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EXPERIMENTAL METHODS IN GAS REACTIONS

EXPERIMENTAL METHODS IN GAS REACTIONS

BY

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PREFACE

WITHIN recent years the study of the kinetics of gas reactions has assumed a prominent rôle in chemistry. One of the consequences of that development has been the appearance of a large number of monographs dealing with every aspect of the subject. Nearly all texts, as is natural, are confined to a discussion of the results of experiments rather than to the methods whereby the data have been obtained. The present book is an attempt to remedy the matter and repair an obvious omission.

It is designed mainly to give a reasonably complete account of the methods of investigating all types of gaseous reactions, together with sufficient theory in order that there should be the minimum gap between theory and practice. While it is intended that the beginner will benefit from the work, the text is arranged in such a way that it may serve as a book of reference for those chemists and physicists engaged in dealing with gas reactions, with high vacua or with any investigation where a knowledge of the preparation and handling of gases is required. A chapter is also included on photochemical technique, which is not necessarily confined to experiments with gases. There is also an omission—a chapter on macro-gas analysis. The reason is that there are several excellent books on the subject.

Grateful acknowledgment is made to Messrs. W. Edwards & Co. for loaning blocks for some of the figures, for permission to reproduce information from their catalogues, for advance details of new vacuum devices and for help in many other ways. The authors are indebted to Mr. T. Carlton Sutton for an unpublished description and a drawing of his capillary method of gas analysis.

Finally especial thanks are accorded to Dr. J. L. Bolland for the painstaking care with which he has pointed out mistakes and obscurities in the manuscript, for checking the references and for the laborious task of proof reading.

The authors' names on the title page are in alphabetical order.

A. F.
H. W. M.

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K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie* (Steinkopff), Figs. 140, 143, 145.

Chemical Engineer's Handbook (McGraw-Hill), Table 40, p. 269.

L. Dunoyer, *Vacuum Practice* (Bell), Fig. 7.

International Critical Tables (Hermann ; McGraw-Hill), Tables 18, 19, 20, 21.

Journal of Chemical Physics, Fig. 64.

Journal of the Chemical Society, Figs. 12, 55, 168.

Journal of Scientific Instruments, Fig. 31.

Journal of Industrial and Engineering Chemistry, Fig. 221.

G. W. C. Kaye, *High Vacua* (Longmans), Figs. 24, 60, 63.

M. Knudsen, *Kinetic Theory of Gases* (Methuen), Fig. 68 c.

Proceedings of the Royal Society, Figs. 135, 167, 170, 217, 231, 233, 234, 235, 237, 240, 252, 266.

Review of Scientific Instruments, Fig. 159.

Transactions of the Faraday Society, Figs. 36, 136, 137, 138, 147, 148, 156, 157, 158.

Zeitschrift fur physikalische Chemie, Figs. 85, 87, 165, 169, 244.

FOREWORD

Our knowledge of the cause of chemical reactivity is still far from complete, and modern development of the many theoretical aspects of this problem has in turn demanded experimental data, both more extended and more accurate than has been found necessary in the past. Fundamentally the conditions obtaining in reactions when in the gaseous phase are the simplest, and the results of experiments on such systems most readily interpreted. The various developments of the experimental technique necessary for the manipulation of gases and the devices constructed for their transport and for the measurement of temperature and pressure have been increased both in variety and in number. Many of these devices are of such complexity that their utilisation is of doubtful value, but on the other hand, where a high degree of accuracy is required much time may be lost in developing a suitable technique, only to find that it, or some minor variant thereof, has already been described in the now extensive and scattered literature. It was with this object of providing the experimentalist with information on methods of practical value, together with the relevant data not easily accessible, that Drs. Melville and Farkas have written this book. Many of the methods described therein have stood the test of entering daily service in our laboratory. Others, which are described in the literature, have only been inserted after enquiries have been made as to their actual suitability for use by research students. I feel sure that workers in many other laboratories will find that the volume is of use in extending their methods of attack on problems connected with reaction kinetics.

ERIC K. RIDEAL

CONTENTS

CHAPTER I

THE ELEMENTS OF THE KINETICAL GAS THEORY AND OF CHEMICAL KINETICS

PAGE

A. KINETICAL GAS THEORY

1. DIMENSIONS OF MOLECULES - - - - - - - 1
2. NUMBER OF MOLECULES - - - - - - - 4
3. THE MOLECULAR VELOCITY - - - - - - - 4
4. DISTRIBUTION OF VELOCITIES - - - - - - - 5
5. COLLISIONS - - - - - - - - - - 6
   (*a*) COLLISIONS BETWEEN MOLECULES - - - - 6
   (*b*) COLLISIONS WITH A SURFACE - - - - - 8
   (*c*) TRIPLE COLLISIONS - - - - - - - 10
6. VISCOSITY - - - - - - - - - - 10
7. THERMAL CONDUCTIVITY - - - - - - - 12
8. DIFFUSION - - - - - - - - - - 14
9. VISCOSITY AND HEAT CONDUCTIVITY AT LOW PRESSURES - 16
   (*a*) VISCOSITY - - - - - - - - - 16
   (*b*) HEAT CONDUCTIVITY - - - - - - - 18
10. EFFUSION OF GAS THROUGH HOLES - - - - - - 18
11. STREAMING THROUGH TUBES - - - - - - - 19
   (*a*) MEAN FREE PATH LARGE COMPARED WITH THE OPENING 19
   (*b*) POISEUILLE FORMULA - - - - - - - 20
12. DISTRIBUTION OF ENERGY AND PARTITION FUNCTION - 20
   (*a*) INTERNAL PARTITION FUNCTION FOR A MONATOMIC GAS 21
   (*b*) INTERNAL PARTITION FUNCTION FOR A DIATOMIC GAS 21
      (α_1) HARMONIC VIBRATIONS - - - - - 22
      (α_2) ANHARMONIC VIBRATIONS - - - - 22
      (β_1) RIGID ROTATION - - - - - - 22
      (β_2) ROTATION WITH VIBRATION - - - - 23
      (γ) NUCLEAR SPIN - - - - - - 23
   (*c*) INTERNAL PARTITION FUNCTION FOR POLYATOMIC GAS 24
      (α) VIBRATION - - - - - - - - 24
      (β) ROTATION - - - - - - - - 25
      (γ) NUCLEAR SPIN - - - - - - 25
13. EQUILIBRIA - - - - - - - - - - 25

PAGE

B. Elements of Chemical Kinetics
1. General - - - - - - - - - - - 29
2. Dependence of the Reaction Rate on Pressure - 33
3. Dependence of the Reaction Rate on Temperature 37
4. Dependence of the Rate of Photochemical Reactions on Light Intensity - - - - - - - 39
5. Explosive Reactions - - - - - - - - 40

CHAPTER II

APPARATUS FOR CONTROL OF PRESSURE AND TEMPERATURE

A. Vacuum Pumps
Water Pump - - - - - - - - - - 42
Rotary Oil Pumps - - - - - - - - - 43
Rotary Mercury Pump - - - - - - - - 45
Condensation Pumps - - - - - - - - 47
Circulating Pump - - - - - - - - - 53
Variation of Pumping Speeds with Pressure - - 55
Töpler Pump - - - - - - - - - - 57
Determination of Pump Speeds - - - - - 59
'Getters' - - - - - - - - - - 60

B. Control of Gases
Glass Taps - - - - - - - - - - 61
Needle Valves - - - - - - - - - 63

C. Vacuum Joints
Low Vapour Pressure Oils and Greases - - - 67
Metal-glass Joints - - - - - - - - - 68

D. Measurement of Pressure
Barometric Pressure Gauge - - - - - - 71
U-tube Manometer - - - - - - - - 72
McLeod Gauge - - - - - - - - - 73
Pirani Gauge - - - - - - - - - - 76
Small Mercury U-tube Manometers - - - - 81
U-tube Oil Manometer - - - - - - - 82
Rayleigh Gauges - - - - - - - - - 82
Inverted Cup Gauge - - - - - - - - 84
Bourdon Gauge - - - - - - - - - 85
Rohn Gauge - - - - - - - - - - 87
Ionisation Gauge - - - - - - - - - 87
Viscosity Gauges - - - - - - - - - 89

PAGE

Absolute Low Pressure Manometers - - - - 92
Gaede's Vacuscope - - - - - - - - - 94
Harteck-Wrede Slit Gauge - - - - - - 95
Calibration of Manometers - - - - - - 96

E. Control of Pressure

Manostat - - - - - - - - - - 99
Manometer and Source for Hot Vapours - - - 101
Flow Meters - - - - - - - - - - 102

F. Measurement of Temperature

Vapour Pressure Thermometer - - - - - 104
Disappearing Filament Optical Pyrometer - - - 111
Thermo-electric Thermometers - - - - - 113
Platinum Resistance Thermometer - - - - 121
Temperature Distribution in an Electrically Heated Wire - - - - - - - - - - - 123
Compensated Filament Method - - - - - 125

G. Temperature Regulation

Resistance Furnaces - - - - - - - 127
Regulation of Furnace Temperature - - - - 129
Liquid Baths for High Temperatures - - - - 133
Time Switches - - - - - - - - - 134
Production of Low Temperatures - - - - 135
Low Temperature Thermostats - - - - - 137
Constant Level Device for Liquid Air - - - 140

H. General Set-up of Apparatus for Gas Reactions - - 141
Cleaning Mercury - - - - - - - - - 142

CHAPTER III

PREPARATION AND ANALYSIS OF GASES

A. General Methods of Preparation and Storage

Gas Holders - - - - - - - - - - 146
Storage and Transportation of Gases - - - - 148
Drying Materials - - - - - - - - - 149
Electrolysis of Sodium through Glass - - - 149
Pumped-out Liquid Air Traps - - - - - 150

B. Preparation of Gases

Hydrogen - - - - - - - - - - 151
Deuterium - - - - - - - - - - 152
Atomic Hydrogen - - - - - - - - - 153
Para-hydrogen - - - - - - - - - 154
Oxygen - - - - - - - - - - - 156

B. Preparation of Gases—*continued* PAGE

Ozone - - - - - - - - - - - 156
Atomic Oxygen - - - - - - - - - 157
Chlorine and Atomic Chlorine - - - - - 158
Hydrogen Chloride - - - - - - - - 159
Hydrogen Bromide - - - - - - - - - 159
Hydrogen Iodide - - - - - - - - - 160
Carbon Monoxide - - - - - - - - - 161
Carbon Dioxide - - - - - - - - - 161
Carbon Oxysulphide - - - - - - - - 161
Nitrogen - - - - - - - - - - 162
Ammonia - - - - - - - - - - 162
Trideuteroammonia - - - - - - - - 162
Nitric Oxide - - - - - - - - - - 163
Nitrous Oxide - - - - - - - - - 164
Nitrogen Peroxide - - - - - - - - 164
Methane and Methyl Deuteride - - - - - 165
Ethane - - - - - - - - - - 165
Methyl and Ethyl Radicals - - - - - 166
Ethylene - - - - - - - - - - 166
Cyanogen - - - - - - - - - - 167
Acetylene and Dideuteroacetylene - - - - 167
Hydrocyanic Acid - - - - - - - - - 168
Hydrogen Sulphide - - - - - - - - 168
Sulphur Dioxide - - - - - - - - - 168
Phosphine and Trideuterophosphine - - - - 168
Arsenic Trihydride - - - - - - - - 169
Antimony Hydride - - - - - - - - - 170
Silicon Hydrides - - - - - - - - - 170
Boron Hydrides - - - - - - - - - 172

C. Micro-gas Analysis

Low Pressure Method - - - - - - - - 175
Shakespear Katharometer - - - - - - - 178
Capillary Burette Methods - - - - - - - 180
Analysis by Low Temperature Distillation - - 187
Estimation of Para-hydrogen, Deuterium, Ortho-deuterium and Hydrogen Deuteride - - - 190
Analysis of Ternary Mixtures by Thermal Conductivity Measurements - - - - - - - - 196
Gas Density Balance - - - - - - - - 199

D. Vapour Pressures of Gases - - - - - - - 201

CHAPTER IV

PHOTOCHEMICAL TECHNIQUE

PAGE

A. Absorption Spectra of Gases - - - - - - - 207

B. Sources of Radiation

The Mercury Lamp - - - - - - - - 214
Condensed Sparks - - - - - - - - 227
Tungsten Filament Lamps - - - - - - 228
Tungsten Arc Lamps - - - - - - - 228
Electrodeless Metal Vapour Lamps - - - - 229
Hydrogen Lamp - - - - - - - - 230

C. Control of Radiation

Filters - - - - - - - - - - 232
Wire Gauze Screens and Perforated Plates - - 237
Sectors and Allied Devices - - - - - - 238
Reaction Vessels - - - - - - - - 241
Monochromators - - - - - - - - 249

D. Measurement of Radiation Intensity - - - - 250
Thermopiles and Galvanometers - - - - - 250
Chemical Actinometers - - - - - - - 254
Photoelectric Quantum Counters - - - - 258
Photoelectric Cells - - - - - - - 260
Photoelectric Photometer - - - - - - 263

CHAPTER V

EXPERIMENTAL METHODS FOR THE INVESTIGATION OF CHEMICAL REACTIONS

A. Reaction Vessels - - - - - - - - - 266
1. Vessels of Glass and Silica - - - - - 266
2. Vessels of Refractory Materials - - - - 270
3. Metal Vessels for High Pressures - - - - 270
(*a*) Wall Thickness - - - - - - 270
(*b*) Gas-tight Joints between the Cover and the Vessel - - - - - - - - 271
(*c*) Fittings - - - - - - - - 272
4. Wall Reactions - - - - - - - 275

B. Progress of the Reaction with Time - - - - 278
1. Manometric Methods - - - - - - 279
2. Heat Conductivity Methods - - - - - 281
(*a*) General - - - - - - - - 281
(*b*) Ternary Gas Mixtures - - - - - 287
(*c*) Low Pressure Gauges - - - - - 288

PAGE

C. Optical Methods - - - - - - - - - 288
1. Interferometry - - - - - - - - - 289
2. Polarimetry - - - - - - - - - 290
3. Spectroscopic Methods - - - - - - - 290
(*a*) Concentration Measurements of H, O, N-atoms 290
(*b*) Infra-red Spectroscopy - - - - - - 290
4. Photometry - - - - - - - - - 292
5. Gas Density Methods - - - - - - - 296

D. Flow Methods
1. Theoretical - - - - - - - - - 296
(*a*) Space-time-yield - - - - - - - 296
2. Production and Measurement of Flow - - - 299
3. Examples of Application - - - - - - - 302
4. Reactions of Atoms and Radicals - - - - 307
5. Dilute Flames - - - - - - - - - 308

E. Factors influencing the Progress of the Reaction
1. Time - - - - - - - - - - - 313
2. Temperature and Pressure - - - - - 314
(*a*) Adjustment of Pressure - - - - - 314
(*b*) Mixing of Gases - - - - - - - 316
(*c*) Low Pressure - - - - - - - - 316
(*d*) Order of the Reaction - - - - - 317
(*e*) High Pressures - - - - - - - 320
3. Illumination
(*a*) Thermostats - - - - - - - - 326
(*b*) Reaction Cells with Plane-parallel Windows 326
(*c*) Vessels for Short Wave Ultra-violet - - 327
(*d*) Special Windows - - - - - - - 328
(*e*) Light Sources for Short Wave Radiation - 329
(*f*) Some Experimental Arrangements: Bodenstein's Apparatus - - - - - - - 330
(*g*) Mercury Sensitized Reactions - - - 331
(*h*) Experimental Arrangement for the Short Wave Region - - - - - - - 332
(*i*) Budde and Draper Effect - - - - 334
(*j*) Large Light Intensities - - - - - 335
4. Catalysts
(*a*) Metallic Catalysts - - - - - - - 335
(α) Compact Form - - - - - - 335
(β) Metals in Form of Powders - - - 338
(γ) Colloidal Metals - - - - - 339
(*b*) Oxide Catalysts - - - - - - - 340

PAGE

(c) Charcoal - - - - - - - - - 341
(d) Supported and Composite Catalysts - - 342
(e) Arrangement and Temperature Control of Filaments - - - - - - - - 343
(f) Catalytically Active Metal Films - - 348
(g) Poisoning and Sintering - - - - - 348
(h) Shaking - - - - - - - - - 350
(i) Reactions in the Adsorption Layer - - 351
(j) Some Typical Arrangements - - - - 352
(α) Wire Catalysts - - - - - 352
(β) Powder Catalysts - - - - - 352
5. Electric Activation - - - - - - - - 353
(a) Electrons and Ions of Controlled Speed - 354
(b) α-rays - - - - - - - - - 355
(c) Glow Discharge - - - - - - - 356
(d) Impulse Discharge - - - - - - 358
(e) Electrodeless Ring Discharge - - - 358

F. Explosive Reactions
1. Determination of Pressure and Temperature Limits of Explosive Reactions - - - - - 359
(a) Theoretical - - - - - - - - 359
(b) Experimental Methods - - - - - 361
(α) Capillary Method - - - - - 361
(β) Withdrawal Method - - - - 362
(γ) Pipette Method - - - - - 362
(δ) Compression Method - - - - 362
(ε) Streaming Method - - - - - 363
2. Artificial Ignition - - - - - - - 364
3. Wall-less Inflammation - - - - - - 365
4. Rapid Reactions and Induction Periods - - - 366
5. Explosions at very High Pressures - - - - 367
6. Optical Observations - - - - - - 367
7. Various Methods - - - - - - - 369
8. Precautions - - - - - - - - 369

Appendix
A. Some Important Physical Constants - - - 371
B. Bibliography - - - - - - - - 371

Author Index - - - - - - - - - - 375

Subject Index - - - - - - - - - - 384

CHAPTER I

THE ELEMENTS OF THE KINETIC THEORY OF GASES AND OF CHEMICAL KINETICS

A. KINETIC THEORY OF GASES

ACCORDING to this theory, gases are composed of molecules which are in perpetual motion. It is not possible to make statements with regard to the motion executed by each or any of the molecules, but it is possible to describe statistically such quantities as mean velocity, mean number of collisions, mean displacement of a molecule in unit time, and to show the connections between the motion of the molecules and the macroscopically measurable quantities such as specific heat, viscosity, and heat conductivity.

It is assumed that the reader is acquainted with the elements of the theory, and hence it will only be necessary to summarise the principal formulae, laws and data.

1. Dimensions of Molecules

The molecules which constitute matter are characterised by shape and dimensions.

The shape of the monatomic molecules is spherical, and that of the diatomic molecules, ellipsoidal. The form of the polyatomic molecules is determined by the distance between the nuclei of the atoms constituting the molecule and the angles between the lines joining the nuclei. Of course, the actual dimensions of the molecule are larger than the internuclear distance, since this does not include the electron cloud.

The data characterising the shape and dimensions of molecules can be determined by different methods, such as diffraction of electrons, band spectroscopy, or gas kinetical measurements.

Whereas it is justifiable to expect similar values for the internuclear distances which are independent of the method of determination, this is no longer the case for the diameter of molecules. This behaviour becomes explicable if we recall the cloud-like structure of the electron shell around the nucleus and remember that the interaction, and so the effective diameter, varies as ions, electrons, atoms or molecules are used to determine the dimensions of a molecule. Table 1 shows the radii of some molecules as determined by different methods.

Tables 2 and 3 summarise the data on the diameters of the most common molecules as determined from gas kinetical measurements; their internuclear distances and other data about the arrangement of the atoms in the molecule are also included.

TABLE 1

Molecular radii in Å units ($=10^{-8}$ cm.) (after Landolt-Bornstein, *Physikalisch-chemische Tabellen*, Table 38; Herzfeld, *Jahrb. Rad.*, **19**, 259, 1922; Zemansky and Mitchell, *Resonance Radiation and Excited Atoms*, Cambridge University Press, 1934, p. 204).

I. From data on: Viscosity, heat conductivity and diffusion.
II. Viscosity.
III. Volume correction in van der Waals' equation.
IV. Volume correction in Wohl's equation.
V. Heat of evaporation.
VI. Diffraction of slow electrons.
VII. Dielectric constant.
VIII. Quenching of mercury fluorescence.

	I	II	III	IV	V	VI	VII	VIII
Argon	1·82	1·43	1·43	1·17	1·8	2·77	1·19	—
Carbon monoxide	1·89	—	2·28	1·48	1·95	—	1·27	1·35
Carbon dioxide	2·31		1·61	1·31	2·0	1·83	1·42	0·88
Chlorine	—	1·85	1·65	1·34	2·15	—	1·65	—
Helium	1·10	1·00	1·24	1·07	1·5	1·41	0·614	—
Hydrogen	1·36	1·09	1·38	1·12	1·55	2·04	0·675	1·65
Krypton	2·07	1·59	1·57	4·27	—	—	1·36	—
Mercury	—	1·80	1·19	0·96	—	—	—	—
Neon	—	1·17	—	—	—	1·28	—	—
Nitrogen	1·90	1·58	1·57	1·28	1·95	1·75	1·21	0·29
Oxygen	1·81	1·48	1·45	1·18	1·8	—	1·17	2·52
Water	2·29	1·36	1·44	1·17	—	—	—	0·67
Xenon	2·44	1·75	1·71	1·39	—	—	1·60	—

TABLE 2

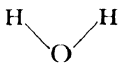
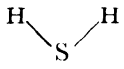
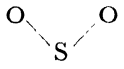
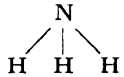
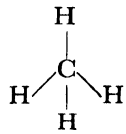
After H. Sponer, *Molekulspektren*, Springer, Berlin, 1935

		Diameter in Å	Internuclear distance (10^{-8} cm.)
Ammonia	NH_3	1·6	—
Argon	A	2·8	—
Benzene	C_6H_6	4·1	—
Bromine	Br_2	3·4	2·28
Carbon dioxide	CO_2	3·2	—
Carbon monoxide	CO	3·2	1·13
Chlorine	Cl_2	3·6	1·98
Ethylene	C_2H_4	3·6	—
Helium	He	1·9	—
Hydrogen	H_2	2·3	1·07

	Diameter in Å (10^{-8} cm).	Internuclear distance
Hydrogen chloride - - - HCl	2·9	1·27
Hydrogen bromide - - - HBr	3·1	1·41
Hydrogen iodide - - - HI	—	1·61
Iodine - - - - - I_2	3·8	2·66
Mercury - - - - - Hg	3·5	—
Nitrogen - - - - - N_2	3·1	1·09
Nitric oxide - - - - NO	2·9	1·14
Nitrous oxide - - - - N_2O	3·2	—
Oxygen - - - - - O_2	2·9	1·20
Water - - - - - H_2O	2·6	—

TABLE 3

According to Sponer (*loc. cit.*)

	Shape	Distances in Å	Angles
Triatomic linear molecules			
CO_2 - - - -	O – C – O	C – O = 1·16	
CS_2 - - - -	S – C – S	C – S = 1·6	
N_2O - - - -	N – N – O	N – N = 1·12 N – O = 2·38	
HCN - - - -	H – C – N	C – H = 1·06 C – N = 1·15	
Polyatomic linear molecules			
C_2H_2 - - - -	H – C – C – H	C – C = 1·20 H – C = 1·05	
$(CN)_2$ - - - -	N – C – C – N	C – N = 1·2 C – C = 1·5	
Triatomic angular molecules			
H_2O - - - -		O – H = 0·955	104° 40′
H_2S - - - -		S – H = 1·35	92° 20′
SO_2 - - - -		S – O = 1·37	
Pyramidal molecules			
NH_3 - - - -		H – H = 1·61 N – H = 1·01	H – N – H 109°
Tetrahedral molecules			
CH_4 - - - -		C – H = 1·1	H – C – H 109° 28′
CH_3Cl - - - -	as CH_4	C – Cl = 1·85 C – H = 1·1	
$CHCl_3$ - - - -	as CH_4	Cl – Cl = 3·0	

The shape and dimensions of the molecules are not appreciably altered if one atom is replaced by its isotope, this being true even for an interchange between hydrogen and deuterium. It may be noted that the hydrides and halides of P, As and Sb are built similarly to NH_3 and that the tetrahalides of Si, Ti, Sn and C are tetrahedral molecules like CH_4.

2. Number of Molecules

One mole of gas contains $6{\cdot}064 \times 10^{23}$ molecules. This number is denoted by **N** and is usually referred to as Avogadro's number, or in the German literature as Loschmidt's number.

On the assumption of ideal gas laws (no interaction between molecules and negligible volume of the molecules), one mol of gas is contained in 22,414 cm.^{3} at 0° C. and 760 mm. Hg pressure. This quantity is the molar volume. Thus at 0° C. one cubic centimetre of gas contains $2{\cdot}705 \times 10^{19}$ molecules at 760 mm. Hg pressure and $3{\cdot}559 \times 10^{16}$ molecules at 1 mm. Hg. At the temperature T° K. and the pressure p mm. the number of molecules per cm.^{3} is $9{\cdot}717 \times 10^{18}\, p/T$.

3. The Molecular Velocity

From elementary theory the speed of the molecules can be deduced in the following way. Consider a mole of gas confined in a cubical box of the volume v and assume that each molecule has the same velocity u and that one-third of the total is moving parallel to each one of the three edges of the cube. One molecule will traverse the box $u/\sqrt[3]{v}$ times in one second and hit each wall $u/2\sqrt[3]{v}$ times. Since $\mathbf{N}/3$ molecules travel in each direction and at each impact the change of molecular momentum is $2Mu/\mathbf{N}$, the total change of momentum is (M = molecular weight)

$$\frac{2Mu}{\mathbf{N}} \cdot \frac{\mathbf{N}}{3} \cdot \frac{u}{2\sqrt[3]{v}} = \frac{Mu^2}{3\sqrt[3]{v}} \qquad \text{.....(1)}$$

and is equal to the force f exerted on any one of the walls. The area of the wall being $v^{\frac{2}{3}}$, the pressure,

$$p = f/v^{\frac{2}{3}} = \frac{Mu^2}{3v}, \qquad \text{.....(2)}$$

or since

$$pv = \mathbf{R}T \quad (\mathbf{R} = \text{gas constant}) \qquad \text{.....(3)}$$

$$\frac{Mu^2}{3} = \mathbf{R}T \qquad \text{.....(4)}$$

and

$$u = \sqrt{3\mathbf{R}T/M}. \qquad \text{.....(5)}$$

This formula is valid also in the exact theory if we take into consideration

the velocity and direction distribution of the molecules. In that case u denotes the root-mean square velocity, being defined as

$$\mathbf{N}\quad u^2 = u_1^2 + u_2^2 + u_3^2 + \ldots + u_N^2, \qquad \ldots\ldots(6)$$

$u_1, u_2, \ldots u_N$ denoting the velocities of each molecule.

With $\mathbf{R} = 8{\cdot}313 \times 10^7$ erg/degree/mole we have

$$u = 1{\cdot}5792 \times 10^4 \sqrt{T/M} \text{ cm. sec.}^{-1} \qquad \ldots\ldots(7)$$

This velocity is sometimes referred to as the effective velocity. From formula (5) we find introducing the density $\rho = M/v$, $u = \sqrt{3p/\rho}$, p being expressed in dynes/cm.^{2}. Besides this velocity we shall have to deal with the average velocity and the most probable velocity.

4. Distribution of the Velocities

The deduction of the law governing the distribution of the molecular velocities is due to Maxwell.

If N_0 molecules are present in a cm.^{3}, the number of molecules with the velocity between c and $c + dc$ is

$$dN_c = N_0 \frac{4}{\sqrt{\pi}} \left(\frac{M}{2\mathbf{R}T}\right)^{\frac{3}{2}} e^{-\frac{c^2 M}{2\mathbf{R}T}} c^2\, dc. \qquad \ldots\ldots(8)$$

The most probable velocity is given by $\frac{d^2 N_c}{dc^2} = 0$ and is

$$\alpha = \sqrt{2\mathbf{R}T/M} = 1{\cdot}2894 \times 10^4 \sqrt{T/M} \text{ cm. sec.}^{-1}. \qquad \ldots\ldots(9)$$

The average velocity is

$$\bar{c} = \int_0^\infty c \frac{dN_c}{N_0} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{2\mathbf{R}T}{M}} = \sqrt{\frac{8\mathbf{R}T}{\pi M}} = 1{\cdot}4549 \times 10^4 \sqrt{T/M} \text{ cm. sec.}^{-1}. \quad \ldots(10)$$

It will be recognised that the most probable velocity $<$ average velocity $<$ mean square root velocity (u).

In chemical kinetics it is often necessary to know the number of molecules, the velocity of which exceeds a certain value c_0. This number is

$$N_1 = \int_{c_0}^\infty dN_c = N_0 \frac{4}{\sqrt{\pi}} \left(\frac{M}{2\mathbf{R}T}\right)^{\frac{3}{2}} \int_{c_0}^\infty e^{-\frac{c^2 M}{2\mathbf{R}T}} c^2 dc, \qquad \ldots\ldots(11)$$

or introducing

$$c \Big/ \sqrt{\frac{2\mathbf{R}T}{M}} = \frac{c}{\alpha} = x, \qquad \ldots\ldots(12)$$

$$N_1 = \frac{4N_0}{\sqrt{\pi}} \int_{x_0}^\infty x^2 e^{-x^2} dx, \qquad \ldots\ldots(12a)$$

or

$$\frac{N_1}{N_0} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} dx + \frac{2}{\sqrt{\pi}} x_0 e^{-x^2}. \qquad \ldots\ldots(13)$$

The value of the integral is to be found in tables for $x_0 \leqq 3$. For $x_0 > 3$ use may be made of the following expansion with sufficient accuracy :

$$\frac{N_1}{N_0} = \frac{2}{\sqrt{\pi}} e^{-x_0^2} \left\{ x_0 + \frac{1}{2x_0} - \frac{1}{4x_0^3} + \frac{3}{8x_0^5} - \ldots \right\} \quad \ldots\ldots\ldots\ldots (14)$$

The evaluation of this complicated formula * is rather difficult. A simplified expression is obtained by considering the translational motion of the molecules in two dimensions instead of in three. Then putting

$$\frac{Mc^2}{2} = E,$$

$$\frac{dN_c}{N_0} = \frac{1}{RT} e^{-E/RT}\, dE. \quad \ldots\ldots\ldots\ldots (15)$$

This formula is for all practical purposes sufficiently accurate and gives instead of (14)

$$\frac{N_1}{N_0} = \int_{c_0}^{\infty} \frac{dN_c}{N_0} = \int_{E_0}^{\infty} \frac{1}{RT} e^{-E/RT}\, dE = e^{-E_0/RT}. \quad \ldots\ldots\ldots\ldots (16)$$

The numerical values of the average velocities of different molecular species are listed in Table 4 (page 8).

5. Collisions

We deal with three kinds of collisions : (*a*) collisions between molecules (or atoms), (*b*) collisions with a surface, and (*c*) triple collisions.

(*a*) *Collisions between molecules.* In elementary theory we obtain the number of collisions which one molecule suffers in unit time in the following way. We consider two different kinds of molecules (diameter d_1 and d_2, respectively), and assume that one kind of molecules, say 1, is at rest, and that there is only one molecule of the kind 2. Two different molecules collide if their centres approach within a distance of $\frac{d_1 + d_2}{2}$. Let there be N_1 molecules per c.c. of kind 1. If the moving molecule is traversing one c.c. of gas (say an area of 1 cm.^{2} and a layer 1 cm. thick), it has

$$N_1 \pi (d_1 + d_2)^2 / 4 \quad \ldots\ldots\ldots\ldots (17)$$

chances of colliding with a molecule at rest, this being the ratio of the total projected area of the resting molecules on the plane of the area of 1 cm.^{2} to this area itself. The free path (Λ) is then the reciprocal value of this expression,

$$\Lambda = \frac{4}{N_1 \pi (d_1 + d_2)^2}. \quad \ldots\ldots\ldots\ldots (17a)$$

* Cf. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford, 1933, p. 11.

If in one c.c. there are N_2 molecules of the kind 2, and the average velocity of molecule 2 is $\bar{c}=\sqrt{\frac{8\mathbf{R}T}{\pi M_2}}$, we find the number of collisions between molecules 1 and 2 per c.c. per second

$$=\bar{c}\,N_2/\Lambda=N_1N_2\sqrt{\pi}\,(d_1+d_2)^2\sqrt{\mathbf{R}T/2M_2}. \quad \ldots\ldots\ldots\ldots\ldots(18)$$

If one allows for the fact that both molecules are moving and that the molecules have different velocities according to Maxwell's distribution law the mean free path for the molecules of the kind 1 is given by

$$\frac{1}{\Lambda_1}=\pi\sqrt{2}\,N_1d_1^2+\pi N_2\left(\frac{d_1+d_2}{2}\right)^2\sqrt{\frac{M_1+M_2}{M_2}}. \quad \ldots\ldots\ldots\ldots\ldots(19)$$

The first expression on the right-hand side represents the mean free path of molecule 1 for meeting a similar molecule, and the second that for meeting a molecule of kind 2.

From this formula the following collision formulae may be obtained : Number of collisions between molecules 1 and 2 per c.c. per second,

$$2\sqrt{2\pi}\,N_1N_2\left(\frac{d_1+d_2}{2}\right)^2\sqrt{\frac{M_1+M_2}{M_1M_2}\mathbf{R}T}$$

$$=1{\cdot}142\times10^4N_1N_2\,(d_1+d_2)^2\sqrt{\frac{M_1+M_2}{M_1M_2}T}. \ldots(20)$$

Number of collisions per c.c. per second in a gas containing only one kind of molecules,

$$2\sqrt{\pi}\,N^2d^2\sqrt{\mathbf{R}T/M}=3{\cdot}232\times10^4N^2d^2\sqrt{T/M}. \quad \ldots\ldots\ldots\ldots\ldots(21)$$

This formula contains a factor 2 less than (20) in order to avoid counting each collision twice.

Number of collisions one molecule suffers per second :

$$4\sqrt{\pi}\,Nd^2\sqrt{\mathbf{R}T/M}=6{\cdot}464\times10^4\,.\,Nd^2\sqrt{T/M}. \quad \ldots\ldots\ldots\ldots\ldots(22)$$

These formulae are valid at high temperatures when there is no attraction between the molecules. At lower temperatures the mean free path is somewhat dependent on the temperature owing to an attraction between the molecules. According to Sutherland

$$\Lambda=\Lambda_\infty\frac{T}{C+T}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(23)$$

where Λ_∞ is the mean free path at very high temperatures and C a constant. The values of C are listed in Table 5.

The mean free paths and collision frequencies for some molecules are listed in Table 4. In calculating these data the dependence of the mean free path on temperature has been taken into account, and in some cases

slightly different values have been taken for the molecular diameter than those listed in Table 2.

TABLE 4

After Landolt-Bornstein, *Physikalisch-chemische Tabellen*, Table 38.

	Molecular weight	Average velocity at 0° C. m./sec.	Mean free path at 0° C., 760 mm. in Å (= 10^{-8} cm.)	Number of collisions one molecule suffers per sec. at 0° C., 760 mm. × 10^{-9}
Ammonia	17·03	582·7	441	13·2
Argon	39 94	380·8	635	5·99
Benzene	78 04	272·2	138	19 6
Bromine	159·83	190 9	—	—
Carbon dioxide	44·00	362·5	397	9·12
Carbon monoxide	28·00	454·5	584	7·78
Carbon disulphide	76·12	275·6	201	13·7
Carbon tetrachloride	153·83	193·9	206	9·42
Chlorine	70·91	285·6	287	9 97
Cyanogen	52·02	333 4	249	13·4
Ethylene	28·03	454·2	345	13·2
Helium	4 00	1204·0	1798	6 69
Hydrogen	2·015	1692 0	1123	15·1
Deuterium	4·027	1196	1123	10·6
Hydrogen chloride	36·46	398·2	433	9·19
Hydrogen bromide	80·92	267·2	—	—
Hydrogen iodide	127·93	212 5	—	—
Hydrogen sulphide	34·08	411·9	375	11·0
Iodine	253·84	151·5	—	—
Mercury	200·61	170 0	217	7·83
Methane	16·03	600·6	493	12·2
Nitrogen	28·01	454·2	600	7·54
Nitrous oxide	44·01	362·5	387	9·35
Nitric oxide	30·00	439·0	570	7·70
Oxygen	32·00	425·1	647	6·57
Sulphur dioxide	64·06	300·4	290	10·3
Water	18·01	566·5	404	14·0

(*b*) *Collisions with a surface.* To obtain the elementary derivation of the number ($\dot{n}$) of molecules striking a unit area per second we will again assume that the molecules are all moving with the same velocity uniformly divided in three dimensions. An area of, say, 1 cm.^{2} will be hit within a second by 1/6 of all those molecules which are contained in the cylinder, of base 1 cm.^{2} and length $\bar{c}$. The factor 1/6 enters, since only 1/6 of the molecules move in a direction perpendicular to and towards the area. Thus

$$\dot{n} = \frac{1}{6}\mathcal{N}\bar{c} = \frac{1}{6}\mathcal{N}\sqrt{\frac{8\mathbf{R}T}{\pi M}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

If we allow for the distribution of the velocities and directions :

$$\dot{n}=\frac{1}{4}\mathcal{N}\bar{c}=\mathcal{N}\sqrt{\frac{\mathbf{R}T}{2\pi M}}=3{\cdot}637\times10^{3}\mathcal{N}\sqrt{T/M}. \quad \text{.....(24a)}$$

The number of molecules per c.c. at a pressure of p mm. Hg and temperature $T°$ K. is

$$\mathcal{N}=9{\cdot}717\times10^{18}p/T,$$

and therefore

$$\dot{n}=3{\cdot}535\times10^{22}p/\sqrt{MT} \text{ molecules/sec. cm.}^2. \quad \text{.....(25)}$$

In hydrogen ($M=2$) at $p=1$ mm. Hg and $T=293°$ K.

$$\dot{n}=3{\cdot}535\times10^{22}/\sqrt{586}=1{\cdot}460\times10^{21} \text{ molecules/sec. cm.}^2.$$

(*c*) *Triple collisions.* The collision between three particles is called a triple collision. The three particles can collide simultaneously, or the third particle can collide with two others which are already in the state of (double) collision. This latter case is considered in calculating the number of triple collisions (K. F. Herzfeld, *Z. Physik*, **8**, 132, 1922 ; Tolman, *Statistical Mechanics*, p. 245, New York, 1927 ; Steiner, *Z. phys. Chemie*, **B. 15**, 249, 1932).

Let the number of double collisions be Z_2 per c.c. per second. If τ is time during which the two particles are in the state of collision, the concentration of such complexes is $Z_2\tau$. The number of triple collisions is then, according to formula (20),

$$Z_3=2\sqrt{2\pi}\mathcal{N}Z_2\tau\left(\frac{d+d_2}{2}\right)^2\sqrt{\frac{M+M_2}{MM_2}\mathbf{R}T}, \quad \text{.....(26)}$$

or with

$$Z_2=2\sqrt{\pi}\mathcal{N}^2d^2\sqrt{\mathbf{R}T/M}, \quad \text{.....(21)}$$

$$Z_3=4\pi\sqrt{2}\mathcal{N}^3\tau d^2\left(\frac{d+d_2}{2}\right)^2\frac{\mathbf{R}T}{M}\sqrt{\frac{M+M_2}{M_2}}. \quad \text{.....(27)}$$

At 0° C. and 760 mm. Hg the ratio of the triple collisions to double collisions is given by

$$\frac{Z_3}{Z_2}=6\times10^{23}\tau\frac{1}{\sqrt{M}}(d+d_2)^2. \quad \text{.....(28)}$$

The exact values for the life time τ and the effective diameter of the double complexes d_2 is not known exactly, but d_2 will be of the same order of magnitude as d and $\tau=\frac{d}{c}\approx10^{-12}$ sec. With these values

$$\frac{Z_3}{Z_2}\approx10^{-3} \text{ to } 10^{-4}.$$

Another approximation for the relative number of the triple collision is (Λ = mean free path)

$$\frac{Z_3}{Z_2} \approx \frac{d}{\Lambda}. \quad \ldots\ldots(29)$$

6. Viscosity

Consider two horizontal and parallel plates at a distance x, one of which, the upper, is moved with the velocity W. Then the force acting on one cm.^{2} of the stationary plate is

$$F = \eta \frac{\partial W}{\partial x}, \quad \ldots\ldots(30)$$

where $\frac{\partial W}{\partial x}$ is the velocity gradient between the two plates and η is the coefficient of viscosity of the gas. Since the force is equal to the momentum transferred in unit time, we obtain the following kinetic expression for the coefficient of viscosity. In any arbitrary plane between the two plates the molecules arrive from layers situated at a distance of Λ above and below this plane. The difference in the additional velocities (due to streaming) of the molecules in these two layers is $2\Lambda \frac{\partial W}{\partial x}$, and the number of molecules passing per second through 1 cm.^{2} of the arbitrary plane 1/6 $N\bar{c}$ (N = number of molecules per c.c.). Thus we have

$$F = 2\Lambda \frac{\partial W}{\partial x} \cdot \frac{1}{6} N\bar{c}\, m, \quad \ldots\ldots(31)$$

or comparing this with (30),

$$\eta = \frac{1}{3} \Lambda N\bar{c}\, m = \frac{1}{3} \Lambda N\bar{c}\, M/\mathbf{N}, \quad \ldots\ldots(32)$$

or since (cf. (19)) $\Lambda = \frac{1}{N \pi d^2 \sqrt{2}}$,

$$\eta = \frac{1}{3\sqrt{2}} \frac{\bar{c}M}{\pi d^2 \mathbf{N}}. \quad \ldots\ldots(33)$$

From this formula it follows that the viscosity is independent of the concentration. This formula requires modification. First of all, the average value $\Lambda \mathbf{N}\bar{c}$ can be calculated more accurately if the distribution of velocities is taken into account. Allowing for this the factor 1/3 should be replaced by 5/12 in equation (33). Secondly, the mean free path is dependent on the temperature (as shown by Sutherland's formula, (23)), and therefore the viscosity will be more dependent on temperature than the molecular velocity. Thirdly, the validity of this formula is confined to a certain pressure region. Considerable discrepancies appear at high

pressures when the dimensions of the molecules cannot be neglected compared with the mean free path, and at low pressures when the mean free path is comparable with the distance between the moving and stationary plate or with the distance of the decisive dimensions of the apparatus used for the measurement of the viscosity. We shall deal with the behaviour of gases at low pressures in a separate paragraph. The viscosities of some gases are given in Table 5.

The viscosity of gas mixtures is not simply given by the viscosities of the components, since the mean free path of each kind of molecule is slightly modified by the presence of the other.

TABLE 5

Viscosities, η in cm.$^{-1}$ gm./sec.$^{-1}$.

	Temperature in ° C.	$\eta \times 10^7$	C.	References
Air	0	1809	113	1
Ammonia	15	1005	370	2
Argon	15·4	2196	148	3
Bromine	20	1542	533	4
Carbon dioxide	0	1382	263	5
Carbon monoxide	15·1	1730	101	6
Chlorine	15·6	1294	351	7
Ethylene	22	970	259	8
Helium	14·0	1943	81	9
Hydrogen	19·4	875	83	10
Hydrogen chloride	0	1332	357	11
Hydrogen sulphide	17	1251	331	12
Iodine	106	1785	568	13
Mercury	281	5310	942	14
Methane	17	1094	198	15
Neon	15·0	3076	80	16
Nitric oxide	0	1797	162	17
Nitrogen	0	1665	118	18
Nitrous oxide	0	1366	274	19
Oxygen	14·2	1973	136	20
Sulphur dioxide	20	1266	396	21
Water	20	937	961	22

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7. Thermal Conductivity

The formula for thermal conductivity is very similar to that for viscosity, the only difference being that in this case we have to deal with the transfer of heat. We consider again two horizontal and parallel plates, the upper being kept at a higher temperature than the lower. The heat transferred from the hotter to the colder plate per cm.^{2} is

$$H = -k\frac{\partial T}{\partial x}, \qquad \ldots\ldots(34)$$

where k is the coefficient of heat conductivity and $\frac{\partial T}{\partial x}$ the temperature gradient between the two plates. Proceeding in a manner similar to that for deducing the viscosity equation we find

$$H = -\frac{1}{3}A N \bar{c} m c_v \frac{\partial T}{\partial x}, \qquad \ldots\ldots(35)$$

where c_v is the specific heat at constant volume of the gas between the plates. Therefore

$$k = \frac{1}{3}A N \bar{c} m c_v = \eta c_v = \eta \frac{C_v}{M}, \qquad \ldots\ldots(36)$$

where C_v is the molar heat capacity at constant volume. A more accurate calculation shows, however, that

$$k = \kappa \eta \frac{C_v}{M} \text{ where } \kappa > 1. \qquad \ldots\ldots(37)$$

For monatomic gases $\kappa = 2{\cdot}5$. According to Eucken this is due to the circumstance that fast molecules possessing a large amount of kinetic energy transport it very rapidly ; consequently, the actual transport of

energy is larger than that calculated from formula (36). The energy of diatomic gases is composed of translational and rotational energy. Since the rotational energy is not preferentially transported by fast molecules we may put $\kappa_{\text{rot}} = 1$, and since

$$C_v = 5\mathbf{R}/2 = C_{v,\,\text{rot}} + C_{v,\,\text{trans}}$$

and $$C_{v,\,\text{rot}} = \mathbf{R},$$

we obtain $$k = \left(2{\cdot}5 \times \frac{3}{2} + 1\right)\frac{\mathbf{R}}{M}\eta = 1{\cdot}9\,\frac{C_v}{M}\eta. \quad \ldots\ldots\ldots\ldots\ldots\ldots (38)$$

(At low temperatures when the rotational levels are not fully excited the corresponding value of $C_{v,\,\text{rot}}$ is to be used.) In fact, for gases such as H_2, N_2, O_2, NO, etc., $\kappa = 1{\cdot}87 - 1{\cdot}97$. For triatomic and polyatomic gases, κ has values ranging between 1·5 and 1·75.

What has been said with regard to the dependence of the viscosity on temperature, pressure and composition is valid also for the heat conductivity. The thermal conductivities are listed in Table 6.

TABLE 6

Thermal conductivities, k in cal./cm. sec. degree $\times 10^5$.

	t° C.	k	References
Acetylene	0	4 44	1
Air	0	5·83	2
Ammonia	0	5·13	1
Argon	0	3·88	3
Benzene	0	2·09	4
Carbon			
monoxide	0	5·63	2
dioxide	0	3·43	5
disulphide	0	1·61	1
tetrachloride	100	2·05	4
Chlorine	0	1·83	1
Chloroform	0	1·52	4
Ethane	0	4·26	1
Ethylene	0	4·07	1
Ethyl alcohol	20	3·58	4
Ethyl ether	0	3 10	4
Helium	0	33·6	1
Hexane	0	2·60	4
Hydrogen	0	40·6	2, 6
Deuterium	0	28·7	7
Hydrogen sulphide	0	3·04	1
Methane	0	7·14	1
Methyl chloride	0	2·22	4
Mercury	203	1·85	8

	$t°$ C.	k	References
Neon	0	11·04	5
Nitrogen	0	5·80	9
Nitric oxide	0	5·55	1
Nitrous oxide	0	3·74	2
Nitrogen peroxide	55	8·88	10
Oxygen	0	5·89	9
Pentane	0	2·93	4
Sulphur dioxide	0	1·95	1
Water	46	4·58	4

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8. Diffusion

Diffusion is analogous to heat conductivity and viscosity, but involves transport of mass. If we have a mixture of two gases, 1 and 2, in a space, the transport of the gas 1 and 2 respectively through one cm.^{2} in one second in the direction x is given by

$$\dot{N}_1 = D\frac{\partial N_1}{\partial x} \quad \text{and} \quad \dot{N}_2 = D\frac{\partial N_2}{\partial x}, \qquad \text{.....(39)}$$

where D is the coefficient of diffusion and $\frac{\partial N}{\partial x}$ is the concentration gradient.

If the pressure does not change during the diffusion process or when $N_1 + N_2 = \text{constant}$,

$$\frac{\partial N_1}{\partial x} = -\frac{\partial N_2}{\partial x}. \qquad \text{.....(40)}$$

If again we proceed as on page 10 and regard two kinds of molecules with the same mass (m) and diameter (d) (this case of self-diffusion is actually realised with the ortho- and para-modifications of hydrogen or of deuterium) when $u_1 = u_2$ and $\Lambda_1 = \Lambda_2$, we have

$$\dot{N}_1 = \frac{1}{3}\bar{c}\Lambda\frac{\partial N_1}{\partial x}, \qquad \text{.....(41)}$$

or

$$D = \frac{1}{3}\bar{c}\Lambda = \frac{\eta}{m(N_1 + N_2)}. \qquad \text{.....(42)}$$

This formula becomes more complicated if the two kinds of molecules have different masses and diameters :

$$D = \frac{1}{3(N_1+N_2)}(\bar{c}_1 \Lambda_1 N_2 + \bar{c}_2 \Lambda_2 N_1). \quad \ldots\ldots\ldots\ldots\ldots\ldots (42a)$$

Λ_1 and Λ_2 are given by formula (19) on page 7.

We note that the coefficient of diffusion varies with temperature as the viscosity and is inversely proportional to the concentration (or pressure) since the expression

$$(\bar{c}_1 \Lambda_1 N_2 + \bar{c}_2 \Lambda_2 N_1)$$

is independent of the concentration.

It is possible to obtain the diffusion coefficient for a mixture of any two gases from their viscosities in the following way :

From the viscosity formula (33) we obtain d_1 and d_2 expressed in terms of η_1 and η_2 respectively ; from formula (19) Λ_1 and Λ_2 expressed in terms of d_1, d_2 and $d = d_1 + d_2$; and finally, from formula (42a), D using the values for Λ_1 and Λ_2. Naturally, the results will not be very accurate since the influence exerted by the two kinds of molecules on each other is neglected.

Formula (42) can be transformed into the form

$$D = \epsilon\eta/\rho, \quad \ldots\ldots\ldots\ldots\ldots\ldots (43)$$

where ρ is the density. The empirical value for ϵ is between 1·3 and 1·5.

The more usual definition of the diffusion coefficient is as follows. Consider a mixture of two gases in a vertical tube, at constant pressure and temperature. The concentration of the two gases (N) is uniform in horizontal layers, but varies along the vertical x axis. The diffusion coefficient is then defined by

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N}{\partial x^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (44)$$

where t = time. The diffusion coefficients for some gases are listed in Table 7.

It was shown by Einstein that the displacement $\bar{x}$ executed by a particle during time t in a medium with a diffusion coefficient D is given by

$$\bar{x}^2 = 2Dt. \quad \ldots\ldots\ldots\ldots\ldots\ldots (45)$$

Since the diffusion coefficients of most gases are of the order of a few tenths cm.^{2}/sec. at N.T.P. the displacement $\bar{x}$ is about 1 cm./sec. The number of collisions one particle suffers while travelling the distance $\bar{x}$ is given by $t\frac{\bar{c}}{\Lambda} = \frac{\bar{x}^2}{2D}\frac{\bar{c}}{\Lambda}$ (formula (18), page 7) or, since $D = \frac{1}{3}\bar{c}\Lambda$, by $\frac{3}{2}\left(\frac{\bar{x}}{\Lambda}\right)^2$.

TABLE 7

Diffusion coefficients at 0° C. and 760 mm.

	Cm.²/sec.			
	In CO_2	In H_2	In air	References
Ammonia	—	—	0·198	1
Benzene	0·0527	0 294	0·0751	2
Bromine	0·086	0·56	—	3
Carbon dioxide	—	0 538	0·142	4
Carbon monoxide	0·131	0·649	—	4
Carbon disulphide	0·0630	0·369	0·883	2
Ethylene	—	0·483	—	4
Ethyl ether	0·0552	0 296	0·0775	2
Ethyl alcohol	0·0685	0·378	0·1016	2
Hydrogen	0·538	1·285	—	5, 6
Methane	0·159	0·625	—	4
Methyl alcohol	0 0880	0·5001	0·1325	2
Nitrous oxide	0·098	0 535	—	4, 5
Oxygen	0·180	0·68	—	4, 5
Sulphur dioxide	—	0·483	—	5
Water	0·132	0·687	0·198	2

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9. Viscosity and Thermal Conductivity at Low Pressures

With decreasing pressures the mean free path increases. When the pressure is low enough the mean free path becomes comparable with, or even larger than, the dimensions of the vessel enclosing the gas. It is obvious that in such cases the molecules can pass between the walls of the vessel without colliding with each other, and therefore the formula for viscosity and thermal conductivity cannot now be valid.

(*a*) *Viscosity.* If we consider again the moving and stationary plate as on page 10 we find that all molecules colliding with the moving plate are coming from the stationary plate and have the additional velocity component o, and all molecules colliding with the stationary plate have a velocity component W, since there are no collisions between the two

plates owing to the large mean free path. Thus there is no velocity gradient between the plates, the additional velocity being $\frac{W_0}{2}$ at any place between the plates. Consequently there is a discontinuity in the velocity at the moving and stationary plate of $\frac{W_0}{2}$. In other words, it seems as if the gas would 'slip'. The momentum transferred per cm.^{2} and per second is given by

$$\frac{\mathcal{N}}{6} m \bar{c} W_0 = \frac{2}{3} \sqrt{\frac{M}{2\pi \mathbf{R} T}}\, p W_0. \quad \text{.....(46)}$$

Thus at low pressures the viscosity is proportional to the pressure (p).

For the intermediate pressure region when the mean free path is neither larger than nor negligibly small compared with the dimensions of the vessel, the momentum transferred is given by

$$\frac{\mathcal{N}}{6} m \bar{c} W' = \frac{\mathcal{N}}{3} \Lambda \bar{c} m \frac{\partial W}{\partial x}, \quad \text{.....(46a)}$$

where W' is the velocity of the molecules at a distance Λ above the stationary plate and $\frac{\partial W}{\partial x}$ the velocity gradient between the plates. Both at the upper and lower plates the velocity drop is

$$W' = 2\Lambda \frac{\partial W}{\partial x},$$

and therefore

$$\frac{\partial W}{\partial x} = \frac{W_0 - 2W'}{d - 2\Lambda} = \frac{W_0 - 4\Lambda \frac{\partial W}{\partial x}}{d - 2\Lambda}, \quad \text{.....(47)}$$

or

$$\frac{\partial W}{\partial x} = \frac{W_0}{d + 2\Lambda}, \quad \text{.....(47a)}$$

d being the distance between the plates. Thus the slipping causes an apparent increase in the distance of the plates by an amount equal to twice the mean free path.

In general not all molecules colliding with the moving or stationary plate will take up the velocity corresponding to the plate, but only a fraction $f < 1$, hence we obtain instead of (46a)

$$\frac{f}{6} \mathcal{N} \bar{c} m W' = \frac{\mathcal{N}}{3} \bar{c} \Lambda m \frac{\partial W}{\partial x}, \quad \text{.....(48)}$$

and instead of (47a)

$$\frac{\partial W}{\partial x} = \frac{W_0}{d + (2 - f)/f \,.\, 2\Lambda}, \quad \text{.....(49)}$$

where f is the coefficient of slip.

(*b*) *Thermal conductivity.* Thermal conductivity at low pressures can be calculated by employing the same principles as those used for viscosity. Thus the heat flowing between two plates of temperature T_1 and T_2 at a distance d apart per cm.^{2} per second is

$$H = k \frac{T_2 - T_1}{d + 2\frac{2-a}{a}\Lambda}, \quad \text{.....(50)}$$

where k is the ordinary heat conductivity at higher pressures and a the thermal accommodation coefficient (in general different from the coefficient of slip). It will be recognised that at very low pressures when $d \prec \Lambda$ the heat given up will be given by (cf. formulae (24a and 36))

$$H = \frac{1}{4} N \bar{c} m c_v a (T_2 - T_1), \quad \text{.....(51)}$$

i.e. proportional to the concentration or pressure. This is the principle of the Pirani manometer (cf. page 76).

The heat given up between two coaxial cylinders is of special importance, since this case is realised by an electrically heated wire stretched axially in a cylindrical vessel. In general we find

$$H = k \frac{T_1 - T_0}{ln \frac{r_1 + \Lambda}{r_0} + \frac{2\Lambda}{a r_1}}, \quad \text{.....(52)}$$

where T_1 and T_0 are temperatures of the wire and the vessel respectively, r_1 and r_0 the radii of the wire and vessel respectively, and a the accommodation coefficient of the gas on the wire. This formula shows that as long as the mean free path is negligible compared with the radius of the wire the heat given up is independent of the pressure.

10. Effusion of Gas through Holes

The simplest case is the effusion of gas through a small hole at low pressure when the mean free path is larger than the opening. In this case the concentration of the gas is not altered by the diffusion process in the neighbourhood of the opening at a distance of the mean free path. Thus the number of molecules effusing is the same as the number of molecules impinging on an area of the wall of the same magnitude as that of the hole (σ) (cf. formula (24a), page 9),

$$\dot{n}\sigma = \frac{1}{4} N \bar{c} \sigma = 3{\cdot}637 \times 10^3 N \sigma \sqrt{T/M}. \quad \text{.....(53)}$$

If a mixture of gases is effusing or if there is gas on both sides of the opening, each kind of molecule behaves independently.

At higher pressures in the neighbourhood of the opening, the distribution of velocity is considerably altered, and all the molecules obtain an additional velocity towards the opening. Thus a stream is formed, and the amount of gas leaving is proportional to the difference in pressure on the two sides of the opening.

11. Streaming through Tubes

(*a*) *Mean free path large compared with the opening.* The number of molecules entering a tube is the same as that entering an opening of the same area. Inside the tube no collision takes place between the molecules. The collisions between the wall of the tube and the molecules are not always elastic, but the impinging molecules are scattered in every direction, and not only in the direction of flow. Consequently, some molecules will be reflected back to the inlet opening, the fraction of these being larger the longer the tube.

Let the pressure at one end of the tube (length L) be p_1 and the temperature T_1, and at the other, p_2 and T_2 respectively. The number of molecules entering each side per cm.^{2} per second will be given by

$$\dot{N}_1 = \frac{N_1 \bar{c}_1}{4} = p_1 \mathbf{N} / \sqrt{2\pi M \mathbf{R} T_1}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (54)$$

and

$$\dot{N}_2 = \frac{N_2 \bar{c}_2}{4} = p_2 \mathbf{N} / \sqrt{2\pi M \mathbf{R} T_2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (54a)$$

It can then be shown that the number of molecules streaming from side one to side two is

$$B = \frac{1}{2} A (\dot{N}_1 - \dot{N}_2)/L, \quad \ldots\ldots\ldots\ldots\ldots\ldots (55)$$

for cylindrical tubes $A = 2d^3\pi/3$ (d = diameter) or

$$B = \frac{\mathbf{N} d^3 \pi}{3 L \sqrt{2\pi M \mathbf{R}}} \left(\frac{p_2}{\sqrt{T_2}} - \frac{p_1}{\sqrt{T_1}} \right). \quad \ldots\ldots\ldots\ldots\ldots\ldots (56)$$

This formula is of great importance for working with high vacuum pumps. It will be recognised that if at one end of the tube the pressure is maintained at zero, the amount of gas leaving through this tube is proportional to the third power of the diameter of the tube. Thus a tap with a small hole in the key, say, 2 mm. in diameter and 1 cm. in length, offers the same resistance to pumping as 125 cm. of 10 mm. tubing or 10 metres of 20 mm. tubing.

Another consequence of this formula is that if two vessels at different temperatures are connected by a narrow tube, then at equilibrium

$$\frac{p_2}{\sqrt{T_2}}=\frac{p_1}{\sqrt{T_1}}, \quad \text{.....(57)}$$

or

$$\left(\frac{p_1}{p_2}\right)=\sqrt{\frac{T_1}{T_2}}, \quad \text{.....(58)}$$

i.e. the pressures are proportional to the square root of the absolute temperature. This, the so-called Knudsen effect, must be taken into consideration in pressure measurements if manometer and reaction vessel are at different temperatures.

