, or their utilisation has been suggested, for the production of feeding stuffs. Thus, " mineral yeast," a form of *Torula*, can produce both proteins and fat when grown on a medium containing sugars and ammonium salts ; and the organism, *Endomyces vernalis*, can build up a material containing 18 per cent. of fat, 31 per cent. of proteins, and 43 per cent. of carbohydrates. These sources of proteins and fats may be of great importance in tropical countries where carbohydrates are plentiful but proteins are scarce.

CHAPTER XVIII

VITAMINS AND HORMONES

THE fundamental problem of organic chemistry, according to the French chemist, MARCELIN BERTHELOT, was the investigation of the compounds occurring in plants and animals and the proof "beyond all question that compounds identical with those produced by plants and animals can be synthesised from inorganic or mineral matter." This, no doubt, is somewhat too narrow a view to take of the aims and objects of organic chemistry, but the interest of such investigations made a powerful appeal to some of the foremost organic chemists in the second half of the nineteenth century, and led to the elucidation of the constitution and, in some cases, to the synthesis of sugars, essential oils, proteins and other products of the animal or plant organism. During the present century, interest in the compounds produced in plants and animals has been revived, and through the investigations of such substances there has been built up the important and rapidly growing branch of science known as *bio-chemistry*. One of the most notable features of this development has been the close co-operation which has been established between the organic chemist and the physiologist in the investigation of the processes of human nutrition and of the factors involved in the maintenance of health. It is possible to consider here only a few of the more important discoveries which have resulted from this co-operation.

In these days when so much interest is being taken in the health of the people and in the attainment of physical fitness, it can be no matter for surprise—it is, in fact, most desirable —that, especially in days of food scarcity, the subject of nutrition should arouse the widespread interest not only of those responsible for government and administration but also

of the people as a whole ; for health depends on adequate and proper nourishment, and without good health there can be no physical fitness.

Until early in this century, the problem of nutrition seemed to be a comparatively simple one and to find its solution in the supply to each individual of a sufficient amount of the proteins, fats and carbohydrates, together with salts and water, necessary to build up the tissues of the growing body, to repair waste, and to supply the energy necessary for the maintenance of the body temperature and the performance of mechanical work. It was the fear that the supply of food might become inadequate in amount that oppressed Sir William Crookes in 1898 (p. 202), and it was the prospect of famine that stimulated the increased production and use of fertilisers. That fear has, to a great extent, been removed and the problem of producing an ample supply of food to feed the world's starving millions has been solved. At the present day, interest is centred not so much in the quantity of food as in the quality ; not in the amount but in the kind. A sufficiency of proteins, fats and carbohydrates is, of course, still essential, but the danger to health comes, except in times of special crisis, not so much from under feeding, although that is not everywhere absent, as from wrong feeding.

Before the recent discoveries in the science of nutrition had been made, food was thought of mainly as a fuel, and the adequacy of a diet was decided largely on the basis of its fuel value, the amount of energy or the number of calories (p. 80) to which it could give rise by its combustion in the body. In the absence of fuller and more exact knowledge, one had to be content, more or less, with this view, although its inadequacy had been demonstrated by medical experience. It had long been known, for example, that one of the most distressing and fatal diseases to which sailors absent from home on long voyages were subject, was scurvy, a disease affecting not only the skin but the whole system, and which,

if not checked, must end fatally. Even on land, thousands have died of this disease and, during the Great War of 1914–1918, it attacked the Indian soldiers in Mesopotamia (Iraq). And yet, early in the eighteenth century, it had been shown that this disease could be cured by the administration of lemon or orange juice.[1] No drugs, in the ordinary sense, were necessary; only a slight alteration of the diet. Many found it difficult to believe that such a dreadful disease could be cured by such easy means. In a similar manner it gradually came to be realised that other diseases, *e.g.* beri-beri and rickets, could be cured by dietary measures. In other words, it came to be realised that these diseases are due not to the presence of toxins or other harmful substances in the diet or produced in the body, but to the absence of certain essential substances from the diet.