(*b*) *Poiseuille formula.* The Poiseuille formula, valid for the streaming of liquids through a tube, is applicable to the flow of gases through tubes of which the diameter is larger than the mean free path, but which are narrow enough to allow friction to play a large part (the high compressibility of gases must be allowed for). For a short tube, flowing being isothermal, the amount of gas in moles streaming through a tube per second is

$$\frac{\left(\frac{d}{2}\right)^4 \pi (p_2^2-p_1^2)}{16 L \eta \mathbf{R} T}. \quad \text{.....(59)}$$

If correction is to be introduced for slip (cf. page 17), this formula is multiplied by $1+\frac{8}{d}g$, where $g=(2-f)2\Lambda/f$, and f is the coefficient of slip. In formula (59) absolute units are used, i.e. $\mathbf{R}=8{\cdot}313\times 10^7$ erg/degree^{-1} mole^{-1}, and the pressure is expressed in dynes cm.$^{-2}$ (cf. page 71).

12. Distribution of Energy and Partition Functions.

The molecules of a gas contain four different forms of energy :

(1) Translational energy.
(2) Rotational energy.
(3) Vibrational energy.
(4) Electronic energy.

The distribution of each of these kinds of energies when the gas is in equilibrium is governed by the Maxwell law. Whereas a molecule may possess any amount of translational energy, the three other forms of energies are quantised, i.e. the energy may assume only certain discrete values.

The knowledge of the individual energy states is of importance since from these quantities the mean energy, molar heat capacity, summation

of state (partition function), entropy and free energy may be derived. These are the quantities which define chemical equilibria.

Let the individual energy levels of any form of quantised energy be ϵ_1, ϵ_2, $\epsilon_3 \ldots \epsilon_n$, then the number of molecules in the first, second, third nth level will be in the ratio

$$g_1 e^{-\epsilon_1/\mathbf{k}T} : g_2 e^{-\epsilon_2/\mathbf{k}T} : g_3 e^{-\epsilon_3/\mathbf{k}T} : \ldots : g_n e^{-\epsilon_n/\mathbf{k}T}, \quad \ldots\ldots\ldots\ldots(60)$$

where $\mathbf{k}$ is Boltzmann's constant and g_1, g_2, g_3 and g_n are the statistical weights and indicate the multiplicity of the corresponding levels, i.e. the number of discrete levels into which each of these levels would split up in a strong enough external field. The expression

$$f = \sum_{n=1}^{\infty} g_n e^{-\epsilon_n/\mathbf{k}T} \quad \ldots\ldots\ldots\ldots(60a)$$

is then called the summation of state or partition function. The partition function for non-quantised energy is given by a similar expression, only the summation is to be replaced by integration to sum up the continuously variable energy states. The total partition function is the product of different kinds of partition functions which may be divided into translational and internal partition functions :

$$f = f_{\text{trans}} \cdot f_{\text{intern.}} \quad \ldots\ldots\ldots\ldots(61)$$

The translational partition function is given by

$$f_{\text{trans}} = \frac{(2\pi \mathbf{k} MT)^{3/2} \mathbf{R}T}{\mathbf{h}^3 \mathbf{N}^{5/2} P}, \quad \ldots\ldots\ldots\ldots(62)$$

with $\mathbf{k} = 1{\cdot}373 \times 10^{-16}$ erg/degree/molecule, M = molecular weight, $\mathbf{R} = 8{\cdot}313 \times 10^{7}$ erg/degree^{-1} mole^{-1}, $\mathbf{h} = 6{\cdot}55 \times 10^{-27}$ erg/sec., $\mathbf{N} = 6{\cdot}06 \times 10^{23}$, and P = pressure in atmospheres.

The internal partition function has different forms depending whether it refers to monatomic, diatomic or polyatomic gases.

(*a*) *Internal partition function for a monatomic gas.* For a monatomic gas

$$f_i = f_E f_K, \quad \ldots\ldots\ldots\ldots(63)$$

where f_E is the multiplicity of the lowest electronic level and $f_K = g_K = 2i + 1$ is the multiplicity due to the nuclear spin i. The spin multiplicity arises since a spin vector of the value i can take up $2i + 1$ different positions in an external magnetic field, e.g. for $i = \frac{1}{2}$, $g_k = 2$, namely parallel and anti-parallel ; for $i = 1$, $g_k = 3$, namely parallel, perpendicular and anti-parallel, and so on.

(*b*) *Diatomic gas.* For diatomic molecules

$$f_i = f_E f_V f_R f_K, \quad \ldots\ldots\ldots\ldots(64)$$

f_V being the partition function for vibrational energy and f_R that for

rotational energy. f_E and f_K have the same meaning as that for a monatomic gas.

(α_1) *Harmonic vibrations.* The frequencies of harmonic vibrations are given by

$$\omega_v = \omega_0 (v + \tfrac{1}{2}), \quad \ldots\ldots(65)$$

where v, the vibrational quantum number, can assume the integral values of 0, 1, 2, and so on. The energy is defined by

$$\epsilon_v = \mathbf{hc}\,\omega_v = \mathbf{hc}\,\omega_0 (v + \tfrac{1}{2}) \quad \ldots\ldots(66)$$

($\mathbf{c}$ = velocity of light).

The energy $\epsilon_0 = \frac{1}{2}\mathbf{hc}\omega_0$ for $v = 0$ is called the zero point energy, since it persists even at absolute zero. The partition function for vibrational energy is

$$f_v = e^{-\epsilon_0/\mathbf{k}I} + e^{-\epsilon_1/\mathbf{k}T} + e^{-\epsilon_2/\mathbf{k}T} + e^{-\epsilon_3/\mathbf{k}I} + \ldots \quad \ldots\ldots(67)$$

This being the sum of a geometric series

$$f_v = e^{-\epsilon_0/\mathbf{k}T}\left(1 - e^{-(\epsilon_1 - \epsilon_0)/\mathbf{k}I}\right)^{-1} = e^{-\mathbf{hc}\,\omega_0/2\mathbf{k}I}\left(e^{\mathbf{hc}\,\omega_0/\mathbf{k}T} - 1\right)^{-1}. \quad \ldots\ldots(68)$$

(α_2) *Anharmonic vibrations.* If the vibrations are not strictly harmonic the following formula is valid for the energy and frequency of the vibration :

$$\omega_v = \frac{\epsilon_v}{\mathbf{hc}} = \omega_e\left(v + \frac{1}{2}\right) - x_e\omega_e\left(v + \frac{1}{2}\right)^2 + y_e\omega_e\left(v + \frac{1}{2}\right)^3 + \ldots, \quad \ldots\ldots(69)$$

x_e and y_e being the anharmonic constants. ω_e is the frequency for infinitely small amplitude, and is to be distinguished from ω_0, the zero point frequency for $v = 0$ with finite amplitude. Except when the highest accuracy is required, the terms after the third may be neglected. The values of ω_e, $x_e\omega_e$, $y_e\omega_e$, etc., are derived from spectroscopic observations. For anharmonic vibrations, the summation of state has to be carried out term by term.

(β) *Rotation.* It is necessary to distinguish between two kinds of rotation, depending upon whether the internuclear distance is constant or variable, (*a*) rigid rotator, and (*b*) rotator coupled with vibrator.

(β_1) *Rigid rotator.* The rotational energy is given by

$$\epsilon_R = \frac{\mathbf{h}^2}{8\pi^2 I} J(J+1) = \mathbf{hc}\,B\,J(J+1), \quad \ldots\ldots(70)$$

where

$$B = \frac{\mathbf{h}}{8\pi^2 \mathbf{c}\,I},$$

J being the rotational quantum number, and I the moment of inertia.

In general, the calculation of the corresponding partition function is rather complicated, but in certain cases it may be simplified considerably :

(1) If the molecules consist of different nuclei and $\sigma = \mathbf{h}^2/8\pi^2 I \mathbf{k} T < 1$, we may substitute integration for summation ; thus

$$f_R = \sum_{J=0}^{\infty} (2J+1)\, e^{-\sigma J(J+1)} = \int_0^{\infty} (2J+1)\, e^{-\sigma J(J+1)}\, dJ = \frac{1}{\sigma} = \frac{8\pi^2 I \mathbf{k} T}{\mathbf{h}^2}. \quad \ldots(71)$$

For other values of σ the following approximation is valid :

$$f_R = \frac{1}{\sigma} + \frac{1}{12} + \frac{7}{480}\sigma + \ldots . \quad \ldots(72)$$

(2) If the molecules consist of identical nuclei, but the nuclei have no spin (e.g. O_2),

$$f_R = \frac{8\pi^2 I \mathbf{k} T}{\mathbf{h}^2 S}, \quad \ldots(73)$$

S being the symmetry number, e.g. for O_2 $S = 2$.

(3) If the nuclei are identical and have a spin i, the summation of the rotational states must be performed for even and odd rotational quantum numbers separately :

$$f_R = g_e \sum_{J=0,2,4,\ldots}^{\infty} (2J+1)\, e^{-\sigma J(J+1)} + g\sigma \sum_{J=1,2,3,}^{\infty} (2J+1)\, e^{-\sigma J(J+1)}, \quad \ldots(74)$$

the statistical weights g_e and g_0 for even and odd J being $i(2i+1)$ and $(i+1)\times(2i+1)$, respectively or *vice versa*, depending upon whether the statistics of the nuclei correspond to the Fermi-Dirac statistics (e.g. H_2, $i = \frac{1}{2}$) or to the Bose-Einstein statistics (e.g. D_2, $i = 1$).

(β_2) *Rotation with vibration.* For a vibrating rotator the rotational energy is given by

$$\epsilon_{R,v} = \mathbf{hc}\,[B_v (J+\tfrac{1}{2})^2 + D_v (J+\tfrac{1}{2})^4], \quad \ldots(75)$$

where B_v and D_v depend on the vibrational quantum number as follows :

$$B_v = B_e - \alpha(v+\tfrac{1}{2}) + \gamma(v+\tfrac{1}{2})^2 + \ldots , \quad \ldots(76)$$

$$D_v = D_e + \beta(v+\tfrac{1}{2}) + \ldots . \quad \ldots(77)$$

Since $\alpha > 0$ and $\gamma < \alpha$ with increasing temperature, B_v decreases, i.e. the moment of inertia I increases. Since in general $\mathbf{hc}B_v < \mathbf{k}T$, it is possible to replace the summation in the partition function by integration and obtain an explicit form for

$$f_{R,v} = \sum 2m\, e^{-\frac{\mathbf{hc}}{\mathbf{k}T}(B_v m^2 + D_v m^4 + \ldots)}, \text{ with } m = J + \tfrac{1}{2}. \quad \ldots(78)$$

(γ) *Nuclear spin.* The contribution of the nuclear spin to the partition function is

$$f_K = (2i_1+1)(2i_2+1), \quad \ldots(79)$$

if i_1 and i_2 denote the nuclear spins of the two atoms of the molecule. For homonuclear molecules when $i_1 = i_2 = i \pm 0$, only those relative positions of the nuclear spins of the atoms are possible which correspond to

the resultant spins of $2i$, $2i-1$, $2i-2$, $2i-3$, ... 0. These values belong alternately to symmetric and antisymmetric (underlined) states which have to be regarded separately :

$$\text{for symmetric states,} \quad f_{K_s} = (2i+1)(i+1) \; ;$$

$$\text{for antisymmetric states,} \quad f_{K_a} = (2i+1)i.$$

The contribution of the nuclear spin is of great importance in the case of hydrogen and deuterium (cf. A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, Cambridge University Press, 1935).

(*c*) *Polyatomic gases.* In general, the state of affairs is very much more complicated with polyatomic molecules than with diatomic molecules, and only in special cases is it possible to deduce exact formulae for energy, partition function, entropy and free energy.

(α) *Vibration.* In general, a molecule composed of n atoms is capable of $3n-6$ fundamental modes of vibration, since a complex of n particles has $3n$ degrees of freedom, 3 of which are reserved for translation and 3 for rotation. Any other vibrational frequency of the molecule can be represented as the sum of two or more fundamental frequencies. For linear molecules the number of fundamental frequencies is $3n-5$, since such a molecule is only capable of 2 rotations.

The vibrations may be divided into two kinds : $n-1$ valence vibrations (frequency denoted by ν), in which the motion of the nuclei takes place along the chemical bonds, and $2n-5$ deformation vibrations, denoted by δ, in which the motion is perpendicular to the bonds.

The vibrations can again be subdivided into :

(1) Parallel vibrations, denoted by $\parallel$, arising when the change of electric moment associated with this vibration is parallel to the axis of symmetry.

(2) Perpendicular vibrations, denoted by $\perp$, arising when the change of electric moment is perpendicular to the axis of symmetry.

For molecules with a centre of symmetry we may further distinguish between :

(3) Symmetrical vibrations, denoted by *s*, when the motion is symmetrical with regard to the centre of symmetry.

(4) Antisymmetrical vibrations, denoted by *a*, when this is not the case.

The $3n-6$ vibrations need not be all different ; in molecules of high symmetry, two or more frequencies are identical. The fundamental frequencies of H_2O, for example, are as follows :

$$\nu_{\parallel} = 3600 \text{ cm.}^{-1},$$
$$\nu_{\perp} = 3756{\cdot}35 \text{ cm.}^{-1},$$
$$\delta = 1595{\cdot}4 \text{ cm.}^{-1}.$$

The vibrational energy of polyatomic molecules is given by

$$\epsilon_v = \mathbf{hc} \Sigma \omega_n (v_n + \tfrac{1}{2}), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (80)$$

where the summation is to be extended over all fundamental frequencies. The partition function may then be computed by addition.

(β) *Rotation.* In the rotation of polyatomic molecules in general, three moments of inertia, I_A, I_B, and I_C, are involved. There are, however, certain special cases in which the state of affairs is simpler.

(1) For linear molecules, such as CO_2, C_2H_2, for example, two of the moments are equal : $I_A = I_B$ and the third $I_C = 0$. The rotation of these molecules is similar to that of diatomic molecules. The rotational energy is

$$\epsilon_R = \mathbf{hc}\, B\, J(J+1). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (70)$$

(2) For spherical molecules (e.g. CH_4) all three moments of inertia are equal, $I_A = I_B = I_C$, and the expression for the rotational energy is similar to that in formula (70).

(3) For molecules of the symmetrical top type (NH_3, C_2H_6, etc.), in which two moments of inertia are equal and the third different, $I_A = I_B \neq I_C$, it is still possible to express in exact formulae the rotational energy, but these formulae are too complicated to be dealt with here.

(4) For the rotational energy of molecules of the asymmetrical top type, in which all three moments of inertia are different, exact formulae are in general no longer available. In cases when two of the moments of inertia are not different by a large amount, approximate formulae may be derived similar to those for molecules of the symmetrical top type.

(γ) *Nuclear spin.* The calculation of the contribution of the nuclear spin to the partition function of polyatomic molecules is carried out according to the same principles as those employed in the case of diatomic molecules. This question, however, cannot be treated here in detail. During a chemical reaction, the nuclear spins of the reaction partners are conserved and their contributions to entropy and free energy cancel out. Consequently, it is permissible to neglect the contribution of the nuclear spin altogether, provided the values thus obtained are only used in calculating chemical equilibria in conjunction with other values not containing the contribution of the nuclear spin.

13. Equilibria

The equilibrium constant of the chemical equilibrium

$$nA + mB \rightleftharpoons rC + sD, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (81)$$

$$K_p = \frac{p_C{}^r \cdot p_D{}^s}{p_A{}^n \cdot p_B{}^m}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (82)$$

(p = partial pressure of the reactants in atmospheres) is connected with the partition function by

$$-\mathbf{R}T\ln K_p = -r[\mathbf{R}T\ln f^\circ - E_0^\circ]_C - s[\mathbf{R}T\ln f^\circ - E_0^\circ]_D + n[\mathbf{R}T\ln f^\circ - E_0^\circ]_A + m[\mathbf{R}T\ln f^\circ - E_0^\circ]_B = -\mathbf{R}T\Delta\ln f^\circ + \Delta E_0^\circ, \quad \ldots\ldots\ldots\ldots(83)$$

where the superscript ° indicates that the partition function refers to the standard state $p = 1$ atm. and E_0 is the energy at absolute zero.

If one regards the energy of atoms at absolute zero as the zero level of energy, E_0° is the energy of dissociation into unexcited atoms at absolute zero and atmospheric pressure. The dissociation energies for some molecules are given in Table 8.

Substituting equations (61) and (62) into (83) we obtain

$$-\ln K_p = \frac{\Delta E_0^\circ}{\mathbf{R}T} - \Delta\left\{\frac{5}{2}\ln T + \frac{3}{2}\ln M - 7{\cdot}267/\mathbf{R}\right\} - \Delta\ln f_{\text{intern}}, \quad \ldots\ldots(84)$$

since

$$\mathbf{R}\ln\frac{(2\pi\mathbf{k})^{\frac{3}{2}}\mathbf{R}}{\mathbf{h}^3\mathbf{N}^{5/2}} = -7{\cdot}267.$$

TABLE 8

Energies of Dissociation in Cals.

		Ref.			Ref.
H_2	102·72	1	I_2	35·39	11
HD	103·54		HF	~140	12
D_2	104·52		HCl	101·6	13
Na_2	17·5	2	HBr	87·7	14
K_2	11·8	3	HI	~66	15
N_2	169·4	4	NO	121·4	16
P_2	115·44	5	SO	116·5	17
O_2	116·4	6	CO	159	17A
S_2	101·7	7	$CO_2 \rightarrow CO + O$	125·8	18
F_2	~64·6	8	$N_2O \rightarrow NO + N$	88·5	
Cl_2	56·87	9	$H_2O \rightarrow HO + H$	117·8	19
Br_2	45·22	10	$SO_2 \rightarrow SO + O$	134·1	20

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Formulae for the measured equilibrium constants are given in Table 9.

TABLE 9

References		
1	$\frac{1}{2}Br_2+\frac{1}{2}I_2\rightleftharpoons IBr$	$\log K_p=1270/4{\cdot}573T+0{\cdot}3816$
2	$CH_4+CO_2\rightleftharpoons 2CO+H_2$	$\log K_p=-57903/4{\cdot}573T+13{\cdot}875$
3	$CH_4+H_2O\rightleftharpoons CO+3H_2$	$-\log K_p$: 3·74 (673 °K.), 3·02 (703), 2·56 (723), 2·12 (744), 1·72 (763)
4	$CH_4+2H_2O\rightleftharpoons CO_2+4H_2$	$\log K_p$: −1·49 (500 °C.), −0·02 (600), 1·18 (700)
5	$CH_4+2H_2S\rightleftharpoons CS_2+4H_2$	$\log K_p$: −4·7 (90 °C.), −2·7 (100), −1·8 (110), +1·1 (120), +3·0 (130)
6	$2CH_3OH\rightleftharpoons(CH_3)_2O+H_2O$	$\log K_p$: 1·68 (403 °K.), 1·19 (503)
7	$C_2H_5Cl\rightleftharpoons C_2H_4+HCl$	$\log K_p=4{\cdot}96-2925/T$
8	$C_2H_6\rightleftharpoons C_2H_4+H_2$	$\log K=-27798/4{\cdot}573T+2{\cdot}01\log T-0{\cdot}471$
9	$C_3H_8\rightleftharpoons C_3H_6+H_2$	$\log K_p=-25920/4{\cdot}573T+2{\cdot}01\log T+0{\cdot}04$
10	$n\text{-}C_4H_{10}\rightleftharpoons H_2+cis\text{-}CH_3\text{-}CH=CH\text{-}CH_3$	$\log K_p=-25580/4{\cdot}573T+2{\cdot}01\log T+0{\cdot}04$
11	$n\text{-}C_4H_{10}\rightleftharpoons H_2+trans\text{-}CH_3\text{-}CH=CH\text{-}CH_3$	$\log K_p=-25090/4{\cdot}573T+2{\cdot}01\log T+0{\cdot}04$
12	$n\text{-}C_4H_{10}\rightleftharpoons H_2+CH_3\text{-}CH_2\text{-}CH=CH_2$	$\log K_p=-25790/4{\cdot}573T+2{\cdot}01\log T+0{\cdot}04$
13	iso-$C_4H_{10}\rightleftharpoons(CH_3)_2C=CH_2$	$\log K_p=-23900/4{\cdot}573T+2{\cdot}01\log T+0{\cdot}04$
14	$C_6H_6+3H_2\rightleftharpoons C_6H_{12}$	$\log K_p=43850/4{\cdot}573T-9{\cdot}9194\log T+2{\cdot}28\times10^{-2}T+8{\cdot}565$
15	$C_6H_{14}\rightleftharpoons C_6H_{12}+H_2$	$\log K_p=29110/4{\cdot}573T-2{\cdot}961\log T+7{\cdot}66\times10^{-4}T-1{\cdot}764\times10^{-7}T^2+0{\cdot}11$
16	$C_8H_{18}\rightleftharpoons C_8H_{16}+H_2$	$\log K_p=29110/4{\cdot}573T-2{\cdot}961\log T+7{\cdot}66\times10^{-4}T-1{\cdot}764\times10^{-7}T^2-0{\cdot}4$
17	$Cl_2+CO\rightleftharpoons COCl_2$	$\log K_p=-5710/T+5{\cdot}46$
18	$Cl_2+2NO\rightleftharpoons 2NOCl$	$\log K_c=-3667/T+1{\cdot}5\log T-0{\cdot}079$
19	$Cl_2+SO_2\rightleftharpoons SO_2Cl_2$	$\log K_p=-2250/T+1{\cdot}75\log T-4{\cdot}55\times10^{-}+2{\cdot}2$

References		
20	$CO + H_2 \rightleftharpoons HCOH$	$\log K_p = 1710/4{\cdot}573T - 5{\cdot}431$
21	$CO + 2H_2 \rightleftharpoons CH_3OH$	$\log K_p = 17030/4{\cdot}573T - 9{\cdot}1293 \log T + 0{\cdot}00308T + 13{\cdot}412$
22	$CO + \frac{1}{2}SO_2 \rightleftharpoons CO_2 + \frac{1}{4}S_2$	$\log K_p = 5659/T - 0{\cdot}6915 \log T + 3 \times 10^{-4}T - 3{\cdot}4 \times 10^{-8}T^2 - 0{\cdot}872$
23	$2CO_2 \rightleftharpoons 2CO + O_2$	$\log K_c = -28600/T + 8{\cdot}46$
24	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	$\log K_p = -2170/T + 0{\cdot}979 \log T - 1{\cdot}082 \times 10^{-3}T + 1{\cdot}734 \times 10^{-7}T^2$
25	$2HBr \rightleftharpoons H_2 + Br_2$	$\log K_p = -5223/T + 0{\cdot}553 \log T - 2\ 72$
26	$2HCl \rightleftharpoons H_2 + Cl_2$	$\log K_p = -9586/T + 0{\cdot}440 \log T - 2{\cdot}16$
27	$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$	$\log K_p = 23920/4{\cdot}573T - 5{\cdot}86$
28	$HCOH + H_2 \rightleftharpoons CH_3OH$	$\log K_p = 21036/4{\cdot}573T - 6{\cdot}470$
29	$2HI \rightleftharpoons H_2 + I_2$	$\log K_p = -540{\cdot}4/T + 0{\cdot}503 \log T - 2{\cdot}35$
30	$2H_2O \rightleftharpoons 2H_2 + O_2$	$\log K_c = -24900/T + 1{\cdot}335 \log T - 9{\cdot}65 \times 10^{-5}T + 1{\cdot}37 \times 10^{-7}T^2 - 6{\cdot}65 \times 10^{-11}T^3 - 1{\cdot}08$
31	$H_2O + HD \rightleftharpoons HDO + H_2$	$\log K = 750/4{\cdot}573T - 0{\cdot}1335$
32	$H_2O + SO_3 \rightleftharpoons H_2SO_4$	$\log K_c = -5000/T + 0{\cdot}75 \log T - 5{\cdot}7 \times 10^{-4}T + 4{\cdot}086$
33	$2H_2S \rightleftharpoons 2H_2 + S_2$	$K_p \times 10^4$: 0·89, 3·8, 24·5, 118, 260 at °C.: 750, 830, 945, 1065, 1132
34	$HgBr_2 \rightleftharpoons Hg + Br_2$	$\log K_p = -42170/4{\cdot}573T + 5{\cdot}329$
35	$HgCl_2 \rightleftharpoons Hg + Cl_2$	$\log K_p = -46150/4{\cdot}573T + 5{\cdot}141$
36	$HgI_2 \rightleftharpoons Hg + I_2$	$\log K_p = -33020/4{\cdot}573T + 5{\cdot}308$
37	$2NH_3 \rightleftharpoons 3H_2 + N_2$	$\log K_p = 2098{\cdot}2/T - 2{\cdot}509 \log T - 1{\cdot}006 \times 10^{-4}T + 1{\cdot}859 \times 10^{-7}T^2 + 2{\cdot}10$
38	$2NO_2 \rightleftharpoons 2NO + O_2$	$\log K_p = -5749/T + 1{\cdot}7 \log T - 5 \times 10^{-4}T + 2{\cdot}839$
39	$N_2O_4 \rightleftharpoons 2NO_2$	$\log K_p = -2692/T + 1{\cdot}75 \log T + 4{\cdot}83 \times 10^{-3}T - 7{\cdot}144 \times 10^{-6}T^2 + 3\ 062$
40	$O_2 + 2SO_2 \rightleftharpoons 2SO_2$	$\log K_c = -10373/T - 2{\cdot}222 \log T + 14{\cdot}585$
41	$S_6 \rightleftharpoons 3S_2$	$\log K_p = -64000/4{\cdot}57T - 4/4{\cdot}57 + 3{\cdot}5 \log T + 6{\cdot}2$
42	$3S_8 \rightleftharpoons 4S_6$	$\log K_p = -29000/4{\cdot}57T - 2/4{\cdot}57 + 1{\cdot}75 \log T + 4{\cdot}3$

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B. ELEMENTS OF CHEMICAL KINETICS

1. General

A chemical reaction involves the rupture of bonds between atoms constituting a molecule and/or the formation of new bonds between atoms. Thus we have the following types of simple chemical reactions :

Dissociation = Rupture of bond		$AB \rightarrow A + B.$	(I) .....(85)
Association = Formation of bond		$A + B \rightarrow AB.$	(II) ....(86)
Atomic exchange	Rupture and formation of bonds	$A + BC \rightarrow AB + C.$	(III) ...(87)
Molecular exchange		$AB + CD \rightarrow AC + BD.$	(IV) ...(88)

Whereas general chemistry is only concerned with the final products of these reactions, chemical kinetics enquires about the speed of such processes. The speed, velocity or rate of a chemical reaction is defined as the number of molecules transformed per unit volume per unit time. Two particles, atoms or molecules will have a chance to perform reactions of the type (II), (III) or (IV) if these two particles come within a reasonable distance of each other. If the gas kinetic diameters determine essentially

this distance, the maximum velocity for these reactions is given by the number of collisions between the corresponding particles. For dissociation reactions of the type (I) it is not possible to give such a reasonable maximum value. A comparison of these figures with the experimental determinations of reaction velocities reveals that for most reactions the actual velocities are far smaller than the maximum values. A closer investigation shows that the inertia of chemical reactions is due to a variety of reasons.

One type of inertia is due to the fact that the average energy of the molecules in the initial state is less than that of the molecules in the final state after the chemical change has taken place. Only those molecules react which happen to have, owing to the Maxwell distribution, an energy equal to or larger than the average energy in the final state. This inertia is observed in all endothermic reactions. From the point of view of chemical kinetics the inertia due to other causes is more important, in which occur reactions of the type (II), (III) and (IV). (Reactions (III) and (IV) are supposed to be exothermic.)

The saturated character of the chemical bond between the atoms B and C in the molecule BC is made manifest to an approaching A atom in reaction (III), as a repulsion. This repulsion increases up to a certain value as the distance between the particles A and BC decreases. If now A approaches more closely the repulsion changes gradually to attraction, and simultaneously the particle C is expelled from the molecule. The atom A can approach the molecule BC along different paths, e.g. along the line joining the nuclei BC, from a direction forming an angle of 45° with this line, and so on. In general, each time the maximum value of the repulsion will be different, the smallest of these maxima, i.e. the maximum repulsion exerted on the most favourable path, is called the energy of activation. Only those atom-molecule aggregates will be able to react for which the joint energy equals or exceeds this energy of activation. (F. London.)

In principle the same considerations hold for a reaction of the molecular exchange type (IV), though naturally the state of affairs is more complicated, four particles being involved instead of three. The other main difference between these two types of exchange reactions is that the activation energy for the molecular exchange reaction is much higher than that for the atomic exchange, owing to the saturated character of both particles AB and CD. Since the number of the molecules for which a certain energy E is available depends on temperature (T), mainly as $\exp(-E/RT)$, the atomic exchange reactions will proceed at measurable speed at a much lower temperature than the molecular exchange reaction.

Another kind of inertia exists in the case of reaction $A+B=AB$. Two

atoms cannot form a molecule if they meet unless some energy is dissipated simultaneously, since otherwise the energy of dissociation released in this process would subsequently drive the atoms apart. In general,* this dissipation of energy is not possible by way of light emission, and since there is no other way of reducing the energy of an individual molecule, formation of molecules can not take place when two atoms meet. It was shown by J. Franck that such a union can occur if part of the energy produced is removed by a third body, i.e. if the union takes place in a triple collision according to

$$A + B + M = AB + M. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (89)$$

We have recognised that temperature is one factor which overcomes the inertia of chemical reactions. In this case it is the thermal energy of the particles which is decisive, but any other form of energy might be equally effective. Radiant energy is responsible for the chemical change in photochemical reactions and the kinetic energy of electrons or ions in reactions under the influence of electric discharges. If radiant energy is absorbed by molecules not involved in the photochemical reaction and subsequently transferred to those taking part, then this process is referred to as a sensitised reaction. Collision processes in which electronic energy is thus transferred are called collisions of the second time.

Since all reactions depend on certain kinds of collisions between the molecules, the concentration or pressure will, in general, have an influence on the reaction velocity.

The acceleration of chemical reactions by various kinds of catalysts is well known. The nature of the catalytic action is not yet completely understood, but it appears that catalytic reactions involve the formation of certain intermediate compounds between the reactants and the catalyst. For this reason we shall include the catalyst among the independent variables controlling chemical reactions: time, pressure (concentration), temperature and light intensity.

The rate of chemical reactions measured by the number of molecules transformed in unit time and unit volume is the absolute rate of reaction, and is usually expressed in units of moles per c.c. per second or moles per litre per second. Often it is convenient to refer to the relative rate, which means the fraction of the total number of molecules present changed per unit of time. The ratio of the absolute rate to the relative rate is the concentration. For characterising the relative rate sometimes the ' half life time ' is introduced, that is, the time required for the reaction to go halfway to completion.

* For details cf. L. S. Kassel, *Kinetics of Homogeneous Gas Reactions*. The Chemical Catalog Co., New York (1932).

In most reactions the rate of chemical change is dependent on concentration. If this dependence is known the velocity of the reaction can be described by a single constant—the velocity constant—which depends only on the temperature. The velocity constant represents the absolute velocity of the chemical change at unit concentration. For simpler reactions the dependence of the absolute velocity (v) on the concentrations of the reactants A, B, C, etc., is of the form

$$v = k[A]^m[B]^n[C]^p, \quad \text{.....(90)}$$

where m, n, p, etc., are small numbers, and are called the order of the reaction with respect to the reactant A, B and C respectively. The sum of these orders is the total order of the reaction.

The order of the reaction is not necessarily an indication of the number of molecules involved in the elementary act of the reaction mechanism. In order to express this the terms monomolecular, bimolecular or termolecular reactions are employed to designate reactions involving one, two or three molecules respectively in the elementary act.

The class of chemical reactions in which reaction velocity can be described by a velocity constant will be referred to as stationary reactions. There is another class of chemical reactions in which the velocity increases rapidly during the course of the reaction and may reach immeasurably high values. To this class belong the explosive reactions.

The majority of chemical reactions are not as simple as those described above, but are composed of a number of simpler processes which proceed simultaneously or consecutively. The object of investigating chemical reactions is to disentangle individual processes and to assign to each process its role in the composite reaction, i.e. to find out the mechanism of the reaction in question. A good example of the composite nature of a reaction is the interaction

$$H_2 + D_2 = HD + HD.$$

This reaction does not proceed according to this equation, which represents a reaction of the molecular exchange type. In fact, it involves as steps reactions of the dissociation, recombination and atomic exchange type. Through the dissociation of the hydrogen molecules,

$$H_2 = 2H,$$
$$D_2 = 2D;$$

and the recombination of atoms,

$$2H = H_2,$$
$$2D = D_2,$$
$$H + D = HD;$$

a certain stationary atom concentration is established, and the atoms react according to

$$H + D_2 = HD + D,$$
$$D + H_2 = HD + H.$$

These last two individual reactions are of decisive importance, since the number of HD molecules produced by this reaction in unit time is very much larger than the number of those produced through the processes of dissociation and recombination.

In photochemical reactions the composite nature of a chemical reaction might be further complicated owing to the variety of the products which may be formed. Thus the photochemical primary process might lead to excited molecules, normal or excited atoms, molecule ions or atom ions. The photochemical decomposition of hydrogen iodide might be cited as an example. Originally it was assumed that through the absorption of light an excited HI molecule was formed which decomposed subsequently on impact with a second molecule :

$$HI + h\nu = HI^*,$$
$$HI^* + HI = H_2 + I_2.$$

Later it was shown, however, that in fact the HI molecules are decomposed into atoms in one elementary act, and the resulting H atoms decompose the second HI molecules according to

$$HI + h\nu = H + I,$$
$$H + HI = H_2 + I.$$

Gaseous reactions may be classified according to various view-points. We distinguish between homogeneous and heterogeneous gas reactions. In the former type only gaseous reactants participate, whereas in the latter type gaseous, liquid or solid reactants might be involved. The distinction between stable and explosive reactions has already been referred to ; similarly the classification according to the number of particles participating in the elementary act and according to the order of the reaction have also been mentioned. If the inertia of a chemical reaction is decreased by elevation of temperature, by addition of a catalyst, or by illumination with light, we speak of thermal, catalytic and photochemical reactions respectively.

2. Dependence of the Reaction Rate on Pressure

By means of the velocity constant and the order of the reaction, the progress of a stable reaction can be represented as a function of time.

Thermal reactions. The characteristic equations for the simplest thermal reactions are as follows :

(1) Unimolecular reactions of the type $A = X$.

$$\frac{dx}{dt} = k_1(a-x), \quad \ldots\ldots(91)$$

$$k_1 = \frac{1}{t} ln\, a/(a-x), \quad \ldots\ldots(91a)$$

with a = the initial concentration of A and $a - x$ = the concentration of A at the time t.

(2) Bimolecular reactions of the type $2A = X$.

$$\frac{dx}{dt} = k_2(a-x)^2, \quad \ldots\ldots(92)$$

$$k_2 = \frac{1}{t} \frac{x}{a(a-x)}. \quad \ldots\ldots(92a)$$

(3) Bimolecular reactions of the type $A + B = X$.

$$\frac{dx}{dt} = k_2'(a-x)(b-x), \quad \ldots\ldots(93)$$

$$k_2' = \frac{1}{t(b-a)} ln \frac{(b-x)a}{(a-x)b}. \quad \ldots\ldots(93a)$$

(4) Termolecular reactions of the type $3A = X$.

$$\frac{dx}{dt} = k_3(a-x)^3, \quad \ldots\ldots(94)$$

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]. \quad \ldots\ldots(94a)$$

(5) Termolecular reactions of the type $2A + B = X$.

$$\frac{dx}{dt} = k_3'(a-x)^2(b-x), \quad \ldots\ldots(95)$$

$$k_3' = \frac{1}{t(b-a)^2}\left\{\frac{(b-a)x}{(a-x)a} + ln \frac{b(a-x)}{a(b-x)}\right\}. \quad \ldots\ldots(95a)$$

These equations are only valid for reactions which proceed under constant but variable pressure, and have to be modified if applied to reactions progressing under constant pressure. The equations valid for reactions under constant pressure will be discussed when dealing with flow systems (p. 296).

It is interesting to compare the relative rates of these different types of reactions for a given velocity constant at different concentrations. If the time of half change or half life of the reaction is defined as the value of

$t=\tau$ at which $a-x=\frac{a}{2}$, from equations (91), (92) and (93) the following relations are obtained :

$$\tau_1=\frac{1}{k_1}ln\,2=\frac{0{\cdot}69}{k_1}, \quad \text{.....(96)}$$

$$\tau_2=\frac{1}{k_2}\cdot\frac{1}{a}=\frac{1}{ak_2}, \quad \text{.....(97)}$$

$$\tau_3=\frac{3}{2k_3}\cdot\frac{1}{a^2}=\frac{1{\cdot}5}{a^2k_3}. \quad \text{.....(98)}$$

Values for $k=10^{-6}$ to 10 and $a=10^{-1}$ mole litre^{-1} (corresponding to a pressure of about 1500 mm. Hg at room temperature) to 10^{-4} mole litre^{-1} are tabulated in Tables 10, 11 and 12. The values of τ which are smaller than 10^5 seconds and larger than one second, i.e. which correspond to reaction rates of conveniently measurable speed, are enclosed by a heavy line.

TABLE 10

Reactions of first order.

k_1 in units of sec.$^{-1}$.

$k_1 \backslash a$	10^{-1}	10^{-2}	10^{-3}	10^{-4}
10^{-6}	$6{\cdot}9\times10^5$	$6{\cdot}9\times10^5$	$6{\cdot}9\times10^5$	$6{\cdot}9\times10^5$
10^{-5}	$6{\cdot}9\times10^4$	$6{\cdot}9\times10^4$	$6{\cdot}9\times10^4$	$6{\cdot}9\times10^4$
10^{-4}	$6{\cdot}9\times10^3$	$6{\cdot}9\times10^3$	$6{\cdot}9\times10^3$	$6{\cdot}9\times10^3$
10^{-3}	$6{\cdot}9\times10^2$	$6{\cdot}9\times10^2$	$6{\cdot}9\times10^2$	$6{\cdot}9\times10^2$
10^{-2}	69	69	69	69
10^{-1}	6·9	6·9	6·9	6·9
10	0·69	0·69	0·69	0·69

TABLE 11

Reactions of second order.

k_2 in units of sec.$^{-1}$ mole^{-1} litre.

$k_2 \backslash a$	10^{-1}	10^{-2}	10^{-3}	10^{-4}
10^{-6}	10^7	10^8	10^9	10^{10}
10^{-5}	10^6	10^7	10^8	10^9
10^{-4}	10^5	10^6	10^7	10^8
10^{-3}	10^4	10^5	10^6	10^7
10^{-2}	10^3	10^4	10^5	10^6
10^{-1}	10^2	10^3	10^4	10^5
10	10	10^2	10^3	10^4

TABLE 12

Reactions of third order.

k_3 in units of sec.$^{-1}$ mole $^{-2}$ litre^2.

$k_3 \backslash a$	10^{-1}	10^{-2}	10^{-3}	10^{-4}
10^{-6}	$1{\cdot}5 \times 10^{7}$	$1{\cdot}5 \times 10^{9}$	$1{\cdot}5 \times 10^{11}$	$1{\cdot}5 \times 10^{13}$
10^{-5}	$1{\cdot}5 \times 10^{6}$	$1{\cdot}5 \times 10^{8}$	$1{\cdot}5 \times 10^{10}$	$1{\cdot}5 \times 10^{12}$
10^{-4}	$1{\cdot}5 \times 10^{5}$	$1{\cdot}5 \times 10^{7}$	$1{\cdot}5 \times 10^{9}$	$1{\cdot}5 \times 10^{11}$
10^{-3}	$1{\cdot}5 \times 10^{4}$	$1{\cdot}5 \times 10^{6}$	$1{\cdot}5 \times 10^{8}$	$1{\cdot}5 \times 10^{10}$
10^{-2}	$1{\cdot}5 \times 10^{3}$	$1{\cdot}5 \times 10^{5}$	$1{\cdot}5 \times 10^{7}$	$1{\cdot}5 \times 10^{9}$
10^{-1}	$1{\cdot}5 \times 10^{2}$	$1{\cdot}5 \times 10^{4}$	$1{\cdot}5 \times 10^{6}$	$1{\cdot}5 \times 10^{8}$
10	15	$1{\cdot}5 \times 10^{3}$	$1{\cdot}5 \times 10^{5}$	$1{\cdot}5 \times 10^{7}$

Catalytic reactions. The kinetics of heterogeneous catalytic reactions differ essentially from those of homogeneous reactions : in the latter type of reaction the reaction velocity measured is independent of the volume of the reaction vessel ; in the former type it is dependent on the volume for a given amount of catalyst. For this reason it is more convenient to measure the velocity of catalytic reactions in absolute amounts of change in unit time.

The characteristic equations for catalytic reactions are more varied than those for the homogeneous equations for two reasons : (1) The rate of a heterogeneous catalytic reaction is governed by the concentration of the reactants in the adsorption layer ; (*a*) this can be either independent of the pressure in the gas phase in the case of strong adsorption (saturation), (*b*) be proportional to it if the adsorption is weak (Henry's law), or (*c*) depend on it according to an intermediate law for medium adsorption. (2) The reactants and the reaction products can mutually replace each other in the adsorption layer, and then their concentrations will also depend on the other concentrations. The following equations are valid for the more common cases (cf. G. M. Schwab, *Katalyse vom Standpunkt der chemischen Kinetik*, Verlag Springer, 1931, p. 156 ff.) :

(1) One initial reactant, no inhibition :

(*a*) Weak adsorption : $$\frac{dx}{dt} = kp, \quad \text{.....(99)}$$

x = absolute amount (not concentration).

(*b*) Medium adsorption : $$\frac{dx}{dt} = \frac{kp}{1 + bp}. \quad \text{.....(100)}$$

(*c*) Strong adsorption : $$\frac{dx}{dt} = k. \quad \text{.....(101)}$$

The order of the reaction is in this last case zero, the absolute amount of change is independent of pressure, the relative or fractional change is inversely proportional to the pressure. Zero order is a common characteristic of catalytic reactions.

(2) One reactant, strong inhibition by the reaction product :

$$\frac{dx}{dt} = k\frac{p_A}{p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (102)$$

(3) Two reactants, no inhibition by the reaction products, A adsorbed weakly, B medium :

$$\frac{dx}{dt} = \frac{kp_A p_B}{(1 + b_B p_B)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (103)$$

In this case the velocity goes through a maximum if p_A is kept constant and p_B varied, since B replaces A in the adsorption layer.

(4) Two reactants, one strongly adsorbed ; reaction occurs if second reactant from the gas phase collides with the first in the adsorption layer :

$$\frac{dx}{dt} = kp_B. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (104)$$

3. Dependence of the Reaction Rate on Temperature

The influence of temperature on the rate of chemical reactions has already been indicated. The simplest formula connecting reaction velocity and temperature is the well-known Arrhenius equation :

$$k = Ce^{-A/RT}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (105)$$

$$\log k = \log C - A/4{\cdot}573T, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (105a)$$

$$\frac{d \log k}{dT} = \frac{A}{4{\cdot}573T^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (105b)$$

where k is the velocity constant, A the energy of activation and C a constant. This equation is found to be valid for a great number of reactions, such as thermal, catalytic and photochemical heterogeneous and homogeneous reactions. It should be pointed out that the velocity of complex reactions need not necessarily obey this simple law, if the reaction is composed of a number of individual reactions proceeding either consecutively or simultaneously. If variation of the rate of complex reactions with temperatures does correspond to Arrhenius' equation, the ' apparent ' energy of activation calculated on the basis of this equation must be regarded in general as a mere number characterising its dependence on temperature, and not as the true energy of activation arising in the way described on p. 30.

The following modified forms of the Arrhenius equation are often used :

(1) Homogeneous reactions : correction for the velocity of the molecules :

$$\frac{d\ln k}{dT} = \frac{1}{2T} + \frac{A}{RT^2} = \frac{\frac{1}{2}RT + A}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (106)$$

This correction is only applicable at high temperatures.

(2) Reactions of polyatomic molecules. In polyatomic molecules the internal energy manifests itself as vibrations and rotations. If the total number of vibrations and rotations is n, the vibrations being counted twice, since each vibration has potential and kinetic energy, the fraction of the total number of molecules possessing a total energy greater than E in all of the n 'square terms' is (cf. C. N. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford (1933), p. 127)

$$\frac{e^{-E/RT}(E/RT)^{\frac{1}{2}n-1}}{\Gamma(\frac{1}{2}n-1)}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (107)$$

$$\Gamma(\tfrac{1}{2}n-1) = (\tfrac{1}{2}n-1)! \text{ if } n \text{ even} ;$$

for odd values of n the following relations are to be used :

$$\Gamma(p+1) = p\Gamma(p) \text{ and } \Gamma(\tfrac{1}{2}) = \sqrt{\pi}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (108)$$

Since the velocity constant is proportional to expression (107) :

$$\frac{d\ln k}{dT} = \frac{A - (\frac{1}{2}n-1)RT}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (109)$$

(3) Catalytic reactions. Since the concentration in the adsorption layer is proportional to $e^{\lambda/RT}$, where λ is the heat of adsorption,

$$\frac{d\ln k}{dT} = \frac{A-\lambda}{RT^2} = \frac{A'}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (110)$$

A' is often referred to as the apparent heat of activation. If two kinds of molecules are involved in the reaction, A' may be equal to $A - \lambda_1 - \lambda_2$. If at low temperatures the adsorption layer is saturated and $A < \lambda_1 + \lambda_2$, it may happen that in a low temperature range the velocity increases with increasing temperature, but decreases in a high temperature range.

Sometimes the temperature coefficient is defined as k_{T+10}/k_T, i.e. as the ratio of the velocity constant at temperatures which differ by 10 degrees. On the basis of the above equation (105) it is evident that the temperature coefficient so defined varies with temperature. k_{T+10}/k_T is usually larger than unity, temperature coefficients which are smaller than unity are referred to as 'negative' temperature coefficients. This designation is incorrect, as has been pointed out by B. Lewis and W. Feitknecht (*J.A.C.S.*, **53**, 2922 (1931)), and should be avoided.

4. The Dependence of the Rate of Photochemical Reactions on Light Intensity

The chemical change due to illumination is dependent on the amount of absorbed radiation. If J_0 is the incident light intensity and J_h the light intensity leaving the reaction mixture, the absorbed radiation $J_{abs} = J_0 - J_h = J_0(1 - e^{-\epsilon hc})$, where ϵ is the molar coefficient of extinction, c the concentration of the reactant which absorbs the light in moles/litre and h the thickness of the absorbing layer. In the general case the rate of a photochemical reaction is given by (cf. V. A. Plotnikow, *Allgemeine Photochemie*, Walter de Gruyter & Co., Berlin (1936))

$$-\frac{d(c-x)}{dt} = kJ_0\frac{s}{V}(1 - e^{-\epsilon h(c-x)}) - k\frac{J_0}{h}(1 - e^{-\epsilon h(c-x)}), \quad \ldots\ldots(111)$$

if the intensity is expressed as the number of incident quanta per cm.^{2} per sec., and s is the area of the illuminated surface of the prismatic reaction vessel and $V = hs$, its volume.

For strong absorption when all of the light is absorbed within a short distance from the illuminated surface, $e^{-\epsilon h(c-x)} \ll 1$, and therefore

$$-\frac{d(c-x)}{dt} = kJ_0/h, \quad \ldots\ldots(112)$$

or

$$x = kJ_0t/h, \quad \ldots\ldots(113)$$

i.e. the concentration of the reaction product is proportional to the incident intensity divided by the thickness of the layer, and increases linearly with time. The absolute amount of change, $M = xV = xhs$, is given by $M = hsJ_0t$, that is the absolute amount of chemical change is proportional to the absolute amount of absorbed or incident light. This formula forms the basis for the determination of photochemical quantum yields (cf. p. 254), k being the quantum yield.

For weak absorption, when $e^{-\epsilon h(c-x)}$ has a value near unity,

$$1 - e^{-\epsilon h(c-x)} = \epsilon h(c-x), \quad \ldots\ldots(114)$$

and

$$-\frac{d(c-x)}{dt} = \frac{kJ_0\epsilon h(c-x)}{h} = kJ_0\epsilon(c-x), \quad \ldots\ldots(115)$$

or

$$ln(c/c-x) = kJ_0\epsilon t. \quad \ldots\ldots(116)$$

These equations are valid for photochemical reactions of the type

$$C + h\nu \rightarrow C^*, \quad \ldots\ldots(117)$$

$$C^* \rightarrow X, \quad \ldots\ldots(118)$$

where C and C^* are normal and excited molecules respectively. In these reactions the primary photochemical process is the excitation of

molecules. In a reaction involving a photochemical dissociation of molecules

$$A_2 + h\nu = 2A, \quad \text{.....(119)}$$

$$2A = A_2, \quad \text{.....(120)}$$

the number of dissociated molecules is $k J_{abs}$, and the number of molecules re-formed by recombination $k'[A]^2$. In the stationary state these two quantities are equal, and consequently the stationary concentration of atoms is proportional to the square root of the absorbed amount of radiation. If the rate determining step in the photochemical reaction is the reaction of these atoms, e.g.

$$A + y \rightarrow x, \quad \text{.....(121)}$$

the velocity of the photochemical reaction is also proportional to $\sqrt{J_{abs}}$.

5. Explosive Reactions

Explosive reactions can occur in two different ways. The progress of chemical change is usually connected with the production of heat. If the heat generated is not dissipated by conduction and radiation, the temperature rises, the reaction goes faster and more heat is produced.

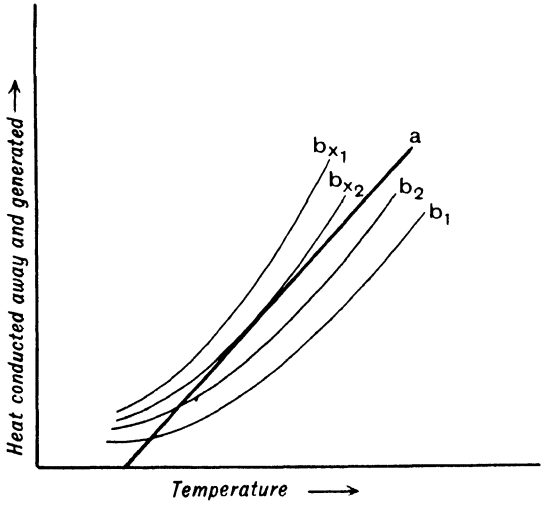


FIG. 1.

If the heat dissipated by thermal conductivity rises faster with increasing temperature than the heat generated, equilibrium is reached when the curve (*a*) in Fig. 1, representing the heat loss as function of the temperature, intersects the curve (*b*) representing the heat generated as a function of temperature. If the experimental conditions (pressure, composition)

are changed, the heat generated will be represented by curves b_1, b_2, etc., and there will be a limiting curve b_{x_1} above which the curves (a) and (b) no longer intersect. Under these conditions the temperature and consequently the reaction velocity will continuously increase, leading eventually to explosion. It will be noticed that a slight change in the experimental conditions will transform a stationary to an explosive reaction.

The other way in which explosions may occur involves the propagation of reaction chains. A reaction of the type :

$$X + A_2 = AX + A, \quad \text{.....(122)}$$

$$A + X_2 = AX + X, \quad \text{.....(123)}$$

$$X + A_2 = AX + A, \quad \text{.....(122)}$$

is called a chain reaction, since one particle—the chain carrier X—can produce a great number of molecules AX (cf. N. Semenoff, *Chemical Kinetics and Chain Reactions*, Oxford (1935), p. 45). Not all chain carriers produce a new carrier and thus continue the chain ; some will be destroyed with a probability β. Others will create two new centres and cause a branching of the chain with the probability δ. The length of the chain, i.e. the number of elementary chemical processes caused by each chain carrier, is $\nu = 1/(\beta - \delta)$, and the reaction velocity is

$$W = n_0/(\beta - \delta) \quad \text{.....(124)}$$

if n_0 is the number of chain carriers produced per second. For $\beta > \delta$ there is a stationary velocity, but for $\beta < \delta$ the velocity continually increases since the number of branches is greater than the number of ruptures, which circumstance leads to explosion provided the reactants are not appreciably consumed during the period of acceleration. Since both β and δ are dependent on experimental conditions, a slight variation of these conditions may cause δ to become greater than β and thus cause an explosion.

CHAPTER II

APPARATUS FOR CONTROL OF PRESSURE AND TEMPERATURE

A. VACUUM PUMPS

THE types of vacuum pumps now in general use may be divided into three classes : (1) water jet injector pumps, (2) mechanical rotary oil pumps, and (3) vapour condensation pumps. To this list the Topler pump may be added, though its use is now generally confined to transferring gas from one part of an apparatus to another and to collecting gases delivered by one of the types of pumps mentioned above.

Water jet injector pump. The familiar ' filter ' pump need not be described in detail, but it may be noted that with a good design of jet and choke tube the vacuum attained may be much lower than the vapour pressure of water, e.g. as low as 7 mm. (quoted by G. W. C. Kaye, *High Vacua*, p. 72, Bell). In order to prevent water sucking back, e.g. through a diminution or cessation of the water supply, a valve shown in Fig. 2 is more compact and reliable than the usual filter flask. A calcium chloride or P_2O_5 tube should be connected to the pump. Though normally the gas discharged by such a pump finds its way into the atmosphere, it may easily be collected by allowing the pump to discharge into a bottle fitted with two taps, one at the bottom to permit the water to escape, and one at the top to draw off the gas as it accumulates. This arrangement will supply air at a sufficient pressure and rate to run a moderate-sized hand blow-pipe. The ordinary filter pump has a speed of 10-30 c.c. per sec., but metal jet pumps have been designed with a speed as great as 500 c.c. per second, the water consumption being no less than 200 gallons an hour. Fig. 3 shows the

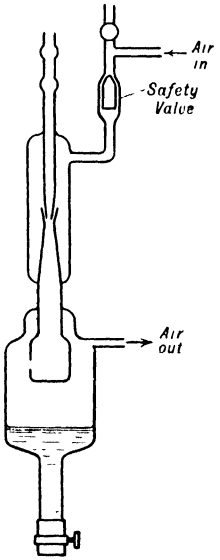


FIG. 2. Water pump.

rate of reduction of pressure in a 10 litre vessel exhausted by water pumps of a speed of 50, 150 and 500 c.c. per second, respectively.

Speed of pumps. The speed of a pump is defined as the volume of gas pumped per unit time at a specified pressure. What is of more practical importance, however, is the time required for the pressure to attain a certain desired value. According to the above definition

$$-\frac{dp}{dt} = \frac{s}{V}(p - p_0),$$

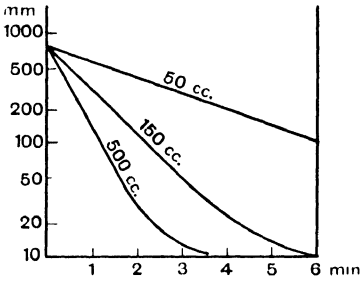


FIG. 3. Velocity of pumping of filter pumps.

where p and p_0 are respectively the pressures at time t and that at $t = \infty$, i.e. the limiting pressure of the pump. V is the volume being exhausted. Integration of the equation at once gives (assuming the speed independent of pressure)

$$s = \frac{V}{t_2 - t_1} \ln \frac{p_1 - p_0}{p_2 - p_0}.$$

Rotary Oil Pumps

For ordinary laboratory purposes the rotary oil pump has superseded the reciprocating type. It runs more quietly, needs no attention or lubrication, and is compact. From atmospheric the pressure may be reduced to 10^{-5} mm. The principle of the pump is due to Gaede, and a section of a recent make of pump is shown in Fig. 4. It consists of an iron casting A, bored and ground accurately cylindrical. Within A, a cylinder B rotates in an anti-clockwise direction, its axis being so positioned that it bears against A at D. Two plates E and F, kept apart by a spring G, bear against A. As B rotates the gas in I is compressed and finally ejected through the steel ball valve K. Meanwhile gas collects in H and finally is cut off from communication with the reservoir being exhausted when F passes the orifice attached to J. The Cenco pumps are designed on the same principle, but the vane separating the expansion and compression compartments is stationary, and the inner cylinder A (Fig. 5) rotates excentrically on a shaft whose axis coincides with that of the outer case B. The vane C is pressed into contact with A by the spring S. The working parts are immersed in oil, and in general two stages are mounted on a common spindle.

A further modification has recently been made to rotary types of pump. One disadvantage of the above arrangement is the frictional losses incurred by the rotor rubbing against the stator. To obviate this, Gaede

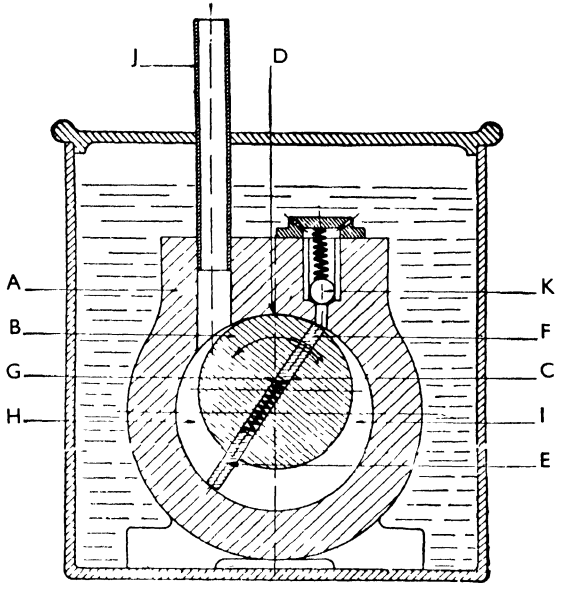


FIG. 4. Gaede rotary oil pump.

now makes a composite rotor consisting of an outer cylinder C running on ball bearings supported by an inner cylinder B, as is shown in Fig. 6.

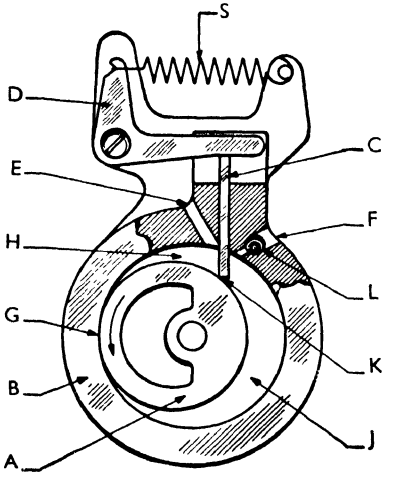


FIG. 5. Hyvac rotary oil pump.

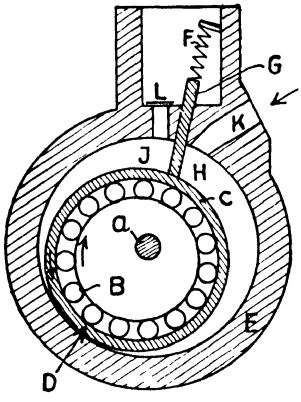


FIG. 6. Cylinder pump.

The outer cylinder thus rolls instead of slides on the inner surface of the stator. The outlet valve is sometimes connected to a tube whereby the gases discharged by the pump may be collected in a suitable reservoir.

By careful construction both types of pumps can be made equally efficient. When such pumps are stopped, especially the older types, oil may leak back into the vacuum system. If this trouble is experienced the vacuum should always be let down on stopping the pump. The Cenco and Gaede series of pumps are now fitted with an oil trap, which prevents leakage occurring.