It was, more especially, by the work of Sir F. GOWLAND HOPKINS, at Cambridge, in 1906, and, later, of Professor MCCOLLUM and Miss MARGUERITE DAVIS, in America, that definite proof was obtained that health cannot be maintained on a diet of protein, fat, carbohydrate and salts only, but that small quantities, sometimes very minute quantities, of other substances, which were given the general name of *vitamins*, are necessary. By the application of this new knowledge, results, sometimes of a spectacular character, have been obtained in the prevention and cure of a number of diseases, the cause of which had long been obscure. It has also come to be realised that there may be a wide gap between perfect health and obvious disease; and that, even when there is no obvious disease, improvement of health, vigour and enjoyment of life may be brought about by an increase of the vitamins in the diet. It is now realised that minor ailments, carious teeth, slight rickets, gastric disturbances, etc., may be the result of mistakes in feeding and lack of vitamins. For this reason, greater attention is now also being

[1] Even in the seventeenth century, lemons and oranges were used for the cure of scurvy among the crews on the ships of the East India Company

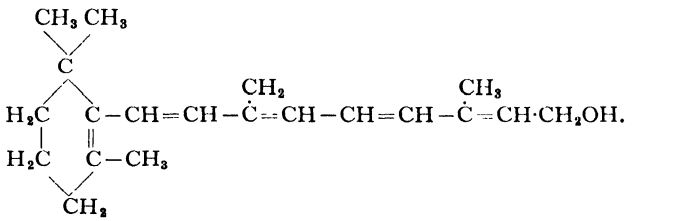
given to improving the quality or vitamin content of foodstuffs, a matter which is of especial importance in these days of a more sophisticated civilisation, when so much of our food is " processed " and thereby sometimes rendered deficient in vitamins.

The discovery of the existence and importance of vitamins initiated a search for and an investigation into the sources and nature of these " accessory food factors," as they were first called; and this investigation has been and is being carried out with great energy and success. Already some fifteen vitamins have been distinguished, and their number is continually being increased. Moreover, not only have the physiological effects of these vitamins been investigated, but their chemical composition and constitution have been the subject of intensive study; and so successful has this been that a number of these vitamins can now be produced, and are being produced, synthetically, on an industrial scale. Through the extraction from natural sources and standardisation of the potency of vitamins, as well as through their chemical synthesis in the laboratory or factory, it is now possible to enrich foods, when so desired, with vitamins in definite and controlled amount.

Ignorance of the nature and chemical individuality of the vitamins, when first discovered, led to their being designated by the letters of the alphabet, and this nomenclature is still to some extent retained. Some of the vitamins, however, originally thought to be single, have been shown to be mixtures of several vitamins, which have to be distinguished by numerals, *e.g.* vitamin B_1, vitamin B_2, etc.

Vitamin A.—This vitamin is of importance in promoting growth in children. It also improves the health of the skin and of the mucous membranes of the respiratory passages, and for this reason it gives increased resistance to bacterial infection. When this vitamin is absent from the diet for prolonged periods, night blindness, or inability to see in a dim light, and later, xerophthalmia, an infective condition of the eyes, supervene.

Chemical investigation has shown that the forerunner of vitamin A is a hydrocarbon, *carotene*, which has a large and complex molecule and a composition represented by the formula $C_{40}H_{56}$. This compound is found widely distributed in the vegetable kingdom : in tomatoes, apricots, bananas ; in carrots, spinach, lettuce and grass, and in various marine algæ. Carotene, when taken into the animal organism, is decomposed by water (hydrolysed) with production of vitamin A, a compound which has been shown by chemists to have its molecule built up as indicated by the formula :



It is formed by the splitting of the carotene molecule into two parts and the combination of each part with two atoms of hydrogen and one atom of oxygen.

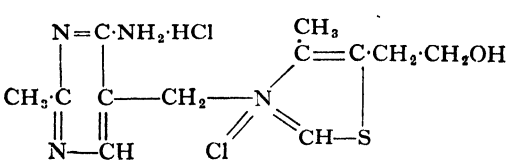
Man may obtain the necessary supply of vitamin A either from the carotene present in various vegetable foodstuffs or, ready formed, from foodstuffs, *e.g.* milk, butter, eggs, etc., derived from animals which have formed it from the carotene in their food. Any excess of the vitamin above that needed to satisfy immediate requirements is stored in the liver. A well-nourished person, therefore, possesses a certain reserve of vitamin A on which he can draw during periods (*e.g.* winter months), when fresh supplies of carotene or of ready-formed vitamin may not be so readily available. By far the richest natural sources of vitamin A are fish-liver oils, especially halibut-liver oil. This vitamin has been formed from the carotene present in the green marine algæ and has been stored up in the liver of the fish. From these fish-liver oils the vitamin is now extracted and placed on the market in a standardised and highly concentrated form, so that it is

now very easy to make good any deficiency of this vitamin in the diet. In Great Britain it is now always added to margarine. Although the chemical constitution of carotene has been elucidated and its synthesis effected in the laboratory, the compound has not so far been produced industrially.

Vitamin A is necessary to regenerate visual purple, the light sensitive substance in the retina, and it has been found that daily doses of carotene relieve eye-strain, reduce fatigue and increase the efficiency of workers engaged in matching colours.

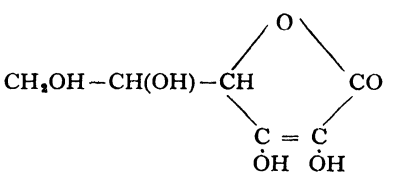
Vitamin B_1.—Deficiency of this vitamin leads to the dangerous neuritic disease known as beri-beri. This disease was particularly prevalent among Eastern peoples whose food consisted mainly of fish and rice. The vitamin is present in the germ or embryo of the rice and so long as the natural rice was used, beri-beri did not occur. When, however, polished rice, from which the germ has been removed, replaced the natural grain, the disease became rampant, and in the eighties of last century sailors of the Japanese Navy suffered greatly until the diet of meat and polished rice was supplemented by whole barley, in which vitamin B_1 is present. Foodstuffs which are rich in vitamin B_1 are yeast, wheat germ, egg yolk, lentils and ox liver. Since the vitamin is not stored in the body, adequate amounts of it must be supplied in the daily diet.

The composition and molecular structure of vitamin B_1 have been ascertained by chemists; and the compound, $C_{12}H_{17}ClN_4OS.HCl$, to which the name *aneurine* (in America, *thiamine*) has been given, is now produced synthetically on an industrial scale. How complex is this structure which chemists have succeeded in building up will be understood from the formula:



Vitamin B_2, which is present in yeast, egg-white, tomatoes and other foods, has been shown to be a complex of a number of different vitamins. One of these is a growth-promoting vitamin, and another is effective in preventing the disease called pellagra. The former constituent has been shown to be identical with the yellow pigment *riboflavin*, obtained from whey, and has the composition represented by the formula $C_{17}H_{20}N_4O_6$. The riboflavin content of milk is rapidly reduced by exposure to sunlight. The latter constituent was found to be identical with *nicotinic acid*, a compound which had been known to chemists long before its vitamin activity was recognised in the B_2 complex.

Vitamin C.—This is the antiscorbutic vitamin; the vitamin which is effective in preventing scurvy. This vitamin, which was known to be present in fresh green vegetables and in citrus fruits,[1] was, in 1932, isolated in a pure crystalline state and in relatively large amount from Hungarian red pepper (paprika), and in the following year its constitution was ascertained and its synthesis effected. This compound, identical with vitamin C, is known as *ascorbic acid*, and has the constitution



Ascorbic acid (vitamin C) is now produced industrially from glucose. It is optically active and rotates the plane of polarised light to the right. The lævo-rotatory acid can also be prepared, and this is found to have no anti-scorbutic effect. This is a further example of the difference in behaviour of two optically active isomers towards the molecularly asymmetric living tissues to which reference has already been made (pp. 306, 323).

[1] Zakatalsk nuts, grown in Russia, are said to have a vitamin C content about forty times that of lemons or oranges.

Ascorbic acid, now an article of manufacture and so made readily available to all, may suitably be added to jams and other preserves.

Vitamin D.—Rickets, which is generally associated with an imperfect calcification of the bones and teeth, is brought about not only through the absence of the necessary calcium salts and phosphates but also through absence or deficiency of vitamin D, a term now used to denote a group of different substances which have anti-rachitic properties. Even when the necessary salts are present, this vitamin is required for their proper utilisation. Although the obvious signs of rickets—curvature of bones, knock knees, etc.—may be absent, radiological examination may reveal the presence of this disease in apparently healthy children. In adults, also, deficiency of vitamin D may be the cause of the imperfect utilisation of calcium and phosphorus salts which may finally manifest itself in osteomalacia (a softening of the bones).

The most effective natural source of vitamin D is cod-liver oil or halibut-liver oil. The vitamin is present, also, in milk, butter and eggs, but in winter the amount may be small and may have to be supplemented by doses of cod- or halibut-liver oil, or of the pure vitamin.