Precautions for Oil Pumps

In mounting oil pumps it is customary to connect pump and electric motor by a rubber-canvas belt. It is essential that a motor of sufficient power be used to rotate the pump at its maximum speed. The oil for the pump must have a vapour pressure less or equal to that of the best vacuum attainable by the pump. Such compression pumps cannot deal with vapours, apart from the fact that vapours usually dissolve in the oil. These must be excluded by a liquid air trap. When pumping large volumes of undried air deterioration of the oil will gradually ensue, and hence a phosphorous pentoxide tube is essential. Care must be taken, however, that sudden inrushes of air do not blow pentoxide dust into the body of the pump. If, in the event of an accident, mercury finds its way into the pump no damage will be done, as these pumps are constructed entirely of iron or steel. A set of spare springs is a useful accessory. The vanes and valves must, of course, be kept covered with oil.

The Gaede Rotary Mercury Pump

This is a simple type of mechanical pump introduced many years ago and is practically fool-proof. Unfortunately it requires a backing pump, such as a good filter pump, to reduce the pressure to a few millimetres. It is especially useful for performing distillations of organic liquids under a high vacuum, since vapours do not contaminate the mercury.

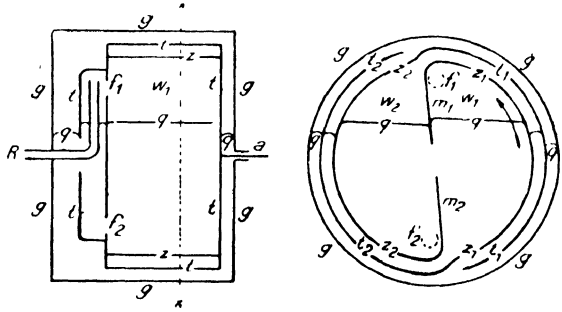


FIG. 7. Gaede rotary mercury pump.

Fig. 7 shows a section of the pump, which consists of an iron case *g* containing a porcelain drum rotated by a spindle *a*. Tube *R* communi-

cates with the apparatus to be exhausted, and the case is exhausted by a filter pump. The right-hand diagram in Fig. 7 is a section through *xx*. There are essentially two partitions, $m_1z_1l_2$ and $m_2z_2l_1$. As the drum revolves in an anti-clockwise direction, the volume w_1 will increase, and gas will therefore flow into it via R and f_1. f_1 dips below the surface of the mercury at q, connection with R being thereby cut off; the volume of w_2 decreases until the gas is finally expelled into the outer case along the channel separating the partition z_2 and t_2. The pump can attain a vacuum of 10^{-5} mm. if the mercury vapour is removed by a liquid air trap (cf. Dunoyer, *Vacuum Practice*, p. 27 : Bell).

The vacua attained and the pumping speeds of a number of commercial rotary pumps are summarised for convenience in Table 19.

A circulating pump working on a similar principle has been described by E. L. Harrington, (*Rev. Sci. Instr.*, **3**, 476 (1932)).

High Vacuum Pumps

The best mechanical oil pumps reduce the pressure in a vessel to 10^{-5} mm. under the most favourable circumstances. This pressure is not low enough for many purposes, and recourse must therefore be made to a new principle in order to obtain better vacua. Theoretically the Töpler pump (see below) has no limiting pressure, but it will be evident from what follows that its speed at low pressures is exceedingly small and its use therefore impracticable. Gaede designed an ingenious pump—the so-called molecular pump (*Phys. Zeit.*, **13**, 864 (1912) ; *Electrician*, **70**, 48 (1912)) -which depends for its functioning on arranging a rapidly moving surface to impart to molecules an additional directed component of velocity so as to drag them out of a reservoir. The pump is shown diagrammatically in Fig. 8, one cylinder rotating within another cylinder. To obtain the requisite speed of pumping there must be as many collisions as possible between fixed and moving surfaces, which implies a small clearance—0·05 mm. in practice—between rotor and stator. Very high speeds up to 12,000 revolutions per minute are also required to maintain a reasonable pressure ratio between inlet and outlet parts. Holweck (see Dunoyer, p. 33) has improved the Gaede pump by attaching the rotor of an induction motor to the rotor of the pump and running the whole in the fore vacuum. The power input is thereby decreased to a few watts. With a backing pressure of several millimetres, pressures of 10^{-6} mm. are obtained, the

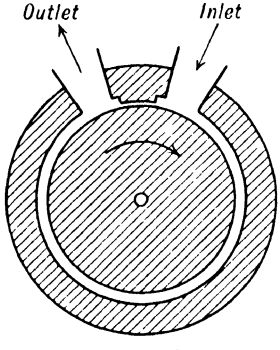


FIG. 8. Molecular pump.

speed of the pump being some 2000 c.c. per sec. at a rotor speed of 4000 revolutions per minute. For the majority of purposes a pump working within such fine limits does not find extensive application, since the condensation pump possesses many superior features.

Condensation Pumps

The development of the condensation pump was initiated by W. Gaede (*Ann. d. Phys.*, **46**, 357 (1915)), who devised a diffusion pump. The principle of the pump is as follows : vapour streams down a tube *AB*, a side tube *OC* communicating with a reservoir containing gas. When pressure and size of the tubes are such that the mean path of the gas in the vapour

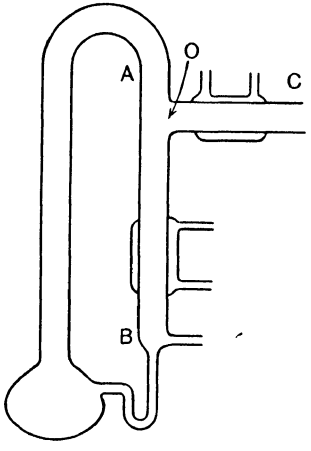


FIG. 9. Diffusion mercury pump.

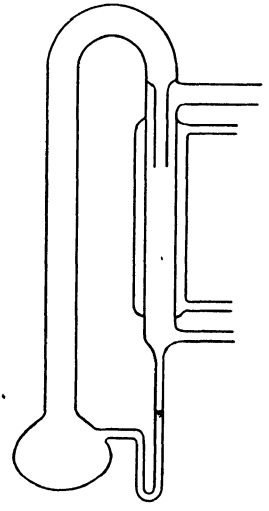


FIG. 10. Condensation mercury pump.

is comparable with the diameter of the orifice *O*, gas will *diffuse* into the vapour stream and thus be removed from the reservoir. To prevent the vapour accumulating in the reservoir, a condenser is slipped over *OC*, and likewise over *AB*, so that the vapour may be condensed and returned to the boiler. Mercury is obviously one of the ideal liquids on account of its comparatively low vapour pressure (0·001 mm.) at room temperature. The size of the orifice is critical ; if too small, diffusion is slow ; if too large the stream of vapour moving towards the condenser on *OC* tends to force the gas back into the reservoir. I. Langmuir (*G.E. Review*, **19**, 1060 (1916) ; *J. Franklin Inst.*, **182**, 179 (1916)) modified the design to that shown in Fig. 10. One advantage immediately accrues. The molecules of the diffusing gas are given a velocity component in the direction of the vapour stream, and the greater the velocity of the vapour stream

the greater the pumping speed. Though Gaede's criterion for jet width and pressures still holds in practice, it is found that the Langmuir pump has no sharply marked optimum working conditions. Theoretically there is no limit to the vacuum attainable, but the lowest pressures measurable are of the order 10^{-8} mm., and there the limit is probably imposed by the evolution of gas from the reservoir and/or the gauge used for measuring the pressure. The mercury vapour must, of course, be trapped by a liquid air-cooled surface, the saturation pressure of mercury at $-183°$ C. being absolutely negligible.

Many types of condensation pumps have been described in the literature made of glass and of metal, and with as many as four stages attached to a common boiler which may be heated by gas or by electric power. Only a few of the more modern types and their performance can be described here. In chemical work a high fore-vacuum pressure is a greater

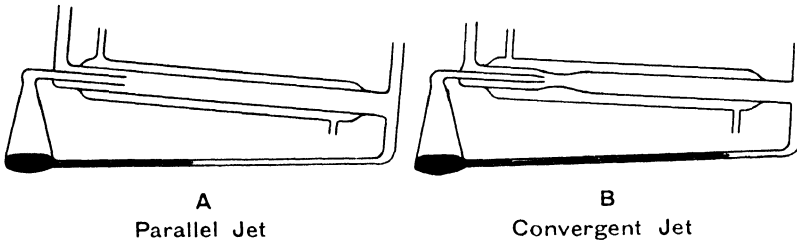


FIG. 11. Waran mercury pump.

desideratum than high pumping speed, since in general the total pumping speed is limited entirely by the numerous traps and taps found in a chemical apparatus. The theory of the diffusion at slits has been discussed in detail by W. Molthan (*Z. f. technische Physik*, **7**, 377, 452 (1926)). Two important advantages of the condensation pump over the rotary pump are its ability to pump vapours and its usefulness in circulating gases in a closed system at low pressures.

Two very simple condensation pumps have been described by H. P. Waran (*J. Scientific Instr.*, **1**, 51 (1923)), and are easily made in Pyrex, requiring only limited skill in glass-blowing to ensure satisfactory operation. Model *A*, with a convergent jet and choke tube (2-3 mm. in diameter), will produce a pressure of 0·1 mm. when backed by a filter pump. Model *B* has a parallel jet, 8 mm. in diameter, and will produce the highest vacua if the backing pressure is less than 0·5 mm. The two pumps may thus be joined in series, giving an efficient though somewhat slow pumping set. Waran pumps may be made very small—total volume 10 c.c. (H. W. Melville, *J.C.S.*, 1243 (1934))—and thus become useful in circulating gases in systems of small total volume. One applica-

tion is shown in Fig. 12. Here it was necessary to withdraw water vapour from the gases at pressures not exceeding 20 mm., and to maintain them

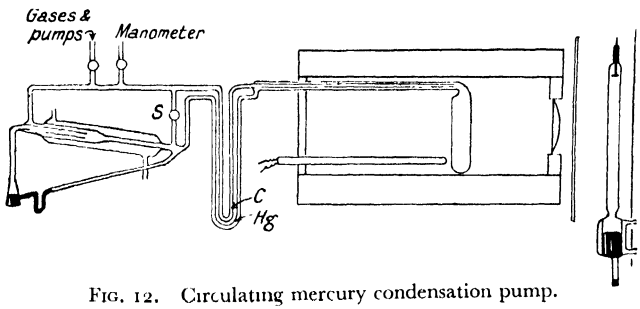


FIG. 12. Circulating mercury condensation pump.

saturated with mercury vapour while the reaction vessel itself was enclosed within a furnace. A short-circuiting tap, *S*, permits the stationary pressure to be ascertained at any moment. A tiny flame from the jet of an ordinary bunsen burner suffices to keep the mercury distilling at a useful speed.

A simple type of two stage glass pump is shown in Fig. 13, fitted conveniently for electric heating. An input of 500 watts gives a vacuum of the order 10^{-7} mm. with a backing pressure of a few millimetres and the high speed of 12,000 c.c. per sec.

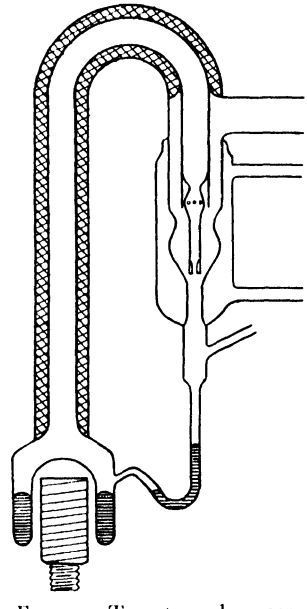


FIG. 13. Two stage glass mercury pump.

Glass pumps are fragile, and therefore metal pumps were designed early in the development of the condensation pump. Typical of single stage pumps is the Kaye Annular Jet Single Stage pump, the internal construction of which is shown in Fig. 14. Mercury vapour from the boiler ascends the centre tube and is deflected downwards by a suitable annular jet. The space between the boiler and body of the pump is sealed by a piston. To prevent the condensed mercury from re-evaporating a disc of baked steatite is fused above the division between boiler and pump body. The top of the pump is detachable, so that the jets, etc., may be removed for cleaning purposes. Efficient cooling is provided so that a large boiler pressure may be employed. Attachment to the apparatus is made by the ground joint on the top of the pump.

This pump requires a backing pressure of 0·5 mm., and attains a speed of $2{\cdot}5 \times 10^3$ c.c. per sec. at 10^{-3} mm.

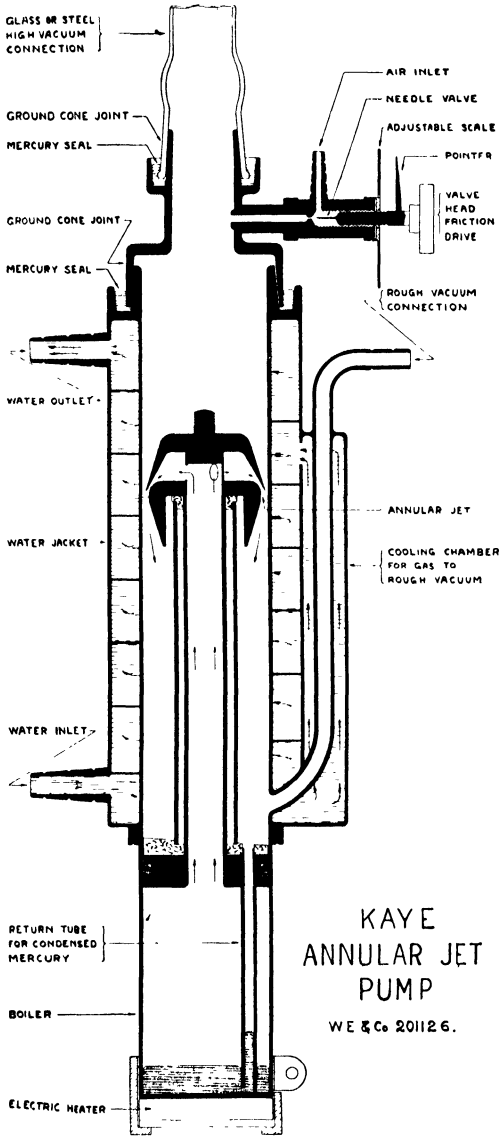


FIG. 14.

Two, three and even four stage metal pumps have been constructed. A four stage pump designed by Gaede is shown in Fig. 15. As will be

seen from the diagram, the first stage is in the form of an annular jet similar to that in the Kaye pump. The succeeding stages are of

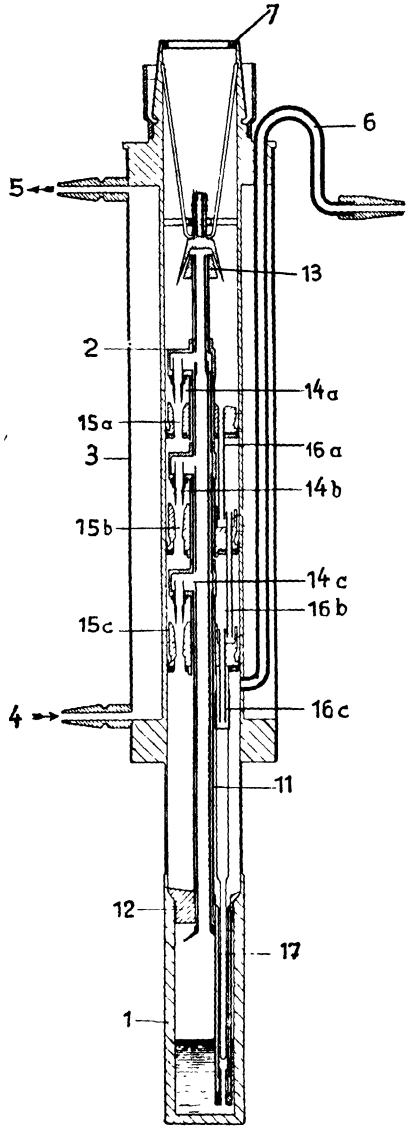


FIG. 15. Section of Gaede four stage diffusion pump.

similar construction. This pump works against the remarkably high backing pressure of 40 mm., with a speed of 16×10^3 c.c. per sec. The

speeds of similar pumps and suitable rotary backing pumps are shown in Table 19.*

When very high pumping speeds are required, the mercury pump has the disadvantage that the liquid air trap invariably reduces the speed. But since the discovery of Burch that low vapour pressure petroleum oils (see p. 67) can be produced to replace mercury, vapour traps become unnecessary, and hence greater pumping speeds may be obtained. Two types of oil pumps are produced commercially by Metropolitan-Vickers Co. Model *P* has a speed of 10^4 c.c. per sec. at 10^{-4} mm. with a backing pressure of 0·4 mm., while Model *Q* has a speed of 2×10^4 c.c. per sec. at 10^{-4} mm. with a backing pressure of only 0·05 mm. It is usual, therefore, to back Model *Q* with *P*, and this in turn with a rotary oil pump (*P* and *Q* are connected via a vacuum reservoir of several litres capacity), rather than adopt the procedure of having multiple stage pumps enclosed in one barrel.

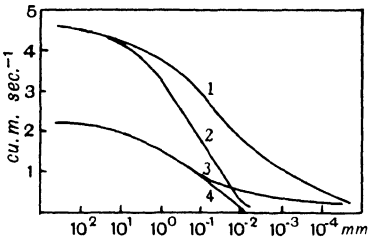


FIG. 16. Speeds of rotary oil pumps.

Speeds of pumps are usually quoted at a single pressure, which does not give an extensive idea of their performance at other pressures. In Figs. 16 and 17 are plotted some curves for typical rotary oil pumps and diffusion pumps described above, so that for any given problem involving pumping at a specified pressure the best combination of pumps may be selected. The characteristics of the pumps shown in Fig. 16 are as follows :

	Displacement	Ultimate vacuum (mm.)
1 -	1400 c.c.	10^{-5}
2 -	1400 c.c.	2×10^{-3}
3 -	550 c.c.	10^{-5}

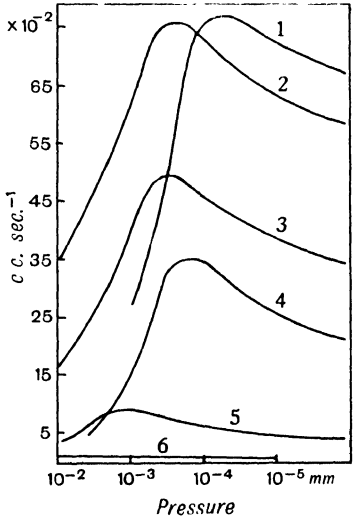


FIG. 17. Speeds of diffusion pumps. 1. Single stage oil (Q). 2. Three stage mercury (Gaede). 3. Two stage mercury (Gaede). 4. Oil diffusion (P). 5. Single stage diffusion (Gaede).

Besides the Burch petroleum oils, K. C. D. Hickman and C. R. Sanford (*Rev. Sci. Instr.*, **1**, 140 (1930)) have found that esters of phthalic acid

* For high speed pumps, see Estermann and Byk (*Rev. Sci. Instr.*, **3**, 482 (1932)), and Ho (*ibid.*, **3**, 133 (1932)).

have suitable properties for use in condensation pumps. *n*-dibutyl (V.P. at 25° C., 10^{-4} mm.) and *n*-butyl benzyl phthalate (V.P. at 25° C., 10^{-5} mm.) appear to be the most satisfactory in respect of stability towards prolonged boiling at high temperatures. In virtue of the low vapour pressures of the phthalic esters, traps may be dispensed with, or at the best need only be cooled with solid carbon dioxide and acetone mixture. Hickman and Sanford experimented with a large variety of single stage pumps to find the most suitable design. It may be mentioned that it is not practicable to construct multi-stage pumps, since the temperature of the boiler has to be raised so high that decomposition of the esters occurs, and it is then impossible to obtain a good vacuum. A typical pump with dimensions is shown in Fig. 18. The ester condenses on the walls as a smooth film without entrapping bubbles of gas, so that the liquid may be allowed to return to the boiler in the opposite direction to the vapour stream. Even a water-cooled condenser may be dispensed with; in its place copper wire, looped at short intervals to provide radiating fins, is wound round the tube above the jet chamber. The speed of such a pump, with *n*-dibutyl phthalate filling, is a few thousand c.c. per sec., a backing pressure of 0·5 mm. being required. An electric heater dissipating 50 watts is sufficient to operate the pump at full speed.

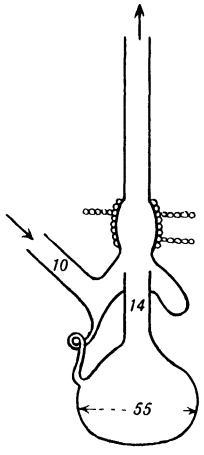


FIG. 18. Di-butyl phthalate pump. (Dimensions in mm.)

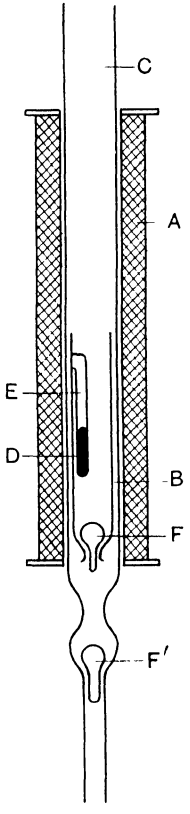


FIG. 19. All glass circulating pump.

The phthalic esters cannot be used in metal pumps on account of corrosion on prolonged boiling.

In operating both oil and ester pumps it is absolutely essential to allow the backing pump to reduce the pressure to the working backing pressure of the condensation pump, in order to prevent the organic liquid becoming too hot and thereby decomposing or being attacked by oxygen.

All-glass circulating pump for pressures in the neighbourhood of atmospheric. (F. Porter, D. C. Bardwell and S. C. Lind, *Ind. and Eng. Chem.*, **18**, 1086 (1926).) The pump (Fig. 19) consists of a piston *B* fitted with a valve *F*. Attached to the piston is a tube *E*

which contains a soft iron rod *D*, 5 cm. long and 0·3 cm. in diameter. The rod is fixed in the tube with wax, and the whole moved up and down by means of the solenoid *A*. The ball and socket valves *F* and *F'* are hollow glass spheres (*ca.* 0·25 cm. diameter and 0·025 gm. wt.) making a ring contact with the sockets. The seat of *F'* is ground with a hemisphere of larger radius of curvature than that of the valve. The upper socket, in order to avoid weakening, is not ground. The stems of the valves are made long enough to keep the balls upright. The actuating current will depend on the number of turns on the solenoid. In the model described 0·5 amp. is required, and is interrupted three times a second by an oscillating relay. A 50-watt 100-volt lamp is connected across the break, so that the current is never completely interrupted, but oscillates between 0·5 and 0·3 amps. The piston therefore does not fall to the bottom of the tube.

The capacity is 7 litres per hour when pumping against a pressure difference of 2-3 mm. of mercury, but will, of course, depend on the fit of the piston in the cylinder.

Brenschede (*Z. phys. Chem.*, **A, 178**, 74 (1936)) describes a very efficient electromagnetic circulation pump incorporating 'KPG' tubes of Jena glass. These can be obtained up to a width of 50 mm. and with a uniform diameter within 0·01 mm. Schwab and collaborators (*Z. phys. Chem.*, **B, 12**, 65 (1933)) maintain a slight circulation of gas in catalytic experiments by using a thermosyphon, depending on a temperature gradient in the circulatory system.

TABLE 13

Performance of Vacuum Pumps

(For tests of a number of commercial pumps see I. Estermann and H. T. Byk, *Rev. Sci. Instr.*, 3, 482 (1932))

	Vacuum attained	Speed, c.c. per sec.
Injector filter pumps	12-15 mm.	10-30

	Backing pressure	Speed, c.c. per sec.
Rotary mercury pumps		
Gaede	10-20 mm.	100-150

Rotary oil-immersed pumps		Displacement (c.c. per sec.)	Vacuum attained (mm.)
Hyvac (two-stage)	at 450 r.p.m.	210	0·001
Gaede small (single-stage)	,, 400 ,,	250	0·1
Gaede iron (single-stage)	,, 400 ,,	550	0·002
Gaede iron (two-stage)	,, 400 ,,	550	0·00001
Megavac (two-stage)	,, 600 ,,	950	0·001
Hypervac (two-stage)	,, 450 ,,	3500	0·00005
Gaede Simplex Type, X1	,, 400 ,,	1390	0·002
Duplex	,, 400 ,,	1390	0·00001

	Displacement (c.c. per sec.)	Vacuum attained (mm.)
Edwards, Type A 1	1310	0·01
,, ,, A 2	4600	0·01
,, ,, A 3	6900	0·01
,, ,, B 1	1030	0·0001
,, ,, B 2	3470	0·0001

Mercury vapour pumps (steel)	Backing pressure (mm.)	Speed c.c. sec.$^{-1}$ at 10^{-3} mm.
Single-stage		
Kaye	1·5	5,000-7,000
Gaede (large)	0·15	150,000
Two-stage		
Gaede 'G'	15	2,500
Gaede 'B'	8	10,000
Three-stage		
Gaede 'E'	20	15,000
Four-stage		
Gaede 'D'	40	15,000
Kaye, Type III	0·5	2,500
Kaye, Type IV	0·15	20,000
Kaye, IV, 3 F	2·0	20,000

Single-stage			Limiting press. (mm.)
M.V. oil diffusion pump, Type 3	0·05	20,000	10^{-7}
M.V. oil diffusion pump, Type 2	0·4	4,000	10^{-7}

Variation of pumping speeds with pressure. The rate of pumping of any mechanical pump falls off rapidly as the ultimate vacuum is approached, and hence ample overlap should be allowed for backing pumps.

Pressure (mm.)	Single stage rotary oil pump, Type A 1400 c.c. displacement at 450 r.p.m.	Two stage rotary oil pump, Type B 1100 c.c. displacement at 350 r.p.m.	Two stage rotary oil pump, Hyvac 210 c.c. displacement at 450 r.p.m.
5	750	—	—
1	500	—	—
0·5	400	650	—
0·1	200	400	—
0·05	120	350	—
0·025	30	300	100
0·01	—	250	90
0·005	—	200	60
0·001	—	125	15
0·0005	—	115	—
0·00025	—	85	—

Effect of diameter of connecting tubing on pumping speeds. It is pointless to employ a pumping unit of large capacity if the pumping speed is limited by the tubes connecting the reservoir to be evacuated with the pumps. The following equation :

$$S = \frac{1}{W + 1/S_0},$$

gives the connection between available pumping speed S in litres per sec. as a function of the pump speed S_0, and of the ' resistance ', W, of the tubing to the flow of gas. If the mean free path of the gas is comparable with the diameter of the connecting tubes, $W = L/r^3$ (cf. formula 56, p. 19), where L is the length and r the radius of the tube in mm. ; e.g., the Kaye pump (type III) has a speed of 2,500 c.c.-sec.$^{-1}$ at 10^{-3} mm. Suppose the connecting tube is 1000 mm. long and 10 mm. in diameter, $W = 10^3/125 = 8$, and hence S is reduced to 0·2 litres per sec. The speed is thus reduced to one-tenth by a length of what is normally regarded as ' wide ' tubing. It will be at once obvious how much taps of narrow bore cut down pumping speed. If there are variations in the bore of the connecting tube, then $W = \frac{L_1}{r_1^3} + \frac{L_2}{r_2^3} + \ldots$, where L_1 and L_2 refer to the separate sections.

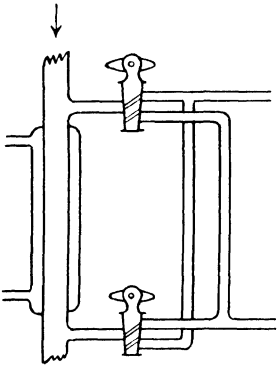


FIG. 20. Arrangement of taps for reversing the direction of pumping.

The following table also indicates the important effect of the diameter of connecting tubing. When long narrow connecting tubing is used the smaller pump (A) is almost as effective as the high speed type (B).

Dimensions of Tubing		Max. speed of pumps at $4{\cdot}5 \times 10^{-5}$ mm.		Available speed, including tubing at pressure $4{\cdot}5 \times 10^{-5}$ mm.	
Length (cm.)	Bore (cm.)				
100	1	A 2,000	c.c. sec.$^{-1}$	118	c.c. sec.$^{-1}$
100	1	B 12,000	,,	124	,,
100	2	A 2,000	,,	667	,,
100	2	B 12,000	,,	924	,,

Method of reversing direction of pumping of circulating pumps. The arrangement of two double way taps is shown in Fig. 20, which is self-explanatory.

Oil trap for rotary oil pumps. When some types of rotary oil pumps are stopped, for example, at night or for longer periods, the oil may rise

into the vacuum system. To prevent this, the vacuum must be let down ; a convenient arrangement incorporating a trap for this purpose is shown in Fig. 21.

Water trap for rotary oil pumps. If an apparatus is of considerable volume and air is admitted frequently and then pumped out through an oil pump, atmospheric moisture dissolves in the oil and impairs the ultimate vacuum of the pump. In absence of a liquid air trap, the phosphorus pentoxide trap shown in Fig. 22 is suitable for protecting the oil. Care must be taken that sudden inrush does not blow the pentoxide into the pump. The movable boat *B* permits of the replenishment of the P_2O_5 at intervals.

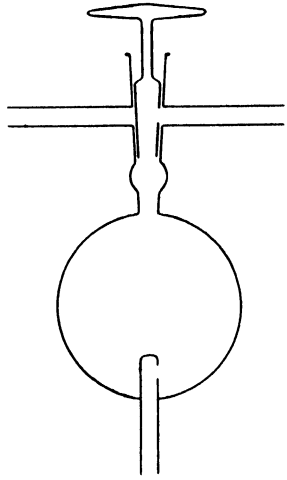


FIG. 21. Oil trap.

The Töpler pump. Before the advent of rotary and of condensation pumps, high vacua were obtained by means of the Töpler or the Sprengel pump. The latter has practically disappeared from use, but the former, though not now used for producing high vacua, finds extensive application in modern practice for collecting gases delivered by more rapid pumps and for transferring gas from one part of an apparatus to another. Since its introduction by Töpler in 1862

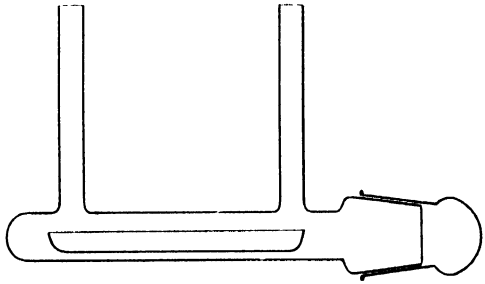


FIG. 22. Phosphorus pentoxide tube.

it has undergone many modifications. Essentially it consists of a bulb *B* (*ca.* 500 c.c. capacity, Fig. 23), which is evacuated by raising mercury until it is expelled through the capillary tube *R* (usually *ca.* 1 mm. in diameter). The mercury is lowered, the thread in *R* breaking until communication is established with the vessel to be

exhausted at *V*. Raising the mercury in *B* compresses the gas which is expelled through *R*. The speed of the pump is simply the volume of *B* multiplied by the number of strokes per sec. Since the time of a stroke is of the order of sixty seconds (if less, there is always a danger of knocking *R* off *B*), and the volume of *B* at most 500 c.c., the speed ·10 c.c./sec.—compares unfavourably with that of rotary oil pumps. To prevent mercury entering the exhaustion tube *V* the leading

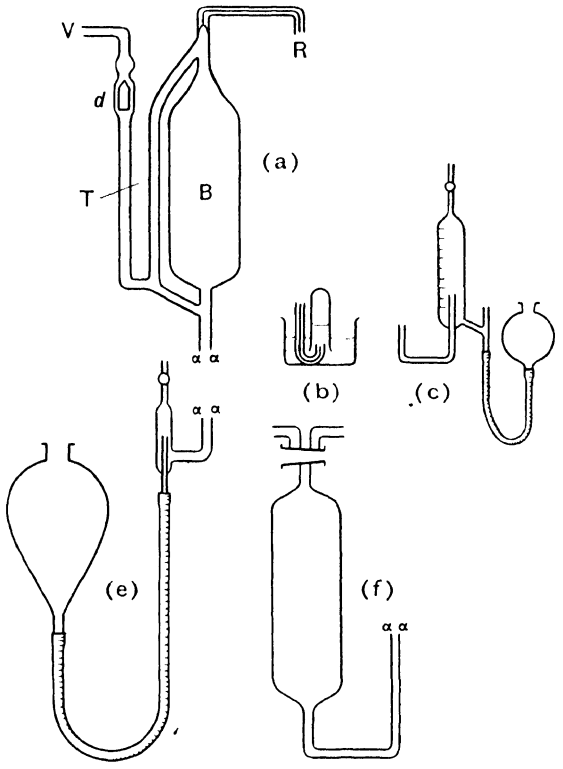


FIG. 23. Topler pump.

in tube is raised to a suitable height, at most 80 cm., which makes the pump rather cumbersome. A more compact arrangement is obtained by substituting the valve *d*. The bulb at *B* may be connected to one or other of the reservoirs shown in *e* and *f* at $\alpha\alpha$. That shown in *e* is the more useful, since the gas in *R* may be easily compressed to atmospheric pressure and thus ejected into the atmosphere. To prevent bubbles of air finding their way into *B*, a small trap with a tap is fixed above the

rubber tube leading to the mercury reservoir. The gas compressed by the pump may be collected in a small test-tube as shown at *b*, or in a graduated vessel as shown at *c*. If, however, the gas is to be transferred to another reservoir, for example, then the capillary may assume the form shown at *a*. In the latter case the mercury reservoir is more conveniently replaced by that shown in *f*, in which a filter pump suffices to lower the mercury. The degree of compression is, of course, now limited by the difference in length between the capillary *R* and the level of the mercury in *f*. To render the operation of the pump less tedious several automatic designs have been proposed (cf. B. D. Steele, *Phil. Mag.*, **19**, 863 (1910) ; F. Porter, *Ind. and Eng. Chem.*, **16**, 731 (1924) ; A. Stock, *Z. Elektrochem.*, **23**, 35 (1917) ; A. T. Williamson, *Rev. Sci. Inst.*, **3**, 782 (1932)) ; also a combined diffusion and Töpler pump installation, E. R. Weaver and M. Shepherd (*J.A.C.S.*, **50**, 1829 (1928)). When removing gas from reservoirs at low pressure, e.g. <1 mm., the speed of pumping may be raised by using the Töpler pump to back a multistage condensation pump.

Pump Speeds

Mercury pellet method. A simple method of measuring the speed of high vacuum pumps has been described by G. W. C. Kaye (*High Vacua*, p. 162 : Bell). A litre bulb (Fig. 24) is connected directly to the

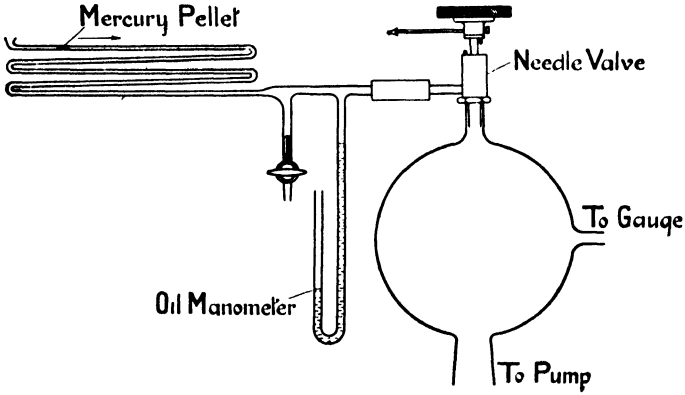


FIG. 24. Apparatus for measuring the speed of pumping.

pump and an attached gauge measures the pressure of gas in the bulb. Air is admitted through the reducing valve ; the rate of admission is measured by the displacement of the mercury pellet contained in a 2 mm. capillary, 100 cm. long, while the oil manometer measures any slight

pressure difference between the atmosphere and the gas in the capillary. If greater sensitivity is required a finer capillary may be used, but the disadvantage is that the mercury tends to stick. By this means the speed of a pump may be determined as a function of the working pressure.

'Getters'

A 'getter' is a substance dispersed in a vacuum tube, after sealing off from the vacuum line, to maintain a good vacuum throughout the life-

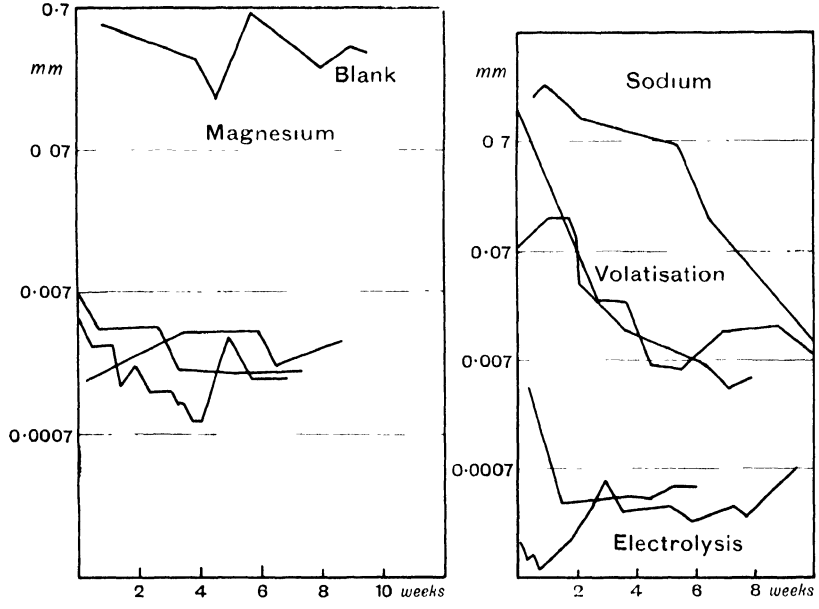


FIG. 25. Performance of getters.

time of the tube. When high speed vacuum pumps were not available, such getters reduced the time required to obtain a good vacuum in a bulb. Dewar was the first to make use of well out-gassed charcoal cooled in liquid air to improve his vacua. For example, in a 2 litre bulb with air at 2·19 mm., 20 grams of charcoal cooled in liquid air reduced the pressure to $2{\cdot}5 \times 10^{-4}$ mm. Charcoals have been improved since Dewar's experiments: S. Dushman (*J. Frank. Inst.*, **211**, 721 (1931)) cites an experiment where the pressure in an ionisation gauge was reduced from 10^{-5} to 5×10^{-9} mm., the limit of the sensitivity of the gauge. F. Soddy (*Proc. Roy. Soc.*, **A, 78**, 439 (1906)) volatilised calcium to achieve a good vacuum. Calcium does not react with the inert gases, and hence

it is very useful for ridding these gases of traces of air and other impurities. The use of red phosphorus as a getter in vacuum electric lamps dates from 1894 (Malignani). Nowadays should it be necessary to obtain and maintain a good vacuum in a radio valve or diode rectifier, a piece of magnesium or calcium is attached to the anode. When the bulb has been heated to the highest temperature the glass is allowed to stand for an hour or two, and the electrodes bombarded with electrons to free them from adsorbed gases. The tube is sealed off from the vacuum line, and the getter then volatilised by heating it with an induction furnace. Sodium may also be used as a getter by making pellets of NaCl and calcium, placing in a nickel case and flashing in the usual way. Better results are obtained by electrolysing the metal through the bulb (see p. 149). To show the results to be expected with this treatment the above diagrams (Fig. 25) are taken from Dushman's article (*loc. cit.*).

B. CONTROL OF GASES

Vacuum Taps and Cut-offs

Glass taps. Glass taps must be carefully chosen for incorporation in a vacuum apparatus. Those with hollow barrels are usually superior to samples with solid keys. The taps shown in Fig. 26 have the advantage

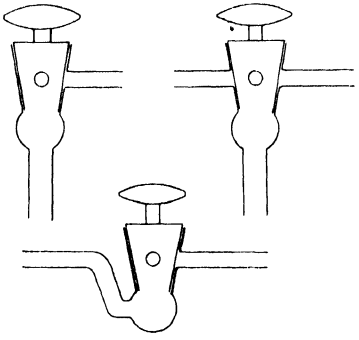


FIG. 26. Vacuum glass taps.

that the barrels are kept in position by atmospheric pressure. Good taps can easily be recognised by spreading a little grease on the barrel and rotating a few times. The lubricant should spread as a perfectly transparent layer over the ground surfaces. In general mercury sealed taps are unnecessary. Oblique bore taps are an additional precaution against leakage from one side of the tap to the other. It often happens that the

gases being used attack or dissolve in tap lubricants. Many greaseless cut-offs have been devised, and a few examples are described below.

Mercury cut-offs. Three types are illustrated in Fig. 27. The first is not necessarily confined to work at pressures more than a few milli-

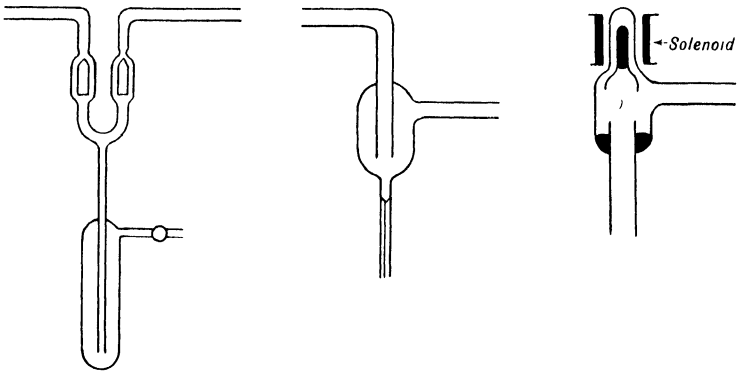


FIG. 27. Mercury cut-offs.

metres, for the limbs need only be made 80 cm. long to enable it to function at pressures up to atmospheric. Long limbs may also be avoided if small float valves be inserted in each limb to prevent mercury entering the vacuum line.

Greaseless glass valve. (M. Bodenstein, *Z. phys. Chem.*, **B**, **7**, 387 (1930).) This valve is made wholly of glass. The seat of the valve is a capillary tube into which a pointed rod of glass is forced. The necessary movement of the seat relative to the rod is obtained by means of glass bellows *B*. The whole is assembled in a metal frame, as is shown in Fig. 28, with a nut to actuate *R*. The movement of *R* is 0·5 – 1 mm., and hence the connecting tubing need not have spirals to allow of change of position. A similar type of valve constructed of platinum and platinum-iridium has been described by M. Bodenstein and W. Dux (*Z. phys. Chem.*, **85**, 297 (1913)).

Greaseless valve for high vacua. (H. C. Ramsperger, *Rev. Sci. Instr.*, **2**, 738 (1931).) This valve will handle halogens, NO_2, other corrosive gases, and vapours. It is not suitable for ammonia or ammoniacal vapours, as the 'seat' of the valve consists of a block of silver chloride, as shown in Fig. 29. The seat bears on the end of a pyrex glass tube, and is actuated by a screw attached to silver bellows coated with silver chloride. Full details of the method of forming the bellows by silver plating on top of 'Tombac' tubing, are given (*loc. cit.*). In this connection it is worth mentioning that silver tube can be joined to pyrex or glass by platinising with 'liquid' platinum and making

the seal with silver chloride, since the latter wets platinum easily (cf. page 69).

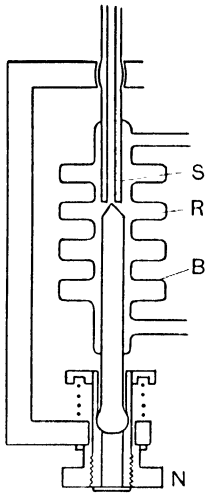


FIG. 28. Bodenstein all-glass non-lubricated tap.

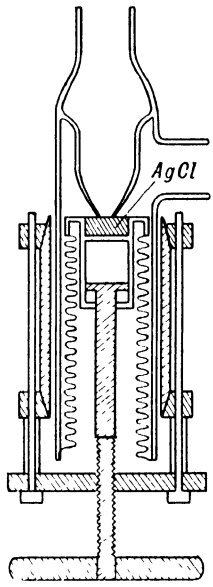


FIG. 29. Ramsperger's greaseless tap.

A silver valve (similar to that of Bodenstein and Dux's platinum valve) is described by H. J. Schumacher and G. Steiger (*Z. phys. Chem.*, **B, 13,** 157 (1931)). Prytz's cut-off is suitable for the admission of small amounts of gas into a vacuum apparatus (Fig. 30). *P* is a porous plate of clay or glass (see below) sealed into the glass and covered with mercury. The end of the tube *B* is closed with a similar plate. If the two plates are brought into contact some gas will enter the tube *B* from the storage vessel. For other patterns of this valve see A. Stock (*Z. Elektrochem.*, **23**, 33 (1917), and **39**, 256 (1933)). No difficulty is met with in sealing in clay discs into glass if the discs are lens-shaped. Porous fritted plates of pyrex glass can be made by a method described by B. Lewis and W. Feitknecht (*J. Amer. Chem. Soc.*, **53**, 2912 (1931)).

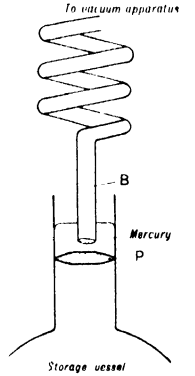


FIG. 30. Prytz's cut-off.

Micrometer needle valve. In gas kinetics it is often necessary to admit a steady flow of gas from a vessel at high pressure to one in which the pressure is much lower. In some experiments the pressure may have to

be adjusted to within fine limits by withdrawing gas from a vessel through a fine but adjustable leak. To perform these duties a metal valve having

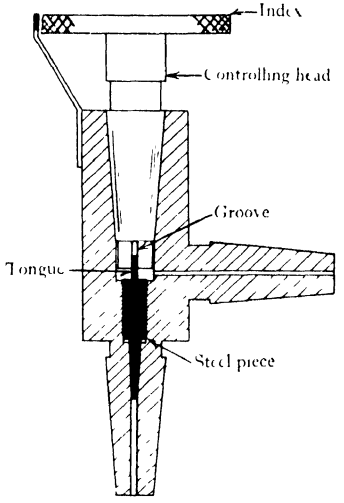


FIG. 31. Micrometer needle valve.

vacuum-tight connections is useful, and is moreover more flexible than a single capillary. There are several forms of such valves. One design is described by L. Saggers (*J. Sci. Instr.*, **12**, 93 (1935)) (Fig. 31). It consists of a brass barrel having two standard male conical pieces so that corresponding female joints may be slipped into position. A steel screw having a conical valve bearing into a brass socket is actuated by a controlling head having a slot at its base and working in a carefully ground conical joint.

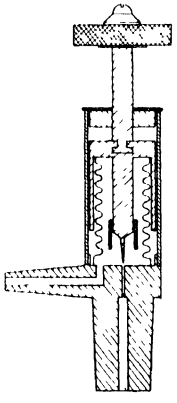


FIG. 32. Regulating valve.

Another form of regulating valve is shown in Fig. 32,* in which the cone for operating the steel needle is dispensed with. As will be seen from the sketch, movement of the needle is permitted by the use of Tombac corrugated bellows, suitable guides being inserted to ensure that the needle enters the seat symmetrically.

All-glass capillary valves for gases. (J. J. Hopfield, *J. Opt. Soc. Am.*, **12**, 391 (1926).) While the steel-brass regulating valve described above is eminently suitable for controlling the flow of gases which do not attack steel or brass nor dissolve in the grease used for lubricating the cone which operates the steel needle, an all-glass valve is sometimes a necessity.

* Manufactured by W. Edwards & Co.

A simple valve is shown in Fig. 33. It consists of a capillary *C* into which a glass needle *N* slides. The position of *N* is controlled by energising the

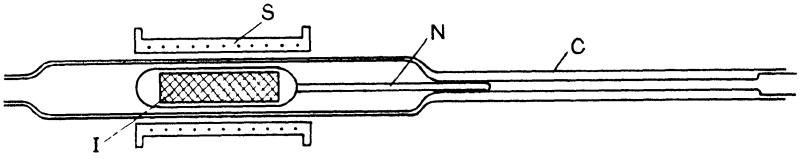


FIG. 33. All-glass needle valve.

solenoid *S*, so that the iron rod *I* and *N* may be moved along the axis of the tube. To avoid sticking, the glass tube surrounding *I* is best placed on four small glass feet. The diameter of *C* and *N* will depend on the volume of gas passing and the degree of control required. It is possible to reduce the flow to 0·1 c.c. per sec. at N.T.P. with atmospheric pressure on one side of the capillary and a vacuum on the other.

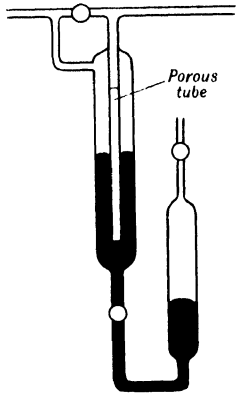


FIG. 34. Valve for regulating the flow of gas.

Variable valves for controlling gas flow. O. H. Wansbrough-Jones (*Proc. Roy. Soc.*, **A, 127,** 530 (1930)) has described a simple adjustable valve which consists of a porous tube, the effective length of which may be varied by immersing it in mercury as shown in Fig. 34. A more elaborate type of valve working on the same principle has been designed by L. Wolf and S. van Reichel (*Z. Elektrochem.*, **39,** 143 (1933)).

All-glass cut-off. (J. Willard, *J. Amer. Chem. Soc.*, **57,** 2328 (1935).) The construction of this cut-off is shown in Fig. 35. It is made partially of pyrex and of silica. To shut this valve the silica tube is heated strongly near the tip of the pyrex tube, the tip thus fusing. To open, it is necessary to evacuate one side, heat the capillary, and, if the gas is at a reasonably high pressure—a few millimetres—on one side, the capillary tube will blow out.

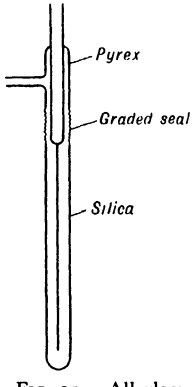


FIG. 35. All-glass cut-off.

A cut-off for high temperatures. When working with vapours it is often necessary to heat the connections to the reaction vessel in order to obtain the required vapour pressure. The usual procedure is to wind those parts of the apparatus containing the vapour with nichrome wire and heat electrically. This may result in melting the grease on the stop cocks, thus giving rise to leaks.

The trouble can be overcome by the use of mercury cut-offs or by a device (Fig. 36) due to J. E. Carruthers and R. G. W. Norrish (*Trans. Faraday Soc.*, **32**, 200 (1936)). These methods are only applicable provided mercury vapour does not in any way interfere with the course of the reaction. The mode of operation is : *A* is opened and the vapour admitted to the reaction vessel. *A* is then closed, and *B* opened to admit mercury from *C* to a point *E*. Any gas trapped between *A* and *D* is removed by carefully opening *A*. Mercury driven out of the space *AE* when the reaction vessel is to be pumped out is collected in a small side tube.

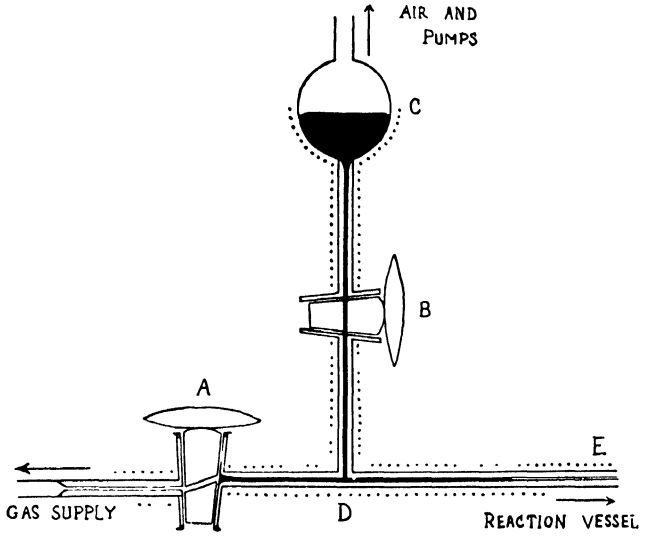


FIG. 36. Mercury cut-off for vapours.

Tombac tubing. When it is necessary to join two pieces of high vacuum apparatus so that they can be moved relatively to each other, this is often accomplished, if the movement is not large, by means of a long spiral of glass tubing, though cutting down speed of pumping. This difficulty is dispensed with by employing Tombac tubing, which consists of a seamless metal tube folded up into corrugations. A tube of 6 mm. internal diameter may be bent into a circle of radius 150 mm., while a 50 mm. tube may have a radius of curvature of 470 mm. These tubes can be obtained with plain ends, and hence may be fixed to glass by vacuum wax, or better, by soldering to a layer of copper deposited on a platinised glass tube. Such tubing is also valuable when it is necessary to move components in an evacuated bulb relative to each other.

C. VACUUM JOINTS

Low Vapour Pressure Oils and Greases

The pioneer experiments of C. R. Burch (*Proc. Roy. Soc.*, **A, 123,** 271 (1929)) on the molecular distillation of petroleum products have found extensive application in vacuum work in the production of a series of oils and greases of exceedingly low vapour pressure. The characteristics of these compounds are shown in the table below.

TABLE 14

Low Vapour Compounds prepared by Technical Products Ltd.

Designation	Vapour pressure	S.G. 15°/4°	Viscosity	Uses
Oil 'A'	- 10^{-5} mm. at 20° C.	0·874	Red. time 255 at 20° C.	Oil condensation pump. Oil U-tube manometer.
Oil 'B'	- 10^{-7} mm. at 20° C.	0·871	Red. time 356	Oil condensation pump, but more suitable for exhausting valves.
Oil 'J'	- 10^{-3} mm. at 250° C.	—	Red. time 100 at 140° C.	Sealing oil, lubricant for special taps.
Oil 'K'	- 10^{-3} mm. at 300° C.	—	Higher viscosity than 'J'	Similar to 'J': used where larger viscosity desirable.
Grease 'L'	- 10^{-3} mm. at 300° C. 10^{-11}* mm. at 20° C.	—	Same consistency as vaseline	Sealing ground joints, lubricating taps.
Grease 'M'	10^{-3} mm. at 200° C. 10^{-7} mm. at 20° C.	—	—	Similar to 'L', but less expensive.
Grease 'N'	- Not given, but low enough for thermionic experiments.	—	—	Rubber grease for taps.

Sealing Compound Q is a substance resembling putty in its mechanical properties. It is quite firm at temperatures up to 30° C., but above this becomes soft, so that it can easily be moulded into position and made to adhere to moist surfaces. It is specially useful for making temporary vacuum joints where the surfaces are not a good fit, and on ground surfaces not flat enough to permit of grease 'L' being employed. The joint may easily be broken by gentle softening of the compound. The vapour pressure is considerably higher than that of grease 'L', and hence the compound cannot be used where an extremely high degree of evacuation

* Calculated.

is desired. Sealing Wax ' W ' is a black pitch-like material which softens at 80-90° C. At 180° C. its vapour pressure is about 10^{-3} mm., which would imply a vapour pressure less than 10^{-6} mm. at room temperature. It is useful for sealing windows to vacuum apparatus, and for making joints between silica and glass tubing.

Metaphosphoric acid. When Ramsay grease or Apiezon grease cannot be used in a vacuum system on account of their susceptibility to attack by corrosive gases or because of solution of gases in the grease, lubrication, though somewhat less satisfactory, can be obtained by applying metaphosphoric acid to the ground surfaces. It may be mentioned that the vapour pressure of water above the acid is not negligible. To keep stop-cocks vacuum tight after repeated turning, A. Pinkus (*Bull. Soc. Chim. Belg.*, **43**, 462 (1934)) cuts two grooves in the barrel and lubricates the top and bottom of the barrel with Ramsay or Apiezon grease.

Inorganic lubricants. (W. A. Boughton, *J. Amer. Chem. Soc.*, **52**, 2421 (1930).) The ground parts of the taps are silvered in the usual way, three successive thick layers being deposited. The amalgam for lubrication consists of 5 gm. solder, 5 gm. Wood's metal, 2·5 gm. Zn and 80 gm. mercury. It is said to wet clean polished glass surfaces.

Vapour pressure of waxes and greases. (R. M. Zabel, *Rev. Sci. Instr.*, **4**, 233 (1933).) Measurements of the vapour pressure of a number of typical substances, such as picein, sealing wax, de Khotinski cement, glyptal lacquer and Ramsay grease, show that the vapour pressure is usually less than 10^{-3} mm. The vapour pressure of Ramsay grease has also been measured by H. Meyer (*Z. Physik.*, **67**, 264 (1931)) and by W. Espe and I. Kroczek (*Z. f. tech. Physik*, **13**, 443 (1932)).

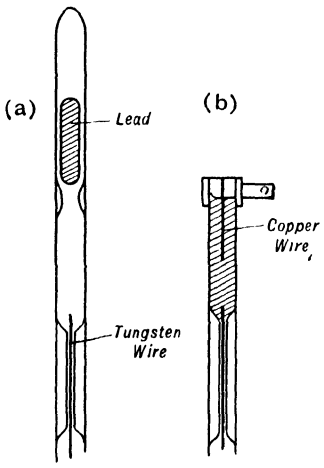


FIG. 37. Metal silica joints.

Metal-glass Joints

Metal-silica joints. (Sand, *Proc. Phys. Soc.*, **26**, 127 (1914).) Lead may be used as a sealing medium, since it wets silica when molten. The tube through which the wire (tungsten or molybdenum) is to be sealed is drawn out as shown in Figs. 37 (*a*) and (*b*). The lower capillary forms a close fit around the tungsten and is connected to a pump. After evacuation the silica is collapsed on to the tungsten. Next the lead is melted and allowed to trickle down into the lower chamber. The upper chamber is opened to the atmosphere, so that the molten lead is firmly

pressed into position. The tube is cut as shown in Fig. 37 (*b*), and a suitable copper lead inserted. A 1 mm. tungsten wire will carry at least 5 amp. continuously.

Copper-glass seals. A convenient method of joining small glass tubes (pyrex or soda) to copper tubes has been described by H. de Laszlo (*J. Sci. Instr.*, **10**, 296 (1933)). The copper tube is of 6·5 and 6·0 mm. external and internal diameters respectively. A piece of hard steel, 1·5 cm. long and exactly 6·0 mm. in diameter, is inserted in the tube until 3 mm. protrudes. A taper cut of 2° is made on a lathe, thus tapering about 5 mm. of tube, which is polished with emery paper and the steel plug withdrawn. The polished tube is next coated with copper borate. The tube is inserted in the chuck of a lathe and slowly rotated, while a fine gas-oxygen flame is allowed to play on it 3 cm. from the open end until the end is of a uniform grey-black colour. On cooling below 100° C. a saturated solution of borax in water is painted on. The heating is then repeated. On cooling, the tube should be covered with an even glaze of reddish purple copper borate. Tubes in this condition may be stored indefinitely until required.

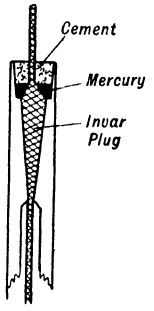


FIG. 38. Copper glass seals.

Sealing to soda glass or pyrex is carried out in the following manner. A piece of glass is chosen such that 3 mm. of the feathered end of copper tube can be inserted into it. The tube and glass are rotated together, while an air-gas flame is directed on the glass tube about 2 mm. from the end of the copper tube. At a red heat the copper borate melts and forms a continuous ring between glass and metal. The seal is annealed in a smoky flame.

The resistance to sudden changes of temperature is dependent wholly on the glass ; pyrex is, of course, superior to soda in this respect. A method of making larger seals is described by H. W. B. Skinner and J. H. Burrow (*J. Sci. Instr.*, **7**, 290 (1930)).

An alternative but less satisfactory type of seal, employed in some mercury lamps, is to grind in an invar taper as shown in Fig. 38. For safety this is best sealed with mercury, the latter being kept in place by a cement of high melting point if the joint is subject to high temperatures.

Metal-silica joints for withstanding temperatures from −190 to 200° C. (S. D. D. Morris, *J. Sci. Instr.*, **11**, 232 (1934).) A method of making a joint which is not vacuum-tight unless covered with a film of wax or resin is as follows. The silica surface is roughened by rubbing with carborundum powder and platinised with ' liquid ' platinum, painting on several coats and burning off the oil between each coating. The

platinum is then copper-plated. In order to obtain an even fine-grained deposit the following bath is used.

$CuSO_4, 5H_2O$ - - - -	150 gm.
Conc. H_2SO_4 - - - -	50 ,,
Alcohol - - - - -	50 ,,
Water - - - - -	1000 ,,

If the joint is to withstand rapid temperature variation the copper is soft-soldered to a low expansion alloy such as invar.

In order to obtain a vacuum-tight joint fulfilling the same conditions a tapered joint is necessary, the metal forming the outer cone so as to grip the inner cone of silica more strongly. A rod or tube of low expansion alloy is bored out so as to have a 1 in 10 taper. The silica is correspondingly tapered, the two being finally ground together. The metal cone is then tinned and the silica cone inserted while the solder is molten. On cooling the metal grips the silica tightly, thus forming a vacuum-tight joint.

Carrying capacity of wires used in Vacuum Tubes

Current-carrying Capacity in Amps.

Diameter (mm.)	Vac. steel (Fe-Ni alloy) as supports	Vacu Cu-Ni as supports	Ni wire as supports	Copper-clad lead-in wire
0·1	0·15	—	0 4	—
0·2	0·6	—	1 1	—
0·25	—	0·5	—	2·0
0·5	3·5	1·2	7·0	7·0
0·7	—	—	—	15·0
1 0	14·0	3·4	20 0	—
2·0	—	—	60 0	—

Method of attaching fluorite windows to glass. (F. Palmer, *Phys. Rev.*, **45**, 557 (1934).) In the method shown in Fig. 39, the upper surface of the glass is ground flat. Before the window is placed in position the channel is filled with granules of silver chloride. The apparatus is placed in a furnace, and the temperature raised to 470° C. and kept there for a minute to melt the AgCl. When cool more AgCl is added, and the process is repeated until the outer level of the cold chloride is slightly above the level of the orifice. When the apparatus is cold, the fluorite window is laid over the orifice, but is supported now at its outer edge by the chloride. The temperature is raised to 450° C. and then slowly until, as the chloride melts, a thin layer

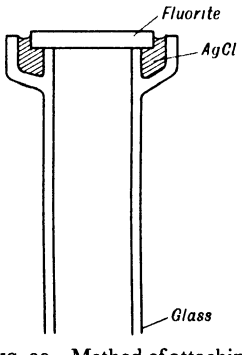


FIG. 39. Method of attaching fluorite windows to glass tube.

runs in suddenly between the window and the ground surface of the orifice. The heating is then stopped immediately. The joint may safely be baked to 430° C.

D. MEASUREMENT OF PRESSURE

The units in which pressure is expressed are summarised in the following table.

1 mm. Mercury (0° C., lat. 45°, $g = 980{\cdot}6$ dynes)	1333 dynes cm.$^{-2}$
1 atmosphere	760 mm. Hg. $1{\cdot}013 \times 10^6$ dynes cm.$^{-2}$
1 bar (British)	10^6 dynes cm.$^{-2}$ $0{\cdot}75 \times 10^3$ mm. Hg.
1 microbar (British)	1 dyne cm.$^{-2}$ $0{\cdot}75 \times 10^{-3}$ mm. Hg.
1 micron (μ) Hg	10^{-3} mm. Hg. 1·33 dynes cm.$^{-2}$
1 $\mu\mu$ Hg	10^{-6} mm. Hg. $1\ 33 \times 10^{-3}$ dynes cm.$^{-2}$

Accurate barometric pressure gauge. For the majority of kinetic experiments, pressures in the neighbourhood of atmospheric are easily measured by setting a millimetre scale behind an ordinary barometer or a simple **U**-tube manometer. The relative accuracy of each measurement is of the order 0·2 mm., but the absolute accuracy may be much worse. If an absolute accuracy of 0·05 mm. is aimed at, many additional precautions must be taken. A large **U**-tube manometer is constructed and the difference in levels measured by a cathetometer. The precautions are discussed by A. F. O. Germann (*J. Phys. Chem.*, **19**, 437 (1915) ; *J. Chim. Phys.*, **12**, 78 (1914)), and a form of suitable gauge is shown in Fig. 40. The main limbs are of 20 mm. tube, the short and the long limbs being made from the same length of tube. The mercury reservoir leads to an air trap as shown, and a small clamp *C* is affixed so that the mercury levels can be adjusted accurately. The whole apparatus is cleaned in the usual way with chromic acid, washed with distilled water, dried, evacuated and flamed. Mercury is then allowed to run in, and the gas of which the pressure is to be measured is admitted to the left-hand limb. Three thermometers are used to read the temperature of the instrument, so that the density of mercury may be calculated. Similarly thermometers are attached to the scale of the cathetometer in order that correction for the expansion of the scale may be made. Precise details of the operation and of the corrections to be applied are given by

Germann (*loc. cit.*), but perhaps the method of making clear the position of the meniscus may be described. A card is placed behind the meniscus, divided horizontally with a white and a black portion (M. W. Travers, G. Senter and A. Jacquerod, *Phil. Trans.*, **A, 200,** 111 (1903)). The line of division, with the black side uppermost, is placed 1-2 mm. above the meniscus, the mercury surface then appearing as a jet-black line which is easily brought into coincidence with the cross wires of the cathetometer telescope.

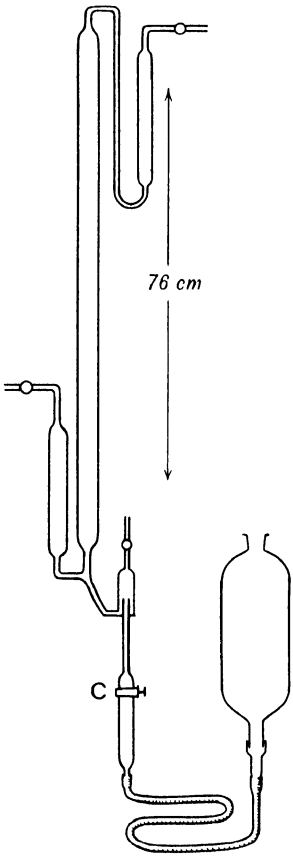


FIG. 40. Accurate barometric pressure gauge.

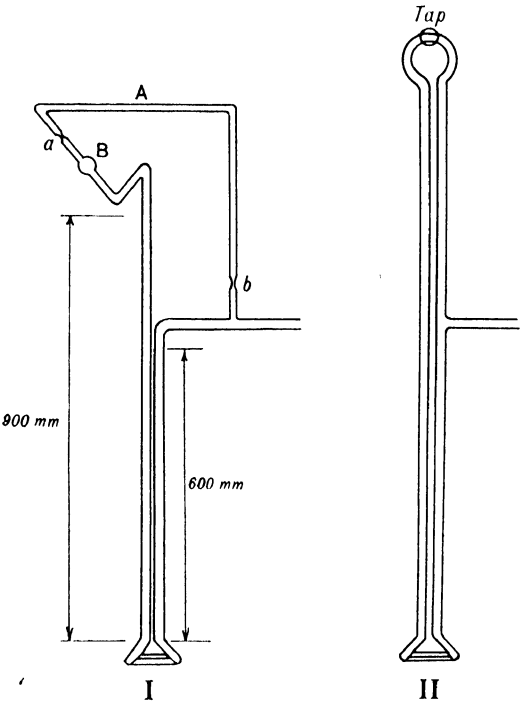


FIG. 41. U-tube manometer.

Large U-tube manometer. Two patterns are shown in Fig. 41. The constriction at the base of the manometer I serves to damp the movement of the mercury. The left-hand limb is evacuated by the auxiliary tube *A*, while the mercury is heated to free it from moisture and air. (For another method of filling, cf. p. 81, and the vapour pressure thermometer, p. 104.) The auxiliary tube is then sealed off at *a* and *b*. It is important to keep the dimensions indicated in the drawing in order to

avoid the mercury's splashing over into the horizontal tube, and to prevent air from entering the right-hand limb, should the pressure increase in the apparatus over one atmosphere. Trap B catches any air which may be given off by the mercury in the right-hand limb after sealing off. It is operated by tilting the manometer to the right. Well-evacuated gauges give a characteristic metallic click if the mercury hits the glass tube. The use of the second pattern, II, is self-explanatory. It can be evacuated any time by opening the tap, which must be very reliable and vacuum-tight.

The McLeod Gauge

This well-tried gauge depends for its action on the compression of a known volume V of gas to a smaller volume v in which the pressure p is measured. If p_0 is the original pressure, then

$$p_0 = \frac{v}{V} p.$$

One of the most useful forms of the gauge is shown in Fig. 42. B is the compression bulb, and C_1 the capillary in which the pressure of gas is measured by comparison with the level in the immediately adjacent capillary of similar bore, C_2. In order to obtain a well-defined cut-off, C.O., an internal seal is inserted, as is shown in the diagram. The end of the compression bulb ends in a drawn-out tube to prevent violent surges of the mercury in B. Similarly to prevent accident, the tube leading to the atmosphere on the two-way tap is drawn down to a fine capillary, such that the mercury takes about 30 sec. to reach C_1. A filter pump is suitable for lowering the mercury. If the length of the gauge is less than the barometric height, it is advisable to have a mercury trap S sealed on at the top to prevent mercury finding its way into other parts of the apparatus. Suitable dimensions for the bulb B are 200 c.c. and 0·2 c.c. for the volume of C_1. A millimetre difference in mercury level then corresponds to 0·001 mm. pressure. C_2 should not be much longer than 200 mm., and hence the maximum pressure which can be measured is 0·2 mm. There is a considerable gap between this pressure and the lowest which can be measured in the usual type of barometric gauge, and so it is

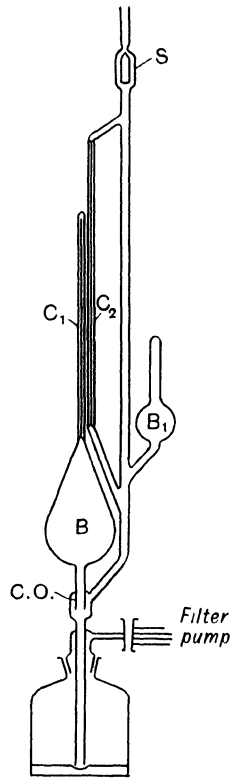


FIG. 42. McLeod gauge.

desirable to have a subsidiary compression bulb *B*, with a compression ratio of perhaps 10-50 to fill this gap. It may be mentioned that this gap is also conveniently bridged by the use of the Bourdon gauge, described on p. 85. The advantages of this type of McLeod gauge over most of previous designs is that it is self-supporting, and is readily fused to a vacuum apparatus standing on a table or attached to a ' grid '. It will be evident from what has been said above that the sensitivity of the gauge has no limit, but obviously it is impracticable to have much larger compression chambers, and the diameter of the closed capillary cannot in practice be reduced below 0·5 mm. With the above dimensions a pressure of 10^{-5} mm. may be detected. To render the gauge more sensitive Pfund (*Phys. Rev.*, **18**, 78 (1921)) has adopted the device of incorporating a small Pirani gauge at the top of the closed capillary, and measuring the pressure according to one of the methods described on p. 79. A sensitivity of 10^{-7} mm. is claimed for this method (cf. also R. T. Cox, *J. Opt. Soc. Amer.*, **9**, 569 (1924)). A ' shortened ' McLeod gauge is described by H. J. Reiff, *Z. Instr.*, **34**, 97 (1914).

A further design of a gauge evolved by the General Electric Co., which does not require accurate setting, is shown in Fig. 43. In this modification the mercury is brought opposite the closed end of the capillary by opening the tap to the atmosphere and withdrawing or adding the necessary amount of mercury. To compensate for variations in atmospheric pressure, the tube leading from the reservoir is made of wide bore capillary tubing. The closed end of the capillary carries a scale with graduations in mm. or other suitable units.

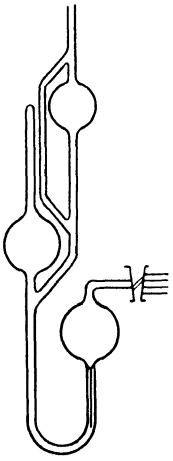


FIG. 43. G.E.C. pattern McLeod gauge.

Calibration. Calibration is best effected before the gauge is assembled. The volume of the closed capillary can then be determined by filling with mercury and weighing. If more than one graduation mark is required, then the volume of each part up to the graduation mark must be measured. The volume of the compression bulb is likewise determined by means of mercury, a small correction being made for the fact that when the bulb is filled it is upside down by measuring the height of the meniscus above the level of the cut-off tube. A similar correction requires to be made in the case of the closed capillary, though for most purposes the calibration mark may be made at the point of contact of the mercury with the glass. If an uncalibrated gauge is obtained the capillary may be calibrated by dropping a weighed

amount of mercury into the gauge, evacuating, and running the droplet into the closed capillary. A series of such determinations then give the relationship between volume and length of the tube. An alternative way of calibrating a new gauge has been described by R. J. Clark (*J. Sci. Instr.*, **5**, 126 (1928)).

Method of reading McLeod Gauge. After having steeped the gauge in chromic acid in the usual way, washed thoroughly with distilled water and roughly dried by connection to a filter pump warming the whole gauge by a luminous gas flame, the gauge is fused to the vacuum line. To rid the walls thoroughly of moisture it is best placed in a large furnace and baked out at 300° C., a liquid air trap being interposed between gauge and pump. If a furnace is not available, careful flaming with a hand blow-pipe is almost as effective. There are two ways of testing whether the water vapour has been eliminated for all practical purposes. One is to use a Pirani gauge during exhaustion, which will readily detect small pressures of vapours of which the McLeod gauge gives no indication. The second gives only a qualitative demonstration that evacuation is completed. The mercury is raised in the two capillaries to the maximum height, and then is very slowly lowered. A good vacuum—10^{-6} mm.—is indicated by the mercury sticking in the closed capillary, so that a negative pressure of a few mm. is produced. This is often known as a 'sticking' vacuum.

There are two methods of operation. The first may be made to give pressure readings directly. It is convenient, in order to save further calculation, to mark the closed capillary such that the compression ratios are $10^3 : 1$, $10^4 : 1$, and $10^5 : 1$. Then, by setting the mercury opposite these marks, the pressure in millimetres of mercury may be directly read on a millimetre scale affixed behind the capillary. In practice it is convenient to have the zero of the scale opposite the $10^3 : 1$ compression mark. In order to obtain closely concordant readings it is advisable to raise the mercury higher than need be, and slowly lower it with gentle tapping to the desired point. The concordance in the readings should be within 0·2 mm.

The other method consists in raising the mercury to any level, measuring the difference in height in the two capillaries, the volume of gas contained in the closed capillary, and calculating the pressure in the usual way.

When using the smaller compression bulb for high pressure measurements the difference in levels of the mercury divided by the compression ratio does not give the pressure accurately. If p is the original pressure and V/v the compression ratio, then

$$g \cdot \rho \cdot \Delta H = p\,(V/v - 1),$$

where ΔH is the difference in height of the mercury columns in the capillary tubes and p the density of mercury. When $V/v = 10^3$, this reduces to the form given before ; but in the present circumstance, when $V/v \doteq 10$, then the correction must be applied.

The gauge depends for its applicability on the validity of Boyle's Law, and hence it may be used for H_2, N_2, O_2, CO, CH_4, the rare gases. W. Gaede (*Ann. d. Physik*, **41**, 289 (1913)) mentions that oxygen forms a scum on the surface of the mercury, thus causing the mercury to stick. This is removed by gently heating the capillary. With the more easily condensable gases, such as CO_2, SO_2, C_2H_2, C_2H_4, C_2H_6, N_2O, NH_3, it is easy to calculate from the compressibility what correction must be applied to the observed pressure (M. Francis, *Trans. Faraday Soc.*, **31**, 1325 (1935)). For an imperfect gas, $p_0V_0/p_1V_1 = 1 + \lambda$,

TABLE 15

Gas	CO_2	SO_2	C_2H_2	C_2H_4	C_2H_6	N_2O	NH_3	PH_3
λ	0·007	0·0234		0·007		0·007	0·0150	0·0091

where p_0 and p_1 refer to a very low pressure and to one atmosphere respectively. λ is characteristic of each gas, and a table of these coefficients is given above for some common gases. If the compression ratio in the McLeod is high, then it may be shown that

$$p = p_c \frac{v}{V}(1 + \lambda p_c),$$

where p_c is the observed pressure. Since p_c does not in general exceed 200 mm., the correction for SO_2, for example, is less than 1 per cent. The real trouble encountered is in the sorption of these gases by the walls of the apparatus. This is a disturbance which cannot be eliminated. It may be mentioned that NH_3 and SO_2 are particularly bad in this respect.

A robust form of McLeod gauge has been introduced by W. Edwards & Co., in which rubber is entirely dispensed with. The upper part is made of glass (Fig. 44) and fitted to the lower steel tube by a standard ground joint and to the apparatus by another similar joint. The mercury reservoir is also of steel, and is arranged so that it may readily be clamped in any position.

Pirani gauge. This is one of the most convenient of low pressure manometers, and has the practical advantage that it may be used with gases and vapours, corrosive or otherwise. Its only disadvantage is that it is not absolute and must be calibrated by another gauge. Another disadvantage, which may at times be turned to a useful purpose in the

analysis of binary mixtures at low pressures, is that calibration must be effected for each gas employed. It depends for its action on the fact that the thermal conductivity of a gas at low pressures is proportional to its pressure, and that therefore a heated wire suspended in a gas will lose part of its energy by impact of 'cold' molecules upon its surface (cf. p. 16). M. V. Pirani was the first to suggest this principle for use as a low pressure manometer (*Verh. d. deutsch. Physik. Ges.*, **8**, 686 (1906)), and a modified form was introduced by C. F. Hale (*Trans. Amer. Electrochem. Soc.*, **20**, 243 (1911)). Further improvements were made by N. R. Campbell (*Proc. Phys. Soc.*, **33**, 287 (1921)), and the conditions for attaining maximum sensitivity pointed out by Knauer and Stern (*Z. Physik*, **53**, 766 (1929)). (Cf. also R. G. J. Frazer, *Molecular Rays*, p. 37, Cambridge.) A sensitivity of 10^{-8} mm. has been attained. A hot wire loses energy (*a*) by conduction through the gas, (*b*) by loss through the ends, and (*c*) by radiation. By making the wire sufficiently long and thin the end losses may be practically eliminated. A thin narrow strip is even better still in this respect. (See also L. F. Stanley, *Proc. Phys. Soc.*, **41**, 194 (1929).) The energy lost by conduction is

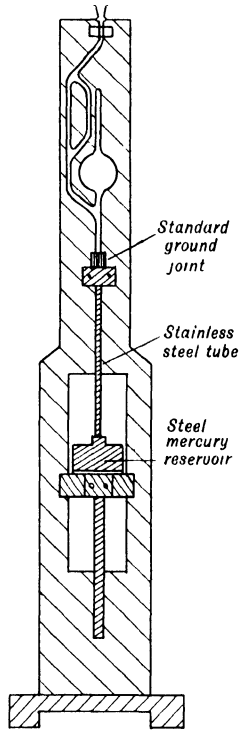


FIG. 44. Glass steel McLeod gauge.

$$\frac{\alpha C_v}{(2\pi M\mathbf{R}T_w)^{\frac{1}{2}}}(T_w - T_g)p \,.\, A,$$

where α is the accommodation coefficient of a gas whose specific heat at constant volume is C_v, molecular weight M and pressure p. T_w and T_g are the temperatures of the wire and gas respectively, and A is the surface area per unit length.

The energy lost by radiation is

$$A \,.\, \epsilon \,.\, c(T_w^4 - T_g^4),$$

where ϵ is the emissivity and c the radiation constant. If E is the energy supplied per unit length, then

$$E = \frac{\alpha C_v}{(2\pi M\mathbf{R}T_w)^{\frac{1}{2}}} \cdot (T_w - T_g)p \,.\, A + A \,.\, \epsilon \,.\, c \,.\, (T_w^4 - T_g^4).$$

Hence

$$\frac{dT}{dp} = -\frac{\alpha C_v (2\pi M\mathbf{R}T_w)^{-\frac{1}{2}}(T_w - T_g)}{4\epsilon \,.\, c \,.\, T^3 + \alpha C_v (2\pi M\mathbf{R}T_w)^{-\frac{1}{2}} p} = -\frac{\alpha C_v (2\pi M\mathbf{R}T_w)^{-\frac{1}{2}}(T_w - T_g)}{4\epsilon \,.\, c \,.\, T^3},$$

when p is small. Or,

$$\frac{dT}{dp} = -\frac{\alpha C_v (2\pi M\mathbf{R}T_w)^{-\frac{1}{2}}}{4\epsilon \cdot c \cdot T_w^2}, \text{ if } T_w > T_g.$$

Therefore

$$\frac{dR}{dp} = \frac{dR}{dT} \cdot \frac{dT}{dp} = -\frac{a \cdot \alpha C_v (2\pi M\mathbf{R}T_w)^{-\frac{1}{2}}}{4\epsilon \cdot c} \cdot \frac{1}{T_w^2},$$

where a is the temperature coefficient of resistance and R the resistance. The maximum sensitivity is thus given when a is large, ϵ small, and α large, though the latter is difficult to control. Roughening the surface to increase α also increases the emissivity, and hence these factors nearly cancel. T_w must be small, which implies a small bridge current and a corresponding drop in the accuracy with which the change in resistance may be measured. The compromise for a given gauge is most quickly found by trial and error. The lower T_w the longer the wire takes to reach thermal equilibrium. Maximum sensitivity is also promoted by low wall temperature, but obviously this is limited by the condensability of the gas.

The form of such a gauge resembles that of a small electric lamp. When constructing the gauge it is often easier to make it as shown in Fig. 45, but without the wire. The tube is then cut at the dotted line, and the wire or ribbon soldered or spot-welded to the nickel supporting leads and the whole resealed. 0·01 mm. platinum or nickel wire is suitable. Its resistance at room temperature will be of the order of 100 ohms for 50 mm. If the gauge is to be immersed in liquid air it is advisable to fill the tube carrying the leads with paraffin wax to prevent condensation of atmospheric moisture therein. Some authors recommend that a spring be attached to the wire, but if the wire is kept as taut as possible during attachment to the supports this appears to be unnecessary for moderately sensitive gauges.

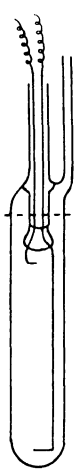


FIG. 45. Pirani gauge.

The gauge is then set up in a Wheatstone network with a similar evacuated gauge balancing that to be used as manometer. Both gauges are immersed in the same cooling liquid. To obtain maximum sensitivity, the resistance of the other arms of the bridge and of the galvanometer should be approximately identical. Frazer (*loc. cit.*) cites an example where a gauge has a nickel hairpin filament, 140 mm. long, 50μ wide and 4μ thick, and resistance 60Ω. With a galvanometer of sensitivity 3×10^{-9}

amp. per scale division at 1 metre, the deflection at a distance of 2 metres for hydrogen was 1·2 divisions per 10^{-8} mm. For ordinary purposes a sensitivity of 10^{-5} mm. is ample. (Cf. also Paneth and Peters, *Z. phys. Chem.*, **A, 134**, 383 (1928).)

Method of operation. For small pressures the bridge galvanometer deflection is proportional to the pressure. Apart from this restricted method, there are two ways in which the gauge may be used. The most common is to measure the voltage required to maintain the bridge balanced, the simple circuit shown in Fig. 46 being used. A 2-volt cell is sufficient to raise the temperature of the wire some 100° C. above that of its container. A high resistance voltmeter with a well-graduated scale is suitable, and if the sensitivity required is not to exceed 10^{-4} mm. a table type 'unipivot' galvanometer makes the whole assembly very compact. One of the arms of the bridge is made adjustable, so that a suitable range for the gauge may be selected to suit the immediate experimental requirements.

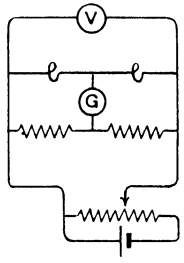


FIG. 46. Electrical circuit for Pirani gauge.

Calibration is most easily effected by means of a McLeod gauge. The energy input to the wire is equal to k_1V^2, k_1 being a constant and V the voltage. The heat loss by conduction along the leads and by radiation is proportional to the excess temperature T_E of the filament over the surroundings. Let this be $T_E k_2$ and the energy loss by conduction $T_E f(p)k_3$. Then

$$k_1 V^2 = T_E k_2 + T_E k_3 f(p),$$

and

$$k_1 V_0^2 = T_E k_2,$$

where V_0 is the voltage required for balancing when $p = 0$. Hence

$$\frac{V^2 - V_0^2}{V_0^2} = \frac{k_3}{k_2} f(p).$$

Up to a pressure of 0·1 mm. $f(p)$ is accurately linear. Beyond this it is advisable to calibrate the Pirani by the McLeod gauge. In this way it may be used up to pressures of several mm. k_3/k_2 depends on the nature of the gas owing to factors discussed on p. 77. In practice it is found that this ratio is about the same for the heavier gases such as N_2, O_2, CO, CO_2, while for H_2 it is about twice that for N_2, etc. On account of this difference, analysis of binary mixtures, one component of which is hydrogen, can be carried out. For example, suppose the composition of a $H_2 - N_2$ mixture is to be determined. First calibration curves for H_2

and N_2 are made separately (Fig. 47). Then the unknown mixture is introduced, its pressure is measured by the McLeod gauge, and also the voltage required to balance the bridge giving point P. From the position of P on the line P_1P_2 the composition may then readily be calculated. The accuracy of this method of analysis is about 1 per cent.

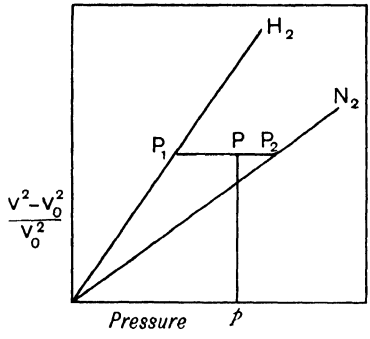


FIG. 47. Calibration of Pirani gauge.

Normally the Pirani gauge is calibrated with mercury vapour present (0·001 mm. at room temperature). If, however, there are traps cooled in liquid air attached to the system, the calibration should be repeated with a trap interposed between Pirani and McLeod gauges in order to eliminate mercury vapour. The area of the inlet and outlet tubes of this trap where cooled by liquid air must be of equal bore. Otherwise, owing to thermal effusion, the calibration will be erroneous. (Cf. J. K. Roberts, *Proc. Roy. Soc.*, **A**, **135**, 192 (1932).) The factor causing the greatest lag in the operation of the gauge is the diffusion of gas into it.

Another method of using the Pirani gauge is to apply a constant voltage across the bridge and alter the resistance of one of the arms (by a dial resistance box) to bring it to balance point. If R_0 and R are the resistances of the variable arm when $p = 0$ and $p = p$ respectively, then it is convenient to plot $(1/R - 1/R_0)$ against p for calibration purposes, though the plot is not exactly linear.

With corrosive gases such as the halogens the usual form of Pirani gauge is not suitable. G. K. Rollefson (*J. Amer. Chem. Soc.*, **51**, 804 (1929)) has overcome the difficulty by constructing a gauge wholly of pyrex glass. 6 mm. tubing is drawn down to a fine capillary and sealed into a suitable vessel. Mercury is then run into the capillary, and the gauge set up in the usual manner. No data about the maximum sensitivity are given. Another way of eliminating the metal filament is to use glass or silica covered wire drawn by the Baker Process. In this process the metal is melted inside the glass and the composite melt drawn into a fine fibre. The combined diameter does not exceed 0·02 mm. The ends of the wire have to be bared for attachment to supports, but the joint, and also the supported wire, may be coated with one of the numerous vacuum waxes to prevent corrosion. It is of interest to note that if copper leads are used on an ordinary Pirani gauge with ammonia corrosion occurs after prolonged use.

Where platinum and nickel cannot be used, the gauge may be made of Pyrex with tungsten leads and wire. Tungsten wires 0·01 mm. thick may be obtained commercially, and so the sensitivity need not be greatly inferior to a gauge of the more normal construction.

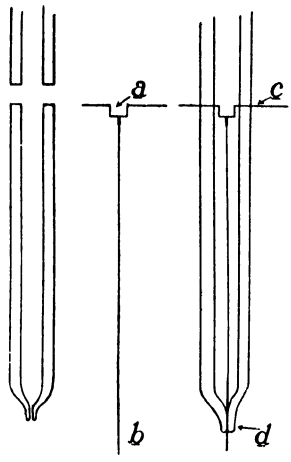


FIG. 48. Micro-Pirani gauge.

Micro-Pirani Gauge

In some experiments it may be necessary to make the volume of a Pirani as small as possible (see below). Fig. 48 shows the method of construction of gauge of volume 0·05 c.c. (H. W. Melville and H. L. Roxburgh, unpublished experiments) made from capillary tube 1 mm. in diameter. 50 mm. of platinum wire, 0·01 mm. in diameter, is spot-welded to 0·3 mm. platinum leads, as shown in Fig. 48. A length of 1 mm. capillary tubing is drawn down at one end, so that the lower platinum lead just slips through. The wire plus leads is slipped into position, and the upper seal made in the way shown. A finely pointed flame is applied for a moment in order to make the lower seal. The weight of the lower leads keeps the fine wire taut during the seal, and the construction of the upper lead insures that the wire shall be central in the tube.

This gauge may be incorporated in an instrument for measuring the pressure and composition of small quantities of gas mixtures, one component of which has a much higher or lower thermal conductivity than the remainder of the constituents (for details see Chap. III, p. 194).

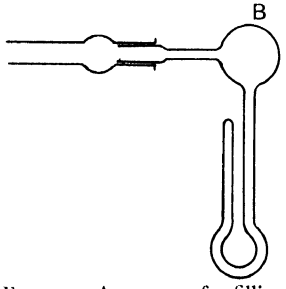


FIG. 49. Apparatus for filling mercury U-tube manometer.

Small Mercury U-Tube Manometers

In a vacuum line it is convenient to have a number of simple U-tube mercury manometers. It is difficult to free the closed limb completely from air. The device shown in Fig. 49 eliminates this difficulty. The U-tube is attached to the bulb *B*, which is filled with the requisite amount of mercury, the manometer being inverted. The whole is pumped out and flamed to get rid of the moisture, *B* is then rotated, the mercury running into the U-tube, which is then cut off.

U-tube Oil Manometers

As a consequence of the production of oils of very small vapour pressure by Burch (*Proc. Roy. Soc.*, **A, 123**, 271 (1929)), working in conjunction with Metropolitan Vickers Ltd., a useful manometric liquid has become available. To double the sensitivity, one of the limbs, B_2, may be made much wider than the other (Fig. 50), the position of the meniscus being read by a low-power microscope. Before use the oil must be thoroughly degassed by heating in a good vacuum. During this process considerable frothing occurs. The bulbs B_1 and B_2 allow the bubbles to break, and prevent oil spray reaching greased taps in the vicinity. With a microscope having a magnification of approximately 10, so that a movement of 0·01 mm. of the meniscus may be detected, a sensitivity of 0·001 mm. is easily attained. If large pressures are to be measured, sufficient time must be allowed for drainage of the oil from the manometer walls. The manometer fitted with a tap as shown in the sketch is very suitable for use as a differential instrument. Unfortunately it cannot be employed for all gases; for example, ethylene and ammonia are quickly absorbed by the oil, but H_2, N_2, O_2, etc., are not appreciably dissolved. Other suitable liquids for such a manometer are *n*-dibutyl phthalate and concentrated sulphuric acid (owing to its high density the sensitivity is only half that of the oil manometer). K. Hickman (*J. Sci. Instr.*, **5**, 161 (1934)) has described an elaborate modification of the simple oil manometer, the liquid used being *n*-dibutyl phthalate. To obviate the necessity of periodically pumping out the closed limb of the gauge by opening the tap connecting the two limbs, a separate butyl phthalate pump is detailed for this purpose alone.

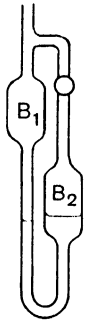


FIG. 50. U-tube oil manometer.

More Sensitive Direct-reading Mercury Manometers

Many attempts have been made to increase the sensitivity of U-tube mercury manometers, but these are all limited by the tendency of the mercury to stick to glass. A sensitivity of 10^{-3} mm. is the best that can be expected. The easiest device is simply to tilt the limbs of the manometer; another consists in joining the vertical limb by a horizontal capillary tube containing a bubble of air (or sulphuric acid) separating the mercury in the two limbs. The position of the air-mercury interface is measured on a suitable scale. The magnification so obtained is simply the ratio of the area of the limb to that of the capillary (cf. B. J. P. Roberts, *Proc. Roy. Soc.*, **A, 78**, 410 (1906)).

Lord Rayleigh (*Phil. Trans.*, **A, 196**, 205 (1901)) constructed the gauge shown in Fig. 51. The two limbs were made wide to avoid trouble with sticking, and each was fitted with glass points just touching the mercury. When a pressure is applied to the right limb, for example,

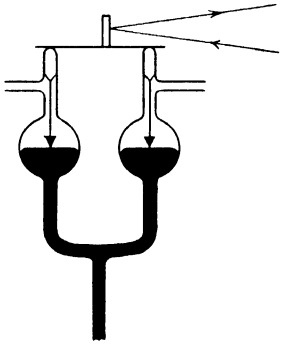


FIG. 51. Rayleigh manometer.

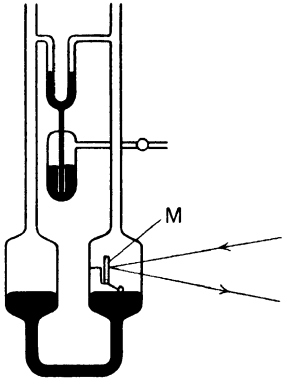


FIG. 52. Shrader-Ryder manometer.

the displacement of the mercury is compensated by tilting the whole manometer in a vertical plane. A mirror attached to the manometer combined with the usual lamp and scale permitted pressures up to 1·5 mm. to be measured to within 10^{-3} mm. This gauge was made less cumbersome by J. E. Shrader and H. M. Ryder (*Phys. Rev.*, **13**, 321 (1919)), who kept the gauge fixed and measured the displacement of the mercury by means of a mirror and float, as shown in Fig. 52.

By paying elaborate attention to detail E. K. Carver (*J. Amer. Chem. Soc.*, **45**, 59 (1923)) has succeeded in making the U-tube manometer sensitive to 0·0001 mm. To attain this degree of sensitivity sticking of the mercury was practicaly eliminated by using extremely wide limbs, by placing the instrument wholly in a thermostat, and by adopting a complicated system for mounting the instrument, which would not in general be convenient for placing close to the usual vacuum apparatus. Carver's method of mounting the mirror may, however, be used advantageously in the less sensitive manometers. The bar carrying the platinised mirror *M* (Fig. 53) has two fine steel points, which rest in a hole and in a groove of the glass stirrup. The float *F* also carries a needle, which bears in a socket placed in an arm attached to the mirror bar. It may

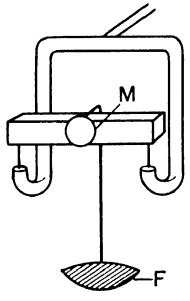


FIG. 53. Reflecting system for Rayleigh manometer.

be mentioned that Carver succeeded in sealing a polished Pyrex window to one limb by heating the surrounding glass to a temperature below the melting point and making the joint by means of a portable blow-pipe.

For modified Rayleigh Gauges, see also K. Newbury and C. L. Utterback, *Rev. Sci. Inst.*, **3**, 593 (1932); K. Scheel and W. Heuse, *Zeit. Instr.*, **29**, 344 (1909); M. Thiesen, *Zeit. Instr.*, **6**, 89 (1886); **24**, 276 (1904); E. Hering, *Ann. d. Physik*, (4) **21**, 320 (1906); C. F. Mundel, *Zeit. phys. Chem.*, **85**, 435 (1913); M. Knudsen, *Ann. d. Physik*, (4) **33**, 1435 (1910).

T. G. Pearson (*Z. phys. Chem.*, **A**, **156**, 86 (1931)) has described a further modification, shown in Fig. 54. *A* and *B* are evacuated, and by

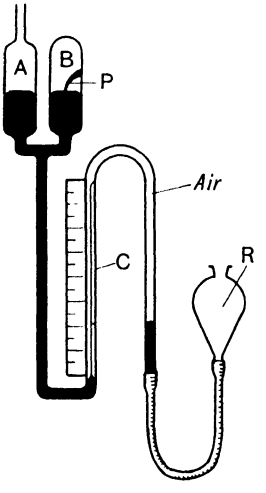


FIG. 54. Pearson manometer.

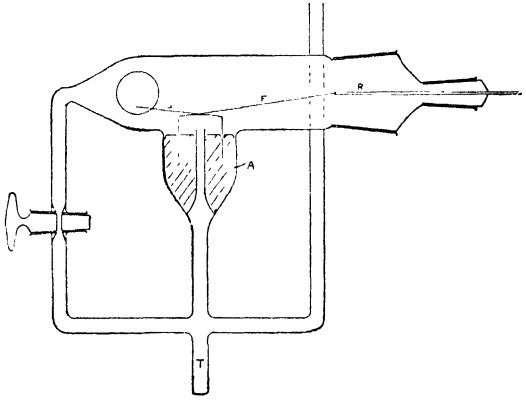


FIG. 55. Inverted cup gauge.

means of *R* the level of the mercury is adjusted to touch the tip of *P* when the mercury stands at some point in the capillary *C*. The gas is then admitted to *A* and *R* lowered until the top of *P* is just uncovered. The position of the mercury in *C* is again read. If p is the difference in the readings in *C*, and r_A and r_C are the radii of *A* and of *C*, then the pressure in mm. in *A* is pr_C^2/r_A^2. In one model the ratio r_C^2/r_A^2 was 177 to 1 and the sensitivity 0·005 mm.

Inverted Cup Gauge

Finally another design may be mentioned which works on an entirely different principle (H. W. Melville, *J. Chem. Soc.*, 2509 (1931)). The manometer consists of a small mounted glass cup, *C*, floating in mercury, as shown in Fig. 55. The simple theory is as follows. Suppose the whole

apparatus is evacuated, then the cup will sink into the mercury until the weight of liquid displaced is equal to the weight of the cup. If a pressure Δp is exerted on, say, the outside of the cup, the total force exerted downwards on the cup is proportional to $\pi r^2 . \Delta p$, where r is the radius of the cup. This will result in the cup sinking further into the mercury by a distance Δx, the weight of the mercury displaced being equal to

$$\Delta x . 2\pi rt . \rho,$$

where t is the thickness of the cup and ρ the density of mercury. For equilibrium

$$\Delta p \pi r^2 = K . \Delta x . 2\pi rt\rho,$$

where K is a constant depending only on the units used to express p. The sensitivity $\Delta x/\Delta p$ is $r/2Kt\rho$. If $r = 1$ cm., $t = 10^{-2}$ cm., and the smallest value of Δx which can be detected is 10^{-3} cm., a sensitivity of 0·001 mm. can be reached.

The cup of the instrument is made by drawing and blowing 1 cm. tube, and cutting into suitable lengths by covering with wax, drawing a furrow in the wax and etching through with hydrofluoric acid. The cup is attached to a bifilar suspension to prevent lateral movement. The small ground joint is eccentric with respect to the large one, so that the cup may be positioned accurately in the side limb.

Bourdon Gauge

This type of gauge and its modifications depend for their action on the movement of a thin diaphragm of glass, soft, Pyrex, or silica under the applied pressure. They are extremely useful in being direct reading, and have the merit that they may be sealed to the reaction system. (Cf. E. Ladenburg and E. Lehmann, *Verh. d. deut. phys. Gesell.*, **8**, 20 (1906); M. G. Johnson and D. McIntosh, *J. Amer. Chem. Soc.*, **31**, 1138 (1909).) They may also be used differentially, but the sensitivity is not greater than 0·002 mm., and usually 0·01 mm. is a good figure. One of the most convenient forms of glass gauge is shown in Fig. 56, which consists essentially of a flattened bulb to which there is attached a long pointer to magnify the motion of the bulb. The whole is enclosed in a glass envelope, which should be as free from striae as possible in order to avoid 'blind' spots when observing the motion of the pointer. The latter is read by a low-power microscope with an eye-piece scale. Owing to imperfections and to size of the glass envelope, the

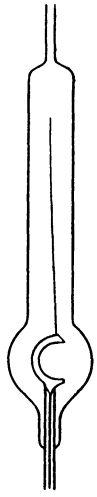


FIG. 56. Bourdon gauge.

magnification cannot be made greater than that capable of detecting a movement of 0·01 mm.

Alternatively an image of the pointer, illuminated by a strong source of light, may be thrown on a scale, or the movement of the pointer caused to tilt a suitably disposed mirror. The more sensitive the gauge the more prone it is to vibration. If a mercury or oil pump is sealed to the apparatus, it is essential that the body of the gauge be firmly clamped, preferably in a vertical position. One disadvantage is the fragility of the flattened bulb. S. G. Foord (*Jour. Sci. Instr.*, **11**, 126 (1934)) has overcome the trouble by designing the gauge as shown in Fig. 57. In this modification the movement of the bulb *B* is limited by a safety ring of glass, *P*, which is attached to the capillary leading to the collapsed bulb. The movement of the pointer *A* deflects a thin fibre, to which a mirror *H* is attached. The whole is placed in a water jacket, so that the gauge may be used differentially. The ground joint facilitates the adjustment of the lever system. With a scale 1 metre away, a few millimetres deflection per mm. change of pressure may be obtained with a bulb sufficiently robust to withstand a pressure of one atmosphere. Another advantage of this mode of construction is that when the arm *A* comes into contact with *P*, further increase of pressure still causes a smaller—*ca.* 1/20—movement of the mirror. This reduction in sensitivity is very useful when balancing the gauge by admitting gas to the envelope. It may be mentioned that a linear relationship exists between applied pressure and deflection. A gauge working on the same principle, but made completely of silica, was first devised by M. Bodenstein and W. Dux (*Z. phys. Chem.*, **85**, 300 (1913)), and consisted of a long thin spiral of flattened silica tubing carrying a mirror at the end to detect the extent of 'unwinding' of the spiral. A recent design by the Thermal Syndicate is shown in Fig. 58, and a usable sensitivity of 0·002 mm. is claimed for the instrument. Unfortunately the repair of such a gauge when broken is an expensive item.

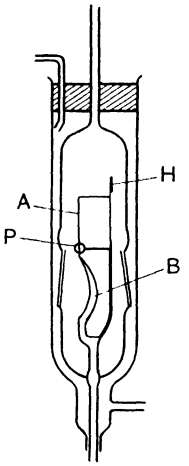


FIG. 57. Foord gauge

Many modifications of this type have been made. For example, the diaphragm has been made flat and attached to the end of a piece of glass tube, and its movement magnified by the usual arrangement of lamp, mirror and scale. In another example the diaphragm was coated with metal foil, opposite to which was another metal plate, so that the two formed a condenser (S. C. Lind and R. Livingston, *J. Amer. Chem. Soc.*,

54, 94 (1932)). The change in capacity of the system on applying pressure is then made to change the resonant frequency of an oscillatory circuit of a thermionic valve, the frequency of which is detected by the sensitive heterodyne method. Again the construction of the diaphragm may be so arranged that, should the pressure exceed a certain value, a distinct click is detectable as the glass adopts a new configuration. This is the so-called 'clicker' gauge (Daniels and Bright, *J. Amer. Chem. Soc.*, **42**, 1131 (1920).)

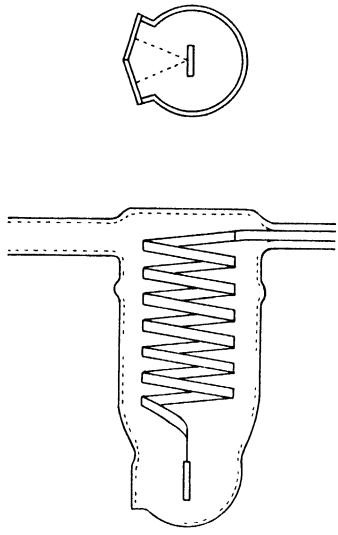


FIG. 58. Quartz spiral gauge.

Rohn gauge. (*Z. Elektrochem.*, **20**, 539 (1914).) This depends for its action on the fact that the e.m.f. generated by a thermocouple, heated by external radiation, depends on the pressure of gas surrounding it. W. E. Garner and F. E. T. Kingman (*Trans. Faraday Soc.*, **27**, 326 (1931)) have made this instrument free from appreciable lag—it attains equilibrium within a few seconds—by using a Moll single thermojunction, illuminating this with a 4 v. 12 watt lamp and measuring the e.m.f. with a Moll galvanometer. The usable range is 10^{-4}–1 mm. The calibration must be effected for each gas to be dealt with, and is not linear, though in Garner and Kingman's gauge for a limited range, viz. 10^{-1} – 10^{-2} mm., the galvanometer deflection is approximately proportional to the logarithm of the gas pressure.

Ionisation gauge. The ionisation gauge (E. O. Buckley, *Proc. Nat. Acad. Sci.*, **2**, 683 (1916) ; Masamichi So, *Proc. Phys. Math. Soc.*, Japan, **1**, 76 (1919) ; S. Dushman and C. G. Found, *Phys. Rev.*, **17**, 7 (1920) : **23**, 734 (1924)) is one of the most sensitive manometers available. Since, however, the Pirani gauge may also be made very sensitive, the ionisation gauge, at any rate for most chemical purposes, is not particularly useful. The mode of working is as follows. Electrons from a thermionic cathode are accelerated by a voltage considerably greater than the ionisation potential of the gas whose pressure is to be measured. As a result the molecules of the gas are ionised by electron impact, and the positive ions so formed are collected by an electrode maintained at a negative potential with respect to the thermionic cathode. At low pressures the number of positive ions produced is proportional to the thermionic current and to the pressure of gas in the tube. A triode valve is suitable for such a

gauge, but it is advisable to use one with a molybdenum anode (e.g. Marconi L.S. 5), in order that this electrode may be thoroughly degassed after sealing to the vacuum line. The usual connections of the triode are reversed, the grid acting as the anode and the anode as the positive ion collector. The valve may also be used normally, but the gauge is not then so sensitive. The usual circuit arrangement is shown in Fig. 59. The milliammeter and ammeter are inserted so that the emission of the filament may be kept steady. *G* must be a microammeter to measure the positive ion current. The voltages naturally depend on the valve, and in Dushman and Found's set up were +240 on anode, −22 volts on collector. A plot of their calibration curves is shown in Fig. 60 (Fig. 88, Kaye, p. 150), where ionisation current is graphed against argon pressure. The larger the thermionic emission the greater the sensitivity, but the sooner does the curve depart from linearity. It is estimated that the manometer is sensitive to 10^{-8} mm. Unlike the Pirani gauge, the zero of the ionisation

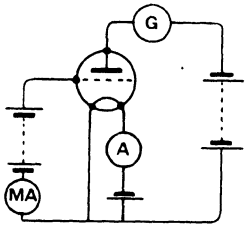


FIG. 59. Electrical circuit for ionisation manometer.

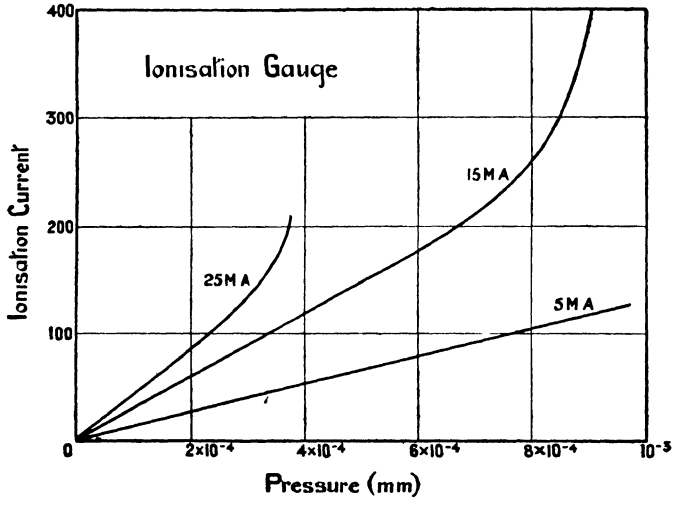


FIG. 60.

manometer is well defined in that it definitely indicates the presence of any gas, whereas the normal procedure with a Pirani is to pump until the lowest reading is attained, having made certain there are no leaks in the vacuum system.

In using gases other than those of the inert group it must be remembered

that possible interaction with a hot filament may vitiate pressure measurements completely. E. K. Jaycox and H. W. Weinhardt (*Rev. Sci. Instr.*, **2**, 401 (1931)) describe in detail the construction of a gauge which is rather a different type compared with that of Dushman and Found. In order to obtain greater sensitivity, particular attention is paid to the insulation. Two thoriated filaments are used—one for bombarding the grid and anode, and the other for operating the gauge. Barkhausen oscillations are also eliminated by the disposition of the elements in the tube. A circuit is also given to show how the gauge may be used for automatic registration and for the operation of relays. The sensitivity is about 10^{-8} mm.

Cf. also H. Simon, *Z. tech. Physik*, **5**, 221 (1924) ; for amplifier for ionisation gauge, see C. G. Found and N. B. Reynolds, *J.O.S.A. and R.S.I.*, **13**, 217 (1926) ; M. D. Sarkey, *Electronics*, April 1931, p. 594.

'Viscosity' gauges. When a body is allowed to vibrate in an enclosure containing a gas the vibrations decrease in amplitude, due (1) to the inelasticity of the supports, and (2) to the viscosity of the surrounding gas. The viscosity does not depend on pressure until the free path of the molecules in the gas becomes comparable with the dimensions of the apparatus (Kundt and Warburg, *Pogg. Annal.*, **155**, 340 (1875)). The logarithmic decrement of the vibrating system then depends on pressure, and in principle may be made the basis of a manometer (W. Sutherland, *Phil. Mag.*, **43**, 83 (1897)). M. Knudsen (*Ann. d. Phys.*, **44**, 525 (1914)) has gone into the question quantitatively; and has constructed a manometer which consists of an oscillating sphere enclosed in another larger sphere. The Langmuir-Dushman gauge (I. Langmuir, *Phys. Rev.*, **1**, 337 (1913) ; S. Dushman, *Phys. Rev.*, **5**, 212 (1915)), on the other hand, contains two discs, one of which is attached to a magnet borne on pivots, so that the whole may be set in motion by a rotating magnetic field. The other disc, placed directly above the first, receives a torque by the impact of molecules upon it, and so is deflected. To illustrate the approximate theory of this type of gauge the disc pattern will be considered. If the pressure is low enough the viscous drag B on one plate, moving past another at a speed u, can be shown to be given by

$$B = \frac{k}{\alpha}\sqrt{\frac{2}{\pi}}p \cdot u\sqrt{\frac{M}{RT}},$$

where $k \doteqdot 1/3$ and α is a coefficient which is a function of the accommodation coefficient of the gas on the moving surfaces. The viscous couple opposing the motion of the disc per unit angular velocity is

$$2\int_0^r \frac{k}{\alpha}\sqrt{\frac{2}{\pi}}p \cdot \sqrt{\frac{M}{RT}}\,2\pi r^3 dr = \pi r^4 \frac{k}{\alpha}\sqrt{\frac{2}{\pi}}\sqrt{\frac{M}{RT}}p = c_1.$$

Let that due to the suspension system be c_2. If a is the amplitude of the oscillation, then k, the logarithmic decrement, is defined by

$$\frac{da}{dt} = -ka,$$

or

$$k = ln\, 2/t_{\frac{1}{2}},$$

where $t_{\frac{1}{2}}$ is the time required for a to fall to half its initial value. But

$$k = (c_1 + c_2)/2I,$$

and hence

$$\pi r^4 \frac{k}{\alpha} \sqrt{\frac{2\bar{M}}{\pi \mathbf{R}\bar{T}}}\, p + c_2 = 2I\, ln\, 2/t_{\frac{1}{2}}.$$

c_2 is easily evaluated when $p = 0$. Like the Pirani gauge, a manometer of this nature is not an absolute instrument, since the value of α cannot be calculated. It therefore requires calibration.

A practical and useful form, though extremely simple in construction, has been devised by F. Haber and F. Kerschbaum (*Z. Elektrochem.*, **20**, 296 (1914)), following an observation of I. Langmuir (*J. Amer. Chem. Soc.*, **35**, 107 (1913)). The gauge consists of single quartz fibre, 9 cm. long

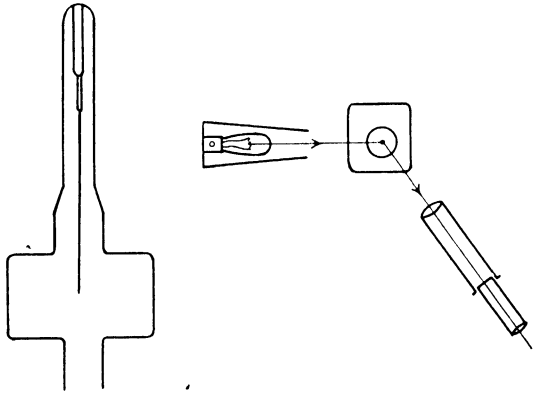


FIG. 61. Quartz fibre manometer.

and 0·2 to 0·4 mm. in diameter, mounted as shown in Fig. 61. Illumination is best done with a dark background, and the amplitude of the motion is observed by a microscope fitted with an eyepiece scale. A gentle tap is all that is necessary to set the fibre vibrating. Some practice is necessary, for it is not easy to persuade the fibre to vibrate in one plane. From the above simple theory it will be evident that

$$t_{\frac{1}{2}}^{-1} = A + B\sqrt{\bar{M}}\, p,$$

where B is a characteristic constant for the gas employed. For example,

in one of the gauges $t_{\frac{1}{2}}$ for $p = 0$ was 89 sec., dropping to 50 sec. on admitting 0·0065 mm. air. The above equation holds sufficiently well up to 0·02 mm. To show the range of pressures measurable, the following results may be quoted for a thin fibre—0·2 mm.—having a large value of $t_{\frac{1}{2}}$ for $p = 0$.

Pressure (mm.)	$t_{\frac{1}{2}}$ (sec.)
0 00002	750
0 00017	720
0·0010	460
0·0112	119
0 0136	100
0 0315	46
0·048	32
0·0724	23
0 1203	16

To surmount the difficulty of the non-planar motion of the fibre, A. S. Coolidge (*J. Amer. Chem. Soc.*, **46**, 680 (1924); **45**, 1637 (1927)) has adopted a bifilar suspension, as shown in Fig. 62. The apparatus, with the exception of the fibres, 9 cm. long, 0·004 mm. diameter, is made of Pyrex. The two fibres are joined by a glass tip to decrease the frequency, and therefore rate of damping of the vibrations, in order that the logarithmic decrement may be measured at pressures so high that the ordinary fibre would be brought to rest in a few seconds. The guard ring prevents breakage, and the projecting points permit of the determination of the time required for the amplitude of vibration to fall to a series of values to be noted, in order to save time in observation. Above 0·1 mm. the above equation ceases to hold, and it is then necessary to calibrate the gauge by a large number of measurements. In this way it may be used up to 1 mm. pressure. As was pointed out in the introduction, the uncertainty in the value of the accommodation coefficient precludes the employment of the gauge as an absolute instrument. None the less Coolidge found empirically that the value for B in the above equation is identical for C_2H_2, CS_2, SO_2, SiF_4, H_2O, NH_3, H_2 and air. Temperature control had to be precise. E. B. King (*Proc. Phys. Soc.*, **38**, 80 (1925)) has made still another form of the gauge shown in Fig. 63, in which the oscillations are photographed. The working part of the gauge is made wholly of silica to avoid temperature control troubles. Two fibres are used, the horizontal one being fused at the ends, so that it reflects light

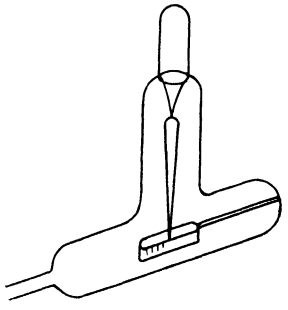


FIG. 62. Bifilar quartz fibre manometer.

from a lamp through a lens and prism on to a photographic plate. The fibre is set into oscillation by bringing up a magnet to the side of the apparatus, a small piece of iron having been fixed at the junction of the fibres. The right-angled prism is rotated so that a trace of the damped oscillation may be spread along the plate ; naturally the method is more tedious than direct observation of the decrement.

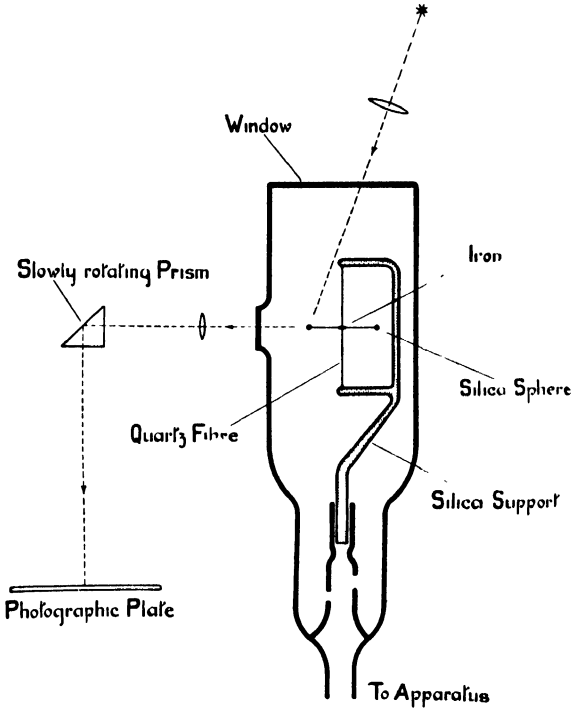


FIG. 63. King's quartz fibre manometer.

According to K. F. Bonhoeffer and L. Farkas (*Z. physik. Chem.*, **132**, 243 (1928)) the damping of the quartz fibre manometer is considerably decreased by making a constriction on the fibre by pulling it somewhat when it is sealed to the stem.

Absolute low pressure manometer. Let two parallel plane plates be placed in an enclosure containing gas at a pressure p_2 such that the mean free path is large compared with the distance between the plates, and the temperature of the sides of the plates facing each other is T_1 and that of the enclosure T_2. Then p_1, the mean pressure between the plates, will be given by $p_1 = p_2\sqrt{T_1/T_2}$ (see p. 20). The plates will be repelled by a force $p_1 - p_2 = p_2(\sqrt{T_1/T_2} - 1)$ dynes per cm.^{2}. It is important to note

that this is independent of the nature of the gas, and hence if an arrangement can be made to measure this pressure an absolute manometer is obtained. The construction of such an absolute manometer has been achieved by M. Knudsen (cf. *Kinetic Theory of Gases*, p. 42 : Methuen), but as it is by no means an easy task, various modified designs, requiring calibration, have been suggested. Since these are but rarely used in practice no description of them will be given here. Knudsen has described his manometer in his book (*loc. cit.*) ; L. Dunoyer (*Vacuum Practice*) gives a complete account of the problems and their practical solution ; and finally W. Gaede has designed a manometer (*Z. f. tech. Physik*, **12**, 664 (1924)) which has been placed on the market.