In 1919 it was discovered that rickets was associated with absence of sunlight and could be cured, or alleviated, by exposure to sunlight or to the light of short wave length (ultraviolet light) emitted by a mercury vapour lamp. Later, in 1924, it was found that foods could be rendered anti-rachitically active by irradiation with ultraviolet light. The explanation of this action of sunlight or of ultraviolet light, whether emitted by the sun or by a mercury vapour lamp, was obtained when, in 1927, it was found that a substance, *ergosterol*, which is present in plants (*e.g.* ergot), yeast, etc., is converted by the light into a compound which is anti-rachitically active. This compound was isolated in the crystalline state in 1932 and was called *calciferol.* It was, at

first, thought to be identical with the vitamin D from cod-liver oil, but this is not the case. Calciferol, sometimes referred to as vitamin D_2, is not so anti-rachitically potent as the natural vitamin, referred to as D_3, present in cod-liver oil or formed by the action of the sun's rays or of ultraviolet light on the cholesterol (dehydrocholesterol) present in the fat glands of the skin of animals. This natural vitamin appears to be formed on the surface of the skin and is then absorbed by the body. This fact suggests that the anti-rachitic benefits of sun-bathing may be destroyed by subsequent bathing in water, unless sufficient time is given for the D_3 to be absorbed by the body.

Pure calciferol is now an article of commerce and can be used, when necessary, to supplement the natural supply of vitamin D in the daily diet. Addition of calciferol is now usually made to margarine.

Besides those just discussed, other vitamins are known—pyridoxin (B_6), biotin (H), tocopherol (E), etc.—and the synthetic production of some of them has already been worked out.

Hormones

Besides the vitamins which, as we have seen, are essential for the proper nutrition of the body and the prevention of certain diseases, other substances are required if health is to be maintained and if the various metabolic changes in the body are to take place in a normal and satisfactory manner. These substances, unlike the vitamins, are produced by the living animal cells in the ductless or endocrine glands, and are passed directly into the blood stream. Deficiency or excess of these substances brings about physiological abnormalities or disease. The purpose of these glandular secretions is to excite or arouse certain responses or reactions and, for this reason, they are called hormones.[1] They are, however, not always stimulating or activating, they may

[1] From the Greek *hormaō*, to excite or to arouse.

also be restraining. They are, in general, regulators of the metabolic changes in the body.

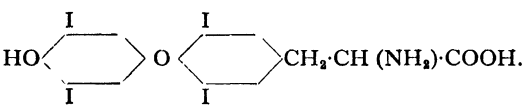
Reference has already been made to *adrenaline* and its use in bloodless surgery (p. 322). This hormone has the composition and structure represented by the formula $(OH)_2{:}C_6H_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NH{\cdot}CH_3$, and is now produced synthetically from *catechol*, $C_6H_4(OH)_2$, a substance which is formed in the dry distillation of catechu or cutch, a hard gum secreted by certain Indian species of *Acacia* and used in tanning and in calico-printing.

In the suprarenal glands, the adrenaline is probably stored as a readily decomposable compound with a protein, and during periods of emotional disturbance its production increases. When adrenaline is introduced into the blood, " it produces all the vascular and visceral reactions which accompany the emotions of danger, excitement and fright. The hair stands on end, the face becomes pale, the heart thumps urgently on the chest wall, the arterial blood pressure rises rapidly, the muscular coat of the bronchioles relaxes and leaves the airway clear for vigorous breathing, and glucose, the fuel of the muscular machine, is poured from the carbohydrate depot of the liver into the blood stream." The presence, however, of minute quantities of this hormone in the blood is necessary for the maintenance of a healthy tone.

Thyroxine.—This is the active principle of the hormone, thyroglobulin, formed in the thyroid gland. The hormone is needed in order to maintain the " basal metabolic rate," or the rate of heat production through oxidation in the body at rest, at its most advantageous value. If the thyroid secretion is absent or deficient in amount in infancy, cretinism, or a halt in the mental and physical development, occurs; and in adults there is a slowing down of the life processes, accumulation of fat, and a mental dullness and sluggishness. These are the symptoms of the disease known as myxœdema.

tion of extract of the thyroid gland. If there is hypertrophy of the thyroid gland, leading to an excessive production of the hormone, the consumption of oxygen is unduly accelerated, the life processes take place too rapidly, and the restlessness and nervous debility characteristic of Graves' disease, supervene.

In 1915 the active principle of the thyroid gland hormone was isolated in a crystalline form and called *thyroxine*; and in 1926 its constitution was determined and its synthesis effected. Thyroxine was thus shown to be a compound containing iodine and to have the formula,



This compound is now synthesised industrially at a cost lower than that of the substance extracted from the thyroid gland, and can be used in place of the extract in the treatment of cretinism and myxœdema. The naturally-occurring thyroxine is lævo-rotatory, while the synthetic product is, of course, inactive (racemic). This product, however, can be resolved into two oppositely active isomers—dextro-rotatory and lævo-rotatory thyroxine. The lævo-rotatory form is three times more active physiologically than the artificially produced dextro-rotatory isomer, another example of the difference in action of two optically active isomers on natural tissues.