Absolute manometer for measuring pressures up to 0·05 mm. V. Deitz (*J. Chem. Physics*, **4**, 575 (1936)). The principle of the manometer consists in measuring the pressure experienced by a quartz disc suspended in a chamber containing the vapour or gas being examined. One such manometer has been designed by W. H. Rodebush and C. E. Coons (*J. Amer. Chem. Soc.*, **49**, 1953 (1927)). The model shown in Fig. 64 is an improved pattern, especially made for measuring the vapour pressure of potassium chloride and caesium iodide. As will be seen from the diagram, the manometer is easily adaptable for other purposes. The only disadvantage of this absolute manometer is that gas or vapour has to be continuously applied to the measuring chamber owing to leakage past the silica disc. The main part of the apparatus is made of transparent fused silica. The disc *L* is of fused silica, 2·5 cm. diameter and not more than 1 mm. thick. This has an upper ground surface to seat accurately on *J*. The disc is supported by a silica fibre, which terminates in an iron core *C* enclosed within a glass tube. This in turn is supported on another silica fibre attached to a 10-inch cantilever arm ending in a fine point *B* for purposes of observation through a microscope. A solenoid *D* when energised exerts an upward pull on *C*. The ground seat *J* is sealed to tube *F*, which in turn is attached to the rest of the apparatus by a waxed joint. Tube *H* is also fused to *G* and ground on the upper surface so as to make good contact with *F*. *G* is waxed to *F* as shown, and water-cooled if there is a furnace around the lower part of *F*. In practice the current in the solenoid is adjusted until the disc just falls off its seat

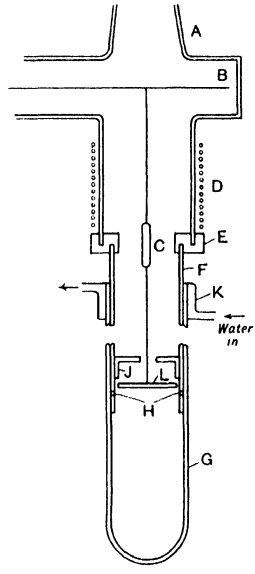


FIG. 64. Absolute low pressure manometer.

as observed by means of the cantilever arm. The manometer may be calibrated directly with a McLeod gauge. In the pattern illustrated the current required to keep the disc attached to its seat was 670 mA., while at a pressure of about 0·03 mm. it fell to about 100 mA. It may also be calibrated directly by removing the disc and hanging weights on the quartz fibre. A vacuum of 10^{-5} to 10^{-6} mm. has to be maintained on the upper side of the silica disc. The ground joint *A* is closed by a tube containing liquid air.

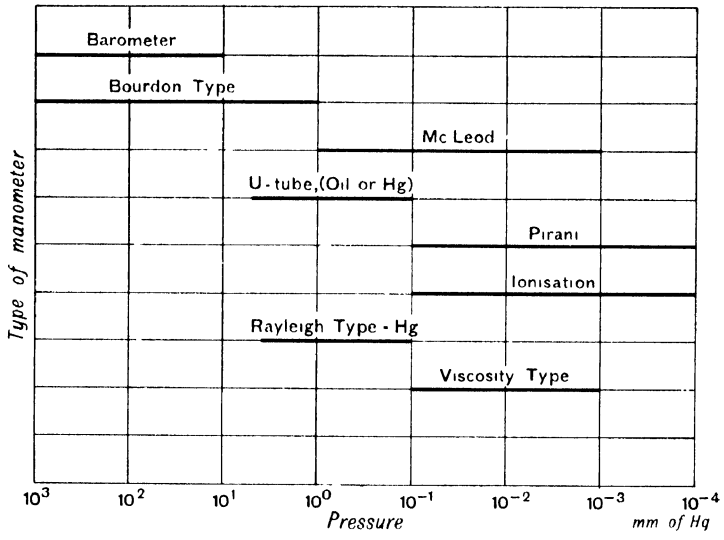


FIG. 65.

Fig. 65 shows the ranges in which the above gauges can most conveniently be employed, the criteria being linearity of response and at least an accuracy of 1 per cent.

Gaede's vacuscope. Gaede has described a compact U-tube manometer and small McLeod gauge, which is suitable for measuring pressures from 10^{-2} mm. to 80 mm. The form of the gauge is shown in Fig. 66. It is attached to the apparatus by pressure rubber tubing. It is evacuated in the horizontal position. If a high pressure is to be measured, it is then tilted into position 2 and the gas allowed into the gauge, the difference in levels giving the pressures. If, however, the pressure is low, the gas is admitted to the gauge, which is then tilted into position 3. Since the capillary of the McLeod gauge is small compared with the diameter of the body of the gauge, the position of the mercury meniscus at *g* is practically independent of the pressure, and hence the capillary may be calibrated directly to read pressure in mm. of mercury. The volume of

mercury in the gauge must, of course, be such that the level in *g* is opposite to the top of the capillary. Owing to the small degree of compression small pressures of vapours may be estimated with some degree

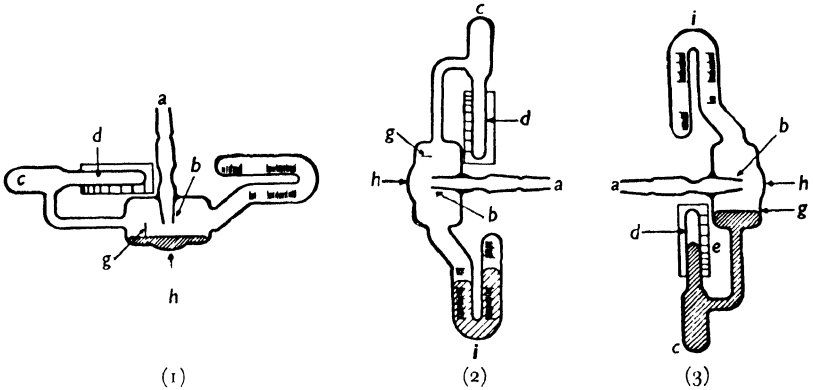


FIG. 66. Gaede vacuscope.

of accuracy. This makes the vacuscope useful in the distillation of organic compounds under reduced pressure.

Wrede-Harteck slit gauge for atomic hydrogen. (E. Wrede, *Z. Physik*, **54**, 53 (1929); P. Harteck, *Z. phys. Chem.*, **A139**, 98 (1928).) If a stream of atomic hydrogen passes an orifice *O*, the pressure being such that the mean free path of the hydrogen atoms is greater than the diameter of the orifice, then, from the condition for equilibrium, it may be shown that the pressure outside the orifice is greater than the pressure in the closed space on the other side of the orifice *O* Fig. 67 (*a*). H. M. Chadwell and T. Titani (*J. Amer. Chem. Soc.*, **55**, 1363 (1933)) use a sintered glass plug instead of a single orifice. This happens because atomic hydrogen enters *O* and combines to H_2 in the tube attached to one arm of the manometer. If therefore a differential manometer is connected to the tube through which the atomic hydrogen is flowing by two tubes, one of which is larger and the other which is smaller than the mean free path of atomic hydrogen, it will show a deflection. In general 100 per cent. atomic hydrogen is not dealt with, and the gauge is therefore used to determine the percentage of atomic hydrogen in a mixture of atoms and molecules. The condition for equilibrium is that equal masses of gas shall traverse the orifice in opposite directions. Hence applying the effusion equation and supposing p_1 and p_2 to be the pressures in the flow tube and in the tube attached to the orifice,

$$p_2\sqrt{\frac{M_{H_2}}{T}} = xp_1\sqrt{\frac{M_H}{T}} + (1-x)p_1\sqrt{\frac{M_{H_2}}{T}},$$

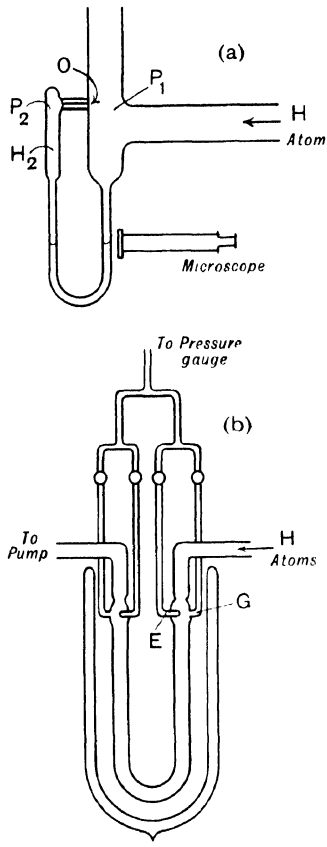


FIG. 67. Harteck's slit gauge.

where x is the fraction of atomic hydrogen in the stream. Solving for x,

$$x = \frac{1 - p_2/p_1}{1 - 1/\sqrt{2}},$$

and for $x = 1$, $p_2/p_1 = \sqrt{2}$.

The arrangement adopted by Harteck (*loc. cit.*) is shown in Fig. 67 (*b*), the apparatus being set up for the purpose of measuring the viscosity of atomic hydrogen. The diameter of the orifice was 0·04 mm., and the diameter of the U-tube 6 cm. The manometer used for measuring the pressures was a hot wire instrument. In one series of experiments the pressure of streaming molecular hydrogen at E and G was 0·490 mm. When the discharge was switched on the pressure in E rose to 0·552 mm., while that in the tube attached to the orifice at G was 0·440 mm., and therefore $x = 0{\cdot}68$. At these pressures it will be evident that a differential oil manometer is also suitable for measurement of pressure. Having regard to conditions specified above, it is obvious that the gauge is only useful within a limited pressure range.

Calibration of sensitive manometers. The calibration of a McLeod gauge may be made by measuring the volume of its constituent parts. Calibration can also be effected by a simple type of apparatus used by M. Knudsen (*Ann. d. Phys.*, **44**, 581 (1919)), which consists of a number of bulbs (Fig. 68 (*a*)) in series. Gas at a pressure measurable accurately on an ordinary barometer is expanded from one bulb to another until the desired pressure range is reached. This apparatus cannot be used satisfactorily for calibrating gauges at very low pressure, since the presence of taps precludes thorough baking out—a vital necessity for such a purpose.

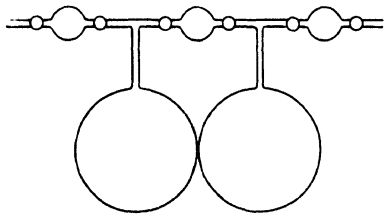


FIG. 68 (*a*). Apparatus for calibration of manometers.

To overcome the difficulty Dushman and Found (*Phys. Rev.* **17**, 7 (1920) ; **23**, 734 (1924)) have devised the apparatus shown in Fig. 68 (*b*), which makes use of the laws of flow of gas at low pressures investigated thoroughly by Knudsen (see e.g. *Kinetic Theory of Gases* : Methuen). The principle of the method is to allow gas at a pressure high enough to be read accurately on a McLeod gauge to stream through a fine capillary into an evacuated container to which the gauge is connected. The gas is passed into A. Trap V_1 is shut and V_2 opened at a known time. The use of mercury traps allows the whole apparatus to be baked out. From the dimensions of the capillary and the volume of

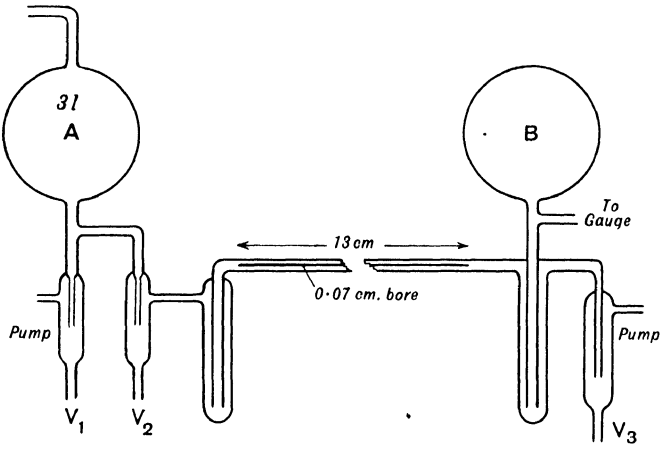


FIG. 68 (*b*).

the gauge system, the pressure at any instant may be calculated in the following way. (Dunoyer, *Vacuum Practice*, p. 109 : Bell.) Let d and l be the diameter and length of the capillary tube, p_A and p_B the respective pressures in A and B at the time t, and the mean pressure $p=\frac{p_A+p_B}{2}$. If v is the volume of gas flowing per second measured at the mean pressure and ρ the density at 1 microbar (1 dyne cm.$^{-2}$), then Q, the mass flowing per sec., is $v\rho p$. According to Knudsen, when the mean free path is large compared with diameter of the tube through which the gas is flowing (cf. p. 19),

$$vp=\frac{\pi}{3\sqrt{2}}\cdot\frac{d^3}{l}\cdot\frac{1}{\rho^{\frac{1}{2}}}(p_A-p_B),$$

$$Q=\frac{\pi}{3\sqrt{2}}\cdot\frac{d^3}{l}\cdot\rho^{\frac{1}{2}}(p_A-p_B).$$

If V is the volume of B plus that of the gauge, then in time dt the pressure will have risen dp and

$$Q\,dt = V\rho\,dp,$$

and hence

$$\frac{dp}{dt} = \frac{\pi}{3\sqrt{2}} \cdot \frac{d^3}{l} \cdot \frac{1}{\rho^{\frac{1}{2}}} \cdot \frac{p_A}{V},$$

since $p_B \ll p_A$ and p_A is nearly constant, or

$$p = \frac{\pi}{3\sqrt{2}} \cdot \frac{d^3}{l} \cdot \frac{1}{\rho^{\frac{1}{2}}} \cdot \frac{p_A}{V} \cdot t.$$

Knudsen (*Kinetic Theory of Gases*, p. 44 : Methuen) has elaborated the expansion chamber apparatus shown in Fig. 68 (*b*) to get more precise pres-

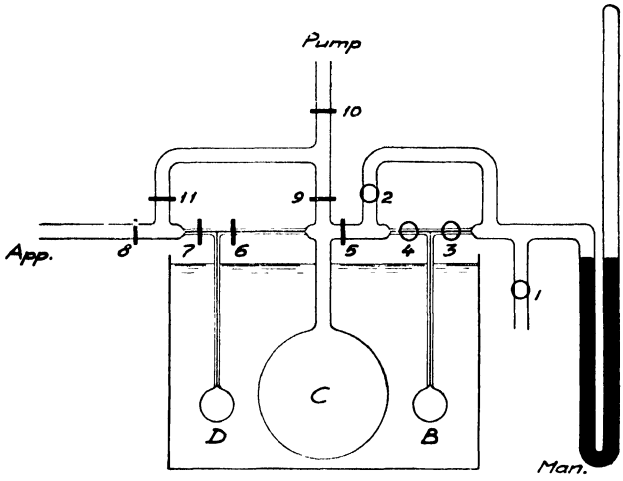


FIG. 68 (*c*).

sure regulation. The apparatus is shown in Fig. 68 (*c*), the expansion bulbs being thermostatted. The manometer has a 2 cm. diameter limb, so that the pressure may be measured to within 0·05 mm. The symbol O stands for an ordinary tap ; ⧺ denotes a mercury cut-off.

Certain precautions must be taken in calibrating a gauge with a McLeod gauge as standard in which a liquid air trap is used to freeze out the mercury-vapour. In order to prevent errors in the readings, it is essential to have the diameter of the inlet and outlet tubes of the trap identical. The simplest trap consists of a U-tube dipping into liquid air. To show the magnitude of the effect, the extreme case occurs when the diameter of one tube is large and the other small compared with the mean free path of the gas. In the large tube (Fig. 69) the pressures below and above the level of the liquid air are equal, but in the small tube, owing

to the effect of effusion, the pressure below the level of the liquid air is $(T_1/T_2)^{\frac{1}{2}}$ times that above the level of the liquid air (T_1 is the higher temperature and T_2 the lower). J. K. Roberts (*Proc. Roy. Soc.*, **A**, **135**, 194 (1932)) has made measurements on helium and argon to find at what pressure corresponding to a mean free path λ_1 for a tube of given diameter d_1 this effect obeys the effusion correction exactly. For helium and argon, if d_1/λ_1 is greater than 2 the correction holds exactly. λ_1(He) at 1 mm. pressure is 0·02 cm., and λ_1(A) at 1 mm. pressure is 0·0075 cm. For pressures above that at which the exact correction is made, it is best to make separate calibration experiments to determine the correction to be applied for any given gas.

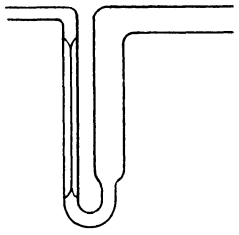


FIG. 69.

In the case where the mean free path is not indefinitely small compared with the diameter, M. Knudsen (*Ann. d. Physik*, **34**, 593 (1911)) has deduced the following expression :

$$p_1 - p_2 = \frac{\lambda\, 10^4}{7{\cdot}28\, d}(T_1 - T_2) \text{ dynes cm.}^{-2}.$$

E. CONTROL OF PRESSURE

Manostat for adsorption experiments. (H. S. Taylor and C. O. Strother, *J. Amer. Chem. Soc.*, **56**, 586 (1934).) The reservoir R_a (Fig. 70) is adjusted to the desired pressure. As the gas is sorbed the mercury rises and makes contact with the tungsten point at *E*. This operates the relay, which in turn generates electrolytic gas in *E.C.*, thus forcing the mercury in *R* down, the level rising in the burette *B* until the contact is broken at *E*. Several amperes are necessary to operate *E.C.* to avoid time lag. S_3 is for blowing off gas at the end of a run. S_1 is kept open to the sorbent.

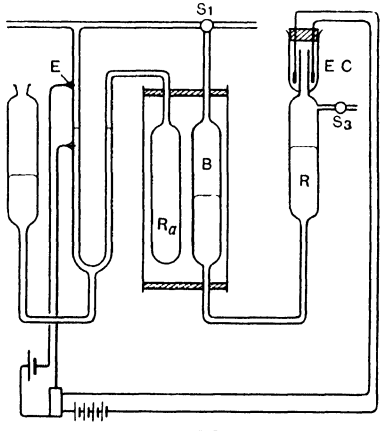


FIG. 70. Manostat.

In some experiments, e.g. adsorption or desorption work, it may be necessary to maintain the pressure in the reaction system at a well-defined value, while in addition provision has to be made for measuring the volume of gas adsorbed or desorbed during the process. The con-

struction of the necessary manostat is then not simple, but the following apparatus devised by T. Soller, S. Goldwasser and R. A. Beebe (*J. Amer. Chem. Soc.*, **58**, 1703 (1936)) permits the pressure to be kept constant to about 0·01 mm. at any pressure up to atmospheric, since the device works differentially. The main idea is that a differential manometer fitted with a mirror actuates a photo-electric relay, which in turn opens a needle valve, thus allowing gas to enter the system under observation. The controlling manometer may either be of the Rayleigh type (p. 83) or of the Bourdon type modified by Foord to carry a reflecting mirror. The main part of the apparatus is shown in Fig. 71 (*a*). First it is necessary

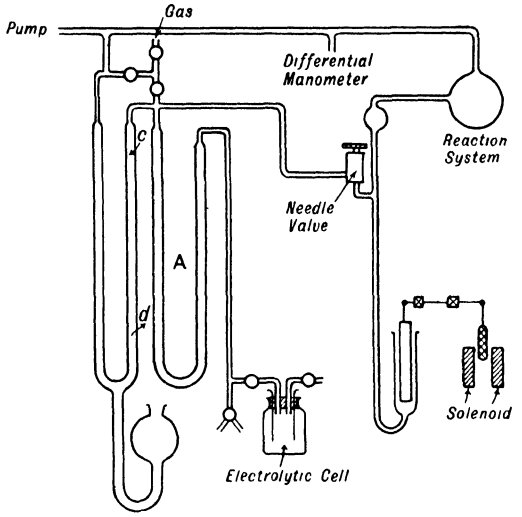


FIG. 71 (*a*). Photoelectrically controlled manostat.

to have a rough manostat to control the gas on the high pressure side of the needle valve. This consists of two U-tubes, one of which is fitted with sealed-in platinum or platinum-tipped tungsten wires at *c* and *d*. A mercury reservoir is used to set the pressure initially. When the pressure falls, the mercury, upon which a platinum-tipped iron plate floats, rises to make contact at *c*, thus switching on by means of a relay an electrolytic cell, through which 3 amperes are allowed to pass. This raises the level of the mercury in the larger U-tube, and brings the pressure of gas up to the correct value. The steel needle valve is of similar construction to those described on p. 64, but in order to have a positive cut-off a steel ball is recessed into the base of the valve, as shown in Fig. 71 (*b*). The body of the valve must, of course, be of steel. When the pressure in the reaction system changes the beam of light reflected from the mirror of the manometer falls on the photo-electric cell. The photo-

current is amplified by a two-stage directly coupled circuit, shown in Fig. 71 (*c*), when it works a relay, thus energising the solenoid and so allowing the mercury to uncover the orifice of the needle valve. The apparatus is stated to be sensitive enough to admit 0·008 c.c. of gas at N.T.P. at a dose. If gas is to be withdrawn from the reaction system the apparatus is much simplified, as it is then only necessary to have a vacuum pump on the other side of the needle valve. The first valve is a radio frequency pentode. Each valve must be supplied from a separate winding on the feeding transformer, self-rectification occurring. The voltage applied to the cell will depend on the type used; a potentiometer is included in the circuit to vary the sensitivity of the circuit. A straight filament exciter lamp of 30 watts or more is suitable. The relay must be capable of taking an input of about 20 mA., and controlling 10 amps., as 100 watts are required to energise the solenoid. The core of the solenoid must be suitable for working on alternating current. (A circuit diagram for American photo-cells and valves is described in the original paper.)

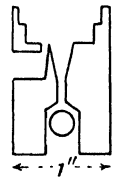


FIG. 71 (*b*).

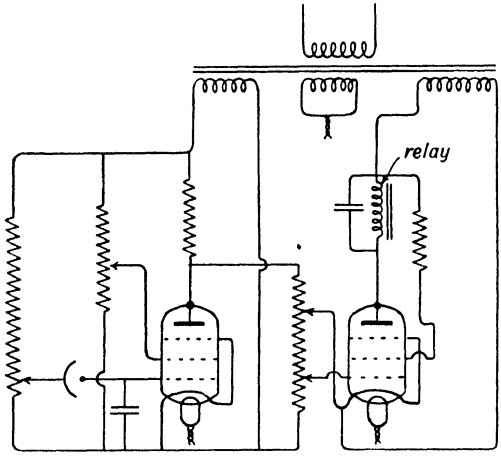


FIG. 71 (*c*).

Manometer and source for hot vapours. (C. T. Zahn, *Rev. Sci. Instr.*, 1, 299 (1930).) This is a device for supplying or maintaining the pressure of a vapour at any desired and easily measurable value up to the temperature of the boiling point. The normal procedure is simply to use a mercury manometer, or where mercury is undesirable a balanced Bourdon gauge, but vapours generally dissolve in taps connecting the Bourdon gauge to the apparatus. This difficulty is overcome in the present instance by using the liquid itself as the isolating liquid and balancing manometer.

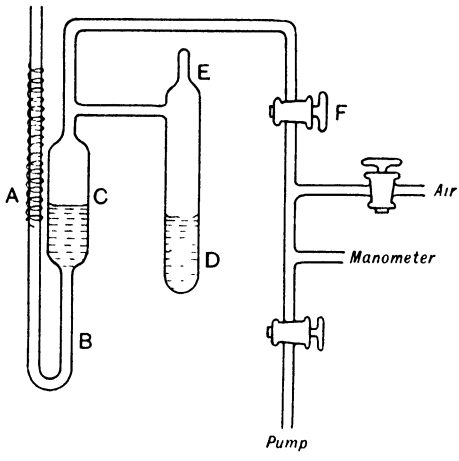


FIG. 72. Manometer and source for hot vapours.

The mode of operating will be clear from Fig. 72. Liquid is run in at *E* into *D* and distilled over to *C*. The apparatus is evacuated and the connecting tubing, wound with nichrome wire, heated to the desired temperature. Air is passed through *F* until the desired pressure is reached, as indicated by the mercury manometer. As a result, liquid rises in *A* until it meets the hot tube, thus vaporising until the pressure in the apparatus is equal to that of the air and vapour in *CED*. The capillary *B* prevents violent oscillation of the liquid in the U-tube. The air must be let in slowly to avoid too rapid evaporation in *A*.

Flow meters.

The simplest type of flow meter consists of a constricted tube through which the gas flows, and across the ends of which the gas pressure so developed may be easily measured. A typical flow meter is shown in Fig. 73 (*a*) The manometric liquid may either be mercury, or if greater sensitivity is required a low vapour pressure oil, or if the gases are saturated with water vapour, water is a suitable liquid. The instrument may be calibrated by measuring the dimensions of the capillary, assuming streamline flow and calculating from the observed pressure difference the rate of flow by means of Poiseuille's equation (cf. p. 20) It is easier and more accurate to calibrate by measuring the volume of gas delivered by the capillary at a known pressure, gas aspirators being used for the purpose. A more elaborate type of meter is shown in Fig. 73 (*b*). In this the capillary tubes are interchangeable, each being attached to a standard ground joint. For low pressures the simple U-tube manometer may be replaced by two identical McLeod gauges.

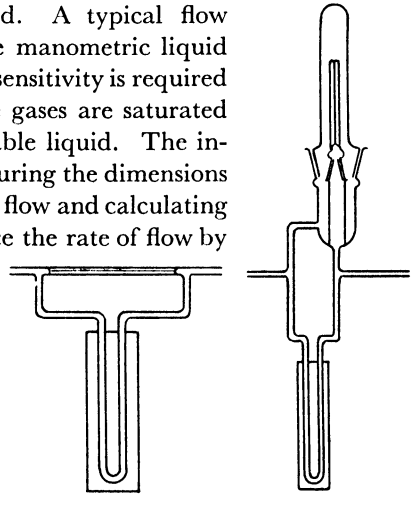


FIG. 73. Flow meters.

F. MEASUREMENT OF TEMPERATURE

In the investigation of gaseous reactions the temperature to be measured may vary from that of liquid hydrogen (20° K.) to the melting point of tungsten (3650° K.). On the one hand the temperature of a liquid or of a furnace may require to be measured, and on the other the temperature of an incandescent filament. In order to facilitate a choice of the appropriate instrument for a particular temperature region, the following diagram (Fig. 74) shows the convenient working ranges of a number of common thermometers. Innumerable designs of such instruments have

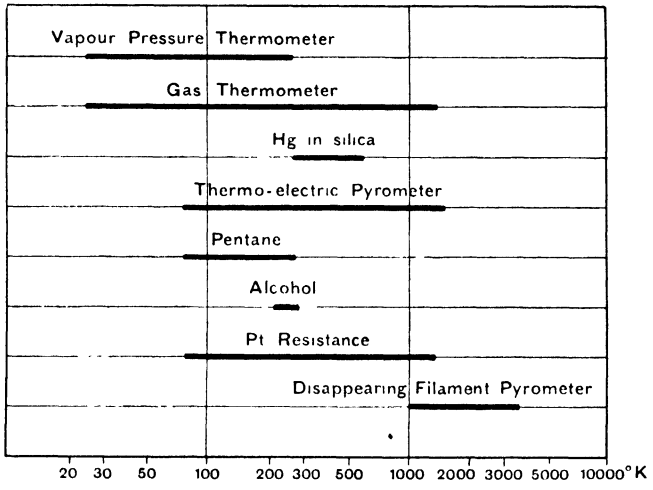


FIG. 74.

been described, and hence space will only permit an account of one or two of the standard types most frequently met with in practice.

The vapour pressure thermometer necessarily has a restricted range on account of the exponential dependence of vapour pressure on temperature, but this very defect may at times prove a distinct advantage, as, for example, in using an oxygen thermometer to determine the temperature of liquid air.

The gas thermometer has a most extensive range if the bulb is fabricated of an element of high melting point, such as iridium, and the gas, e.g. helium, is impermeable to the metal at high temperatures. Such a thermometer requires elaborate manometric arrangements, and often the bulb is inconveniently large for many purposes.

The pentane thermometer is very useful for measuring temperatures from that of liquid air, and the alcohol thermometer is no less useful for measuring the temperature of baths cooled with solid carbon dioxide. For accurate work both these thermometers require calibration against a

vapour pressure or gas thermometer. Next there is the usual mercury glass thermometer, whose upper range may be extended to 550° C. by constructing it of silica glass and filling under pressure with nitrogen.

For temperature ranges from 0° C. to 1400° C. a thermocouple is the most widely-used measuring instrument. The voltage developed may be accurately measured by a potentiometer, or by a high resistance millivoltmeter such that temperatures may be read to within 0·1°. It may, of course, be used at low temperatures.

Perhaps second in importance to the thermo-electric thermometer comes the platinum resistance thermometer. The resistance element of this instrument takes up rather more space than the junction of a thermocouple, and hence it is necessary to have a large space at a uniform temperature to ensure accuracy of working. It cannot, for instance, be used to explore the temperature distribution in a small furnace.

At higher temperatures where silica softens, radiation pyrometers must be employed. In recent practice these are of two types : the first in which the brightness of a heated filament of a tungsten lamp is compared with that of the hot body by superposing it on the hot body used as background, that is, the so-called disappearing filament pyrometer ; and the second in which the brightness of the hot body is compared with standard illumination provided by an incandescent filament run under specified conditions, matching being accomplished by reducing the intensity of one of the sources by crossed Nicol prisms—the half-shadow type. The former type is especially useful for determining the temperature of incandescent filaments.

The vapour pressure thermometer. The vapour pressure thermometer depends on the variation of the vapour pressure with temperature. Vapour pressures of thermometric substances have been determined by F. Henning and A. Stock (*Z. Physik*, **4**, 227 (1921)), using a platinum resistance thermometer, the thermodynamical temperature scale being taken as a basis.

A thermometer constructed according to dimensions given by A. Stock (*Z. Elektrochemie*, **29**, 354 (1923)) is shown in Fig. 75. An amount of mercury sufficient to fill the manometer is placed in bulb *A*, heated and transferred to tube *M* after the instrument has been evacuated. Then tube *B* is cooled, and the thermometric substance is introduced until 1-2 c.c. have condensed in *B*. The apparatus is sealed off at *C* and tube *B* is warmed to room temperature. Excess gas bubbles out through *D*. The pressure in the apparatus is now about 1000 mm. ; therefore tube *B* is again cooled until the pressure falls below atmospheric, and the thermometer is sealed off at *E*. The thermometer is then ready for use. The glass spiral serves to make tube *B* slightly flexible. It is most essential

that the apparatus and gases should be absolutely free of air. Good thermometers rapidly come to the reading point, and show zero pressure if tube *B* is cooled with liquid air (provided easily condensable gas has

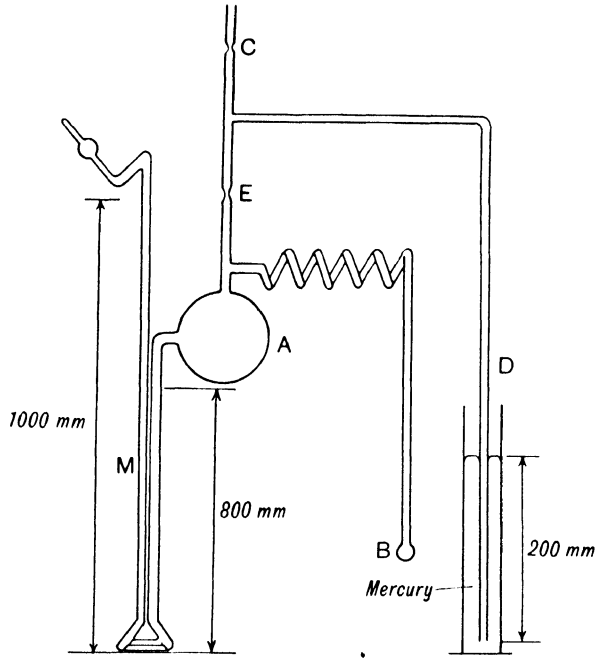


FIG. 75. Vapour pressure thermometer.

been used to fill the thermometer). This thermometer is easily transportable, and its readings correspond to the lowest temperature of tube *B*. The following substances may be used for filling vapour pressure thermometers :

TABLE 16

Substance	Temperature range °C.
Carbon disulphide	Room temperature to −10
Sulphur dioxide	−10 to −50
Ammonia	−30 to −80
Carbon dioxide	−75 to −100
Hydrogen chloride	−85 to −110
Ethylene	−105 to −150
Methane	−160 to −185
Oxygen	−180 to −200
Nitrogen	−195 to −210

These ranges are valid for a thermometer of the dimensions given in Fig. 75. The upper limit can be somewhat extended by using longer

manometers. The preparation of these substances is described on pp. 145 ff. (Cf. also A. Stock, F. Henning and E. Kuss, *Ber.*, **54**, I, 1119 (1921).) Their vapour pressures are given in Table 17.

TABLE 17

Temperature-Vapour Pressure Data for Vapour Pressure Thermometers.

Vapour pressures in mm. Hg. (at 0° C.).

°C.	CS_2	SO_2	
+25	359·8	—	—
+24	346 6	—	—
+23	333·8	—	—
+22	321·3	—	—
+21	309 2	—	—
+20	297·5	—	—
+19	286 1	—	—
+18	275 0	—	—
+17	264·3	—	—
+16	254·0	—	—
+15	243·8	—	—
+14	234·0	—	—
+13	224·5	—	—
+12	215 4	—	—
+11	206 6	—	—
+10	189·1	—	—
+ 9	189 8	—	—
+ 8	181·8	—	—
+ 7	174·1	—	—
+ 6	166·7	—	—
+ 5	159 5	—	—
+ 4	152·6	—	—
+ 3	145·9	—	—
+ 2	139·5	—	—
+ 1	133·3	—	—
0	127·3	—	—
− 1	121·6	—	—
− 2	116·0	—	—
− 3	110 7	1026·2	—
− 4	105·6	984·0	—
− 5	100·7	943·8	—
− 6	95·9	904·3	—
− 7	91·4	866 3	—
− 8	87·0	829·7	—
− 9	82·8	794·1	—
−10	78·8	759·8	—
−11	74·9	726·6	—
−12	71·2	694·6	—

°C.	CS_2	SO_2	NH_3
−13	67·6	663·7	—
−14	64·2	633·9	—
−15	60·9	605·3	—
−16	57·8	577·7	—
−17	54·8	551·0	—
−18	51·9	525·3	—
−19	49 2	500·6	—
−20	—	476 7	—
−21	—	453·9	—
−22	—	432·1	—
−23	—	411·2	—
−24	—	390·9	—
−25	—	371·5	—
−26	—	352·6	—
−27	—	334·7	1034·1
−28	—	317·7	986·5
−29	—	301·4	940·8
−30	—	285·8	896·3
−31	—	270 8	853 7
−32	—	256·5	813 0
−33	—	242·8	773·7
−34	—	229·7	736·0
−35	—	217·1	699·6
−36	—	205·1	664·6
−37	—	193·6	631·0
−38	—	182·6	598·9
−39	—	172·2	568·2
−40	—	162·5	538·7
−41	—	152·9	510·5
−42	—	143·9	483·5
−43	—	135·4	457·7
−44	—	127·3	433·2
−45	—	119·6	409·7
−46	—	112·3	387·2
−47	—	105·4	365·7
−48	—	98·8	345·2
−49	—	92·6	325·7
−50	—	86·7	307·1
−51	—	81·2	289 4
−52	—	75·9	272·5
−53	—	70·9	256·5
−54	—	—	241·3
−55	—	—	226·8
−56	—	—	213·0
−57	—	—	199·9
−58	—	—	187·5

°C.	NH_3	CO_2	HCl	C_2H_4
−59	175·8	—	—	—
−60	164·7	—	—	—
−61	154·2	—	—	—
−62	144·2	—	—	—
−63	134·8	—	—	—
−64	125·9	—	—	—
−65	117·5	—	—	—
−66	109·5	—	—	—
−67	102·0	—	—	—
−68	95·0	—	—	—
−69	88·4	—	—	—
−70	82·2	—	—	—
−71	76 3	—	—	—
−72	70·8	—	—	—
−73	65·6	—	—	—
−74	60 7	—	—	—
−75	56·2	1008·2	—	—
−76	52·0	931·5	—	—
−77	48·0	859·6	—	—
−78	—	792·5	—	—
−79	—	730·1	—	—
−80	—	672·2	1002·2	
−81	—	618·3	949·7	—
−82	—	568·1	899·6	—
−83	—	521·4	851·2	—
−84	—	478·5	805·1	—
−85	—	438·4	760·9	—
−86	—	401·3	718·7	—
−87	—	367·1	678·4	—
−88	—	335·6	640·0	—
−89	—	306·3	603·3	—
−90	—	279·2	568·2	—
−91	—	254·3	534·9	—
−92	—	231·5	503·1	—
−93	—	210·5	472·7	—
−94	—	191·2	443·9	—
−95	—	173·6	416·5	—
−96	—	157·3	390·5	—
−97	—	142·4	365·8	—
−98	—	128·7	342·3	1044·1
−99	—	116·2	320·1	989·6
−100	—	104·8	299·1	936·9
−101	—	94·4	279·3	886·3
−102	—	84·9	260·6	838·0
−103	—	76·2	242·8	791·5

°C.	HCl	CO_2	C_2H_4	CH_4
−104	226·0	68·3	747·0	—
−105	210·2	61·2	704·7	—
−106	195·5	54·7	664·1	—
−107	181·6	48·9	625·2	—
−108	168·4	43·6	588·0	—
−109	156·1	38·9	552·4	—
−110	144·6	34 6	518·4	—
−111	133·8	—	485·9	—
−112	—	—	455·0	—
−113	—	—	425·7	—
−114	—	—	397·9	—
−115	—	—	371·6	—
−116	—	—	346·7	—
−117	—	—	323·2	—
−118	—	—	301·0	
−119	—	—	280·1	
−120	—	—	260·3	—
−121	—	—	241·7	—
−122	—	—	224·2	—
−123	—	—	207·7	—
−124	—	—	192 2	—
−125	—	—	177·6	—
−126	—	—	163·9	—
−127	—	—	151·0	—
−128	—	—	138·9	—
−129	—	—	127·6	—
−130	—	—	117·0	—
−131	—	—	107·2	—
−132	—	—	98·0	—
−133	—	—	89·5	—
−134	—	—	81·6	—
−135	—	—	74·3	—
−136	—	—	67·6	—
−137	—	—	61·4	—
−138	—	—	55·6	—
−139	—	—	50·3	—
−140	—	—	45·5	—
−141	—	—	41·1	—
−142	—	—	37·0	—
−143	—	—	33·2	—
−144	—	—	29·8	—
−145	—	—	26·7	—
−146	—	—	23·9	—
−147	—	—	21·3	—
−148	—	—	19·0	—
−149	—	—	16·9	—
−150	—	—	14·9	1718
−151	—	—	—	1611

°C.	CH_4	O_2	N_2
−152	1508	—	—
−153	1410	—	—
−154	1316	—	—
−155	1227	—	—
−156	1143	—	—
−157	1062	—	—
−158	986	—	—
−159	914	—	—
−160	846 0	—	—
−161	781·5	—	—
−162	721·1	—	—
−163	662·4	—	—
−164	608·3	—	—
−165	558 2	—	—
−166	511·1	—	—
−167	467 2	—	—
−168	426 2	—	—
−169	387·9	—	—
−170	352·3	—	—
−171	319·6	—	—
−172	289·2	—	—
−173	261 3	—	—
−174	235·5	—	—
−175	211 5	—	—
−176	189·4	—	—
−177	169·1	—	—
−178	150 6	—	—
−179	134·0	1125	—
−180	118·5	1023	—
−181	104·7	927	—
−182	92·3	839	—
−183	81·1	757·2	—
−184	71·0	681·4	—
−185	—	611·6	—
−186	—	547·4	—
−187	—	488·5	—
−188	—	434·6	—
−189	—	385·5	—
−190	—	340·7	1428
−191	—	300·2	1289
−192	—	263·6	1162
−193	—	230·6	1043
−194	—	200·9	933
−195	—	174·4	833

°C.	O_2	N_2	
−196	150·9	741	—
−197	129·9	657	—
−198	111·3	580·5	—
−199	95·0	511	—
−200	80·7	459	—
−201	68·2	391	—
−202	57·3	340	—
−203	48·0	295	—
−204	39·9	254	—
−205	33·0	218	—
−206	27·1	183	—
−207	22·1	158	—
−208	17·9	136	—
−209	14·4	112·5	—
−210	11·5	94	—

The disappearing filament optical pyrometer. (Cf., *inter alia*, 'Properties of Tungsten', W. E. Forsythe and A. G. Worthing (*Astrophys. J.*, **61**, 146 (1925)); 'Use of Filters at 6650 Å', E. P. Hyde, F. E. Cady and W. E. Forsythe (*Astrophys. J.*, **42**, 294 (1915)); 'Spectral Emissivity', A. G. Worthing (*Phys. Rev.*, **10**, 377 (1917)); 'Disappearing Filament Pyrometer', W. E. Forsythe (*Trans. Faraday Soc.*, **15**, 21 (1919)). Optical pyrometers may work upon one or other of two principles. In the first the intensity of the total radiation may be measured, and, after suitable correction for emissivity, the temperature calculated from the Stefan-Boltzmann radiation equation. In the second the radiation E_λ at a particular wavelength λ may be measured and the temperature computed from the Wien radiation equation,

$$E_\lambda = c_1 \lambda^{-5} e^{-c_2/\lambda T},$$

where c_1 and c_2 are constants. This equation describes the variation of E_λ with sufficient accuracy if λT is less than 2000. $c_2 = 14350\mu$ deg. (W. Coblentz, *Bull. Bur. Standards*, **13**, 459 (1917).) In this form the pyrometer is simply calibrated from sources at known temperatures, the calibration being based on the gold point at 1336° K. (A. L. Day and R. B. Sosman, *Am. J. Sci.*, **29**, 93 (1910)), and on the palladium point determined accurately by F. Henning as 1828° K. (*Z. f. Instr.*, **30**, 61 (1916)).

The optical arrangements are shown in Fig. 76. S_1 is the source of radiation whose temperature is to be determined. The objective O forms an image, for example, that of a filament, at S_2 in the same plane as the filament of the comparison lamp of the pyrometer. Owing to the departure of the radiation from Lambert's cosine law (A. G. Worthing, *Astro. Phys. J.*, **36**, 345 (1912)), it is essential to have both filaments

parallel to each other, which means that the image of S_1 at S_2 has to be large compared with S_2. Diaphragms D_1 and D_2 limit the cone of light entering the eyepiece E, so that variations in the distance of O from S_1 shall not affect the apparent brightness of S_1. A filter F selects a band of radiation having its maximum at 6650 Å. In operation the source S_1 is brought into focus, and the current in S_2 adjusted until the filaments have the same apparent brightness. The temperature thus read on the instrument does not indicate the true temperature, since metallic filaments do not in general behave as perfect black body radiators. Their true

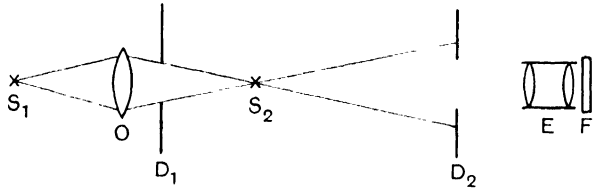


FIG. 76. Optical system for disappearing filament pyrometer.

temperature is therefore somewhat higher. It follows from the Wien equations that if ϵ (the so-called colour emissivity) is the ratio of the normal brightness of the filament to that of a black body at temperature T, that

$$\frac{1}{T}-\frac{1}{S}=\frac{\lambda}{c_2}\ln\epsilon,$$

where S is the temperature determined by the pyrometer. To calculate T, ϵ must be known. This has been measured for a number of metals and the calculation made for the suitable temperature range. The following table shows the corrections for a number of metals.

True temperature	Brightness temperature (S)				
°K (T)	Mo	Ni	Pt	Ta	W
1000	958	956	950	966	966
1100	1049	1047	1037	1058	1058
1200	1139	1137	1124	1149	1149
1300	1228	1226	1211	1239	1240
1400	1316	1315	1296	1329	1330
1500	1403	1403	1381	1418	1420
1600	1489	—	1466	1506	1509
1700	1574	—	1551	1592	1597
1800	1658	—	1634	1680	1684
1900	1741	—	1717	1766	1771
2000	1824	—	1800	1851	1857
2100	1905	—	—	1935	1943
2200	1986	—	—	2018	2026
2300	2065	—	—	2099	2109

True temperature	Brightness temperature (S)				
° K (T)	Mo	Ni	Pt	Ta	W
2400	2143	—	—	2180	2192
2500	2220	—	—	2260	2274
2600	2297	—	—	2339	2356
2700	2373	—	—	2417	2437
2800	2448	—	—	2495	2516
2900	2523	—	—	2571	2595
3000	—	—	—	2647	2673

Brightness temperature for $\lambda = 6650$ Å.

Thermo-electric thermometers. The use of a thermocouple for the measurement of temperature is by far the most convenient for temperatures of about − 180° to 1500° C.* It may be made small, the thermo-electric e.m.f. is readily measured, and when made of suitable alloys the results are reproducible. The number of alloys employed is small, the upper temperature limit being fixed by the melting point and liability to oxidation. A couple of platinum and an alloy of 13 per cent. rhodium and 87 per cent. platinum is now in general use. (Formerly an alloy containing 10 per cent. rhodium was employed, but subsequent improvements in the purification of platinum have necessitated that the rhodium content be slightly increased in modern thermocouples in order that they may generate the same e.m.f. as those of the older combination.) The platinum alloy couple has the disadvantage that the e.m.f. yielded is comparatively small, and other alloys have been introduced to give a larger e.m.f., so permitting the use of more robust measuring instruments. For temperatures up to 800° C. iron constantan or copper constantan couples are very suitable. Constantan is a eutectic alloy (40 per cent. Ni, 60 per cent. Cu), and hence is thermally stable. For temperatures up to 1200° C., alloys of nickel and chromium, such as chromel-alumel and titan, are very stable, and yield a much larger e.m.f. than the platinum couple. The couple must be protected by a sheath of infusible material such as translucent silica or porcelain.

The e.m.f. generated by a thermocouple depends on the difference in temperature between the hot and the cold junction. For measuring temperatures above 0° C., the cold junction is best placed in a bath of crushed ice contained in a vacuum flask. If the temperatures are below 0° the hot junction is maintained at 0° C. With the base alloys it is most convenient to run *both* leads from the thermocouple into the ice bath, where they are connected to the copper wires leading to the potentiometer or millivoltmeter. On the other hand, this may prove expensive with

* For thermocouples suitable between 2 and 90° K., see J. E. Ahlberg and W. O. Lunberg, *J. Amer. Chem. Soc.*, **57**, 2722 (1935).

platinum. For most purposes the difficulty can be surmounted by using compensating leads of base metal which yields an e.m.f. similar to that of the platinum couple. It is essential, of course, that such leads be connected round the right way.

The most accurate instrument for measuring the e.m.f. generated is the potentiometer. A good millivoltmeter with a resistance at least one thousand times larger than that of the thermocouple is almost as satisfactory. When reading up to a maximum of 1000° C. such a meter may be calibrated to 10° intervals and the reading estimated to the nearest degree. The chromel-alumel or titan couples give a very even—nearly linear— scale. The platinum scale is rather crowded below 400° C., but has the advantage of being open above this temperature. Some millivoltmeters (Cambridge Instrument Co.) are fitted with automatic thermoelectric compensators. It is then unnecessary to immerse the cold junction in a constant temperature bath.

Calibration of thermocouples. The Standard Calibration Tables (for use with deviation curve) are given below (*International Critical Tables*, Vol. 1, p. 57). The correction curve is determined for each couple by calibration at three or more fixed points. This curve is constructed by plotting ΔE as ordinate ($\Delta E = E_{obs} - E_{stan}$) against E standard as abscissa. In order to obtain the temperature corresponding to the e.m.f. indicated by the couple, the appropriate value of ΔE (as obtained from its deviation curve) is subtracted algebraically from the observed value of E before the latter is converted into degrees by means of the table. For example, a Cu-constantan couple gave an e.m.f. of 8720 microvolts. From the previously determined deviation curve of the particular couple the value of ΔE at 8720 microvolts is 12 microvolts. The 'standard' e.m.f. is therefore $8720 - 12 = 8708$ microvolts, and from the Cu-constantan table this corresponds to 189·08° C. The fixed junction is normally maintained at 0° C.

If the cold junction is not at 0° C., then the following correction is applied.

A. Let the temperature of the fixed junction be t_c and that of the hot junction be t. Then to the e.m.f. observed, E_{t-tc}, the e.m.f. corresponding to t_c is added. This gives E_t, which may at once be converted into degrees by means of the proper table.

B. The fixed junction temperature is multiplied by the factor

$$f = (dE/dt)_0 / (dE/dt),$$

which is the ratio of the mean e.m.f. temperature gradient between 0° and t_c to the gradient at t, and the product is added to t^1, the uncorrected temperature, that is $t = t^1 + ft_c$. These e.m.f. temperature gradients may

be obtained by taking the reciprocals of the numbers appearing in the difference column of the calibration tables No. 19-21.

Standard Temperatures for Calibration of Thermometers

(1) Boiling point of oxygen $-182{\cdot}96°$ C.
for a pressure p mm. $t_p = -182{\cdot}97 + 0{\cdot}0126\,(p-760) - 6{\cdot}5 \times 10^{-6}(p-760)^2$

(2) Melting point of ice $0°$ C. (273·18° K.)

(3) Boiling point of water $100°$ C.
for a pressure p mm. $t_p = 100 + 0\ 0367\,(p-760) - 2{\cdot}3 \times 10^{-5}(p-760)^2$

(4) Boiling point of sulphur $444{\cdot}60°$ C.
for a pressure p mm. $t_p = 444{\cdot}60 + 0\ 0909\,(p-760) - 4{\cdot}8 \times 10^{-5}(p-760)^2$

(5) Boiling point of naphthalene $217\ 96°$ C.
for a pressure p mm. $t_p = 217{\cdot}96 + 0{\cdot}058\ (p-760)$

(6) Boiling point of benzophenone $305{\cdot}90°$ C.
for a pressure p mm. $t_p = 305{\cdot}90 + 0{\cdot}063\ (p-760)$

(7) Melting point of silver $960{\cdot}5°$ C.

(8) Melting point of gold $1063°$ C.

Subsidiary Points useful for Thermocouple Calibration

(1) Temperature at which solid CO_2 has a vapour pressure of 760 mm. $-78{\cdot}5°$ C.
(2) Boiling point of ammonia - - - - - - - $-33{\cdot}5°$ C.
(3) Melting point of tin - - - - - - - - 231·9° C.
(4) Melting point of lead - - - - - - - - 327 4° C.
(5) Melting point of antimony - - - - - - - 630·5° C.

TABLE 18

Comparison of the E.M.F.'s of Common Thermocouples

	Temperature °C.			Temperature °C.	
E millivolts	Fe-const.	Chromel-alumel	E millivolts	Pt—Pt-Rh	Cu-constantan
5	95	121	1	146	25
10	186	244	2	260	49
15	277	365	3	364	72
20	367	483	4	461	94
25	457	600	5	553	115
30	546	719	6	641	136
35	632	843	8	806	176
40	713	970	10	959	213
45	792	1104	12	1103	250
50	871	—	14	1242	285
55	950	—	16	1379	320
—	—	—	18	1515	353

TABLE 19

Temperatures in °C. and Temperature Differences for every 0·5 millivolt—Chromel-Alumel

E millivolts	0		10		20		30		40	
0	0·0		244·5		482·8		719·2		970·4	
		12·3		12·2		11·7		12·2		13·0
0·5	12·3		256·7		494·5		731·4		983·4	
		12·1		12·2		11·7		12·3		13·1
1·0	24·4		268·9		506·2		743·7		996·5	
		12·0		12·1		11·7		12·3		13·2
1·5	36·4		281·0		517·9		756·0		1009·7	
		12·0		12·1		11·7		12·3		13·3
2·0	48·4		293·1		529·6		768·3		1023·0	
		12·0		12·0		11·7		12·4		13·3
2·5	60·4		305·1		541·3		780·7		1036·3	
		12·0		12·0		11·7		12·4		13·4
3·0	72·4		317·1		553 0		793·1		1049·7	
		12·0		12·0		11·7		12·5		13·5
3·5	84·4		329·1		564·7		805·6		1063·2	
		12 0		11·9		11·7		12·5		13·6
4·0	96·4		341 0		576·4		818·1		1076·8	
		12·1		11·9		11·8		12·5		13·7
4·5	108·5		352·9		588·2		830·6		1090·5	
		12·1		11·9		11·8		12·6		13·7
5·0	120·6		364·9		600·0		843·2		1104·2	
		12·2		11·9		11·8		12·6		13·8
5·5	132·8		376·8		611·8		855·8		1118·0	
		12·4		11·9		11·8		12·6		13·8
6·0	145·2		388·6		623·6		868·4		1131·8	
		12·5		11·8		11·8		12·6		13·9
6·5	157·7		400·4		635·4		881·0		1145·7	
		12·6		11·8		11·9		12·7		13·9
7·0	170·2		412·2		647·2		893·7		1159·6	
		12·5		11·8		11·9		12·7		14
7·5	182·7		424·0		659·1		906·4		(1174)	
		12·5		11·8		11·9		12 7		14
8·0	195·2		435·8		671·0		919·1		(1188)	
		12·4		11·8		12·0		12·8		14
8·5	207·7		447·6		683·0		931·9		(1202)	
		12·3		11·8		12·0		12·8		—
9·0	220·0		459·4		695·0		944·7		—	
		12·3		11·7		12·1		12·8		—
9·5	232·3		471·1		707·1		957·5		—	
		12·3		11·7		12·1		12·9		—
10·0	244·5		482·8		719·2		970·4		—	

TABLE 20

Temperatures (° C.) and Temperature Differences for every 100 Microvolts. Platinum—Platinum-Rhodium (10 per cent. Rh) Standard Range, 630-1083°. Applicability Range, 0-1754° C.

E(μV)	0		1000		2000		3000		4000	
0	0		147·1		265·4		374·3		478·1	
		17·8		12·6		11·2		10·6		10·6
100	17·8		159·7		276·6		384·9		488·3	
		16·7		12·4		11·1		10·5		10·1
200	34·5		172·1		287·7		395·4		498·4	
		15·8		12·3		11·0		10·5		10·1
300	50·3		184·3		298·7		405·9		508·5	
		15·1		12·0		11·0		10·4		10·1
400	65·4		196·3		309·7		416·3		518·6	
		14·6		11·8		10·9		10·4		10·0
500	80·0		208·1		320·6		426·7		528·6	
		14·1		11·6		10·9		10·4		10·0
600	94·1		219·7		331·5		437·1		538·6	
		13·7		11·5		10·8		10·3		10·0
700	107·8		231·2		342·3		447·4		548·6	
		13·4		11 5		10·7		10·3		9·9
800	121·2		242·7		353·0		457·7		558·5	
		13·1		11·4		10·7		10·2		9·9
900	134·3		254·1		363·7		467·9		568·4	
		12·8		11·3		10·6		10 2		9·9
1000	147·1		265·4		374·3		478·1		578·3	

E(μV)	5000		6000		7000		8000		9000	
0	578·3		675·3		769·5		861·1		950·4	
		9·8		9·5		9·3		9·0		8·4
100	588·1		684·8		778·8		870·1		959·2	
		9·8		9·5		9·2		9·0		8·8
200	597·9		694·3		788·0		879·1		968·0	
		9·8		9·5		9·2		9 0		8·7
300	607·7		703·8		797·2		888·1		976·7	
		9·7		9·5		9·2		9·0		8·7
400	617·4		713·3		806·4		897·1		985·4	
		9·7		9·4		9·2		9·0		8·7
500	627·1		722·7		815·6		906·1		994·1	
		9·7		9·4		9·1		8·9		8·7
600	636·8		732·1		824·7		915·0		1002·8	
		9·7		9·4		9·1		8·9		8·7
700	646·5		741·5		833·8		923·9		1011·5	
		9·6		9·4		9·1		8·9		8·6
800	656·1		750·9		842·9		932·8		1020·1	
		9·6		9·3		9·1		8·8		8·6
900	665·7		760·2		852·0		941·6		1028·7	
		9·6		9·3		9·1		8·8		8·6
1000	675·3		769·5		861·1		950·4		1037·3	

E(μV)	10,000		11,000		12,000		13,000		14,000	
0	1037·3		1122·2		1205·9		1289·3		1372·4	
		8·6		8·4		8·3		8·4		8·3
100	1045 9		1130·6		1214·2		1297·7		1380·7	
		8·5		8·4		8·4		8·3		8·3
200	1054·4		1139·0		1222·6		1306·0		1389·0	
		8·5		8·4		8·3		8·3		8·3
300	1062·9		1147·4		1230·9		1314·3		1397·3	
		8·5		8·4		8·4		8·3		8·3
400	1071·4		1155·8		1239·3		1322·6		1405·6	
		8·5		8·4		8·3		8·3		8·2
500	1079·9		1164·2		1247·6		1330·9		1413·8	
		8·5		8·3		8·3		8·3		8·2
600	1088·4		1172·5		1255·9		1339·2		1422·0	
		8·5		8·4		8·4		8·3		8·2
700	1096·9		1180·9		1264·3		1347·5		1430·2	
		8·5		8·3		8·3		8·3		8·2
800	1105·4		1189·2		1272 6		1355·8		1438·4	
		8·4		8·4		8·4		8·3		8·2
900	1113·8		1197·6		1281·0		1364·1		1416·6	
		8·4		8·3		8·3		8·3		8·2
1000	1122·2		1205·9		1289·3		1372·4		1454·8	

E(μV)	15,000		16,000		17,000		18,000	
0	1454·8		1537·5		1620·9		1704·3	
		8·2		8·3		8·3		8·3
100	1463·0		1545·8		1629·2		1712 6	
		8·2		8·3		8·4		8·4
200	1471·2		1554 1		1637 6		1721·0	
		8·2		8·3		8·3		8·3
300	1479·4		1562·4		1645·9		1729·3	
		8·3		8·4		8·4		8·4
400	1487·7		1570·8		1654·3		1737·7	
		8·3		8 3		8·3		8·3
500	1496·0		1579·1		1662·6		1746·0	
		8·3		8·4		8 3		8·3
600	1504·3		1587·5		1670·9		1754·3	
		8·3		8·3		8·4		
700	1512·6		1595·8		1679·3		—	
		8 3		8·4		8·3		
800	1520·9		1604·2		1687·6		—	
		8·3		8·3		8·4		
900	1529·2		1612·5		1696·0		—	
		8·3		8·4		8·3		
1000	1537·5		1620·9		1704·3		—	

TABLE 21

Temperatures and Temperature Differences for every 100 microvolts
Copper-Constantan

E(μV)	−5000		−4000		−3000		−2000		−1000	
0	−169·14		−124·46		−87·86		−55·81		−26·82	
		5·20		4·01		3·42		3·05		2·79
100	−174·34		−128·47		−91·28		−58·86		−29·61	
		5·40		4·09		3·46		3·08		2·81
200	−179·74		−132·56		−94·74		−61·94		−32·42	
		5·04		4 18		3·51		3·11		2·84
300	−185·28		−136·74		−98·25		−65·05		−35·26	
		5·89		4·28		3·57		3·15		3·86
400	−191·27		−141·02		−101·82		−68·20		−38·12	
		6·17		4·39		3 63		3·19		2·89
500	−197·44		−145·41		−105·45		−71·39		−41·01	
		6·81		4·50		3·68		3·22		2·90
600	−203·95		−149 91		−109·13		−74·61		−43·91	
		6 97		4·61		3·74		3·26		2·93
700	−210·92		−154 52		−112·87		−77·87		−46·84	
		7·55		4·73		3·30		3·29		2·96
800	−218·47		−159·25		−116·67		−81·18		−49·80	
				4·87		3·86		3·33		2·99
900	—		−164·12		−120·53		−84·49		−52·79	
				5 02		3·93		3·37		3·02
1000	—		−169·14		−124·46		−87·86		−55·81	

E(μV)	−0		0		1000		2000		3000	
0	0		0		25·27		49·20		72·08	
		2·60		2·59		2 45		2·33		2·23
100	−2·60		2·59		27·72		51·53		74·31	
		2 62		2·57		2·43		2·32		2·23
200	−5·22		5·16		30 15		53·85		76·54	
		2 63		2·56		2·42		2·31		2·22
300	−7·85		7·72		32·57		56·16		78·76	
		2·65		2·55		2·41		2·30		2·21
400	−10·50		10·27		34·98		58·46		80·97	
		2 67		2·53		2·40		2·30		2·20
500	−13·17		12·80		37·38		60·76		83·17	
		2·69		2·52		2 39		2·28		2·20
600	−15·86		15·32		39·77		63·04		85·37	
		2·71		2·51		2·38		2·27		2·19
700	−18·57		17·83		42·15		65·31		87·56	
		2·73		2·49		2·36		2·27		2·18
800	−21·30		20·32		44·51		67·58		89·74	
		2·75		2·48		2·35		2·25		2·17
900	−24·05		22·80		46·86		69·83		91·91	
		2·77		2·47		2·34		2·25		2·16
1000	−26·82		25·27		49·20		72·08		94·07	

E(μV)	4000		5000		6000		7000		8000	
0	94·07		115·31		135·91		155·95		175·50	
		2·16		2·09		2 03		1·97		1·93
100	96·23		117·40		137·94		157·92		177·43	
		2·15		2·08		2·02		1·97		1·93
200	98·38		119·48		139·96		159·89		179·36	
		2·14		2·08		2·02		1·97		1·92
300	100·52		121·56		141·98		161·86		181·28	
		2·14		2·07		2·01		1·96		1·92
400	102·66		123·63		143·99		163·82		183·20	
		2·13		2·06		2·01		1·96		1·91
500	104·79		125·69		146·00		165·78		185·11	
		2·12		2·06		2·00		1·95		1·91
600	106 91		127·75		148·00		167·73		187·02	
		2·11		2·05		2 00		1·95		1·91
700	109·02		129·80		150·00		169·68		188·93	
		2·10		2·04		1·99		1·94		1·90
800	111·12		131·84		151·99		171·62		190·83	
		2·10		2·04		1·99		1·94		1·90
900	113·22		133·88		153 97		173 56		192·73	
		2·09		2·03		1·98		1·94		1·89
1000	115·31		135·91		155·95		175·50		194·62	

E(μV)	9000		10,000		11,000		12,000		13,000	
0	194·62		213·36		231·74		249·82		267·60	
		1·89		1·85		1·82		1·79		1 76
100	196·51		215·21		233·56		251·61		269·36	
		1·89		1·85		1·82		1·79		1 76
200	198·40		217 06		235·38		253·40		271·12	
		1·88		1·85		1·82		1·78		1·76
300	200·28		218 91		237·20		255·18		272·88	
		1·88		1·84		1·81		1·78		1·76
400	202·16		220·75		239·01		256·96		274·69	
		1·88		1·84		1·81		1·78		1·79
500	204·04		222·59		240·82		258·74		276·40	
		1·87		1·84		1·81		1·78		1·75
600	205·91		224·43		242·63		260·52		278·15	
		1 87		1·85		1·80		1·77		1·75
700	207·78		226·26		244·43		262·29		279·90	
		1·86		1·83		1·80		1·77		1·75
800	209 64		228·09		246·23		264·06		281·65	
		1·86		1·83		1·80		1·77		1·74
900	211·50		229·92		248·03		265·83		283·39	
		1·86		1·82		1·79		1·77		1·74
1000	213·36		231·74		249·82		267·60		285·13	

E(μV)	14,000	15,000	16,000	17,000	18,000	19,000
0	285·13	302·42	319·49	336·36	353·08	369·61
	1·74	1·72	1·70	1·68	1·66	1·64
100	286·87	304·14	321·19	338·04	354·74	371·25
	1·74	1·71	1·69	1·68	1·66	1·64
200	288·61	305·85	322·88	339·72	356·40	372·89
	1·74	1·71	1·69	1·68	1·66	1·64
300	290·35	307·56	324·57	341·40	358·06	374·53
	1·73	1·71	1·69	1·67	1·66	1·64
400	292·08	309·27	326·21	343·07	359·72	376·17
	1·73	1·71	1·69	1·67	1·65	1·63
500	293·81	310·98	327·95	344·74	361·37	377·80
	1·73	1·71	1·69	1·67	1·65	1·63
600	295·54	312·69	329·64	346·41	363·02	379·43
	1·72	1·70	1·68	1·67	1·65	1·63
700	297·26	314·39	331·32	348·08	364·67	381·06
	1·72	1·70	1·68	1·67	1·65	1·63
800	298·98	316·09	333·00	349·75	366·32	382·69
	1·72	1·70	1·68	1·67	1·65	1·63
900	200·70	317·99	334·68	351·42	367·97	384·32
	1·72	1·70	1·68	1·66	1·64	1·63
1000	302·42	319·49	336·36	353·08	369·61	385·95

Platinum resistance thermometer. This instrument depends on the variation of electrical resistance for the measurement of temperature. To obtain reproducible results it is essential to use pure materials for the resistance element, and for this reason, as well as for its high melting point and resistance to corrosion, platinum has been chosen for the purpose. The platinum wire is wound on a mica or steatite frame and enclosed within a suitable protecting sheath, such as translucent fused silica, and is adjusted so as to have a definite resistance difference between 0° and 100° C. at 760 mm. pressure. This may be one or two ohms, though forty ohms is used in industrial thermometers, and is termed the Fundamental Interval.

The calibration of the thermometer is carried out in the following manner, originally due to H. L. Callendar (*Phil. Trans.*, **178**, 160 (1887)). Having measured the resistance of the wire at 0° and at 100° C. and assuming a linear relationship between resistance and temperature, then a single measurement of the resistance gives the temperature on the 'platinum scale'. To convert temperatures to the gas scale Callendar has shown that the relationship between the two is given by the formula

$$t - t_{pt} = \delta\{(t/100)^2 - (t/100)\},$$

where t = temperature on the gas scale,
t_{pt} = temperature on the platinum scale,
δ = a constant depending on the purity of the wire.

δ is evaluated by measuring the resistance at 0°, 100°, and 444·60° C., the boiling point of sulphur on the gas scale. For pure platinum, $\delta = 1{\cdot}5$. For convenience the following table, showing the relation between platinum and gas scales, is given.

TABLE 22

Reduction of Platinum to 'Gas' Scale Temperature (° C.)

Platinum	Gas	Platinum	Gas	Platinum	Gas
50	49·6	450	477·0	850	979·1
100	100·0	500	534·9	900	1049·5
150	151·2	550	594·0	950	1122·0
200	203·1	600	654·4	1000	1197·0
250	256·0	650	716·2	1050	1274·5
300	309·7	700	779·4	1100	1355·1
350	364·5	750	844·3		
400	420·2	800	910·8		

The arrangement of the bridge to measure the resistance is shown in Fig. 77. A pair of leads without the platinum wire is mounted in the same sheath as P and connected to the variable arm of the bridge R. Variation in lead resistance is thereby compensated. Without taking especial precautions, temperatures in the range—100° to 1000° C.—may be measured to within 1°. By taking great precautions in the design of the bridge and mounting of the resistance element, the accuracy may reach 0·002°. For most work on gaseous reactions such accuracy of temperature measurement is not necessary in view of much greater uncertainties introduced by other factors.

An alternative method of measuring the resistance is to pass a current through the platinum coil and a standard resistance (maintained at a constant temperature) in series, and compare the respective voltage drops by means of a potentiometer. A diagrammatic representation of the arrangement is shown in Fig. 78.

M. S. Van Dusen (*J.A.C.S.*, **47**, 326 (1925)) has made an accurate comparison of the platinum with the gas thermometer down to about − 190° C.

The Callendar equation used above may also take the form :

$$t = \frac{1}{\alpha}(R/R_0 - 1) + \delta(t/100 - 1)\,t/100.$$

For temperatures below 0° the equation which represents the variation of resistance with temperature becomes

$$t = 1/\alpha(R/R_0 - 1) + \delta(t/100 - 1)t/100 + \beta(t/100 - 1)t^3 10^6.$$

The constant β is calculated by determining the resistance of the platinum coil at the boiling point of liquid oxygen, namely − 182·96° C.

Temperature distribution in an electrically heated wire. (J. K. Roberts, *Proc. Roy. Soc.*, **A, 135,** 198 (1932) ; see also I. Langmuir, S. McLane and K. Blodgett, *Phys. Rev.*, **35,** 478 (1930) ; I. Langmuir and J. B. Taylor, *ibid.*, **50,** 68 (1936).) To obtain the temperature distribution consider an element of the wire between x and $x+dx$. In the steady state

$$K \,.\, A \,.\, \frac{d^2t}{dx^2}\,dx + \frac{1}{4{\cdot}2}\,i^2\rho_0(1+\alpha t)\,\frac{dx}{A} - 2\pi r q t\,dx = 0, \quad \ldots\ldots\ldots\ldots(1)$$

the first term representing the gain of heat by conduction, the second the rate of gain of heat due to the heating current, and the third the

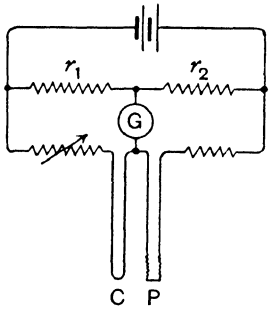


FIG. 77. Electrical circuit for resistance thermometer.

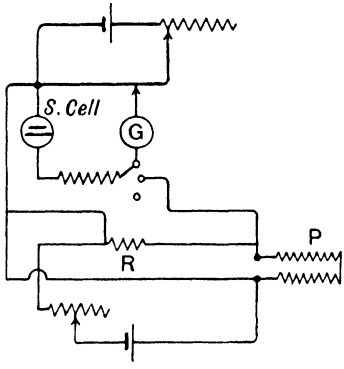


FIG. 78. Electrical circuit for resistance thermometer with potentiometer control.

algebraic rate of gain of heat at the surface. K = thermal conductivity of the material of the wire (cf. Table 23), t = temperature excess at x above the ends, i = current in amps., ρ_0 specific resistance at the bath temperature, α = temperature coefficient of resistance, r = radius of wire, q = heat loss per unit area per degree temperature excess of the wire. Let $q = q_g + q_r$, q_g = heat conducted away by the gas, q_r is that due to radiation.

Hence

$$\frac{d^2t}{dx^2} - mt + n = 0, \quad \ldots\ldots\ldots\ldots(2)$$

where

$$n = \frac{1}{4{\cdot}2} \cdot \frac{i^2\rho}{KA^2}, \quad m = \frac{2\pi r q}{K \,.\, A} - \alpha n.$$

If l is the length of the wire, then for $x=0$ and $x=l$, $t=0$; and if m is positive,

$$t = \frac{n}{m}\left\{\frac{l^{-l\sqrt{m}} - 1}{l^{l\sqrt{m}} - l^{-l\sqrt{m}}}\,(l^{x\sqrt{m}} - l^{-x\sqrt{m}}) + 1 - l^{-x\sqrt{m}}\right\}. \quad \ldots\ldots\ldots\ldots(3)$$

The mean temperature excess $\bar{t}$ is $\frac{1}{l}\int_0^l t\,dx$, and is given by

$$\bar{t}=\frac{n}{m}\left\{1+\frac{2}{l\sqrt{m}}\frac{(l^{l\sqrt{m}}-1)(l^{-l\sqrt{m}}-1)}{(l^{l\sqrt{m}}-l^{-l\sqrt{m}})}\right\}, \quad \ldots\ldots(4)$$

and $(dt/dx)_0$, the temperature gradient at the end, which determines the end loss, is given by

$$\left(\frac{dt}{dx}\right)_0=\frac{n}{\sqrt{m}}\left\{1+\frac{2(l^{-l\sqrt{m}}-1)}{l^{l\sqrt{m}}-l^{-l\sqrt{m}}}\right\}. \quad \ldots\ldots(5)$$

If m is negative, let

$$m'=-m=\alpha n-\frac{2\pi r q}{K\,.\,A}$$

and we obtain $$\bar{t}=\frac{n}{m^1}\left\{\frac{\sin l\sqrt{m^1}}{l\sqrt{m^1}}+\frac{(1-\cos l\sqrt{m^1})^2}{l\sqrt{m^1}\sin l\sqrt{m}}-1\right\} \quad \ldots\ldots(6)$$

and $$\left(\frac{dt}{dx}\right)_0=\frac{n}{m^1}\frac{(1-\cos l\sqrt{m^1})}{\sin l\sqrt{m^1}}. \quad \ldots\ldots(7)$$

The mean temperature is measured experimentally, but it is not possible by substituting the measured value in equation (4) or (6) to determine the value of q. It is therefore necessary to calculate from equation (4) or (6) the values of t for certain assumed values of q, and to obtain the actual value of q by interpolation to the measured value of $\bar{t}$. q_r and q_r+q_g are determined separately.

If the gas is at low pressure,

$$q_g=\frac{1\cdot74\times10^{-7}p\alpha}{\sqrt{mT}}\text{ cals. cm.}^{-2}\text{ sec.}^{-1}\text{ deg.}^{-1},$$

where p = pressure in dynes cm.$^{-2}$, α = accommodation coefficient, m = mass of the molecule and T is the temperature of impinging gas molecules.

TABLE 23

Metal	K (cals. cm.$^{-2}$ sec.$^{-1}$ deg.$^{-1}$)	Temp. coeff. of resistance*	Metal	K (cals. cm.$^{-2}$ sec.$^{-1}$ deg.$^{-1}$)	Temp. coeff. of resistance*
Aluminium	0·504	0·0036	Mercury	0·019	0·00089
Bismuth	0·019	0·004	Molybdenum	0·346	0·0047
Cadmium	0·222	—	Nickel	0·142	0·0054
Copper	0·92	0·0040	Palladium	0·168	0·0036
Gold	0·70	0 0036	Platinum	0·166	0·0037
Iridium	0·141	0·0037	Rhodium	0·210	—
Iron	0·161	0·005	Silver	0·974	0·0036
Lead	0·083	0·0040	Tantalum	0·13	0·0031
Lithium	0·17	—	Tungsten	0·48	0·0052
Magnesium	0·38	0·0039	Zinc	0·265	0·0035

* These values are approximate. For nearly all work the variation of R with temperature must be determined by experiments over the requisite temperature range.

Compensated filament method. When the temperature of a filament is below red heat its temperature cannot, of course, be determined by a micropyrometer. One method of measuring these lower temperatures is to note the watts input and surrounding gas pressure, and calculate the temperature distribution along the filament. This, however, is a difficult calculation, and moreover when completed is not easy to apply to the results: for not only is it necessary to determine the temperature distribution, but also the reaction velocity due to each individual element of the wire.

Another method consists in setting up two exactly similar filaments, one being considerably longer than the other, and measuring the contribution made to the reaction velocity by each and the respective resistances. (See H. W. Melville and H. L. Roxburgh, *J. Chem. Soc.*, 587 (1933); H. W. Melville and S. C. Gray, *Trans. Faraday Soc.*, **32**, 275 (1936). (See also p. 344.) Assuming that the two filaments are equally active, then simple subtraction gives the reaction velocity due to the central portion of the long filament at an approximately uniform temperature. Equality in the activity of filament catalysts is difficult to obtain. A compromise must therefore be struck by not making the small filament too long. For example, with 0·1 mm. diameter tungsten wire at about 500° C., the long filament being 12 cm. and the short 3 cm., the contribution made by the short filament to the total reaction velocity was about 5 per cent.

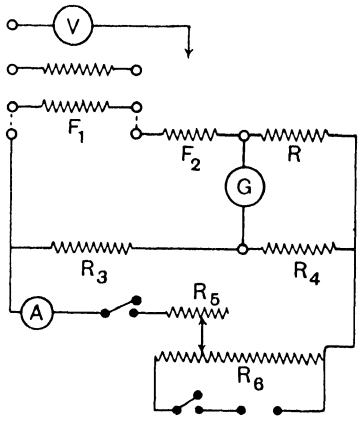


FIG. 79 Compensated filament circuit.

The arrangement of the bridge circuit for carrying out these measurements is shown in Fig. 79. The bridge itself consists of the two filaments, F_1 and F_2, in one arm, a standard resistance R of thick wire, so as to carry the bridge current without appreciably altering in resistance, being placed in the other arm. R_3 and R_4, which may be 100 to 1000 times the resistance of the filament, complete the network, the galvanometer functioning as a null instrument. In order to obtain fine control over the bridge current a voltage somewhat in excess of that necessary is tapped off from the potentiometer R_6. The actual voltage applied to the bridge is then accurately regulated by the variable resistance R_5. The individual values of the filament resistances are then measured by observing the voltage drop across each. This is best done with a potentiometer, but if this is not available a high resistance voltmeter is also

satisfactory, provided its resistance is at least 1000 times that of the filament. A small correction due to the current required to actuate the voltmeter may then be applied.

The procedure in operating the bridge is as follows. With the filaments F_1 and F_2 in operation the voltage drops are measured, and the resistances are calculated from the bridge arms. Having measured the velocity of reaction due to both filaments, F_1 is cut out and an external resistance of exactly the same value substituted. The velocity due to the small filament is thus determined. All the data are therefore to hand for calculating the average temperature of and reaction velocity due to the central portion of F_1. In practice it is simplest to mount one filament in the reaction bulb and spot weld on a current lead towards one end of the filament (cf. also pp. 343 ff.).

Useful Temperatures

Boiling Points :

Liquid helium	−269° C.	Solid CO_2	−78·5° C.
Liquid hydrogen	−252·78° C.	Liquid ammonia	−33·4° C.
Liquid air	−187° C.		

Melting Points :

Mercury	−38·87° C.	Red sealing wax	75-85° C.
Ice	0° C.	Naphthalene	80° C.
Phosphorus	44° C.	Sulphur	115° C.
Soft vacuum wax	50-60° C.		

Temperature by appearance (e.g. of inside of furnace) :

Just visible, dull red	500-700° C.
Cherry red, orange	900-1100° C.
White	1300° C. upwards

Melting Points (Metals) ° C. :

Potassium	62·5	Gold	1063
Sodium	97·6	Copper	1083
Selenium	217	Nickel	1452
Tin	231·9	Steel	1530
Lead	327·4	Palladium	1555
Magnesium	633	Platinum	1755
Aluminium	658·9	Molybdenum	2530
Silver	960·5	Tungsten	3380

Melting Points (Alloys) ° C. :

Wood's metal (1Sn, 2Pb, 1Cd, 4Bi)	60·5
Rose's metal (1Sn, 1 Pb, 4 Bi)	94
Solder (2 Sn, 1 Pb)	180
„ (1 Sn, 1 Pb)	220
„ (1 Sn, 2 Pb)	250
Silver Solder	450-600
Brass	800-1000

G. TEMPERATURE REGULATION

Furnaces. It is a general practice in reaction kinetics to study the properties of an isolated mass of gas confined in a container. The most useful container is fused silica, which thereby limits the maximum temperature at which reaction velocities may be measured to about 1200° C. It may also be necessary to obtain higher temperatures for special investigations, and the upper limit will therefore be fixed at about 2000° C. Should higher temperatures be required it is hardly within the province of this book to discuss the detailed construction of the carbon tube furnace capable of reaching a temperature of 3000° C. (cf. A. S. King, *J. Opt. Soc. Am.*, **12**, 503 (1926)).

Furnaces for the present purpose may be divided into two types. (1) Resistance furnaces, which consist essentially of a core upon which a wire of high resistance is stretched and thermally insulated by some refractory material. (2) High temperature baths of molten metal.

Resistance furnaces. The construction of such a furnace is fairly well defined by the maximum temperature at which it is to operate. In its construction three variables enter : (1) the furnace core, (2) the resistance wire, (3) insulating material.

Furnace core. In order of increasing temperature (the maximum temperature being shown in parentheses) are Pyrex (500° C.), iron,* insulated with asbestos (900°), translucent fused silica (1200°), porcelain (1500°), and alundum or fused aluminium oxide (1800°). Various commercial refractories are available in the intermediate range 1000°-1800°, and for these manufacturers, statements as to temperature range will have to be obtained. It may be added that if porcelain be used, then it must be unglazed, for glazes are much more fusible than the porcelain itself, and would stick to and might attack the heating element. If the core is smooth the winding is best done on a lathe, in order to ensure uniformity, but it is much more satisfactory to obtain the core ready grooved, a great variety of pitches being offered by manufacturers of refractory materials. Winding on Pyrex tube or iron is practically impossible unless moist asbestos paper is first rolled round the core. The wire bites into the moist paper, and when the furnace is put into operation the asbestos acts as weak setting cement, thus keeping the wire in position. Several layers of paper are advisable on an iron core to guard against short-circuiting. The temperature must not be raised above 900° C., at which temperature asbestos melts and the furnace is destroyed.

* Stainless steel is much superior to iron for furnace cores, in spite of its expensiveness.

Translucent fused silica is much cheaper than the transparent variety, and is just as suitable for furnace cores.

Resistance wire. For this a few metals and alloys suffice. The desiderata are high melting point, resistance to oxidation and high electrical resistance. These requirements are met satisfactorily by nichrome wire, an alloy of nickel and chromium (*ca.* 25 per cent. Cr), which operates indefinitely at 1000° C., and may be run up to 1100° C. For temperatures up to 1500° C. platinum must be used. To reach the higher temperatures, viz. 1800° C., molybdenum and tungsten are suitable, but have the disadvantage that the furnace must be run in a hydrogen atmosphere to prevent oxidation. Molybdenum possesses a great advantage over tungsten in that it is readily bent at room temperature, and consequently easily wound on to a furnace core, whereas tungsten requires to be heated to achieve the same end. Such resistance wires are obtainable as ribbon or circular wire. The former, while permitting uniform evenly spaced windings and lying well on a smooth core, is difficult to attach to external leads.

Thermal insulation. Here again the choice of material is governed by the maximum operating temperature, chemical inertness combined with low thermal conductivity being the factors limiting the field. For temperatures below 900° C. so-called magnesia pipe lagging is the most satisfactory material. It consists of about 85 per cent. magnesia, the remainder being asbestos. A layer 5 cm. thick is sufficient for most purposes. For higher temperatures granular magnesia or aluminium oxide is suitable. The thermal conductivity is rather larger than that of the magnesia-asbestos mixture, and in order to obtain efficient insulation at high temperature the normal practice is to have a few mm. of MgO or Al_2O_3 surrounding the core, the whole being enclosed within another alundum tube insulated with magnesia-asbestos pipe lagging.

Construction of furnaces. Having selected the suitable materials, the next problem is to obtain the necessary uniformity of temperature within the zone occupied by the reaction tube. This can, of course, be accomplished by employing a long furnace, which may not always be possible. One solution of the difficulty is to wind the resistance wire more closely at the ends of the furnace. A second and more satisfactory method is to wind the furnace in sections, as shown in Fig. 80, each section having a resistance in parallel with it of such a value as to give the largest uniform temperature zone within the furnace. This, of course, is a matter of trial and error, varying with the size of the furnace, resistance windings, etc. One point may be mentioned in this connection—platinum and

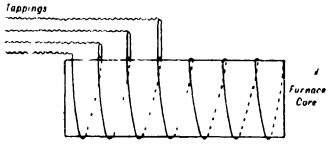


FIG. 80. Method of tapping furnace windings.

molybdenum may easily be welded to leads of thicker metal, e.g. nickel ; nichrome, on the other hand, is not easily welded in the ordinary spot-welder. At the end of the winding enough wire is left in order that a loop may be formed, the two wires being twisted together. A similar loop should be left at a tapping point, as shown in Fig. 80. To give some idea of the uniformity to be expected of an ordinary furnace the following example (C. C. Bidwell, *J. Opt. Soc. Am.*, **12**, 495 (1926)) may be quoted. The core was 18 inches long by $1\frac{1}{4}$ inch diameter, and plugged with two inches of granular alundum at each end. When wound with wire with $\frac{1}{16}$ inch clearance the temperature of a region 6 inches long in the middle of the furnace did not vary by more than 5°, the maximum temperature being 1000° C. With a compensated furnace R. G. W. Norrish and J. Wallace (*Proc. Roy. Soc.*, **A, 145,** 307 (1934)), managed to obtain a length of 20 cm. uniform within 1° at 700° C. Bidwell (*loc. cit.*) has suggested placing the winding inside the core in order to speed up the time of heating. In this construction the winding is formed on a cylinder covered with $\frac{1}{16}$ inch layer of paper, so that it just slides within the furnace core. Current is switched on, the paper chars, the inner cylinder is withdrawn, and the winding finally fixed in place by running in a thin paste of alundum cement.

Molybdenum furnaces. It is necessary to make these furnaces practically gas-tight, so that hydrogen may be circulated to prevent the molybdenum from becoming oxidised. The following dimensions for a core of 10 cm. in diameter have been given by C. C. Bidwell (*J. Opt. Soc. Am.*, **12**, 500 (1926) ; cf. also H. Gerdien, *Z. Elektrochem.*, **39**, 13 (1933)). The alundum core is wound with wire 1-2 mm. in diameter, and is insulated with 10-12 cm. of finely precipitated alumina, the whole being contained in an iron cylinder, preferably with one end welded on, with a hole for leading in hydrogen. The other end of firebrick or alundum may be cemented on with a mixture of water glass and alundum cement thinned with water, and applied in successive thin coats to avoid premature cracking. For annealing or cooling substances in hydrogen which have been treated in the furnace, a 120 cm. core tube is wound for 45 cm. of its length, starting 15 cm. from one end, the alumina insulation extending to 75 cm. The projecting 45 cm. are sheathed with iron tube for part of the length. The object after a suitable time in the hot part of the furnace may then be gradually removed to the cool portion. To avoid explosion the hydrogen is ignited at the inlet plug, and the flame front gradually allowed to extend through the furnace until it emerges at the other hole where it is maintained. The flame should be as small as is consistent with stability.

Regulation of furnace temperature. For small furnaces, e.g. 10 cm. × 40 cm., the input required to attain a temperature of 1000° C. is of the

order of 1 KW. In choosing resistance wire, therefore, the voltage must be considered in addition to adequate current-carrying capacity. Regulation of temperature by sliding wire rheostats is customary, but rather wasteful. If the supply is A.C. an auto-transformer, though expensive in the first place, is a more economical control. This, of course, must be supplemented by a small variable resistance for precise control. A simple economy may be made by centre tapping the furnace, running the two halves in parallel for high temperatures and in series for low temperatures.

With reasonably constant voltage, manual regulation of furnace current is satisfactory for most purposes. When, however, it is necessary to maintain a constant temperature over long periods some degree of automatic

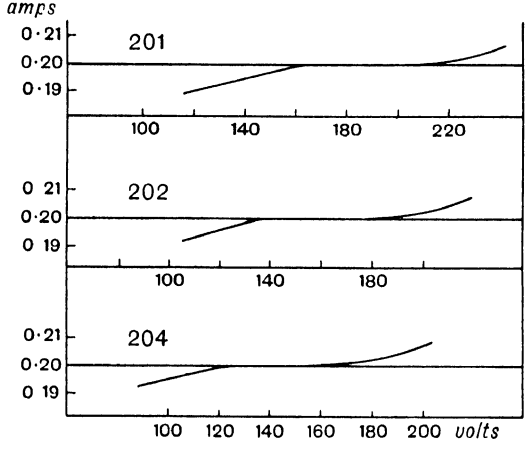


FIG. 81. Regulation curves for barretters.

control is desirable. One way of accomplishing this is to wire a barretter in series with furnace windings. This device consists of a length of iron wire suspended in an atmosphere of hydrogen, the conditions being so arranged that the current passed by the wire is practically independent of the applied voltage over a considerable range. To indicate the regulation to be expected, the characteristic curves for three typical small Osram barretters are shown in Fig. 81. These carry a comparatively small current, and in general several would require to be run in parallel to supply a furnace of normal dimensions.

Thermo-regulators. For temperatures up to 400° C. gas expansion thermo-regulators operating a mercury contact in a U-tube may be used. In order to reduce inaccuracy owing to the variation of the room temperature, capillary tubing is used outside the furnace. If the other limb of the mercury contact tube is closed and kept at constant temperature

the thermo-regulator is independent of the barometric pressure. The temperature is set in the same way as that for the ordinary liquid-filled thermo-regulators. H. S. Taylor and D. V. Sickman (*J. Am. Chem. Soc.*, **54**, 604 (1932)) use the inside of a Pyrex Dewar flask as reaction vessel and the annular space between the double wall as thermo-regulator. J. A. Christiansen's observation is interesting, namely (*Z. physik. Chem.*, **B, 2,** 407 (1928)) that a contact between a steel needle and mercury works satisfactorily for months if the steel needle is connected to the negative pole of the battery, but is corroded after a few interruptions if connected to the positive pole.

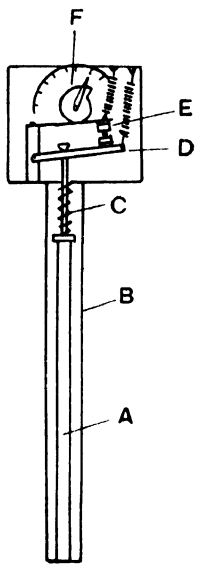


FIG. 82. Bimetallic thermo-regulator.

Somewhat more satisfactory in operation are metal thermo-regulators (cf. Fuchs, *Chemische Fabrik*, **5**, 49 (1932)), which depend on a combination of two materials of different coefficients of expansion. Such materials are aluminium, brass, copper, nickel, chrome nickel, steel, porcelain, invar (steel containing about 36 per cent. nickel) and silica. Aluminium has the highest coefficient of expansion and silica the lowest. The following combinations may be used: (*a*) aluminium and invar to 250° C., (*b*) copper or brass and invar or silica, (*c*) steel or nickel and silica to 600° C., and (*d*) chrome nickel and porcelain to 1000° C. A simple pattern is shown schematically in Fig. 82. Invar rod *A* is pressed to the bottom of the brass tube *B* by spring *C*. If tube *B* expands, the lever *D* is pulled downwards by the rod, and the contact is broken between *D* and *E*. The temperature is set by turning knob *F*. The levers *D* and *E* are pressed down by *F*, the higher the temperature at which the contact is interrupted. Such contacts can only be worked for currents less than 0·15 amp. A very convenient relay with suitable contacts for switching on and off the heating current is a gas expansion mercury relay developed by Heraeus shown in Fig. 83. The thermo-regulator switches on the filament in bulb *A*, the gas in it (N_2) is heated, expands and pushes the mercury over to connect *B* and *C*.

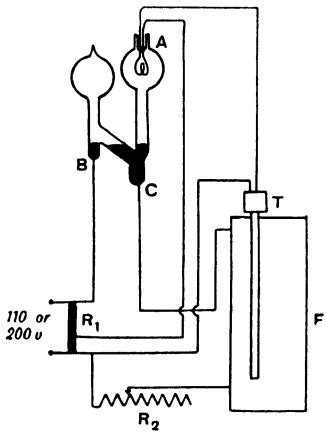


FIG. 83. Thermo-regulator with gas expansion relay. R_1 voltage divider. R_2 variable resistance for adjusting heating current. *T*, thermo-regulator. *F*, furnace.

Automatic furnace temperature regulator. (Metropolitan Vickers Electrical Co., *J. Sci. Instr.*, **13**, 374 (1936) ; cf. also J. C. Swallow and E. M. Cooke, *J. Sci. Instr.*, **6**, 287 (1929).) Apart from the somewhat inaccurate bimetallic thermo-regulator, the only satisfactory method of controlling the temperature of a furnace, say to within 0·4° at 600° C. over 24 hours, is to use a platinum resistance thermometer, in which the bridge galvanometer is replaced by a relay to switch off and on the furnace current. The regulator described below will keep a furnace at 600±0·4° C. over long periods without any attention. It has been

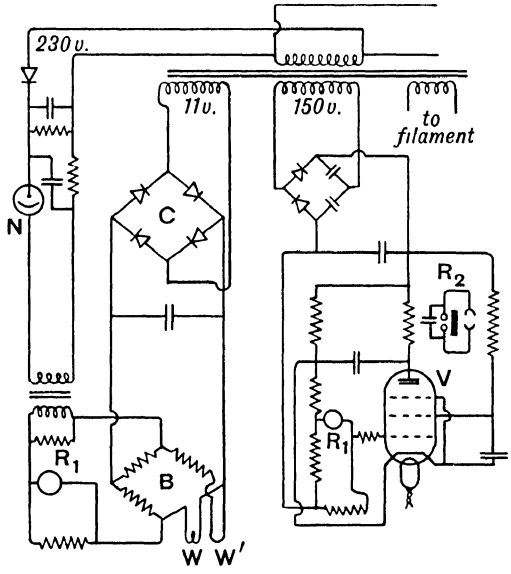


FIG. 84. Electrical circuit for thermostatic control of furnaces.

designed to work from alternating current mains, which possess a number of advantages. The power-relay will control up to 10 amperes. The bridge *B* (Fig. 84) contains the platinum wire *W* and compensating leads *W'*. A variable resistance in one arm of the bridge allows of its being set to any temperature from 20° C. to 600° C. This bridge is supplied with D.C. at 11 v. from the copper oxide rectifiers *C*. When the bridge is unbalanced the contacts of the sensitive relay R_1 are closed, thus decreasing the negative bias on the pentode valve *V* (Mazda A.C.2/Pen.). The anode current thereby increases, thus closing the thermal relay R_2 and so switching on the furnace current. The valve is similarly supplied with high tension current at 200 v. from copper oxide rectifiers, smoothed by chokes and condensers.

The sensitivity of the relay may be altered by a variable resistance in parallel with the windings. In order to prevent sticking contacts in R_1, an impulse is sent through the windings every 20 sec. to break the contacts. This impulse is derived from a condenser, which charges up through a fixed resistance and discharges through the neon lamp N.

The power-relay R_2 is a thermally operated vacuum switch with a delay period of about 2 sec., so that it is not affected by the short impulse from the neon lamp. This relay, though capable of breaking 8 amperes

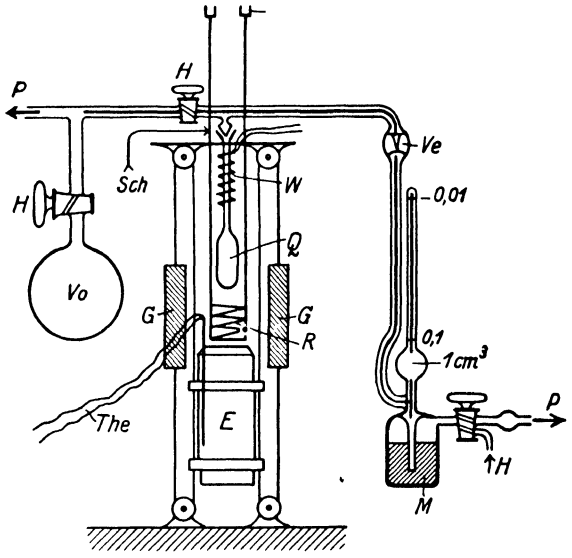


FIG. 85. Electrically heated lead bath.

(the controlling current being 25 mA. at 50 volts), is better placed in the furnace circuit to control only *part* of the furnace current. For satisfactory operation it is evident that the resistances controlling the furnace current should be adjusted to give approximately the temperature required.

Liquid baths for high temperatures. For some purposes in reaction kinetics it may be desirable to mix the reactants at leisure, heat for the required time, and then perform the analysis some time after the run. Clearly the electrically-heated air furnace is not suitable. An electrically-heated bath of molten lead is an efficient substitute, as is shown in Fig. 85 (M. Volmer and H. Briske, *Z. phys. Chem.*, **B, 25**, 87 (1933)). In this the furnace is counterweighted so that it can be rapidly raised around the reaction vessel. To give an idea of the time required to heat a litre

reaction vessel to reaction temperature, the results of M. Volmer and H. Kummerow (*Z. phys. Chem.*, **B**, **9**, 144 (1930)) are shown in Fig. 86. Since it requires at least one minute, the method is not readily applicable

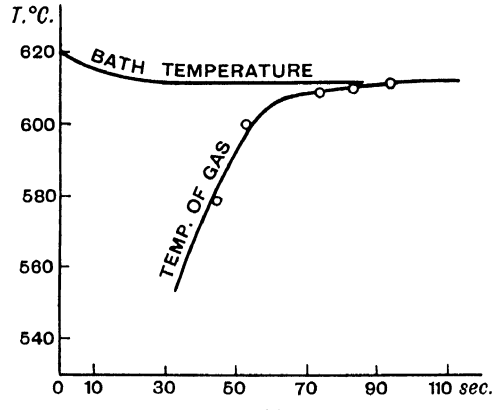


FIG. 86.

to rapid reactions. When dealing with involatile substances such as mercury and it is necessary to have pressures of several hundred millimetres of vapour, the reaction vessel is fitted with a needle valve (shown in Fig. 87) and operated through bellows of tombac tubing (cf. M. Volmer and M. Bogdan (*Z. phys. Chem.*, **B**, **21**, 258 (1933)).

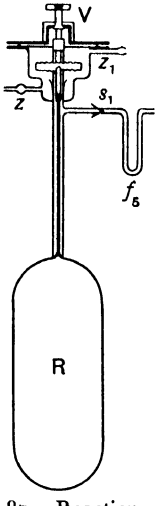


FIG. 87. Reaction vessel for involatile substances.

Time switches for furnaces. The time required to get an electrically-heated furnace up to working temperature may often be comparable with the period of a normal working day. To save time a switch attached to a clock is useful, so that the furnace may be switched on about 6 o'clock in the morning. Spring and electric clocks may be had for the purpose, but a cheap alarm clock with external bell will usually serve equally well. The details of the arrangement will depend on materials available, but the following general description will show the basic idea (Fig. 88). The bell of the clock is removed and a small rectangular block of ebonite, to which is attached a strip of copper, is screwed on the bell spindle. The alarm is set; when it goes off the solenoid *S* is energised, pulling down the armature *A* and so making contact in the mercury switch *M* through which the furnace current flows. *A* will only

remain within the solenoid so long as the clock rings. To prevent A rising again, two small ratchets, R_1 and R_2, are arranged so that R_1 interlocks

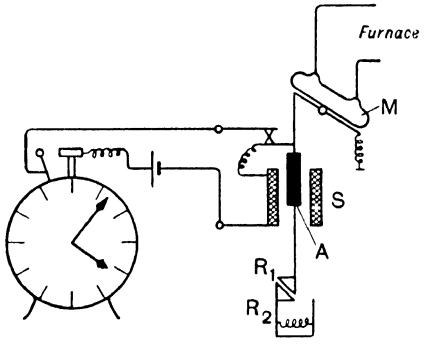


FIG. 88. Time control for electric furnace.

with R_2. The battery need not therefore supply current to keep switch M closed.

Production of low temperatures.

Temperatures down to about $-80°$ C. are most conveniently obtained by the use of solid carbon dioxide ('dry ice') or CO_2 snow. If the former is not available, the latter may be easily made from a cylinder of compressed carbon dioxide, though this is a rather wasteful proceeding. A specially made regenerative cooler reduces the loss, but it must be remembered that the gas has to do external work in order to be cooled to $-80°$ C. The simplest way of obtaining CO_2 snow is to attach a tube to the outlet valve of the cylinder by a nipple, and tie a bag of fine canvas of double thickness around the tube. A more convenient apparatus is the box in Fig. 89. The cylinder must then be tipped up so that liquid flows out from the valve. The latter will probably choke from time to time, but as it warms up it is automatically cleared. To make intimate contact between the refrigerant and the cooled body it is advisable to dissolve the snow in acetone or ether, adding small portions of liquid to the snow in a vacuum flask. This procedure of adding liquid to snow avoids frothing of the solution, which often forces an appreciable fraction of it out of the flask with disastrous consequences if naked flames, e.g. from a diffusion pump bunsen burner, are in the near vicinity. Should it be necessary to add snow to the liquid, small quantities should be added at intervals with frequent stirring to prevent explosive ebullition of the liquid. If liquid air is not available temperatures down to $-120°$ C. may be readily reached by pumping off carbon dioxide from the solid contained

in an ordinary vacuum flask by means of a filter pump. The only objection is that the solid carbon dioxide may gradually recede from the trap, and thus make cooling rather less rapid.

Liquid oxygen, air or nitrogen is the most suitable refrigerant for temperatures from $-183°$ to $-205°$ C. If contained in a good pint-size vacuum flask it will last twenty-four hours, if used, say, to surround a trap to prevent mercury entering an apparatus from a diffusion pump.

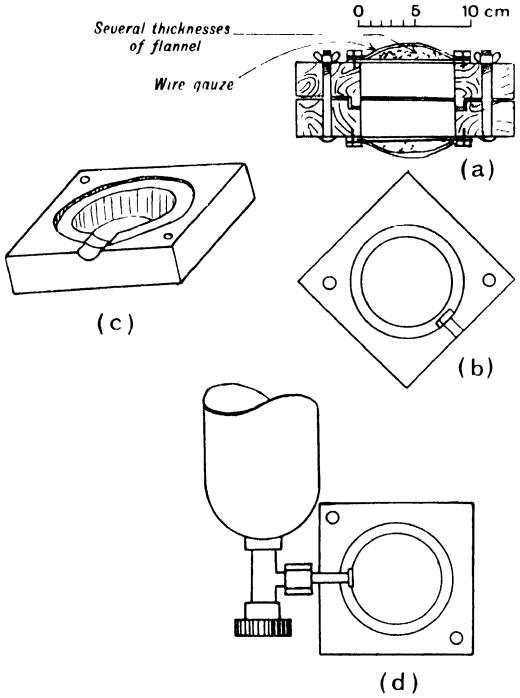


FIG. 89. Box for preparing solid carbon dioxide.

The temperature and composition of liquid air is most readily determined by means of an oxygen vapour pressure thermometer, which simply consists of a glass tube dipping into the liquid and attached to a barometric tube or to a long U-tube mercury manometer. By pumping off liquid air with the apparatus shown in Fig. 104, Chap. III, a temperature of $-205°$ may be reached. Below this temperature liquid hydrogen must be employed.

Method of handling liquid hydrogen. As liquid hydrogen plants are becoming more widespread, a brief description of the precautions in handling and storing this useful refrigerant may be given. Its principal use in chemistry is for freezing out all gases except helium from gases

containing hydrogen. Again it is extremely useful for the preparation of para-hydrogen or ortho-deuterium (see Chap. III). Before entering the laboratory with a flask of liquid hydrogen all naked flames must be extinguished. To prevent too rapid evaporation the liquid is transferred to a vacuum flask immersed in a bath of liquid nitrogen by means of a tube V, as shown in Fig. 90. First V is inserted in the liquid hydrogen flask V_1 and into the vacuum flask V_2 immersed in liquid nitrogen. Tap T is closed, and the pressure exerted by the gaseous hydrogen forces liquid hydrogen into V_3, displacing the air. When the transfer is completed,

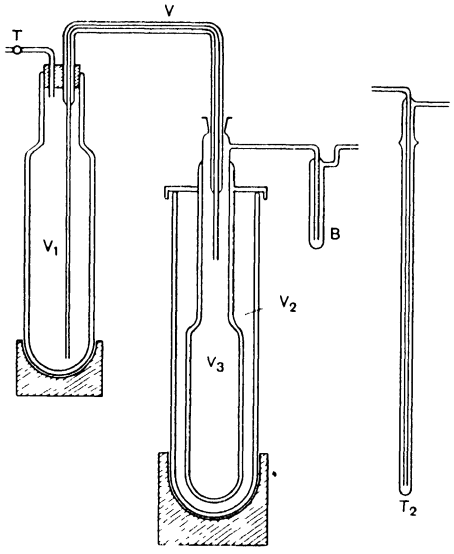


FIG. 90. Apparatus for handling liquid hydrogen.

trap T_2 is inserted and the gaseous hydrogen allowed to escape through bubbler B, the sulphuric acid in which just reaches above the lower lip of the inner tube. The issuing gas is conducted out of a nearby window. After allowing the room to be thoroughly ventilated bunsen burners may be relighted.

Low temperature thermostats. Low temperatures may be prepared by choosing a liquid with a suitable freezing point, and cooling the bath to freezing temperature by pouring liquid air into a closed tube contained in the bath. If, however, it should be necessary to alter the temperature frequently this procedure is not satisfactory. The following arrangement (R. M. Barrer, private communication) is eminently satisfactory for the present purpose. The low temperature bath B (Fig. 91) consists of a vacuum flask filled with pentane or hexane (if temperatures not lower

than −180° C.), in which the reaction vessel *R.V.* is immersed. One or more thermocouples are fixed to the exterior of the reaction vessel. A pentane thermometer may also be used, but then it may be necessary to

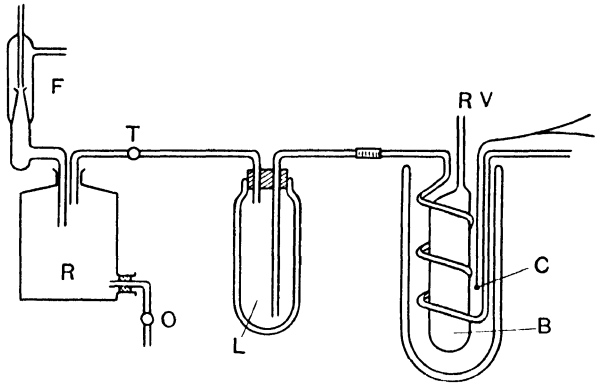


FIG. 91. Low temperature bath (down to −183° C.).

employ a flask with an unsilvered strip to permit the thermometer being read. A coil of ' compo ' tubing surrounds the reaction vessel. Liquid air from a flask *L* is blown over into *B*, the liquid entering the top of the spiral, an arrangement which helps to maintain an even temperature in *B*. To prevent undue loss of liquid air the tubing is covered with cotton wool or, better still, vacuum jacketted tubing is employed. The air pressure for driving the liquid air from *L* is produced by the filter pump-bottle arrangement. When the temperature rises in *B*, *T* is opened and a small amount of liquid air admitted to the coil. Such a device, of course, requires continued attention if the temperature is to be kept within 1° for several minutes at a time. A simple type of rough thermostat is shown in Fig. 92.

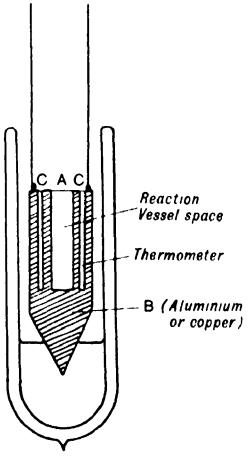


FIG. 92. Simple low temperature thermostat.

Thermostat for temperatures below −183°C. The temperature of liquid air, oxygen or nitrogen bath may be accurately controlled by keeping the vapour pressure constant. Good control is possible by manual adjustment of a needle valve interposed between the pump and the liquid bath. A very satisfactory automatic control devised by W. J. C. Orr (private communication) can be accomplished by the vapour pressure thermometer shown in Fig. 93. The mercury of the manometer operates a relay (connected through the platinum contacts

at *A*) which switches on and off the motor of a Hyvac pump (pumping at *B*) as contact is broken or made respectively. As designed the thermometer can be easily filled with oxygen or nitrogen through tap *C*, nitrogen being used for the temperature range 68-77° K. and oxygen for 77-80° K.

The thermometer may be set to regulate at any desired temperature by adjusting the Hg level at *D*, the temperature being determined from

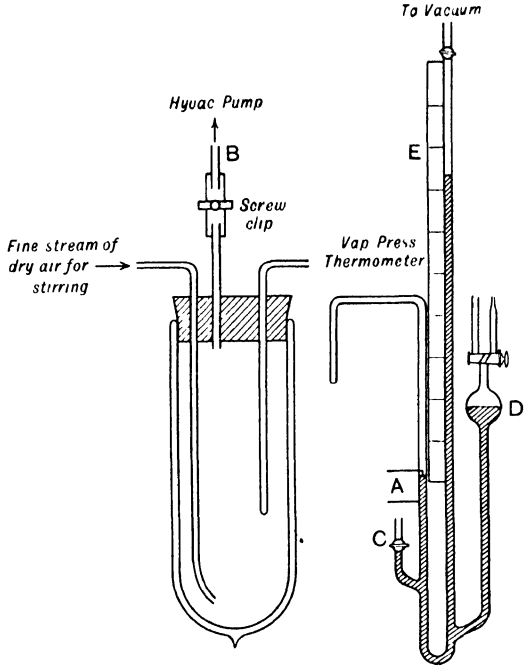


FIG. 93. Automatically controlled low temperature bath for temperatures below −183° C.

the vapour pressure measured on the millimetre scale. For vapour pressures, see p. 106. Using oxygen and nitrogen there is a change in vapour pressure of 40-60 mm. per degree K. throughout the range 68-90° K. In operation the temperature is controlled to within ±0·02° K. Such a thermostat could also be used for higher temperatures with liquids of higher boiling points.

Constant level device for liquid air. (R. B. Scott and F. G. Brickwedde, *Rev. Sci. Inst.*, **2**, 171 (1931) ; cf. also A. C. Egerton and A. R. Ubbelohde, *Trans. Faraday Soc.*, **26**, 236 (1930).) The device is shown diagrammatically in Fig. 94. When the level in vessel V_1 sinks, a float *F* thereby closes the contacts at *C*. This energises the relay *R*, which in

turn causes the solenoid to raise its armature against the spring *Sp*, bringing with it the valve *V*. Air is supplied at *A* under pressure. By raising

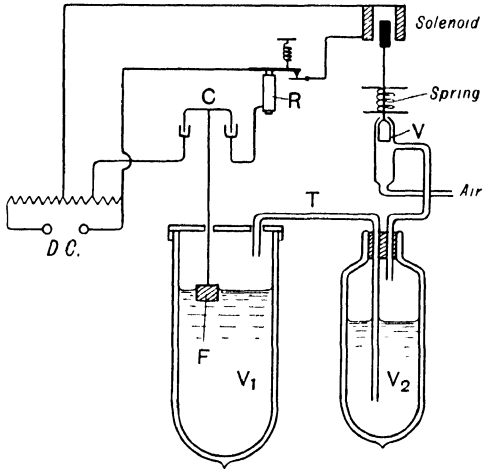


FIG. 94 Constant level device for liquid air

V air flows into V_2 and forces liquid air into V_1. *F* then rises, causing *V* to drop back into the bottom of its container, thereby releasing the pressure in V_2 and so stopping the flow of liquid air.

H. GENERAL SET-UP OF APPARATUS FOR GAS REACTIONS

Though individual apparatus differs a good deal in the study of gas reactions, there is usually a basic similarity in all arrangements. There are, in fact, four distinct portions of such an apparatus :

(*a*) Reaction bulb system.
(*b*) Analytical devices.
(*c*) Gas generating flask and storage reservoirs.
(*d*) The pumping installation.

The separate units likely to be required must be left to the choice of the experimenter, and elsewhere in this book a reasonable selection of the most commonly-used instruments has been given. The normal procedure is to support the glass work on a number of retort stands placed on a suitable table. Much is to be gained in convenience and flexibility by employing a system of crossed rods of the same diameter of the retort stand rods. At the side of this ' grid ' the electrical control gear and switchboard for pumps, gauges, etc., are set upon a table with a rotatory

oil pump underneath. Between the rotary oil pump and the mercury or oil diffusion pump a liquid air trap or phosphorous pentoxide tube (see p. 57) is inserted to prevent water vapour reaching the oil. If the oil pump has a tendency to allow oil to leak back into the vacuum line when it is stopped overnight, it is advisable to put a tap on the tube leading to the diffusion pump so that the vacuum can be let down. On those rotary oil pumps not provided with a male conical joint for connection to the apparatus, the junction between glass and metal is made with vacuum wax in preference to rubber tubing. A small mercury **U**-tube manometer is useful on this section of the vacuum line, though the pressure can be roughly gauged by listening to the 'note' of the oil pump. The lower the pressure the more metallic the click of the pump.

Between diffusion pump and apparatus there should be two taps of large bore, in between which a liquid air trap with demountable bottom (see p. 151) is connected. If corrosive or spontaneously inflammable gases are being pumped, this trap may be taken apart, without stopping the running of the apparatus, and allowed to warm up from liquid air temperature in a fume cupboard. A McLeod gauge attached to this part of the apparatus is very useful for detecting leaks and ensuring that the vacuum pumps are working properly. The only disadvantage is that it does not indicate the presence of vapours, especially of water vapour, and hence the pressure read on the gauge may be 10^{-4} mm., whereas in fact the pressure of water vapour might be 10^{-2} mm. If it should be necessary to have a large number of gas reservoirs on the apparatus, it is in general a good plan to isolate the tube to which these reservoirs are attached by means of an additional tap. With this arrangement the reservoir pressure gauges may then dip into a common mercury reservoir. When setting up the reaction vessel and associated manometric equipment, it is of prime importance to avoid dead space by shortening all connections as far as possible. At low pressures, e.g. 0·1 mm., interdiffusion is rapid enough to establish uniform conditions fairly quickly; at higher pressures diffusion is so slow that serious errors may be made if a considerable fraction of unreacted mixture remains in tubing connected to the reaction vessel.

After having cleaned and washed with distilled water the component parts of the apparatus, the greater part of the moisture is removed by warming and drawing dry air through the tubes. Next the parts are fused together, care being taken to blow through a small tube of calcium chloride, the pumps started, and as much of the apparatus as possible flamed gently with a portable blow-pipe.

Leak testers. By judicious use of taps it is usually possible to locate that part of an apparatus which is leaking, though it is often very difficult

to determine the exact position of the hole. One rather messy but effective way is to cover the suspected parts one at a time with vacuum wax, and after each application test for rate of leakage. When found, the wax is cleaned off and the joint reblown. A more rapid procedure is to employ a small Tesla coil. These can be obtained commercially with a suitable insulated output electrode. The coil is started and gas to a pressure of a few tenths of a mm. allowed to accumulate in the apparatus. The sparks from the electrode are played over the apparatus. When in the vicinity of a small hole the discharge tends to pass through the hole

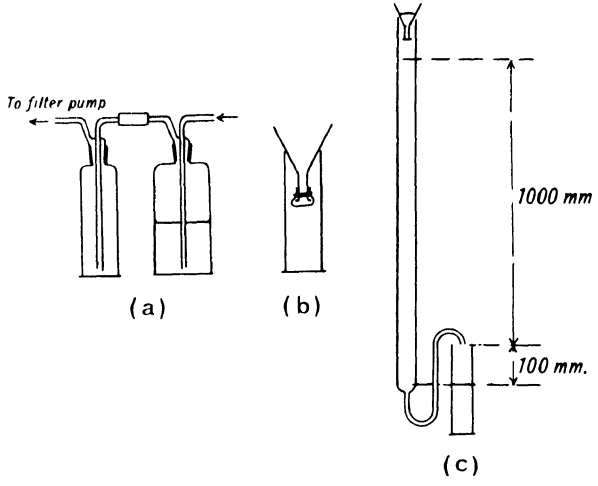


FIG. 95. Apparatus for cleaning mercury.

rather than pass through the glass, with the result that a small patch of light is produced at the entrance to the hole. The smaller the hole the more difficult is it to detect. Care must be taken against making the sparks too long, as there is a tendency for the glass to be punctured.

Cleaning apparatus. Vacuum apparatus which has become dirtied with mercury compounds such as halides or sulphides may be cleaned in the following way : zinc dust is made into a paste with water and the suspension run into the apparatus, so that the walls are covered by a deposit of metallic zinc. Dilute hydrochloric acid is added. The insoluble mercurous compounds are reduced to metallic mercury, which is easily removed with concentrated nitric acid.

Cleaning mercury. If mercury is used for confining gases or for other purposes it must be clean. Dust and other coarse impurities are separated by filtration through chamois leather, using a funnel, as shown in Fig. 95 (*b*). Shaking with benzene or petrol in a thick-walled vessel will free

the mercury from oil or grease. Copper, zinc and lead dissolved in mercury are oxidised and removed by sucking a strong air current through the mercury in a wash bottle, Fig. 95 (*a*). It is advisable to insert a second wash bottle between the filter pump and the mercury bottle in order to

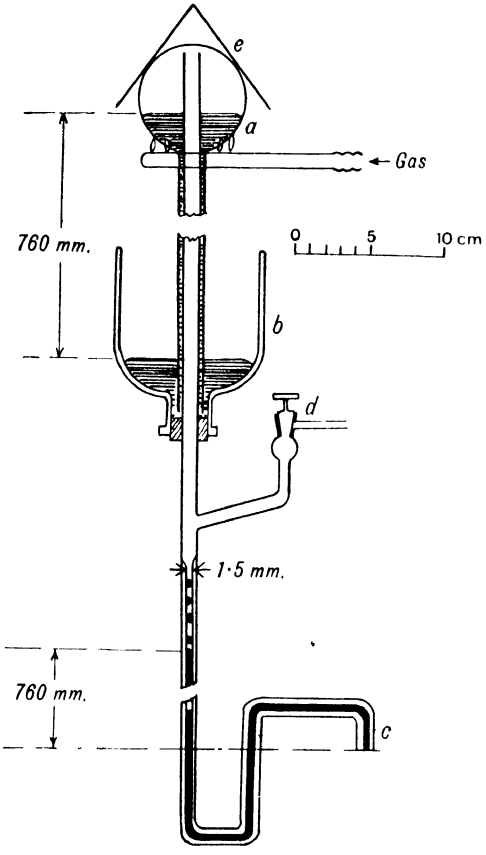


FIG. 96. Mercury still.

prevent mercury entering the pump. Oxidisible metals can also be removed by dilute nitric acid (20 per cent.) containing some mercurous nitrate in the apparatus shown in Fig. 95 (*c*). Before filling the tube with acid some clean mercury is first poured into it. The mercury to be cleaned is added through a funnel closed with chamois leather, Fig. 94 (*b*), and passes through acid in the form of fine drops. Before the final purification by distillation the mercury is dried by heating it to 120° C. in an open porcelain crucible for an hour (in a fume chamber to avoid inhaling poisonous mercury vapour). The distillation is most con-

veniently carried out in the apparatus shown in Fig. 96, which can be easily made (Gouy, *Recueil d'Expériences élémentaires de Physique*, par H. Abraham (Paris, 1904), p. 46). Part *a* is made of a 100-150 cc. Pyrex bulb, *b* from an ordinary bottle by cracking off its bottom. Tube *c* must be fixed very firmly into the neck of a flask *b* by a rubber stopper, iron wire ligatures and picein. When the apparatus is assembled mercury (after having been well dried) is poured into *b*, the tip of tube *c* immersed into some clean mercury, and the still evacuated through tap *d*. Then the mercury rises in *a* and *c*, tap *d* is closed, and the still is ready for use. Bulb *a* is heated by a burner made of a copper tube, the asbestos cap *e* serves to reduce heat loss. The mercury condenses in the upper part of tube *c*, and the drops falling into the capillary part take with them some air, which is left in the still or which is given up by the mercury. Thus the still is automatically and continuously evacuated. In this manner the still will work for weeks. The yield is about 1 kg. of mercury per hour.