The characteristic feature of thyroxine is its content of iodine, and this element, in the form of iodides or other compounds of iodine, must be taken into the body to furnish the necessary iodine. Failure to satisfy this requirement leads to goitre, or an enlargement of the thyroid, due to an attempt to increase the production of thyroxine. Hence the use of iodides in the treatment of goitre. Long ago, burnt sponge was used, and the effectiveness of this remedy

became intelligible when it was shown that sponges, seaweeds, etc., contain iodine in combination. Normally, iodine is taken in with the food or drinking water; and the main sources of this element are fish, crabs, lobsters, oysters, green peas, and beans.

Insulin.—Another hormone which is essential for the maintenance of health is insulin. This is produced in the pancreas and its main purpose seems to be to control the carbohydrate metabolism, or the changes which carbohydrates (sugars and starches) undergo in the body. A diminution in the production of insulin leads to a failure of the body tissues to burn and to store sugar (in the form of glycogen) in the liver. The content of sugar in the blood increases above the normal and brings about the state known as diabetes. Defective production of insulin by the pancreas can be made good by the subcutaneous injection of insulin, but excess must be avoided.

Insulin is a complex protein, the constitution of which is not yet known. It has, however, been separated in crystalline form, and one may therefore hope that its molecular constitution will in due course be unravelled and its synthetic production worked out. At present the active principle is extracted from the pancreas of the ox, pig or sheep, and this extract is used in the treatment of diabetes.

Besides the hormones just mentioned, there exist also a number which are associated with and are indispensable for normal and healthy sex activity, and the appearance of the secondary sex characteristics. Chemists have been very successful in elucidating the nature of the sex hormones, which are related chemically to the compounds cholesterol and ergosterol already mentioned. Not only have some of these hormones been synthesised, but chemists have also prepared substitutes, which are now produced industrially. These synthetic compounds can be successfully used clinically in place of the natural hormones to which, indeed, for many purposes, they are to be preferred.

From the discussion of the phenomena of catalysis (Chap. IX) one could not fail to realise the importance of minute quantities of certain substances in influencing the rate of chemical change ; and in the vitamins and hormones we meet with substances which seem to exercise some sort of catalytic effect in regulating the various chemical processes which go on in the living plant or animal organism. The presence of these substances, even though their amount may be extremely small, is of vital importance for health. The study of how even minute amounts of certain substances may completely change the state of health of man or of the animals is clearly one which exercises a peculiar fascination; and just as it became known, through the investigations of chemists, that certain small amounts of iodine (in a combined state) must be present in the food in order that the secretion of the thyroid gland may be effective, so, in recent years, it has been found that traces of a number of other elements are essential for the health of man or of the animals. Reference has already been made to the importance of trace elements for the health of plants (p. 211).

That iron, which is a constituent of hæmoglobin, is essential for health has long been known, but it is only in recent years that it has become known that the presence of minute quantities of copper is necessary for the efficient transference of the iron into the hæmoglobin, and many cases of pernicious anæmia are due to a deficiency of copper. The daily intake of copper for an adult should be about 4–5 milligrams, and if this is not supplied in the food, health is impaired. In many cases, severe wastage diseases among animals have been cured by the addition of small quantities of copper salts to the diet.

Small quantities of manganese salts are necessary for the proper development of the fœtus, and deficiency of cobalt has been found to be the cause of "bush sickness" in sheep and cattle. It may be cured by adding cobalt salts to the soil (whence it passes into the pasture) or to the salt licks.

As little as 1 milligram of cobalt per day is sufficient to secure health. It may be noted, also, that trace elements, especially zinc and manganese, are intimately connected with the proper utilisation of vitamins by the body and are generally associated with the natural vitamins. They are, of course, not present in the synthetic vitamins.

And now we must conclude. Giving a backward look, we see how out of the mysticism and obscurantism of the earlier alchemistic period there has grown the science of chemistry, which offers to the mind a clear and well-ordered account of the constitution of matter and of the laws of chemical combination. We have seen also how, during the past hundred years, much has been added not only to our philosophic conceptions regarding the universe of matter, but also to the great array of substances which, in various ways, have proved of benefit to mankind. But great as have been the services rendered by chemistry hitherto, its power to contribute to man's comfort and well-being and to the general advancement of civilisation and of culture, is not yet exhausted; nay, rather, the achievements of the past are but an earnest, we may confidently believe, of what will still be accomplished in the future.

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