CHAPTER III

PREPARATION AND ANALYSIS OF GASES

A. GENERAL METHODS OF PREPARATION AND STORAGE

THE preparation of gases may be divided into three distinct operations, some of which are common to a considerable number of preparations, namely, (1) generation, (2) purification, and (3) storage.

Solids or liquids with a low vapour pressure (e.g. H_2SO_4) for generation and purification possess the important advantage that the whole system may be at first evacuated before gas generation is commenced,

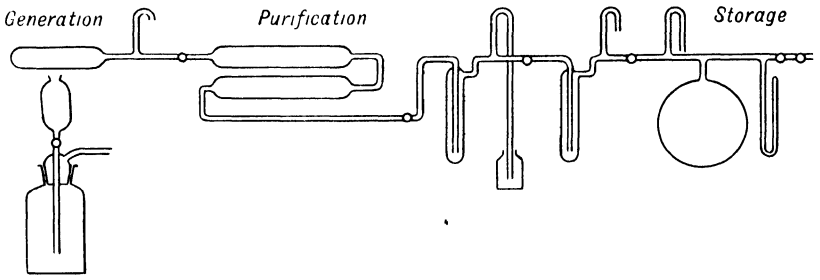


FIG. 97. Apparatus for the generation, purification and storage of gases.

and therefore in the following description these agents will be specified, provided they yield gas of a purity comparable with other methods.

In setting up a gas line it is advisable to construct it wholly of glass, or if this is not possible to use standard ground joints in preference to rubber connections, when the apparatus may then be constructed on the unit principle. A typical arrangement is shown in Fig. 97. To each part of the apparatus shut off by means of taps there is attached a mercury manometer, not only to indicate the pressure of the gas in each section, but also to act as a safety valve should there be a sudden evolution of gas from the generator or from the condensed liquid. For gases which attack mercury, such as Cl_2, Br_2, NO_2, the mercury manometer may be replaced by stout Bourdon gauges (see p. 85) without an outer envelope. For those gases which are condensable in liquid air further purification is desirable by fractional distillation. By means of the two liquid air traps

any desired fraction of the liquid may be retained. If the gas is noxious or inflammable—CO, hydrocarbons—the mercury containers into which the manometers dip should consist of bottles with a two-holed stopper, in order that the escaping gas can be conveyed to a fume cupboard or the open air. Storage bulbs sometimes do not readily seal to soda glass if this is used for the apparatus. A satisfactory method of making a connection is shown in Fig. 98 (*a*), picein or sealing wax being used as sealing material. With large bulbs (5 litres) it is advisable to bind the neck tightly with a layer of 16 s.w.g. copper wire to prevent splitting. For admitting gas to the reaction system a single tap will usually suffice, but if only low pressures are being used, then a doser consisting of two taps in series may be used. Alternatively a three-way tap, shown in Fig. 98 (*b*),

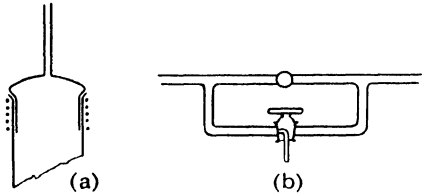


FIG. 98.

is more rapid in action and incidentally fool-proof. The straight through portion of the key is sealed up with picein. Another tap must be used in parallel in order that the bulb can be evacuated.

If the same amount of gas (within, say, 1 per cent.) is to be admitted to the reaction system at each dose, the volume of the doser should be only a few tenths of 1 c.c. with a storage bulb of 1 litre. A more tedious method is to calibrate the doser for different pressures in the storage bulb, and then correct for each addition of gas.

Gas holders. The simplest type of gas holder for a few c.c. of gas is a small inverted test-tube, as shown in Fig. 99. The mercury trough and pipette are necessary for transferring gas from one holder to another. The construction of the trough with one deep tube economises in the volume of mercury required. The small gas holders are removed from the trough by slipping a crucible underneath the surface of the mercury. Tube and crucible are then removed to a wooden burette stand. Gases may be delivered directly to these gas holders from a Töpler pump. Larger quantities of gas (up to 5 litres) are most conveniently stored in large glass bulbs fitted with a good vacuum tap, and preferably with a standard ground joint to permit of their being instantly attached to any portion of an appartus.

It is sometimes necessary to pass a valuable gas into an apparatus or reaction system at a constant high pressure. To enable this to be done

to the last c.c. the gas holder illustrated in Fig. 98 (*c*) is useful. The mercury trough is fixed on the ring of a retort stand, so that it may be moved upwards as the gas supply becomes exhausted. When large quantities of

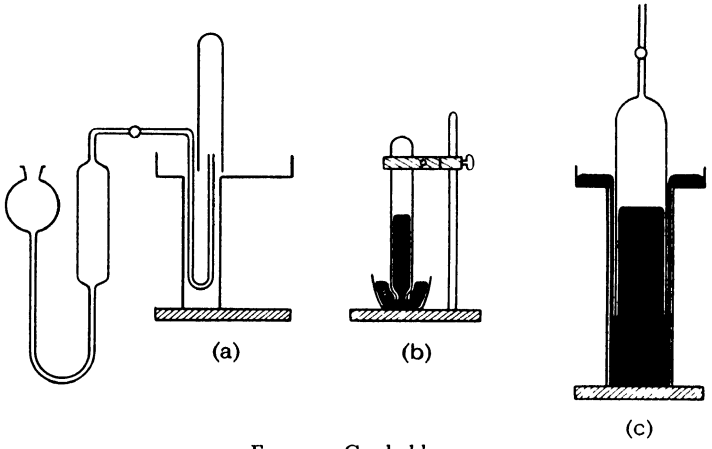


FIG. 99. Gas holders.

gas have to be stored, especially before purification, say for flow experiments, the common aspirator, using water as confining liquid, is most suitable. The stopper with tap is waxed in position, and the levelling bottle is kept above the reservoir to ensure that there is no leakage into

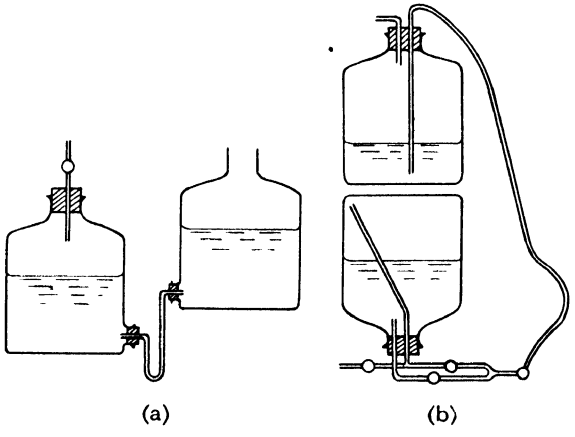


FIG. 100. Large gas reservoirs.

the gas, Fig. 100 (*a*). The arrangement shown in Fig. 100 (*b*) due to H. Moser (*Die Reindarstellung von Gasen*) makes certain that the gas only comes into contact with glass and water. Quantities of gas larger than 5 litres may be stored in small metal gas holders of the usual type.

Corrosive, e.g. Cl_2, and unstable gases are often kept frozen in a liquid air or CO_2 trap until required for experiments. Small vacuum flasks will retain liquid air for twenty-four hours.

Storage and Transportation of Gases

The storage and transportation of quantities of purified gas too small or too inconvenient to be compressed into steel cylinders is best done in sealed glass containers of the construction shown in Fig. 101. The bulb has a tube attached to it with a constriction *C* and a side tube T_1 if the gas to be stored is likely to be decomposed, e.g. H_2S, when the bulb is sealed off. At the lower end there is a small thin bulb *B*. The procedure then is to fill the large bulb (previously having been cleaned with chromic acid, washed with distilled water, pumped out and flamed) from a gas reservoir, and condense by cooling T_1 with liquid air. Sealing off is carried out carefully at the constriction *C*, the walls of which must be thick enough to collapse without sucking in, as shown at (*b*). When required for use, a tap *T* (preferably of the right-angled type) is sealed at *aa*. In the barrel there is a small piece of clean iron *I* (if the gas attacks iron, then the latter must be enclosed in a closely-fitting glass tube). The space between *B* and *T* is evacuated and *I* is allowed to drop on *B* in order to smash it, and so release the gas. If the bulb is attached to an apparatus and cannot be shaken, then a small magnet is used to propel *I* against *B*.

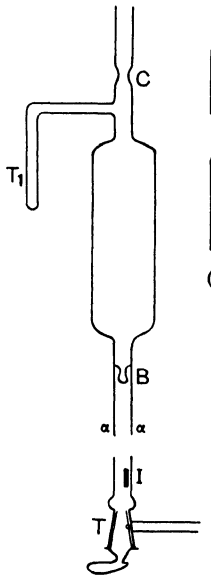


FIG. 101. Reservoir for transportation of gases.

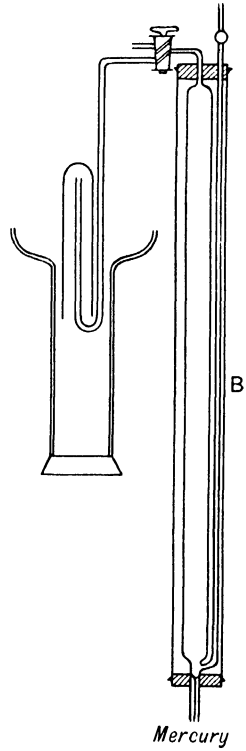


FIG. 102. Gas measuring burette.

Apparatus for measuring volume of gases accurately. Should it be necessary to measure the volume of an amount of gas collected from an apparatus or to make mixtures of known composition, the burette shown in Fig. 102 is suitable. The levelling tube is in the thermostatted jacket *B* containing a thermometer, while the burette itself is graduated in c.c.

Since the levelling tube is of smaller diameter than the burette, a correction for capillarity must be applied. This is obtained directly by allowing air at the same pressure into the two tubes, and reading off the difference in levels by means of a cathetometer.

Drying Materials

Calcium chloride should be free from calcium oxide. Before filling absorption tubes it is advisable to heat them strongly in a stream of dry air. The vapour pressure of water above $CaCl_2$ is 0·3 mm. at room temperature.

Concentrated sulphuric acid (density 1·84) must be free from SO_3 vapour. E. W. Morley (*Am. J. Sc.*, **30**, 1411 (1885)) estimated that sulphuric acid decreased the water content of air to about 10^{-2} mm. at room temperature.

Phosphorus pentoxide is the best drying agent. It often contains lower oxides of phosphorus, whose presence may be detected by heating with silver nitrate or mercuric chloride solution, when the latter are reduced. Purification is a tedious business, but there is now on the market an oxide guaranteed free from lower oxides. H. Moser (*Die Reindarstellung von Gasen*) states that by passing gas at the rate of 2 litres per hour over 25 c.c. P_2O_5 the vapour pressure of water is reduced to less than 10^{-5} mm.

Potassium hydroxide is not so effective as P_2O_5, the vapour pressure of H_2O above it being 0·007 mm.

Magnesium perchlorate. For many purposes phosphorus pentoxide as a dessicating agent has some disadvantages. If used for drying large volumes of gas it becomes liquid, and may clog communicating tubes, and cannot be regenerated *in situ*. To overcome these defects a more efficient agent than the alternative calcium chloride has been recommended by G. F. Smith (*Ind. and Eng. Chem.*, **19**, 411 (1927)), in the form of mixed perchlorates of magnesium and barium containing 25-35 per cent. of the magnesium salt. Although not so efficient as P_2O_5—it is stated to be as good as sulphuric acid—it is granular, offers little resistance to passage of the gases, and may be easily regenerated by heating to 250° C., the vacuum being that provided by a filter pump. Some idea of the performance of these mixed perchlorates may be had from the fact that passing air containing about 8 mm. of water vapour at the rate of 70 litres per hour through a column of reagent 7″ × 1″ reduced the partial pressure of H_2O to 0·007 mm.

Electrolysis of Sodium through Glass for Gas Purification

A clean film of metallic sodium is useful not only as a trap for mercury and water vapour (see p. 162), but also in the purification of a number

of gases. For example, ethylene and gaseous hydrocarbons may be freed from traces of oxygen by leaving them in a bulb containing such a film. Similarly ammonia may be dried in a sodium bulb, for the hydrogen produced may easily be got rid of by freezing the ammonia in liquid air and pumping off the hydrogen. The most satisfactory way of forming such a film is to electrolyse sodium through glass, using a thermionic cathode to supply the necessary electrons to neutralise the sodium ions as they migrate through the glass under an applied potential difference. A suitable arrangement using a 60 watt vacuum electric lamp is shown in Fig. 103 (R. C. Burt, *J. Opt. Soc. Am.*, **11**, 88 (1925)). The bulb is immersed in molten sodium nitrate (M.P. 312° C.) or, better, a mixture of sodium and potassium nitrate contained in an iron crucible. The filament is heated by 200 v. A.C. and the potential for electrolysis is supplied from 100 v. D.C. mains, a regulating resistance and a milliammeter completing the circuit. Currents as large as 300 mA., depositing 0·3 gm. of sodium per hour, may be used. Neither potassium nor lithium can be electrolysed through glass in this manner. Larger bulbs of soda glass are quite easily used, and a short thick filament heated from accumulators functions perfectly.

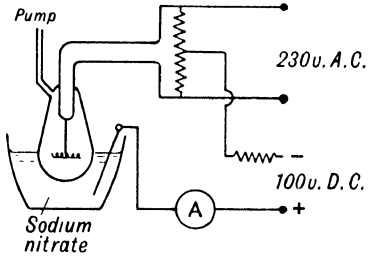


FIG. 103. Electrolysis of sodium through glass.

Pyrex glass can also be employed (E. W. Pike, *Review of Scientific Instruments*, **4**, 687 (1933) ; cf. also M. R. Andrews and J. S. Bacon, *J. Amer. Chem. Soc.*, **53**, 1674 (1931)), but now it is necessary to use a sodium nitrate bath in a nickel crucible at 480-510° C. containing 0·4 per cent. potassium nitrate and 0·8 per cent. calcium nitrate. The latter substances appear to prevent etching of the glass. With a wall thickness of 1-2 mm., 5 mA./cm.^{2} can be passed, thus giving 0·005 gm. of sodium per hour.

Pumped-out liquid air traps.

Those gases which boil about −80° C., such as ethane, ethylene, acetylene, nitrous oxide, hydrogen sulphide, etc., are not frozen out effectively when passed through a liquid air trap. Their vapour pressures at liquid air temperature are of the order 10^{-2} mm. By pumping off the liquid air at reduced pressure, temperatures approaching 70° K. may readily be obtained, at which the vapour pressure falls to about 10^{-5} mm. A suitable trap for the purpose is shown in Fig. 104, though an ordinary vacuum flask fitted with a rubber stopper bored with two holes, one of the trap, the other for the tube leading to the pump, will suffice. A

mercury manometer is attached to measure the pressure, and therefore the temperature, and also to act as a safety valve. Liquid air or oxygen is poured into the vacuum flask, and the pressure above it reduced by a rotary oil pump until the desired temperature is reached, and the tap shut. From time to time as the liquid air evaporates, the pressure must be reduced, but once the low temperature is reached it is not necessary to keep pumping continuously, since the liquid air does not evaporate much more quickly than when boiling at atmospheric pressure. Liquid nitrogen has the disadvantage that if the pressure be reduced too far it solidifies, and hence is not quite so effective a refrigerant. With liquid oxygen a temperature (*ca.* 60° K.) corresponding to a vapour pressure of 8 mm. is easily reached with a pump of the Hyvac type.

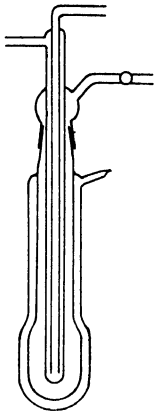


FIG. 104. Pumped-out liquid air trap.

B. PREPARATION OF GASES

Hydrogen. B.P. −252·78° C.

For the preparation of small quantities of hydrogen (not greater, say, than 1 litre) there is no better method than to diffuse electrolytic hydrogen, from zinc and sulphuric acid or from a cylinder, through a palladium tube into an evacuated reservoir. A suitable apparaus for the purpose is shown in Fig. 105. The palladium tube is gold-soldered to a platinum tube of the same diameter, which in turn is fused into the apparatus as shown. Heating is accomplished by a coil of nichrome wire wound on a silica tube. It is convenient to have a tap *T* to by-pass the palladium tube, so that the hydrogen reservoir may be evacuated.

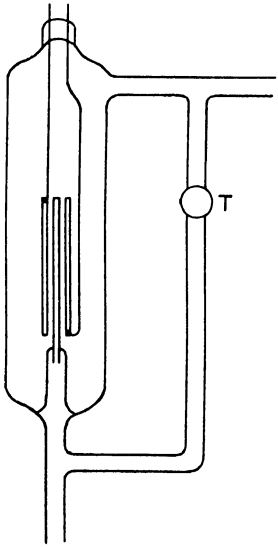


FIG. 105. Electrically heated palladium tube.

For larger volumes of hydrogen this method of purification takes too long. The gas is therefore generated electrolytically from a 30 per cent. solution of caustic soda with pure nickel electrodes. Two typical generators are shown in Fig. 106. To avoid overheating the cylinder containing the electrolyte is cooled

by wrapping lead piping carrying cold water around it. A current of 10 amps. will generate 4 litres of hydrogen per hour. The gas contains a small percentage of oxygen. It is therefore dried roughly with calcium chloride, passed over 30 cm. of platinised or palladised asbestos at 300° C., then over P_2O_5, and through a liquid air trap to remove the final traces of water vapour. Electrolytic hydrogen from a cylinder may be similarly purified. Hydrogen prepared in a Kipp's apparatus from zinc and sulphuric acid may contain as impurities AsH_3, PH_3, H_2S, hydrocarbons, oxygen, CO_2. The gas is therefore passed through 50 per cent. KOH, twice through saturated potassium permanganate, $CaCl_2$, platinised asbestos at 800° C. in a silica tube, $CaCl_2$ and P_2O_5.

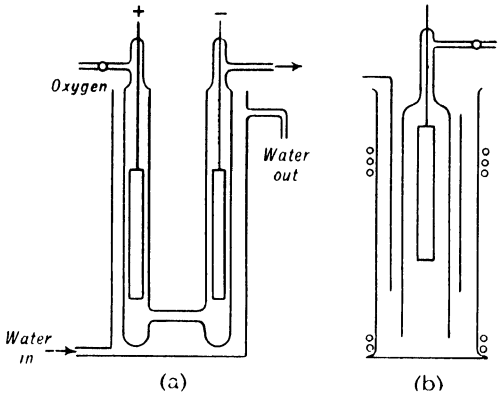


FIG. 106. Electrolytic generators for hydrogen.

Deuterium. B.P. −249.66° C.

Deuterium, in quantity, is likewise best prepared by electrolysis. Now, however, special precautions must be taken to avoid the introduction of hydrogen or water. First the density of the deuterium oxide is measured in the usual way. To render the liquid conducting metallic sodium is added, the metal previously having been boiled in a vacuum (Pyrex must be used—soda glass cracks too easily) to free it from hydrocarbons and from hydrogen. The solution of NaOD is then placed in a cell of the form shown in Fig. 106, except that the anode compartment is closed to avoid contamination of the D_2O with H_2O of the atmosphere. This compartment must be provided with a tap to allow the oxygen to escape. Drying before and after passage through platinised asbestos is carried out with liquid air traps, so that the deuterium oxide is not lost. Small quantities of deuterium are simply made in the Pyrex apparatus shown in Fig. 107, which has a ground joint J perpendicular to the plane of the apparatus to permit of the whole being rotated. First, D_2O is run into

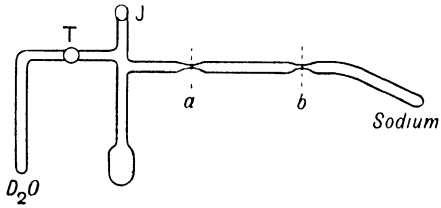


FIG. 107. Preparation of small amounts of deuterium.

the tube shown, frozen in liquid air and pumped free of air. This is repeated a few times. Next, metallic sodium is put into its appropriate compartment, and the apparatus once more evacuated. The sodium is then distilled, the pumps being on continuously, just past the first constriction at *a*, thereby leaving behind oxide, hydroxide and carbonate. The Pyrex tube is sealed off at *a*, and the metal gradually distilled along the tube until it is past the constriction *b*, which in turn is sealed off. When the sodium is cold the apparatus is rotated and a few drops of deuterium oxide allowed to run on to the metal, when immediate evolution of deuterium occurs. Deuterium oxide is trapped by a liquid air trap before the gas enters a gas holder.

Atomic Hydrogen

Atomic hydrogen may be generated by electrical dissociation of hydrogen molecules, or by collisions between optically excited mercury atoms and hydrogen molecules (see Chap. V). In the former method very nearly 100 per cent. atomic hydrogen may be prepared, but in the latter a partial pressure of 10^{-3} mm. in presence of 200 mm. of hydrogen is about the maximum so far attained. R. W. Wood (*Proc. Roy. Soc.*, A, **102**, 1 (1922)) was the first to produce atomic hydrogen electrically; his method has remained unmodified. A typical form of tube is shown in Fig. 108 (*a*). The total length is about 200 cm., and diameter 2 cm. The electrodes are of aluminium sheet, 0·05 cm. thick, fitted into circular end pieces, which are in turn fixed to copper-clad wires passing out at the usual type of pinch seal, as is shown in Fig. 108 (*b*). The hydrogen admitted to the tube must be slightly moist or contain a small percentage of oxygen, e.g. that present in electrolytic hydrogen. Water vapour is then introduced into the discharge tube, poisoning the walls for the recombination of atomic hydrogen thereon. It is also essential to withdraw the gas from a point as close to the middle of the tube as possible, for it is at this point that the atomic hydrogen concentration is highest. At the ends the presence of the metallic electrodes very considerably catalyses the recombination of atoms. Pressures lying between 0·1 and 1·0 mm. are suitable; the colour of the discharge should be fiery purple. A high concentration of molecules is indicated by a steely blue discharge. At these pressures a

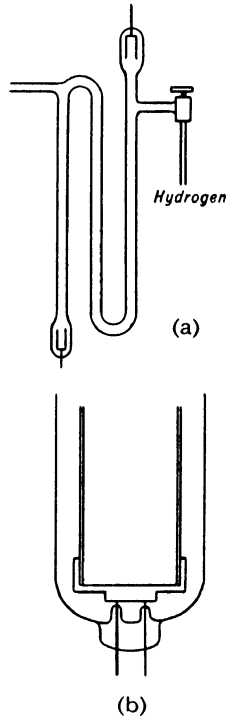


FIG. 108. Wood's tube for the generation of atomic hydrogen.

current of several hundred milliamperes may be supplied at about 5000 volts. It is advisable to cool the tube by blowing a strong current of air over it from an electric fan. If higher currents are used the tube is best immersed in a water bath, and constructed of Pyrex, in which case tungsten will be required for the pinch seals. A fast three- or four-stage mercury diffusion pump backed by an oil pump (see p. 54) are adequate to produce a good stream of atomic hydrogen. As is usual, the diameter of reaction tubes following the Wood's tube will limit the pumping speed. The atomic concentration at the exit of the discharge tube may be measured by the Harteck-Wrede gauge (see p. 95). In this connection see also p. 356. For the chemical properties of atomic hydrogen, see K. F. Bonhoeffer (*Ergebn. exakt. Naturwiss.*, **6**, 201 (1927)).

Para-hydrogen. B.P. −252·87° K.

This modification of hydrogen is best prepared by adsorbing normal hydrogen on charcoal contained in the apparatus shown in Fig. 109. The charcoal tube must be made of Pyrex, so that the charcoal may be out-gassed *in vacuo* at about 500° C. After cooling it is surrounded with liquid air, and hydrogen passed in until adsorption is complete. The time required for conversion may vary from a few minutes to several hours, depending on the activity of the charcoal. After a suitable interval, which can only be estimated by trial (for method of analysis, see p. 190), the liquid air is withdrawn, some of the hydrogen is allowed to escape, and the remainder is collected in a clean reservoir. The time of desorption must not exceed a few minutes, in order to avoid reconversion of the gas. In the presence of mercury and tap grease para-hydrogen may be preserved unchanged for months. By rapidly pumping off the liquid air the equilibrium concentration of para-hydrogen may be increased to 65 per cent. compared with 42-48 per cent. at temperature of liquid air boiling under atmospheric pressure.

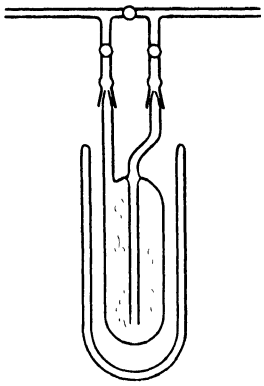


FIG. 109. Preparation of parahydrogen.

In order to prepare pure para-hydrogen liquid hydrogen is necessary. The procedure is exactly the same, except that for economy's sake the vessel containing the liquid hydrogen is best kept immersed in another Dewar flask containing liquid nitrogen (see Chap. II, p. 136). L. Farkas and H. Sachsse (*Z. phys. Chem.*, **B, 23,** 1 (1933)) have described a simple apparatus for the continuous production of pure para-hydrogen. It may be mentioned that 10 gm. of suitable charcoal will adsorb several litres of

hydrogen. Supported nickel catalysts are also particularly active in the conversion, and are especially useful for the continuous production of para-hydrogen (H. S. Taylor and A. Sherman, *Trans. Faraday Soc.*, **28,** 249 (1932)): for example, 15 gm. of the catalyst—Ni-kieselguhr—at −183° C. yielded 100 c.c. equilibrium hydrogen per minute. This catalyst was prepared as follows. Kieselguhr was saturated with nickel nitrate until about 15 per cent. of the preparation consisted of nickel. This was calcined, reduced in hydrogen at temperatures which rose to 130° C. during four hours, rose further to 160° C. in an hour, and was kept at this temperature for fourteen hours. Finally the temperature was raised to 450° and maintained there for about twenty hours.

The following table shows the equilibrium para-hydrogen content at various temperatures (A. Farkas, *Ortho-hydrogen, Parahydrogen and Heavy Hydrogen,* Cambridge 1935, p. 14).

TABLE 24

Equilibrium Para Content of Hydrogen

Temp. ° K.	% p-H_2	Temp. ° K.	% p-H_2	Temp. ° K.	% p-H_2
20	99·82	75	51·86	90	42·75
21	99·73	76	51·13	91	42·27
22	99·60	77	50·41	95	40·48
23	99·45	78	49·73	100	38·51
24	99·25	79	49·05	105	36·82
25	99·01	80	48·39	110	35·30
30	96·98	81	47·75	115	34·00
35	93·45	82	47·13	120	32·87
40	88·61	83	46·53	130	31·03
45	82·91	84	45·95	150	28·54
50	76·89	85	45·37	170	27·09
55	70·96	86	44·82	230	25·42
60	65·39	87	44·39	273	25·13
65	60·33	88	43·76	∞	25·00
70	55·83	89	43·25		

Ortho-deuterium may be prepared in an analogous manner, except that liquid air is not so effective and liquid hydrogen is best employed, as may be seen from an inspection of the following table showing the equilibrium percentage of ortho-deuterium as a function of temperature. It will be observed that 76-78 per cent. ortho-deuterium may be prepared from deuterium adsorbed on charcoal in a pumped-out liquid oxygen trap.

Temp. ° K.	% o-D_2	Temp. ° K.	% o-D_2	Temp. ° K.	% o-D_2
20	97·97	50	79·19	90	68·58
25	95·29	60	74·79	100	67·82
30	92·07	70	71·78	∞	66·66
40	85·12	80	69·82		

Oxygen. B.P. −182·96° C.

For the continuous generation of large volumes of oxygen the electrolytic method is best. A generator of the type used for hydrogen is suitable, the electrolyte being 20 per cent. sulphuric acid and the electrodes of platinum foil. The gas contains traces of hydrogen, which are removed by using platinised asbestos as for hydrogen purification. Smaller quantities of oxygen are most conveniently made by heating potassium permanganate in an evacuated tube. Dust arising from the manganese dioxide formed is filtered out with glass wool. Traces of carbon dioxide are removed by soda lime.

Ozone. B.P. −111·5° C.

This gas is best made by the silent electric discharge through oxygen in an apparatus shown in Fig. 110 due to C. Harries (*Ann.*, **343**, 341

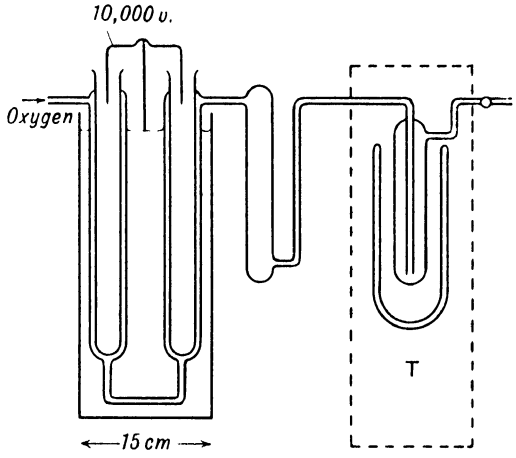


Fig. 110. Ozoniser.

(1905)). The containing jar and inner tubes are filled with dilute sulphuric acid or aqueous copper sulphate solution. The lead and copper wires are connected to a 10,000 volt transformer fed with 50 cycle current. The ozone so formed passes through a soda-lime tube to rid it of any oxides of nitrogen, if there are traces of nitrogen in the oxygen. The ozone is liquified in the liquid air-cooled trap *T*, while the unconverted oxygen is pumped off with a rotary oil pump. Since liquid ozone has a tendency to explode, the trap is best placed in a box large enough to facilitate manipulation of the liquid air flask and fitted with a Triplex or toughened glass window. The box occupies the position shown by the dotted lines. Small amounts of ozone are made at a time and the solid

kept stored continually at liquid air temperature, except when required for an experiment. The purity may be tested by introducing a known volume into a bulb carrying a hot platinum wire and noting the increase in pressure, or alternatively, a solution of potassium iodide is admitted to the sampling bulb and the resulting iodine liberated according to the equation $O_3 + 2KI + H_2O = O_2 + 2KOH + I_2$, titrated with standard sodium thiosulphate.

Atomic Oxygen

('High Frequency Discharge,' O. E. Kurt and T. E. Phipps (*Phys. Rev.*, **34**, 1358 (1929).) The discharge bulb is a 200 c.c. Pyrex bulb wound with six turns of copper tubing, 3 mm. external diameter, connected to a transformer giving 25,000 volts from the secondary and to a condenser having a capacity of 0·015 μF by 8 s.w.g. copper wire. The condenser consists of 15 plates of metal foil 500 cm.^{2} separated by two thicknesses of window glass, the whole being immersed in oil. The spark gap consists of two zinc electrodes 2 cm.^{2}, placed 1·5 cm. apart. A pressure of oxygen 0·007 to 0·45 mm. is satisfactory, and in this particular set-up 0·13 mm. is the optimum pressure.

L. C. Copeland has described a similar set-up (*Phys. Rev.*, **36**, 1222 (1930)), finding in agreement with Kurt and Phipps that the oxygen should contain a little moisture for the maximum rate of production of oxygen atoms. Nitrogen should be absent, although Kurt and Phipps used cylinder oxygen without any apparent deleterious effect. Copeland used a slit gauge (see p. 95) for measuring the extent of dissociation of oxygen. Instead of using one slit a number were made in the following manner. The end of a piece of Pyrex tubing was blown into a bulb 0·1 mm. in thickness. A small section of this thin glass was placed on a carbon plate, and the end of a piece of 1 cm. Pyrex tubing was heated to softening point and pressed against the thin glass, thus sealing it to the end. A piece of $\frac{1}{32}$ inch tungsten wire was mounted in a chuck of a jeweller's lathe, and a fine centred point produced by burning it with an oxygen flame while the lathe was rotating. This fine drill was then heated red hot with an air flame and the thin wall lightly brought to the hot point.

Atomic oxygen may also be produced by means of a Wood's tube. (P. Harteck and U. Kopsch, *Z. phys. Chem.*, **12B**, 328 (1931).) The discharge tube has the form shown in Fig. 108. The overall length is about 70 cm. and the diameter 18 mm. ; the electrodes are of aluminium. The oxygen is admitted through a reducing valve (see p. 64) and the mixture of atoms and molecules drawn off at the opposite point. At a pressure of about 1 mm. the stream velocity should be about 3 metres per sec., cor-

responding to the passage of 4 litres of oxygen at N.T.P. per hour through the tube. Under these conditions the current required (A.C.) is about 300 mA. at 5000 volts. At such streaming velocities the following percentages of atomic oxygen were found :

Distance from discharge (cm.)	% atoms
60	17·5
12	27
10	30
7	80

The concentrations were measured by allowing the atomic oxygen to combine on platinum and estimating the heat so generated.

Diffusion of oxygen into closed system. (J. B. Taylor, *Rev. Sci. Inst.*, **6**, 243 (1935).) Oxygen diffuses through silver, e.g. through a tube 3 cm. long, 0·3 cm. diameter, with walls 5 mil thick, 0·1 c.c. of O_2 per min. at N.T.P., pass when the tube is heated in air at temperatures below the M.P. (960° C.) by a small electric furnace.

Chlorine. B.P. −34·7° C.

This gas is most conveniently prepared in a pure state by dropping pure concentrated hydrochloric acid on to potassium permanganate contained in an evacuated flask. It is washed in permanganate solution, in water (in darkened vessels) and dried with P_2O_5. Four or five fractionations remove the last traces of oxygen (cf. e.g. M. Ritchie and R. G. W. Norrish (*Proc. Roy. Soc.*, **A, 140**, 105 (1933))—an impurity which often acts as an inhibitor in reactions of chlorine. M. Bodenstein (*Z. phys. Chem.*, **B7**, 387 (1930) dispenses with greased taps, and finally purifies his chlorine in an apparatus connected together with glass unlubricated taps (see p. 62).

Atomic Chlorine. (W. H. Rodebush and W. C. Klingelhoeffer, *J.A.C.S.*, **55**, 130 (1933).) For this purpose a Wood's tube is not effective, even with electrodes which are not attacked by chlorine.

The apparatus (Fig. 111) for the production of atoms consists of a reservoir of liquid chlorine maintained at a suitable temperature, e.g. −80° C., and a discharge bulb *E* of 200 c.c. capacity, around which a high frequency current carried by 3 mm. copper tubing is circulated. Excitation is provided by a 2·5 k.v.a. 25,000 volt transformer, with a spark gap of 1 cm. between disc electrodes 3 cm. in diameter. This should be mounted in a sound-proof box with provision for forced ventilation. The condenser *D* consists of 14 plates 20 × 23 cm., separated by 5 mm. of glass. The high frequency coil is centre-tapped and earthed, to prevent the discharge penetrating into the apparatus.

A Wrede gauge (see p. 95) is used to measure the atomic concentration (the orifice is 0·1 mm. in diameter) and is made in the following way. Traps T_1, T_2, T_3 at −80° C. prevent vapour from the oil manometer reaching other parts of the apparatus. The oil manometer I measures the difference in pressure across the slit, and the manometer J the total pressure. Equilibrium is established in two minutes. With this set up, 5 to 10 c.c. of Cl_2 at a pressure of 0·2-0·7 mm. are dissociated 8 to 18 per cent. The differential pressure developed under these conditions is

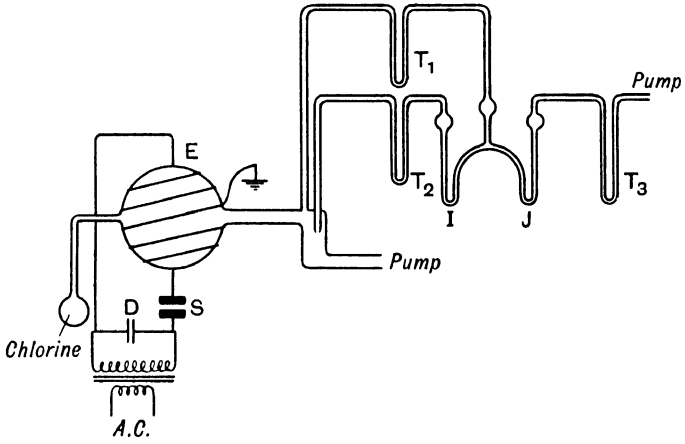


FIG. 111. High frequency generator for atomic chlorine.

of the order of a few tenths of a millimetre of oil, e.g. for 11 per cent. dissociation 0·40 mm. oil, or 0·024 mm. Hg.

After a few hours of operation the discharge bulb becomes coated with a white deposit only slightly volatile at a red heat. This is probably formed by the attack of silica in the glass by chlorine atoms.

A little silver foil is placed in the diffusion gauge to catalyse the recombination of chlorine atoms.

Hydrogen Chloride. B.P. −84·9° C.

Hydrogen chloride is prepared by dropping pure concentrated hydrochloric acid into warm sulphuric acid, dried with phosphorus pentoxide, fractionation following as in the case of chlorine. Hydrogen chloride if pure and dry may be stored over mercury.

Hydrogen Bromide. B.P. −66·8° C.

A mixture of phosphorus pentoxide and freshly ignited sand is introduced into the usual type of generating flask. After evacuation

a 25 per cent. aqueous solution of hydrogen bromide is added slowly from a dropping funnel. If stronger acid is used, or if the rate of addition too quick, the HBr generated will be partly decomposed. The taps in the apparatus are best lubricated with metaphosphoric acid. Small quantities of bromine are removed by passing over red phosphorus, which must be free from lower oxides of phosphorus. This is easily done by boiling for an hour with dilute caustic soda. Water vapour is removed by phosphorus pentoxide, the HBr collected in a liquid air trap and any hydrogen pumped off. This is followed by fractionation.

Deuterium bromide may be produced by passing deuterium and bromine over a platinum catalyst in the apparatus used for the preparation of HI (J. R. Bates, J. O. Halford and L. C. Anderson, *J. Chem. Physics*, **3**, 531 (1935)).

Hydrogen Iodide. B.P. −35·4° C.

The best method for preparing pure hydrogen iodide is due to M. Bodenstein (*Z. phys. Chem.*, **13**, 59 (1894); *ibid.*, **119**, 127 (1926)). The essential part of the apparatus required is shown in Fig. 112.

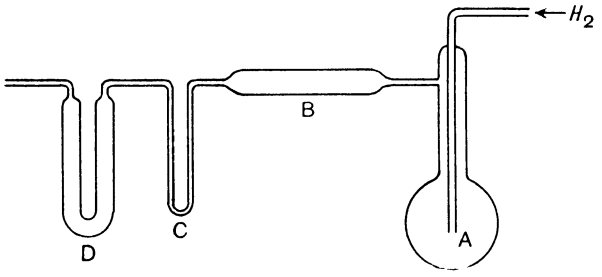


FIG. 112. Preparation of hydrogen iodide.

The flask *A* contains dry resublimed iodine; this leads to a tube *B* containing platinised asbestos, followed by a U-tube cooled to −30° C. to condense out as much iodine as possible. The last traces of iodine are eliminated by a U-tube of red phosphorus. Finally the gas is collected in a liquid air trap and fractionated. In starting the preparation, the platinised asbestos is heated first, and a fairly rapid current of hydrogen is sent through the apparatus. The iodine is gradually heated, the mixture being such that hydrogen is always in excess. The hydrogen stream must be dry and free from oxygen, and also fast enough to prevent back diffusion of the iodine vapour.

Deuterium iodide may be prepared in an exactly similar manner (J. R. Bates, J. O. Halford and L. C. Anderson, *J. Chem. Physics*, **3**, 413 (1935)).

Carbon Monoxide. B.P. −191·5° C.

This gas is prepared by dropping air-free formic acid into concentrated sulphuric acid at 120-150° C. contained in an evacuated flask fitted with dropping funnel ; at lower temperatures evolution of gas is slow. The only impurities are carbon dioxide and acid spray. The gas is therefore passed over soda lime, and then phosphorus pentoxide. In some experiments it is necessary to have well-dried gas. This can be accomplished by passing the gas through a trap filled with glass wool and immersed in liquid air, and finally storing the gas in reservoir containing phosphorus pentoxide.

Carbon Dioxide. B.P. −78·5° C.

1. From sodium bicarbonate. Well-dried sodium bicarbonate is heated in a Pyrex tube fitted with glass wool plugs to catch solid particles. The carbon dioxide is then dried by passing over $CaCl_2$ and phosphorus pentoxide.

2. Carbon dioxide from a cylinder contains O_2, N_2, CO. It may be freed from these gases by fractional distillation, but if, as may sometimes happen, H_2S and SO_2 are also present, the following purification train is necessary : titanous chloride solution, sodium bicarbonate, copper sulphate, concentrated sulphuric acid, hot copper (700° C.) and hot copper oxide (700° C.).

Carbon Oxy-sulphide. B.P. −50·2° C

This gas is prepared by the action of dilute sulphuric acid on ammonium thiocyanate, the essential reaction being

$$HCNS + H_2O = NH_3 + COS.$$

According to H. Moser (*loc. cit.*) 200 c.c. of a saturated solution of ammonium thiocyanate are run into a 5-litre flask containing an ice-cooled mixture of 2000 gm. H_2SO_4 and 1000 gm. water, and fitted with a gas delivery tube. The temperature is raised to 40° C. when a continuous stream of COS is evolved. The gas contains many impurities, NH_3, H_2S, CS_2, SO_2, HCN, CO_2, $(C_2H_5)_2S$, H_2 and H_2O. The HCN, H_2S and CO_2 are removed by bubbling through two wash bottles containing 40 per cent. KOH ; NH_3 and H_2O are removed with concentrated sulphuric acid. The CS_2 and $(C_2H_5)_2S$ are best separated by fractional distillation. The CS_2 can also be removed by bubbling through the following mixture : 1 part triethyl-phosphine, 9 parts pyridine and 90 nitrobenzene ; but the vapour of the mixture has also to be removed, which is no easier than that of removing

CS_2 itself. If ammonium thiocarbamide is available hydrochloric acid gives COS :

$$NH_4.COSNH_2 + 2HCl = COS + 2NH_4Cl$$

(A. Stock and E. Kuss, *Ber.*, **50**, 159 (1917)).

Nitrogen. B.P. −195·8° C.

Nitrogen is usually available in cylinders, and contains about 1 per cent. oxygen, with perhaps a little water vapour, carbon dioxide and inert gases. Such nitrogen is passed over reduced copper at 700° C. in a combustion tube, through soda lime and phosphorus pentoxide.

If the gas is prepared from air, the following purifying train is necesary : a tube of moistened cotton wool to remove dust, one calcium, chloride and one soda lime tower, two wash bottles of alkaline hydrosulphite, two of concentrated sulphuric acid, 150 cm. of red-hot active copper, and finally P_2O_5.

Small quantities of pure nitrogen may be prepared by heating sodium azide in a high vacuum to about 320° C., the heating tube being immersed in a sand bath in case of explosion.

Ammonia. B.P. −33·5° C.

Ammonium salts, which form the starting point in the preparation of ammonia, if prepared from ammonia derived from coal tar distillation, contain organic bases such as pyridine, methylamine, pyrrol, etc. To free ammonium chloride, for example, from such impurities, a saturated solution is boiled with a tenth of its volume of concentrated nitric acid until free from hydrochloric acid. The solution is evaporated and ammonium chloride allowed to deposit. The ammonium chloride is further recrystallised to free it from ammonium nitrate. The chloride is mixed with soda lime and gently heated *in vacuo*. The ammonia is dried by passing through a 50 cm. tube filled with lumps of recently ignited lime, and finally fractionated by means of solid carbon dioxide and preserved in a flask containing metallic sodium. Traces of hydrogen produced during storage may be removed by condensing the gas in a liquid air trap and evacuating the bulb thoroughly.

Synthetic ammonia is free from organic impurities, and need only be dried according to the above directions.

Trideutero-ammonia B.P. −30·9° C.

Trideutero-ammonia or ammonia in small quantity is prepared from magnesium nitride and deuterium oxide or water. The nitride is pre-

pared by passing a slow current of nitrogen over magnesium filings, heated in a combustion furnace to a temperature at which combustion tubing just commences to soften. It is advisable to attach a manometer to the system to check the uptake of nitrogen—a process which requires several hours for completion. The filings are preferably contained in porcelain boats, since magnesium reduces part of the glass to silicon. The nitride must be transferred immediately after preparation to a stoppered bottle, or, better, sealed into a glass tube. The apparatus used for generation of the gas is shown in Fig. 113. The nitride is placed in tube *I*, water in tube *II*, and the whole evacuated, the water meanwhile being frozen by means of liquid air. Liquid air is now put in the nitride container and water vapour allowed to distil over. On allowing the nitride tube to warm up, ammonia is evolved, and collected in a flask containing metallic sodium.

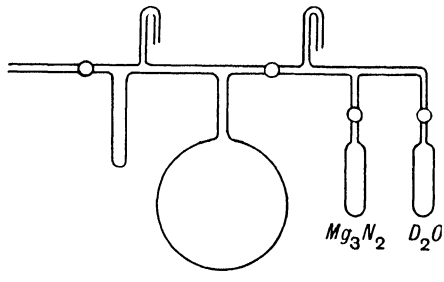


FIG. 113. Preparation of trideutero-ammonia

If preparing heavy and light ammonia by this method it is absolutely essential to use two separate samples of nitride, for, if part of the nitride is decomposed by deuterium oxide and then water is added to prepare light ammonia, it will be found that the light ammonia contains some deuterium owing to interchange between magnesium deuteroxide and H_2O.

Nitric Oxide. B.P. −151·8° C.

A simple method of preparation is due to M. W. Travers (*Gases* p. 50 : Macmillan). Boiled dilute nitric acid, density 1·1 gm./c.c., is run into an evacuated flask. A saturated solution of sulphur dioxide in deaerated water is then added from a dropping funnel.

To free the gas from other oxides of nitrogen the following method is advocated by K. Adwentowski (*Z. comprim. u. verfl. Gase*, **13**, 1, 19 (1911)) It is first passed through a U-tube filled with glass beads moistened with concentrated sulphuric acid, then through a long spiral cooled in a bath of petrol ether at −148° C., whereby nitrous oxide and higher oxides are removed. It is then collected in a liquid air trap, uncondensable gas (e.g. N_2) and some nitric oxide being pumped off. Repeated fractionation is finally necessary to ensure absence of traces of N_2O, NO_2.

Nitric oxide cannot be preserved in a pure state in gas holders containing water.

A second method of preparation (L. W. Winkler, *Ber.*, **34**, 1408 (1901) ; Johnston and Giauque, *J.A.C.S.*, **51**, 3194 (1929) ; W. A. Noyes, *J.A.C.S.*, **53**, 515 (1931)) is based on the reduction of the nitrite ion according to the following equation :

$$2NO_2^- + 4H^+ + 2I^- = 2NO + I_2 + 2H_2O.$$

The apparatus employed is similar to that illustrated in Fig. 97 ; two towers, containing glass beads moistened with concentrated sulphuric acid and with 50 per cent. caustic potash respectively, are inserted in the purification train. Thereafter the gas is dried by passing over calcium chloride and phosphorus pentoxide. 75 gm. KNO_2 and 38 gm. KI are dissolved in 225 c.c. distilled water, and the solution run into the generating flask. A 50 per cent. solution of sulphuric acid is then allowed to drop into this mixture, the flask having previously been evacuated as completely as the vapour pressure of water will allow. Impurities are HI, I_2, NO_2. These are removed by passing the gas over soda lime. A small trace of N_2O may be present, which can be removed along with traces of air by fractional distillation with liquid air. The vapour pressure of NO at the temperature of boiling oxygen is 3·2 mm., and at that of boiling nitrogen 0·1 mm.

Nitrous Oxide. B.P. −89·5° C.

This gas is prepared by heating ammonium nitrate mixed with an equal weight of clean sand to a temperature not exceeding 290° C. Impurities are NO, N_2, NO_2, O_2, CO_2, H_2O. The following purifying train is therefore necessary : ferrous sulphate (NO), aqueous caustic soda (NO_2, CO_2), concentrated sulphuric acid and phosphorus pentoxide (H_2O). Traces of O_2 and of N_2 are removed by repeated fractionation with liquid air.

Nitrous oxide from cylinders used for dental purposes is particularly free from NO and NO_2. It contains a very little air, and therefore requires fractionation with liquid air, preceded by drying with P_2O_5.

Nitrogen Peroxide. M.P. −9° C., B.P. 22·4° C.

This substance is prepared by heating lead nitrate. To avoid explosive decomposition it is advisable to mix the nitrate with clean sand and warm to about 110° C. The gas is collected in a liquid air trap, while the accompanying oxygen is pumped off. The NO_2 is then freed from dissolved oxygen by repeated fractionation.

Methane. B.P. −161·4° C.

For small quantities the decomposition of methyl iodide with a zinc-copper couple is suitable.

Granulated zinc is first washed with very dilute sulphuric acid, then immersed in a 2 per cent. copper sulphate solution. When the blue colour has disappeared the solution is decanted and the treatment with copper sulphate repeated three times. The couple is washed with water and then with alcohol. Whilst wet it is transferred to the generating flask shown in Fig. 114. An alcoholic solution of methyl iodide is added from the dropping funnel, whilst the temperature of the flask is maintained at 40° C.

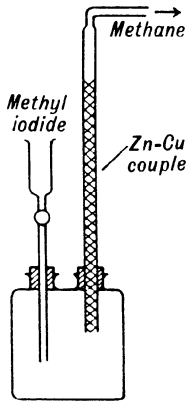


FIG. 114. Preparation of methane

Impurities are CH_3I, C_2H_5OH, H_2, traces of ethane and air. Fuming sulphuric acid removes CH_3I and C_2H_5OH and aqueous KOH, SO_3 vapour. The methane may be freed from hydrogen by condensing it in a trap cooled in liquid air or oxygen boiling under reduced pressure.

For larger quantities the decomposition of aluminium carbide with water is less costly. 100 gm. Al_4C_3 are placed in a 500 c.c. flask and 350 c.c. of water at 90° C. are added quickly. The reaction starts slowly, gradually speeding up to give a constant stream of methane. Impurities are H_2, C_2H_4, CO_2, traces of NH_3, SiH_4 and H_2S. The impure gas is led through two wash bottles of ammoniacal cuprous chloride, two of concentrated sulphuric acid, and one of alkaline hydrosulphite.

Methyl Deuteride. (N. Ginsburg and E. F. Barker, *J. Chem. Physics*, **3**, 668 (1935)) is most easily prepared by the Grignard reaction.

$$CH_3I + Mg = CH_3MgI,$$
$$CH_3MgI + D_2O = CH_3D + MgI(OD).$$

It is recommended that the methyl iodide be dissolved in dibutyl ether rather than the usual diethyl ether, and that the gas be collected over concentrated sulphuric acid in order to get rid of traces of ether. The infra-red absorption spectrum shows that, besides CH_3D, there is some CH_2D_2 present in the gas.

Ethane. B.P. −88·7° C.

This may be made in a very pure state by the hydrogenation of ethylene. A 1 : 1 mixture of hydrogen and ethylene is prepared in a gas holder. The dry mixture is passed through a 70 cm. tube of finely-

divided nickel at 150° C. The latter is made by dissolving nickel in nitric acid, calcining the nitrate and reducing the oxide at 300° C. with hydrogen. After this treatment the gas still contains ethylene and hydrogen. It is therefore passed through two flasks of fuming sulphuric acid, one of 50 per cent. KOH, and finally dried with P_2O_5. The hydrogen is removed by freezing the ethane in a liquid air trap and pumping off.

Free methyl or ethyl radicals can be prepared, according to F. Paneth and W. Hofeditz (*Ber.*, **62**, 1335 (1929)) and F. Paneth and W. Lautsch (*Ber.*, **64**, 2702 (1931)), by thermal decomposition of lead tetramethyl or tetraethyl in a current of hydrogen at 1-2 mm. pressure. Instead of hydrogen, water, carbon dioxide, acetone or hexane can also be used as carrier gas (F. O. Rice, W. R. Johnston and B. L. Evering, *J. Amer. Chem. Soc.*, **54**, 3529 (1932)). The radicals can be detected in a gas stream by their reaction with a mirror of lead or bismuth, which are removed owing to the formation of volatile methyl compounds. Mirrors of arsenic, antimony, tellurium, tin, and germanium are removed not only by radicals, but also by hydrogen atoms. The lifetime of the radicals is of the order of 10^{-2}-10^{-3} sec. They disappear by forming hydrocarbons (cf. also F. Paneth and collaborators, *J. Chem. Soc.* (1935), 366, 372, 380; and F. O. Rice and K. Rice, *The Aliphatic Free Radicals*, Johns Hopkins Press, Baltimore (1935)).

Ethylene. B.P. −103·7° C.

The gas is prepared by the action of alcohol on orthophosphoric acid. A 200 c.c. wide-necked flask is fitted with a stopper carrying a thermometer, a dropping funnel, the end being drawn off to a point, and a delivery tube. The flask is filled with 60 c.c. orthophosphoric acid (s.g. 1·70 to 1·75), connected to an empty flask having a safety manometer through wash bottles containing alkaline hydrosulphite and concentrated sulphuric acid. When the generating flask and empty flask are evacuated the temperature of the acid is raised to 200° C., and the alcohol (rectified spirit) added slowly.

Impurities are an oil, alcohol vapour, water, traces of CO_2 and O_2. To obtain a thoroughly oxygen-free gas H. H. Storch (*J.A.C.S.*, **56**, 374 (1934)) recommends the following procedure. After the normal fractionation with liquid air, the ethylene is passed through a tube $23 \times 2{\cdot}5$ cm., filled with glass wool covered with sputtered sodium. The latter is prepared by alternating small lumps of sodium with layers of glass wool, evacuating at about 300° C. until the glass wool is completely covered with a bright layer of sodium and the pressure reduced to 10^{-3} mm.

Cyanogen. B.P. −20·7° C.

Cyanogen is prepared by heating mercuric cyanide, prepared as follows: aqueous HCN is mixed with enough yellow mercuric oxide to make the solution alkaline to litmus. The solution is filtered and HCN added until the filtrate smells strongly of HCN. The solution is evaporated, during which crystals of mercuric cyanide separate. The dry cyanide is then heated in a hard glass or silica tube, which is connected to a trap cooled in running water to condense mercury vapour and paracyanogen. The gas may then be fractionally distilled.

Acetylene. B.P. −82·4° C.

In preparing acetylene from calcium carbide and water it is advisable to add the carbide to the water by using a Wolff's bottle with a wide tube dipping into water, or by lowering a wire gauze basket containing carbide into water. The following impurities are present: H_2, NH_3, H_2S, SiH_4, PH_3, CO, CO_2, O_2, N_2 and CH_2O. First the gas is led through a 50 cm. tube filled with cotton wool to free it from particles of carbide and calcium oxide, then through aqueous NaOH (50 per cent.), aqueous chromic acid, HCl-$HgCl_2$ solution, alkaline hydrosulphite, and finally dried with $CaCl_2$ and P_2O_5. It is then condensed with liquid air, the non-condensable gases being pumped off.

Acetylene from cylinders is generally purer, but contains in addition acetone. It must therefore be bubbled through two wash bottles filled with a strong solution of sodium bisulphite.

Dideutero-acetylene. (S. C. Lind, J. C. Jungers and C. H. Schiflett, *J.A.C.S.*, **57**, 1032 (1935).) The apparatus required is shown in Fig. 115.

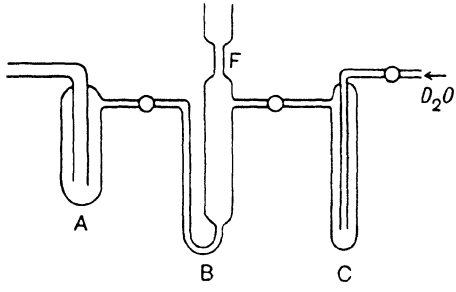


FIG. 115. Preparation of dideutero-acetylene.

A large lump of calcium carbide is selected, the middle portion isolated, crushed and quickly introduced into *B*. *F* is then sealed off and the apparatus (Pyrex glass) baked out at 400° C. for 24 hours. Deuterium oxide is distilled into *C*. Trap *A* is surrounded by liquid air, and the tap

connecting *B* and *C* opened to allow the D_2O vapour to come into contact with the carbide. After all the water has distilled over, the contents of *A* are passed over the residual carbide in *B* to rid the gas of traces of water vapour. Finally the acetylene is collected in *A*, which is then surrounded by a CO_2-acetone mixture at $-78°$ C. and the dideutero-acetylene collected in a suitable gas reservoir.

Hydrocyanic Acid. B.P. 20·8° C.

Potassium cyanide, free from carbonate, is placed in a flask fitted with a dropping funnel. The outlet of the flask is connected to tubes of calcium chloride and of phosphorus pentoxide, followed by a trap cooled in CO_2-ether to $-80°$ C. for collecting the acid. The flask is evacuated and a 50 per cent. (by volume) mixture of sulphuric acid and water slowly dropped on to the KCN. The acid collected in the trap may contain a little carbon dioxide if the KCN is not quite pure. It may easily be separated by fractional distillation.

Hydrogen Sulphide. B.P. −60·8° C.

Hydrogen sulphide is prepared by dropping 10 per cent. sulphuric acid on calcium sulphide contained in an evacuated flask. Impurities are HCl, H_2O, CO_2 and traces of O_2. Oxygen is first eliminated by passing the gas over chromous chloride-acetate paste or 15 per cent. titanous chloride containing a little sulphuric acid to prevent hydrolysis; HCl and CO_2 are absorbed in a concentrated solution of potassium sulphide, and H_2O with phosphorus pentoxide, the whole being followed by fractionation with liquid air. Dry hydrogen sulphide may be stored over mercury.

Sulphur Dioxide. B.P. −10·02° C.

Concentrated sulphuric acid is dropped into a concentrated solution of pure sodium sulphite in an evacuated flask (1 part by weight of Na_2SO_3 and 2 parts water). The gas is dried with P_2O_5 and fractionated. SO_2 from a syphon contains a little air and water vapour when first drawn from a full syphon, and therefore requires drying and subsequent fractionation.

Phosphine. B.P. −87·4° C.

This gas is best made by treating phosphonium iodide with caustic potash, $PH_4I + KOH = PH_3 + KI + H_2O$. The original method of A. Baeyer (*Ann.*, **155**, 269 (1870)), for the preparation of PH_4I has been modified by M. Ritchie (*Proc. Roy. Soc.*, **A 128**, 562 (1930)). 60 gm. white phosphorus is dissolved in a 150 c.c. of carbon disulphide in a

retort leading to a wide water-cooled condenser ; 100 gm. of iodine are then added in small portions, the solution being kept cooled in ice. The carbon disulphide is distilled off on the water bath, a current of CO_2 being passed through the retort during the distillation. 50 gms. of water are added to the phosphorus tri-iodide from a dropping funnel, the mixture being cooled in ice to prevent volatilisation of PH_4I, and finally set aside for 3-4 days. Thereafter the iodide is sublimed out of the mixture by heating in a water bath to 80-90° C. The iodide, of yellowish brown colour, is scraped from the walls of the condenser and purified by sublimation in the vacuum provided by a filter pump. The iodide is placed in a suitable flask that is evacuated, and 20 per cent. KOH solution is added from a dropping funnel. Hydrogen iodide and water are removed from the gas by passing over soda lime and phosphorus pentoxide. The gas is then collected in a liquid air trap, and pumping and fractional distillation continued until the pressure is not greater than 0·007 mm.—the vapour pressure of phosphine at liquid air temperatures.

Trideutero Phosphine has been made (M. de Hemptinne and J. M. Delfosse, *Bull. Acad. roy. Belg.*, **21**, 793 (1935)) from the corresponding heavy phosphonium iodide, but the small yield of gas for a given quantity of heavy water is not advantageous. The gas is more conveniently made by the interaction of calcium phosphide with deuterium oxide in the apparatus shown in Fig. 115, in which the D_2O vapour is continually circulated over the phosphide. To ensure that no PH_3 is generated, it is essential to use freshly prepared calcium phosphide and then to take only the inner portion of the lumps. These are heated strongly *in vacuo* before the deuterium oxide is allowed access to the phosphide. The impure gas collected in the liquid air traps may contain a little D_2O and P_2D_4. These are separated by fractional distillation, a CO_2 bath at $-80°$ C. replacing the liquid air in order to keep back these impurities. The purity may be checked by decomposing a measured volume of the gas on a well outgassed tungsten wire or by determining its density, which is 8·8 per cent. greater than that of PH_3, or by measuring the deuterium content of the gas produced on decomposition (H. W. Melville and J. L. Bolland, *Proc. Roy. Soc.*, **A**, **160**, 384 (1937)).

Arsenic Trihydride. B.P. −54·8° C.

Arsenic trihydride may be generated by the reduction of arsenic compounds with nascent hydrogen. One of the most convenient methods is to drop dilute hydrochloric acid on zinc arsenide contained in an evacuated flask, cooled in ice. The gas evolved contains hydrogen and acid spray, and is therefore passed over soda lime followed by phosphorus

pentoxide. Fractional distillation with liquid air completes the purification. The gas may be stored without decomposition and exposed to daylight, since absorption of light does not commence till a wavelength of 2500Å is reached. (G. H. Cheesman and H. J. Emeléus, *J. Chem. Soc.*, (1932) 2847).

Antimony Trihydride. B.P. −17° C.

Antimony trihydride is prepared by dropping a magnesium-antimony alloy into ice-cold dilute hydrochloric acid. (A. Stock, W. Doht and O. Gutmann, *Ber.*, **35**, 2270 (1902); **37**, 885 (1904)). The alloy is first made by fusing together 20 gm. of finely ground antimony powder and 40 gm. of magnesium powder in an iron boat contained in an iron tube heated to redness. A slow current of hydrogen is passed through the tube to prevent oxidation. The alloy is broken up to pass through a 1/2 mm. sieve. In order to introduce the alloy to the acid without admitting air to the apparatus the device shown in Fig. 116 is used. First, dilute hydrochloric acid is placed in the flask and the alloy run into the hopper above. A glass rod *B* has attached to it an inverted glass cup *C* sealed with mercury, and terminates in a pointed end *D* bearing on a circular seat at the bottom of the hopper *E*. CO_2 is passed into the flask, and *B* withdrawn to admit a small quantity of the Sb-Mg alloy. The gas is passed over soda lime and P_2O_5 and collected immediately in a liquid air trap. Fractionation is then carried out behind a protective glass screen and the gas finally stored in liquid air. The taps in the purification train are best lubricated with phosphoric acid (see p. 68), or are replaced by mercury cut-offs, since rubber grease initiates decomposition of SbH_3.

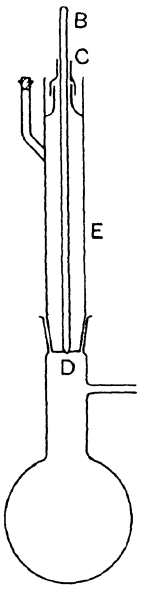


FIG. 116. Preparation of stibine.

Silicon Hydrides. SiH_4, B.P. −112° C.; Si_2H_6, B.P. −15° C.

The best method of preparation consists in adding magnesium silicide to hydrochloric acid, the reaction being $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$, though other hydrides are produced simultaneously. The technique for the preparation of pure samples of SiH_4 and of Si_2H_6 is due to A. Stock and C. Somieski (*Ber.*, **49**, 111 (1916)).*

* See also C. A Kraus and C. L. Brown, *J. Amer. Chem. Soc.*, **52**, 4031 (1930); **56**, 765 (1934).

First, it is necessary to prepare Mg_2Si. Phosphorus-free and sulphur-free silicic acid is mixed with 0·5 N caustic soda and heated until thoroughly dehydrated. A little alkali is necessary, since alkali-free SiO_2 reacts too quickly with magnesium. Two parts by weight of magnesium are mixed with one of SiO_2, and 100 gm. of this mixture put in a one litre iron crucible provided with a little hole, through which a pipe is inserted to lead in hydrogen, as in a Rose crucible. The whole is placed in a large water bath. The reaction is set off by pushing a match into the mixture and igniting the end. The lid is immediately put on and the hydrogen ignited. When the reaction is completed the blue crystals of Mg_2Si are broken up in a hydrogen atmosphere until they will pass a 1 mm. mesh sieve. The addition of the magnesium silicide to the acid must be done in an atmosphere of hydrogen, and for this purpose the following rather complicated apparatus is used (Fig. 117). A glass tube *A*, 4 cm. in diameter, contains a closely fitting inverted tube *B*. This is fitted with a wooden plug, through which tube *E* leading to the generating flask passes easily. The magnesium silicide *C* is placed in *B*. *F* is a mercury reservoir, and *H* a 4-litre flask containing 3 litres of 10 per cent. hydrochloric acid Before mercury is admitted from *F*, dry hydrogen is passed through the apparatus, since the silicon hydrides are spontaneously inflammable. Mercury is run into *A* from *F*. *B* is forced up until the Mg_2Si is level with the top of *E*. A small electric bell movement *K* taps a little of the silicide into H, when evolution of the gas begins, hydrogen meanwhile being bubbled through the apparatus. The rate of addition is regulated, so that the temperature of the acid rises to 50-60° C. and remains there. The gas is washed free from HCl by four wash bottles containing water, and is dried by passage over calcium chloride and phosphorus pentoxide, finally collected in a liquid air trap, and the hydrogen pumped off. The liquid air is replaced by a low temperature bath (see p. 137) at −125° C., at which temperature the vapour pressure of SiH_4 is 230 mm., and the monosilane condensed in

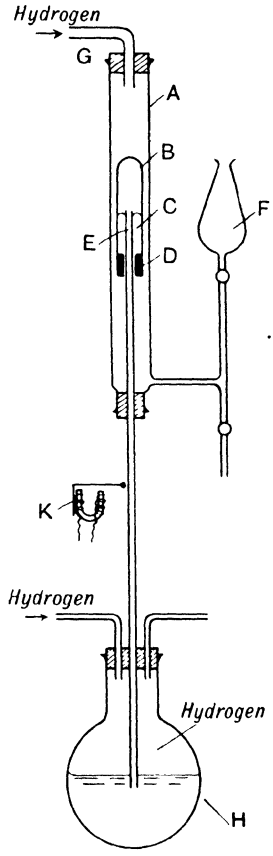


Fig. 117. Preparation of silicon hydrides.

another receiver. This distillation is repeated several times until a constant vapour pressure is obtained. The composition of the monosilane may be determined by shaking with concentrated caustic soda, when four volumes of hydrogen should be produced according to the equation

$$SiH_4 + 2NaOH + H_2O = Na_2SiO_3 + 4H_2.$$

The residue from the distillation of the SiH_4 contains Si_2H_6 and higher homologues. The temperature of the mixture is raised to $-100°$ C., at which temperature disilane has a vapour pressure of 4·5 mm. This is collected in another liquid air trap and fractionated in the usual way. On treatment with caustic soda it should give seven volumes of hydrogen,

$$Si_2H_6 + 4NaOH + 2H_2O = 2Na_2SiO_3 + 7H_2.$$

Before the generating apparatus is dismantled the hydrogen is replaced by CO_2, and traces of silicon hydride carefully got rid of in case of explosion.

Boron Hydrides. B_2H_6, B.P. $-92·5°$ C.; B_4H_{10}, B.P. 176° C.

The technique for the preparation of these hydrides in a pure state is due to Stock and co-workers (A. Stock and C. Massenez, *Ber.*, **45**, 3539 (1912); A. Stock and K. Friederici, *ibid.*, **46**, 1960 (1913); A. Stock and E. Kuss, *ibid.*, **47**, 811, 3124 (1914)). They are prepared by dropping magnesium boride into hot concentrated hydrochloric acid. The boride is prepared in the following way. Anhydrous boron trioxide, passing a 120 mesh (per inch) sieve, is mixed with three parts by weight of magnesium powder. Ten gm. of the mixture are heated in a 50 c.c. iron crucible, provided with a lid bored with a hole to admit a current of hydrogen during the reaction. The reaction is started by heating the crucible with a blast lamp. After the mixture has reacted it is allowed to cool in hydrogen, and the mass broken up to pass a 50 mesh sieve.

The apparatus for the preparation of the boranes is exactly similar to that used for antimony hydride, except that 4N hydrochloric acid at 50° C. is placed in the generating flask, through which a current of hydrogen is passed. The gas is washed with water, dried with calcium chloride and phosphorus pentoxide and collected in a liquid air trap, the hydrogen being pumped off. The temperature of the trap is raised to $-80°$ C., when the pressure should rise to 250 mm. The B_2H_6 is pumped off into another liquid air trap until the pressure begins to fall below 280 mm. Depending on the purity of the reagents, the gas may contain a little SiH_4, H_2S or NH_3, which are very difficult to separate. The composition of the gas may be checked by shaking with caustic soda, when six volumes of hydrogen are produced. Acidification and filtration of the

solution will show whether there is any appreciable quantity of SiH_4. The gas is unstable and spontaneously inflammable. It may be confined over dry mercury.

The mixture remaining in the liquid air trap after the removal of B_2H_6 is pumped off until the pressure sinks to a few tenths of a millimetre. The gas so removed is mostly B_4H_{10}, and must be purified by repeated fractionation. On shaking with caustic soda it gives eleven volumes of hydrogen. This is a very unstable gas, undergoing spontaneous decomposition.

The preparation of the undermentioned less common gases is described in the reference quoted :

Boron Trifluoride (BF_3). O. Ruff, *Z. anorg. Chem.* **206**, 59 (1932); A. F. O. Germann and H. S. Booth, *J. phys. Chem.* **30**, 370 (1926).

Carbon Suboxide (C_3O_2). A. Stock and H. Stolzenberg, *Ber.*, **50**, 498 (1917).

Methylacetylene ($CH_3-C\equiv CH$). P. Libeau and M. Picon, *Compt. rend.* **156**, 1077 (1913) C. H. Hurd, R. N. Meinert and L. U. Spence, *J. Amer. Chem.* Soc., **52**, 1141 (1930).

Propane (C_3H_8). O. Maass and C. H. Wright, *J. Amer. Chem. Soc.*, **43**, 1098 (1921).

Propylene (C_3H_6). G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Amer. Chem. Soc.*, **57**, 876 (1935).

n-Butane (C_4H_{10}). G. Calingaert and L. B. Hitchcock, *J. Amer. Chem. Soc.*, **49**, 754 (1927)

Isobutane ($(CH_3)_3CH$) F. M. Seibert and G. A. Burrell, *J. Amer. Chem. Soc.*, **37**, 2684 (1915).

Butene-1 ($C_2H_5.CH=CH_2$). G. B. Kistiakowsky *et. al.* (*J. Amer. Chem. Soc.*, **57**, 879 (1935)).

Butene-2 ($CH_3-CH=CH.CH_3$). See above.

Methyl Fluoride (CH_3F). E. Moles and T. Baturcas, *J. Chim. phys.* **17**, 537 (1919).

Methyl Chloride (CH_3Cl). J. F. Norris and H. B. Taylor, *J. Amer. Chem. Soc.*, **46**, 753 (1924).

Methyl Bromide (CH_3Br). C. Boulin and L.-J. Simon, *Comptes rend.* **170**, 595 (1920).

Carbonyl Chloride ($COCl_2$). V. Grignard and E. Urbain, *Comptes rend.* **169**, 17 (1919).

Silicon Tetrafluoride (SiF_4). A. F. O. Germann and H. S. Booth, *J. phys. Chem.* **21**, 81 (1917) ; H. S. Booth and C. F. Swinehart, *J. Amer. Chem. Soc.*, **57**, 1337 (1935).

Silicon Hexafluoride (Si_2F_6). G. Martin, *J. Chem. Soc.*, **105**, 2836 (1914).

Nitrosyl Chloride ($NOCl_2$). A. F. Scott and C. R. Johnson, *J. phys. Chem.*, **33**, 1975 (1929).

Nitryl Chloride (NO_2Cl). H. J. Schumacher and G. Sprenger, *Z. phys. Chem.*, **B**, **12**, 115 (1931).

Hydrogen Selenide (H_2Se). L. Moser and E. Doctor, *Z. anorg. Chem.*, **118**, 284 (1921).

Hydrogen Telluride (H_2Te). L. M. Dennis and R. P. Anderson, *J. Amer. Chem. Soc.*, **36**, 882 (1914).

Chlorine Dioxide (ClO_2). H. J. Schumacher and G. Stieger, *Z. phys. Chem.*, **B, 7**, 364 (1930).

Chlorine Monoxide (Cl_2O). M. Bodenstein and G. B. Kistiakowsky, *Z. phys. Chem.*, **116**, 372 (1925).

C. MICRO-GAS ANALYSIS

Micro-analysis of gas mixtures (e.g. analysis of less than 0·1 c.c. of gas) is necessary for two reasons. (1) In dealing with low pressure gas reactions sufficiently large reaction vessels cannot be employed to yield enough gas on compression to employ the ordinary macro-methods requiring at least 10 c.c., though with care 1 c.c. may now be analysed (cf. D. S. Chamberlain and D. M. Newitt, *Ind. and Eng. Chem.*, **17**, 621 (1925); H. R. Ambler, *Analyst*, **54**, 517 (1929)), and hence micro-methods must be employed. (2) If the reaction is carried out at pressures approaching atmospheric and micro-analytical methods are available, then a number of samples of the gas mixture may be withdrawn at intervals and analysed at leisure. Such a method considerably expedites the completion of an investigation by cutting down the number of runs required to furnish the data.

The analysis of binary mixtures is not in general a difficult matter, as a simple physical or chemical process is often sufficient to remove one of the constituents. Nor is there usually much complication if only one component of a mixture has to be withdrawn and measured. Matters become very much more complicated if a complete analysis of a gaseous mixture is required. Much ingenuity has been displayed in the design of the necessary apparatus, which may now be divided into three distinct types. The first is the low pressure method. In this the gas is subjected to physical and chemical processes to remove each constituent one at a time the resulting pressure changes, when the gas is contained in a given volume, being measured by a McLeod gauge. It is estimated that 0·001 c.c. of gas may be analysed by this method. The second may be termed the capillary burette method, in which the gas is treated with beads of suitable reagents and the volume subsequently measured at atmospheric pressure in a graduated capillary. The minimum volume which can be analysed is about 0·02 c.c. Thirdly, the constituents of the mixture may be separated by low temperature distillation with or without previous chemical treatment.

Low pressure method. This method was first developed by I. Langmuir (*J.A.C.S.*, **34**, 1310 (1912)) for his investigations on chemical reactions at low pressures, and a more detailed description of the method with the order of accuracy to be expected given by H. M. Ryder (*J.A.C.S.*, **40**, 1656 (1918)). The apparatus is shown in Fig. 118, and consists essentially of a vacuum line with mercury cut-offs, exhausted by a diffusion pump, and having attached to it an optical lever gauge (see p. 83), a McLeod gauge, and a Töpler pump connected to a small combustion bulb carrying a fine platinum filament. Provision is also made for introducing hydrogen, carbon monoxide or oxygen for combustion

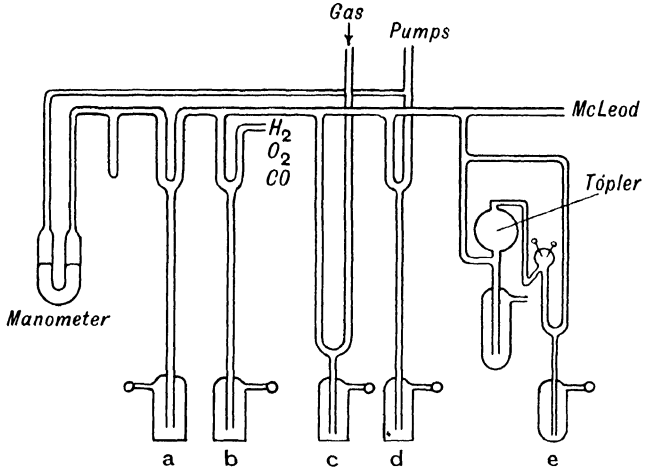


FIG. 118. Low pressure gas analysis apparatus (Ryder).

purposes. Sufficiently small quantities of these gases may be introduced from a reservoir containing gas at a high pressure by a " doser " (cf. p. 146). The amount so introduced is then measured accurately on the McLeod gauge. This implies, of course, that a fixed volume of gauge and connecting tubing is used. It is therefore necessary to raise the mercury in the cut-offs to some definite mark, for variations in atmospheric pressure would introduce appreciable errors in this " fixed " volume. Assuming that the mixture contains H_2O, CO_2, CO and N_2, the following is the procedure. The mixture is admitted through the cut-off *c*. The mercury in *a* is lowered, and liquid air placed around the trap next to the optical level manometer. The non-condensable gas is pumped off by the Töpler and stored for the time being in the combustion bulb. A CO_2 bath at $-80°$ C. replaces the liquid air, thus volatilising the CO_2, the pressure of which is measured by the McLeod gauge, suitable correction being made for the fact that the volume of the system

is larger by that of the tubing between the optical lever manometer and the cut-off *a*. Next, the CO_2 is pumped off. Prolonged pumping must be avoided, as the vapour pressure of water at $-80°$ C. is 10^{-3} mm. A trial will settle how long pumping may be continued without removing an appreciable fraction of the water. The mercury in *a* is raised, the CO_2 bath withdrawn and the pressure of water vapour measured by the manometer. A knowledge of the volume in which the vapour is contained permits the calculation of the volume of H_2O in c.c. at N.T.P. Oxygen in excess of that required to burn the hydrogen and carbon monoxide is admitted, and the pressure measured by the McLeod gauge. The mixture contained in the combustion bulb is next mixed with the oxygen and the total pressure noted. Once more it is compressed, the platinum wire glowed, after which the amounts of water and of carbon dioxide are determined in the above described manner. The volume of hydrogen and carbon monoxide in the original sample may then be calculated. The residual gas now contains only nitrogen and oxygen. Since the amount of oxygen originally added and the amount required in the combustion has been measured, the percentage oxygen in the residual gas is easily computed. It may, of course, be determined by adding a measured amount of carbon monoxide, combusting and noting the amount of CO_2 produced.

To illustrate the sensitivity and accuracy of the analysis the following example may be quoted from Ryder's paper :

Volume of sample, 4·78 mm.³

Gas	% found	% introduced
CO	32·2	28·5
H_2	51·3	57·3
O_2	16·5	14·2

Greater accuracy is obtainable with larger volumes of gas. For mixtures other than those given above, modification in the technique will have to be made to suit the particular case in hand. For example, hydrocarbons except methane, may be condensed by liquid air and the hydrogen removed by the Töpler pump. Acid gases, such as CO_2, SO_2, can be removed by condensing in a side tube, containing soda lime, attached to the main vacuum line by a mercury cut-off. After absorption of the gas the mixture is pumped off with the Töpler pump and the normal analysis resumed. P. A. Guye and F. E. E. Germann (*J. Chim. physique*, **14**, 195 (1916)) have also described an apparatus in which CO_2 is removed by KOH, oxygen by a heated iron wire, and combustion is accomplished by sparking the mixture with oxygen. The McLeod gauge and Töpler

pump are combined into one. So far the only published results relate to the analysis of dry air.

In the **micro-gas analysis apparatus of C. H. Prescott** (*J.A.C.S.*, **50**, 3237 (1928)), designed especially for mixtures of H_2, CO, CO_2 and N_2, the gas is measured in a McLeod gauge and is then pumped through soda lime for removing CO_2, then over heated CuO to oxidise H_2 and CO, the water being removed by passage over P_2O_5 and CO_2 by soda lime. The arrangement of the McLeod gauge and associated Töpler pumps is shown in Fig. 119. The gas enters at *A* and is pumped

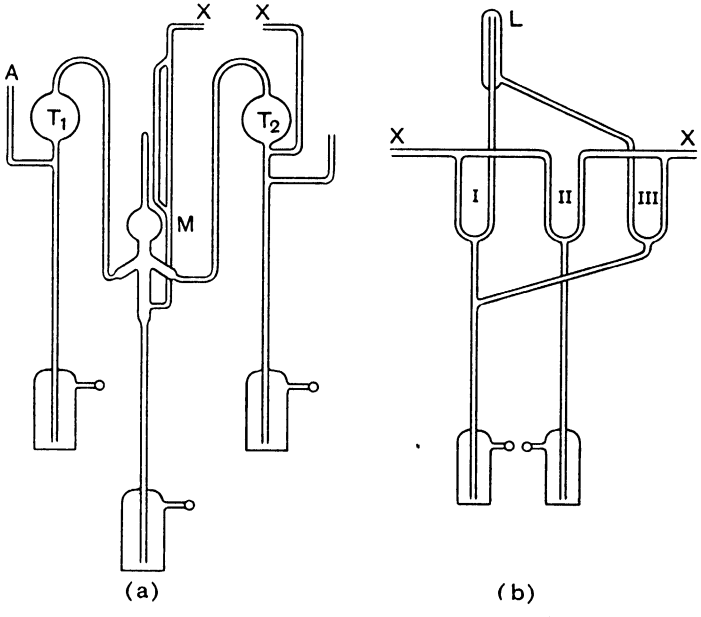


FIG. 119. Low pressure micro analysis apparatus (Prescott).

by T_1 into *M*. By means of T_2 it is then pumped through the absorbing agent in *L*. Three sets of apparatus, shown in (*b*), are connected in series and fused on at *XX*. The phosphorus pentoxide is mixed with powdered pumice for support. All the reagents are, of course, baked out *in vacuo*. By suitable operation of the cut-offs, *I*, *II* and *III*, the gas may be circulated through any reagent at will. After treatment it is once more compressed in *M* and the pressure noted.

An apparatus for the analysis of gases given off by molten glass has been described by Dalton (*J.A.C.S.*, **57**, 2150 (1935)) (Fig. 120). It consists of two Töpler pumps with a McLeod gauge in between and a Pirani gauge, *P*. Two tubes containing copper oxide and freshly reduced copper

are sealed on above the second Töpler. L is a trap. This type of apparatus is suitable for about 1 c.c. of gas. It may be used to analyse mixtures of H_2O, CO_2, SO_2, CO, H_2 and non-condensable gas, e.g. N_2, as follows. The mixture is admitted at S_1, S_2 being shut. It is pumped through L, which is cooled to $-80°$ C., by T_1, the gas being temporarily stored in M. The mercury in T_1 is raised to a fixed mark, L warmed to room temperature, and the pressure of H_2O determined by the Pirani gauge, which, of course, must be previously calibrated. The water is pumped out. The total pressure of gas is measured by M and recirculation commenced, L being cooled to $-150°$ C. to freeze out SO_2. CO_2 is withdrawn by cooling L to $-180°$ C. Oxygen is removed by heating the copper to 350° C., the mixture being compressed during this reaction. Hydrogen is removed with CuO, likewise carbon monoxide. The water and carbon dioxide formed are estimated as described above. Non-condensable gases are estimated by difference.

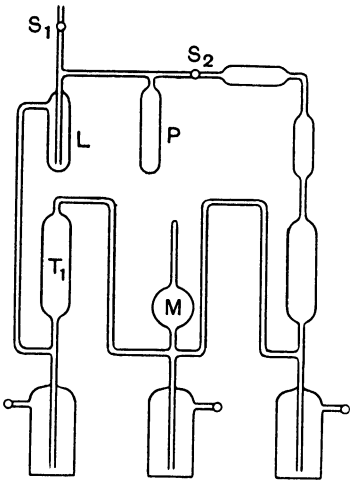
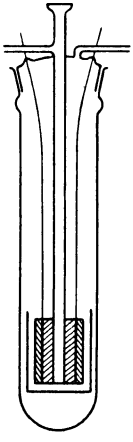


FIG. 120. Low pressure micro-gas analysis apparatus (Dalton).

In this paper a convenient vacuum furnace for this particular purpose is described, suitable for use up to 1450° C. A 1 cm. tube of sillimanite serves as a core. This material can be fused to a Pyrex tube. The sillimanite is wound with tantalum and heat insulated with alundum. A molybdenum shield also prevents excessive loss of heat. To prevent oxidation of tantalum the furnace is operated in a vacuum, as shown in Fig. 121.


FIG. 121. Vacuum furnace.

The Shakespear katharometer. The analysis of small amounts of binary mixtures of gases of different thermal conductivities, e.g. CO and H_2, may be simply carried out by making use of the thermal conductivity gauges used in commercial practice. In addition the method is also useful, but somewhat less accurate, for the estimation of one constituent of a gas mixture which has either a low (e.g. CO_2) or high (e.g. H_2) thermal conductivity compared with other constituents of the mixture, e.g. air. The unit from the Shakespear

katharometer has been used for analysing CO-H_2 mixtures by W. W. Hurst and E. K. Rideal (*J. Chem. Soc.*, **125**, 694 (1924)) and by R. M. Barrer and E. K. Rideal (*Proc. Roy. Soc.*, **A, 149**, 231 (1935)) for $CH_4 - H_2$ mixtures. This device consists of two cells of capacity *ca.* 0·5 c.c., 5·5 mm. in diameter and 15 mm. in length, bored out of a brass or copper block to ensure uniformity of temperature. Suitable small holes cut in the block communicate with glass tubing attached to the apparatus. The wires (30 mm. long and 0·015 mm. in diameter) in the cells are attached to stirrups mounted on insulating plugs. The parts of the block exposed to the gas are gold-plated to prevent corrosion. The set-up used by Barrer and Rideal is shown in Fig. 122. In this the katharometer cells form part of a Wheatstone network, one arm of which is adjustable, a voltage of 4 being suitable for heating the wires. The right-hand cell, C_2, is then filled with one of the gases, e.g. H_2, at a pressure not less than 20 mm., as shown by the manometer *M*, where the thermal conductivity is not very dependent of pressure. Hydrogen to the same pressure is admitted to C_1 and the bridge balanced. C_1 is evacuated and a known mixture admitted to the same pressure by means of the Töpler pump. Once more the bridge is balanced, and thereby a calibration curve may be constructed in order that the composition of an unknown mixture may be read off directly. Employing this method W. W. Hurst and E. K. Rideal estimate they could detect 5×10^{-7} c.c. of H_2 at N.T.P. in $1{\cdot}3 \times 10^{-3}$ c.c. of CO – H_2 mixture.

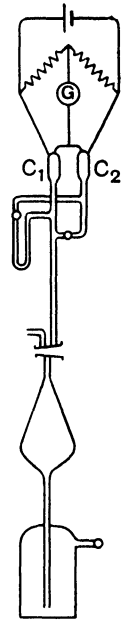


FIG. 122. Shakespear katharometer.

The katharometer may also be used for measuring the thermal conductivity of gaseous mixtures (cf. T. L. Ibbs and A. A. Hirst, *Proc. Roy. Soc.*, **A, 123**, 134 (1929)) for following gaseous diffusion (W. P. Summerhays, *Proc. Phys. Soc.*, **42**, 218 (1930)), in thermal diffusion (see T. L. Ibbs, *Proc. Roy. Soc.*, **A, 107**, 470 (1925)). G. T. Morgan, R. Taylor and T. J. Hedley (*J. Soc. Chem. Ind.*, **47**, 117T (1928)) followed the interaction of CO and H_2 to CH_3OH by this instrument ; Edwards and Elworthy used the indicator for estimating the purity of helium, liable to contain traces of hydrogen. Finally H. A. Daynes has written a monograph (*Gas Analysis by Measurements of Thermal Conductivity* : Cambridge University Press) on the subject of determining thermal conductivity of gases and its application to a great variety of practical problems.

Gas Analysis using Capillary Burettes

In this method the gas is confined in a capillary burette, and the reagents employed are either solid beads or porous beads of inert material saturated with the appropriate liquid reagents. Analysis is carried out in the dry state, and the accuracy claimed by a number of experimenters is of the order of 0·1 per cent. (L. Reave, *J.C.S.*, **125**, 1946 (1924)). J. A. Christiansen (*J.A.C.S.*, **47**, 109 (1925)) and J. R. Huffmann (*Z. anal. Chem.*, **80**, 435 (1930)) were the first to describe apparatus for the purpose (cf. also Schwarz, *J. Amer. Chem. Soc.*, **57**, 963 (1935)). Later experiments by F. E. Blacet, P. A. Leighton and G. D. MacDonald (*Ind. and Eng. Chem.* (anal.), **3**, 266 (1931) ; **5**, 272 (1933) ; **6**, 334 (1934)) have improved the technique to a stage where it is as accurate as that of the commonly used macro methods. Modifications naturally depend on the work in hand, but a description of the latter experimenters' apparatus will indicate the usefulness of the method.

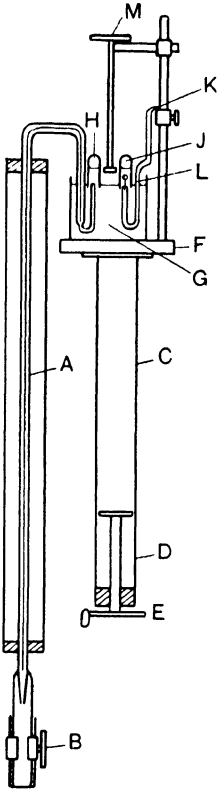


FIG. 123. Capillary burette.

The capillary *A* (Fig. 123), diameter 0·5 mm. and length 45 cm. (vol., 0·112 c.c.) is ruled with or fitted to a millimetre scale. The whole is surrounded by a water jacket. At the base of the burette there is a piece of rubber tubing, closed at one end, which may be compressed by means of a large screw clip. More accurate control of the mercury in the capillary is obtained by waxing a steel tube to the lower part of the burette. A closed rubber tube is clamped to the steel tube. A metal plunger actuated by a screw distends the rubber tube into the mercury reservoir. The outer steel tube may also be used as base to which the burette water jacket is attached.

A small trap serves to eliminate any small bubbles of air or particles of solid matter, which might otherwise choke the fine capillary tube at the end of the burette. This fine capillary is bent as shown in the diagram, so that its end is directly below the gas holder *H*. The arrangement for holding *H* and the beads *K* is shown in Fig. 124. To ensure complete removal of the gas from *H*, the top of the capillary is ground and fire polished to a radius of curvature somewhat less than the hemispherical end of *H*. Before use the burette is completely filled with mercury by inverting it, finally pushing

a piece of glass rod into the rubber tubing and sealing in position. The small bubble of air which invariably remains at the end of the capillary is expelled by slight compression of the rubber tube. The mercury trough *G* may be altered in height by means of the telescopic tube actuated by the handle *E*. The mercury surface is kept clean by applying suction to a tube dipped slightly below the surface, thus removing scum, etc. This operation is most essential in order to prevent impurities finding their way into the gas reservoirs. Since it is essential that the gas holders—four in practice—be brought exactly into the correct position, these latter are held by a revolving table *M*.

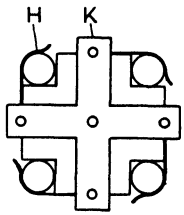


FIG. 124. Gas holders.

The beads of absorbent reagent held in the glass rod *L* are maintained in position by the clamp *K* or in the revolving stand. If it is necessary a Töpler pump may conveniently discharge its contents into one of the gas holders, the outlet tube being arranged similarly to that of the burette. The operation of the apparatus is best described by following the procedure adopted to determine the amount of oxygen in dry air. Air is first removed from the gas holder by placing a glass tube drawn out to a capillary, so that it can be pushed up to the top of *H*. A few tenths of a c.c. of dry air are then admitted to *H*. The platform *F* is lowered until the top of the burette projects above the level of the mercury in *H* when air is drawn into the capillary by unscrewing *B*. *F* is raised again, so that a thread of mercury follows the air into *A*. Next the mercury level in *G* is brought opposite the first calibration mark in the burette, and *B* readjusted to bring the upper end of the air column to the same position. To obtain concordant results this adjustment should be repeated a few times, the temperature and barometric pressure being noted. Gas holder *J*, filled with mercury, is swung round over the top of the burette and the air expelled from the latter into *J*. A bead of white phosphorus on a platinum wire is slipped into *J*; on being returned to its original position care is particularly taken that the glass supporting rod does not touch the sides of *J*. The bead of phosphorus may be made by squeezing a chip of white phosphorus on to the platinum wire and fusing by holding over a warm resistance coil. J. S. Swearingen, O. Gerbes and E. W. Ellis (*Ind. and Eng. Chem.* (anal.), **5**, 369 (1933)) suggest cleaning the bead to facilitate rapidity of absorption of oxygen by washing in water, then in alcohol, finally drying in a stream of inert gas such as CO_2 or coal gas. After a few minutes' contact with the bead, the residual gas is withdrawn and its volume measured as before. To make sure that all the oxygen is absorbed, the treatment with phosphorus is repeated. In performing these operations it is essential on withdrawing the gas to

ensure that the tip of the burette touches the top of *J*, so that all the gas is removed. Water vapour is removed by a bead of phosphorus pentoxide. This is best fused by surrounding the bead with a glowing spiral, since a small flame generates too much moisture. Carbon dioxide is removed by potassium hydroxide which has been allowed to become slightly moist by exposure to atmospheric air. Dry KOH does not absorb CO_2. Hydrogen, carbon monoxide or a *single* hydrocarbon may be determined by adding oxygen from another gas holder, transferring to a combustion tube, sparking and removing the H_2O and CO_2 from the gases. If the gas is saturated with water vapour, the readings given by the micro burette become inaccurate, and hence the measurement of the volume of " wet " gases is precluded. The combustion tube may consist of two platinum wires sealed in at the top of an ordinary gas holder. In this case it is not easy to keep the head of the holder hemispherical. An alternative device is to place a 2 mm. external diameter tube in a 4 mm. tube, both being about 12 cm. in length. Two platinum wires are run through the inner tube and through the annular space between the tubes, so as to project by a few mm. The ends of the tubes are made flush with one another, fused together and bent so that the composite tube may be introduced into a gas holder. The platinum wires are broken off at the surface, leaving an end of perfectly smooth curvature.

Hydrogen and carbon monoxide may be burned without affecting hydrocarbons—so far, up to butane—present simultaneously. The following procedure is adopted. In this case it is necessary to oxidise the gas with cupric oxide at a controlled temperature and withdraw the water vapour simultaneously. The apparatus is shown in Fig. 125. *C* is a copper vessel with tube fitting snugly round the gas holder *H*. The outside carries a sheet of mica *E* wound with a resistance coil *B*, which is thermally insulated by asbestos. *C* is filled with lead or potassium dichromate to obtain a constant temperature, and the current is switched on until the solid is nearly all melted. For this work a Pyrex gas holder is advisable. The bead is made by melting cupric oxide on to the platinum loop, then fusing on an equal amount of potassium hydroxide, when a smooth dark blue bead is obtained. The time required for oxidation

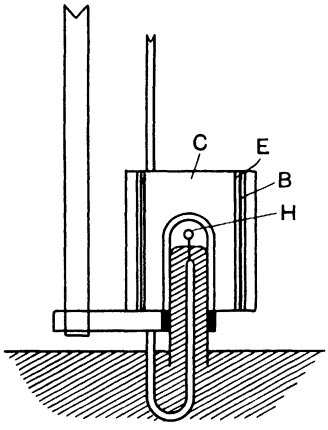


FIG. 125. Apparatus for the micro estimation of hydrogen.

does not exceed 15 minutes. Carbon monoxide is oxidised in the same way, but this gas cannot be selectively oxidised in presence of hydrogen.

Hydrogen chloride. This gas may be absorbed by a bead of potassium hydroxide or a KOH solution on a sintered glass bead.

Ammonia is absorbed by moistened phosphorus pentoxide or sulphuric acid on a sintered glass bead made from 100-150 mesh soft glass. Beads may also be made by fusing a mixture of 70 per cent. porcelain and 30 per cent. kaolin, the former passing a 120 mesh screen and the latter a 200 mesh screen. For some unknown reason the ammonia results are always slightly high. Care must be taken not to have too much liquid in the bead.

On account of capillary correction it is difficult to measure the *absolute* volume of gas in the burette. This may be the reason for the slightly less accurate results with ammonia, which alters the surface tension or angle of contact of the mercury with the glass. Ammonia may also be absorbed by a moistened bead of potassium bisulphate.

Carbon monoxide. Silver oxide (Ag_2O) is precipitated from silver nitrate solution by a strong base, washed and while moist compressed into small pellets. The tip of a platinum wire is covered with a drop of a strong solution of sodium silicate, the latter is covered with a layer of silver oxide, and the whole allowed to dry for 15 minutes. This operation must be done quickly to prevent formation of silver carbonate. Absorption is complete in 10 minutes.

In presence of hydrogen a considerable error, e.g. 1·5 per cent. in a 50 : 50 mixture, is made in this process. The error may be made a minimum by carefully regulating the time of absorption of CO.

Ethylene. A piece of sintered glass is shaped into a sphere 2 mm. in diameter, and a straight platinum wire is attached by fusing a small part of the bead. The bead is *slowly* immersed in fuming sulphuric acid, and then introduced in the usual way to a sample of gas. SO_3 vapour is subsequently removed by a potassium hydroxide bead. All unsaturated hydrocarbons are removed in this way.

Acetylene. A stiff paste is made by moistening cuprous chloride with dilute potassium hydroxide solution, and then moulded on to a platinum loop 2 mm. in diameter. Absorption is complete in 5 minutes. The copper acetylide formed does not detach itself from the bead. The potassium hydroxide takes up all the hydrogen chloride and water vapour formed on the reaction.

Swearingen, Gerbe and Ellis (*loc. cit.*) use a horizontal burette surrounded by an ordinary burette serving as a water jacket, and graduated scale. The mode of operating this burette is self-evident from

Fig. 126. the burette being rotated into the position shown by the dotted line for transferring gas to and from the gas holder.

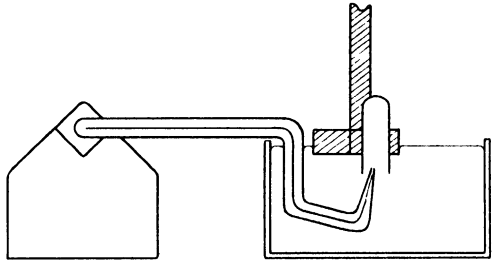


FIG. 126. Horizontal capillary burette.

The following table summarises the extent of this method of analysis. To show its versatility the following nine gases could be separated by removal in the following order : H_2O, CO_2, C_2H_4, O_2, CO, H_2, CH_4, C_2H_6 and N_2.

TABLE 25

Summary of Gases analysed and Reagents used

Gases	Reagents
H_2O	KOH, P_2O_5.
CO_2, HCl or other acid-producing gases	KOH.
Acetaldehyde and other similar vapours	KOH (P. A. Leighton and F. E. Blacet, *J. Amer. Chem. Soc.*, **54**, 3165 (1932)).
Oxygen	Phosphorus (white).
Ammonia and base-producing gases	P_2O_5, H_2SO_4, $KHSO_4$.
Acetylene	Cuprous chloride and potassium hydroxide.
Ethylene and other unsaturated hydrocarbons	Concentrated sulphuric acid ; fuming acid for ethylene.
Carbon monoxide	Silver oxide or cupric oxide KOH explosion.
Hydrogen	Cupric oxide KOH, explosion.
CH_4, C_2H_6 or readily combustible gases	Explosion.
Nitrogen and inert gases	By difference.

Sutton's micro method. An alternative way of conducting analysis by the capillary method has been developed by T. C. Sutton (private communication), paying particular attention to avoiding soiling the reaction chamber with the absorption reagents. The measuring burette is a 0·1 mm. horizontal capillary tube, *AA*, one end of which is expanded and fused to a wider ($d=4$ mm.) short capillary tube *B*, which is used as the reaction chamber (Fig. 127). This tube, together with a compensat-

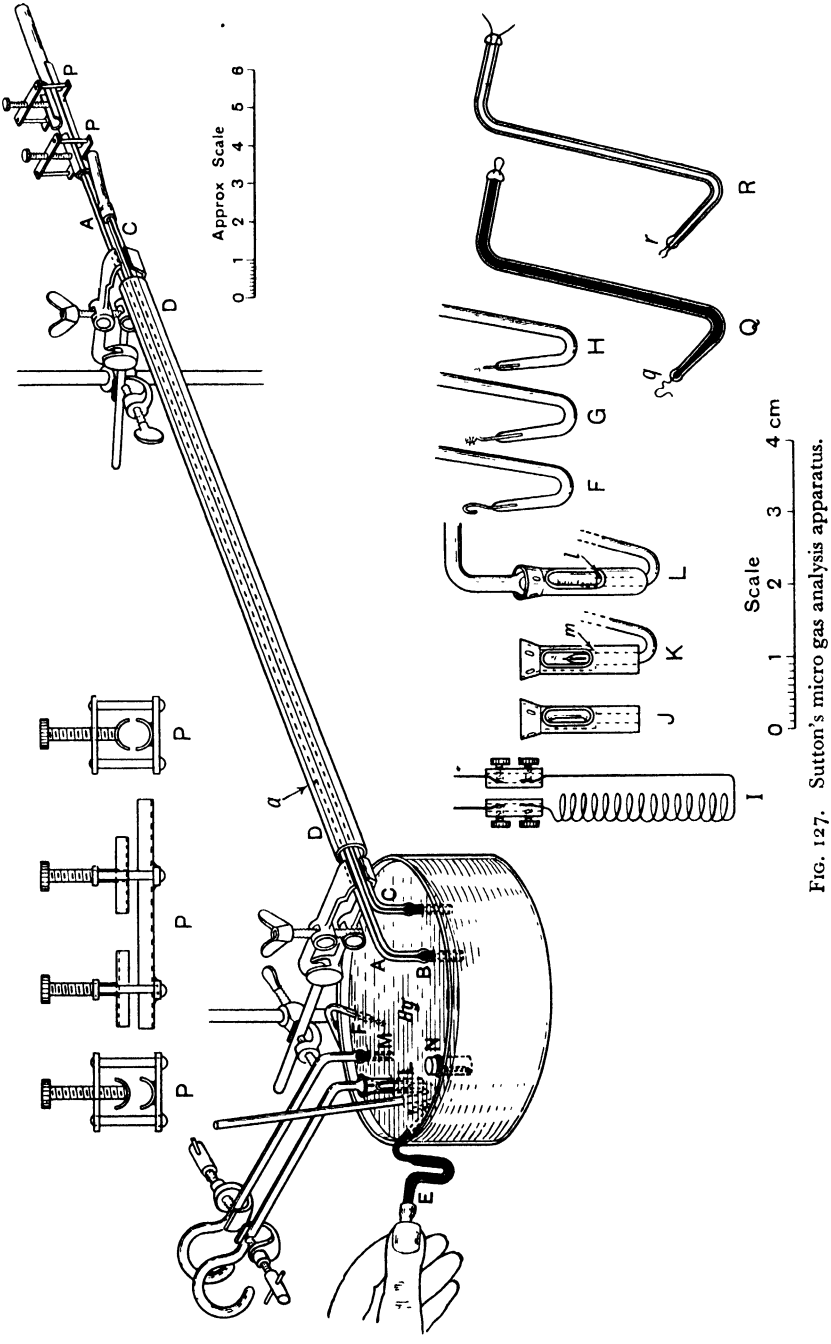


FIG. 127. Sutton's micro gas analysis apparatus.

ing tube *CC*, is placed within a wide glass tube *DD*, which acts as an air-jacket to the two tubes. The measuring chamber *AA* should be calibrated ; it may either be graduated along its whole length, or one reference line, *a*, may be placed upon it and the graduations placed round the jacketing tube *DD* ; the latter method has the advantage that the graduations are on the outside of the apparatus and can be seen clearly. The reaction chamber dips into a wide bowl, Hg, containing mercury. The end of *AA* remote from the reaction chamber is fitted with a rubber " bobby " by means of which mercury may be drawn into the capillary system ; *PP* is a convenient screw fitting for making fine adjustments.

Inverted specimen tubes *N* or the glass vessels *M* make convenient reservoirs for reagents and for the gas to be analysed. To transfer a sample of gas from *M* to *B* use is made of a small glass vessel *E*, drawn to a tip at one end and fitted with a rubber bobby at the other. *E* is filled with mercury, the tip is then placed in the mercury bath, the bobby squeezed between the fingers so as to expel any trace of air and about 0·5 c.c. of mercury, the tip is then passed through the mercury into the gas in *M*, the pressure of the fingers is lessened and a sample of gas drawn into *E*, the tip is immersed again in the mercury and the pressure removed, mercury being drawn into *E* and completely isolating the sample of gas. The tip of a sample of gas of the desired magnitude forced into it. On removing *E*, the screw *PP* is adjusted so as to draw this sample into the measuring tube *AA*.

To assure that the meniscus of the mercury column affects the pressure in the gas column to the same extent, each measurement in *AA* is preceded by a short repeatable routine. By unscrewing *PP* the gas is drawn into *AA* just beyond the fixed mark *a*. *PP* is then screwed down slowly until mercury begins to move into *B* and the meniscus approaches *a* ; this occurs when the excess pressure in the gas column just exceeds the resistance of the meniscus when at *a*. A sample 25 cm. in length will give a consistency of 1 in 400 provided the tube is clean.

In common with other forms of " constant-pressure " apparatus, the required volume measurements are merely relative, and it is sufficient to compare at each stage of the analysis the length of the sample with that of a sample of dry air in the tube *CC* ; the latter indicates any sufficient change in temperature, in atmospheric pressure, or in the relative positions of the measuring system and of the mercury reservoir Hg. In practice it is convenient to compensate for such changes, if any, by using the vessel *E* to adjust the level of mercury in the reservoir until the air sample occupies its original position.

Solid reagents are held by a platinum loop, such as that at *F*, and may be fused by holding the loop within the electrically heated coil *I*. In *G*.

and H the loop is filled with a porous mixture of kaolin and sintered porcelain, made coherent by holding within I; the air in the pores may be replaced by a liquid reagent contained in M or N, by merely passing the loop into the liquid for a few seconds. When not in use the loops may be stored inverted under mercury as at F.

J is a carefully shaped steel tube, essential for clean manipulation without risk of soiling the reaction chamber B. It is placed over a reaction rod as at K, and if the latter is made somewhat elliptical, a slight rotation will fix it there. As the lip of J is wide, the system K may readily be placed around the bottom of either a reagent container M or the reaction chamber B, and as it is sloped it will guide the reagent rod directly into the centre of M or B. The enlargement m assures that a passage l is maintained, without which traces of air may become entrapped within J and forced into M or B.

" Hot wire " reactions may be obtained by placing within B the end of Q; the flexible platinum wire q then forms automatically a loop passing through the gas in B and into the mercury below; an electric current may thus be passed through the mercury column within Q, through Q and through the mercury in the reservoir. By placing the end of R within B in a similar manner sparks may be passed through the gas.

The apparatus thus briefly described enables each reaction employed in macro-analysis to be applied to micro-analysis in a simple, clean and effective way.

In this method the sample remains in the same vessel, BAA, throughout the analysis, and there is thus no risk of loss during transfer.

Micro gas analysis by low temperature distillation. In order to illustrate the principle of this method, first used by N. R. Campbell (*Proc. Phys. Soc.*, **33**, 287 (1921)), consider a bulb B attached to an appendix T of negligible volume and to a pressure gauge G (Fig. 128 (*c*)). Gas is admitted to a convenient pressure and then condensed by surrounding T with a refrigerant. On withdrawing the cooling bath the pressure in B will increase exponentially with temperature according to the usual vapour

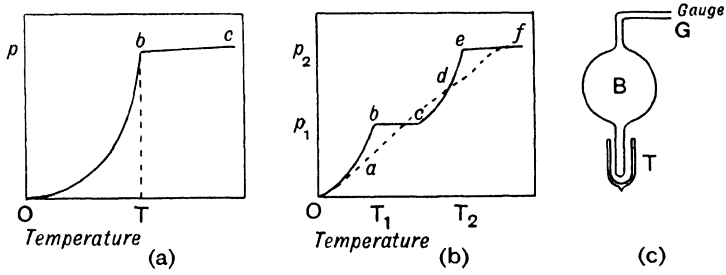


FIG. 128. Micro-gas analysis by low temperature distillation.

pressure-temperature equation as shown by *Ob* (Fig. 127 (*a*)). When the condensed phase disappears the pressure will cease to rise (curve *bc*), T is the temperature of condensation. Next a gas is added with a somewhat higher condensation temperature T_2. On performing the same experiment a composite curve *abcdef* will be obtained, if the condensed phases do not form solid solutions. If p_1 and p_2 are respectively the magnitudes of the ordinates for the two gases, then the percentage of the first is $100p_1/(p_1+p_2)$ and of the second $100p_2/(p_1+p_2)$. In practice the curves do not exhibit sharp breaks, solid solutions and neighbouring or coincident condensation temperatures rendering matters more complicated, as is shown by the dotted line. Furthermore, the ideal horizontal sections *bc*, *ef* are rarely observed. None the less J. J. Sebastian and H. C. Howard (*Ind. and Eng. Chem.* (Anal.), **6**, 172 (1934)) have improved the technique so as to be applicable to the accurate analysis of samples of the order of 1 c.c. at N.T.P. The essential part of their apparatus is shown in Fig. 129, the pressure gauge being a quick-acting McLeod. Campbell originally used a Pirani gauge, which is much superior in rapidity of working to the McLeod gauge, and since the calibration is very nearly the same for all the "heavier" gases (see p. 79) offers no disadvantage on this account. The greatest difficulty to be overcome is that of uniform slow heating of the condensed phase. The condensation tube T is first platinised and then copper-plated (*ca.* 0·3 mm. thick). A thermo-couple of copper-constantan, calibrated at the freezing point of mercury, at $-80°$ C. (CO_2) and at $-197°$ C. (the B.P. of nitrogen), is fixed to this copper sheath. The Dewar flask D_1 is then filled with copper turnings. D_1 is filled with liquid nitrogen, the sample condensed in T, and finally the mercury in the cut-off is brought up to the mark M. The pressure is then noted on the gauge, which should be capable of reading up to 0·2-0·3 mm. The liquid nitrogen in D_1 is then drained into D, which is fitted with a resistance coil to increase the rate of evaporation of the liquid. A temperature rise of 0·5° per minute is suitable. If the rate of temperature rise is not high enough, it may be increased by blowing a slow stream of air through D. A pressure temperature curve is then plotted roughly. The sample may then be recondensed

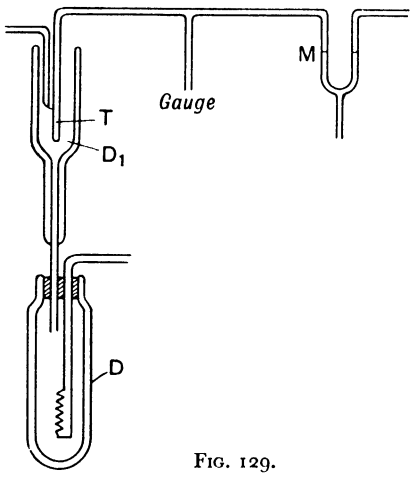


FIG. 129.

and the important parts of the curves measured more exactly. To indicate the range of this method the following table shows the temperatures at which the substances listed have a vapour pressure of the order of 0·01 mm.

TABLE 26

	B.P. ° K.	Temp. ° K. for 0·01-0·05 mm.
Oxygen	90·2	—
Methane	111·7	—
Ethylene	169·4	85- 95
Ethane	184·4	85-100
Acetylene	190·7	85-100
Carbon dioxide	194·6 *	110-120
Propylene	226·1	105-125
Propane	228 6	105-120
Isobutane	262·9	120-133
1-Butene	268·1	130-145
n-Butane	273·6	125-140
Water	373·1	200-220

On condensing the mixture to be analysed at the temperature of liquid nitrogen the non-condensable gas is not necessarily H_2, O_2, N_2, CO or CH_4, since the vapour pressure of ethylene, ethane and acetylene and other gas with a boiling point near 200° K. is quite appreciable, as shown by the above table.

Two examples of the analysis of binary mixtures are shown in Fig. 130. The first forms a heterogeneous condensed phase and the second a homogeneous phase. In Fig. 130 (*a*) it will be seen that at 90° K. 0·0030

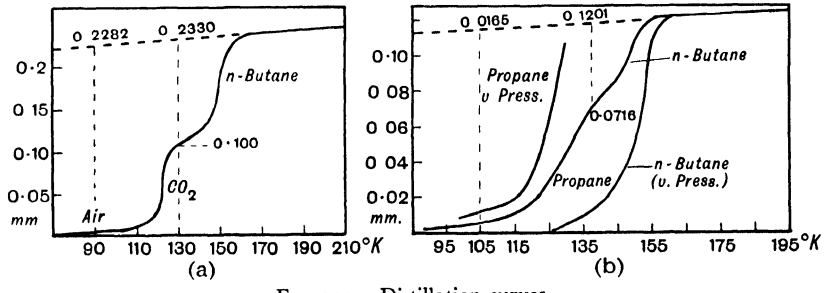


FIG. 130. Distillation curves.

mm. of non-condensable gas are present in 0·2282 mm., or 1·3 per cent. The " kink " in the curve occurs at 130° K., when the pressure of CO_2 and air is 0·0100 mm., the extrapolated value of the total pressure being 0·2330 ; therefore the percentage CO_2 and air is 47·2, i.e. 45·9 per cent. CO_2 compared with 46·5 per cent. prepared. With a propane-butane

* Sublimation temperature at 760 mm.

mixture the evaporation curve merely exhibits slight inflection when butane commences to evaporate. In order to find the position of the kink accurately it then becomes necessary to plot dp/dT against T. The minimum in the curve gives the position of the kink as 138° K., which corresponds to a pressure of 0·0716 mm., the percentage propane and air thus being $100 \times \frac{0{\cdot}0716}{0{\cdot}1201}$, 59·7 or 56·2 per cent. propane, compared with 55·9 per cent. prepared. Even in this unfavourable case the accuracy is very good. Mixtures of more than two components may be analysed in a similar manner. The method is not limited to hydrocarbons, but in all cases, if the qualitative composition of the gas is known, it is advisable to calibrate the apparatus with mixtures of known composition in order to obtain satisfactory results. It may be added that non-condensable gas can always be analysed by one of the methods described elsewhere in this chapter.

Determination of inert gas content of a gas mixture. In experiments where it may be necessary to determine the percentage of the rare gases in presence of others, e.g. N_2, the most efficient way of removing the latter is to bring the mixture into contact with red-hot calcium (F. Soddy, *Proc. Roy. Soc.*, **A, 78**, 429 (1906)). In order that this may be done in apparatus constructed of soda or of Pyrex glass, the calcium is best contained in a quartz tube heated by a spiral of nichrome ribbon wound on the outside, the whole being enclosed in another quartz tube which functions as a radiation shield. At a bright red heat absorption of O_2 and N_2 from air is complete within half an hour (M. Leatherman and E. P. Bartlett, *Ind. and Eng. Chem.* (Anal.), **1**, 223 (1929)).

Analytical methods for the estimation of para-hydrogen, deuterium, ortho-deuterium and hydrogen deuteride. The principles underlying the methods for such analyses are best understood from a consideration of Fig. 131, which shows how the rotational specific heats of the several molecules vary with temperature.

Para-hydrogen. From the figure it will be seen that the rotational specific heat of para-hydrogen below 280° K. is considerably greater than that of normal hydrogen. For the present purpose the most convenient way of detecting a change in the specific heat of a mixture is by measuring its thermal conductivity, which at high pressures is independent of pressure and proportional to $\int C_v dT / \int dT \,.\, m^{-\frac{1}{2}}$, where m is the mass of the molecules of the gas. The thermal conductivity of para-hydrogen is thus greater than that of normal hydrogen. The experimental arrangement used by K. F. Bonhoeffer and P. Harteck (*Z. phys. Chem.*, **B, 4**, 113 (1929)) is shown in Fig. 132. The gauge for measuring the thermal conductivity contains a 100 mm. length of 0·01 mm. platinum wire. This is placed in a bridge and a voltage of 8-10 applied across the bridge. One arm is

variable, and should read to 1 part in 10,000. The values of R for normal hydrogen (R_n) and for para-hydrogen (R_p) are determined. The unknown mixture is introduced and the value of R again determined. A

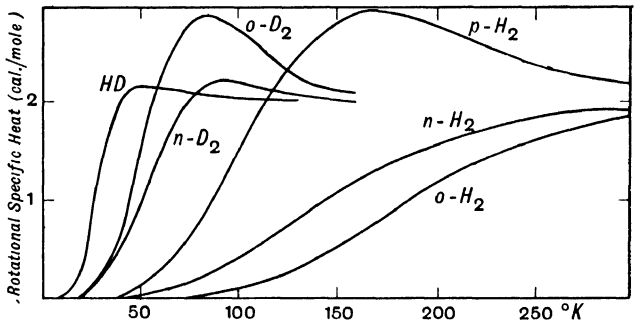


FIG. 131. Rotation specific heats of the modifications of hydrogen (after Urey and Teal, Rev. Mod. Physics, Vol. 6. 1935.)

linear interpolation then gives the para-hydrogen content. Several precautions must be observed if accurate analyses are to be obtained, for the change in resistance is only about 4 per cent. The bridge battery must be stable. Even then it is advisable to measure R frequently for normal

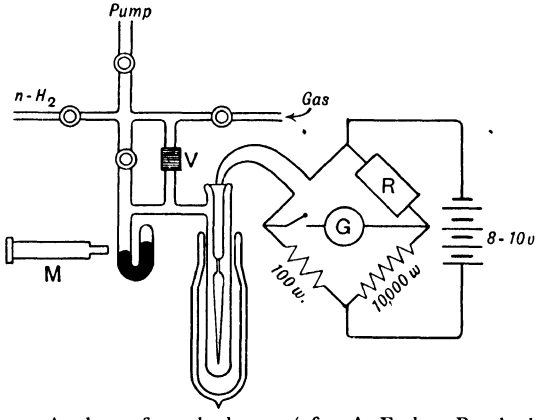
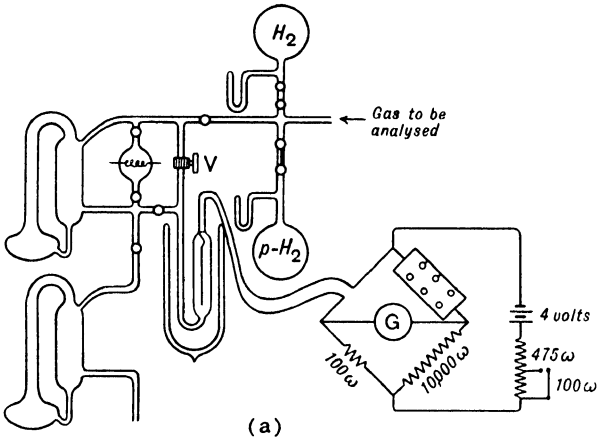


FIG. 132. Analysis of parahydrogen (after A. Farkas, Parahydrogen, Orthohydrogen and Heavy Hydrogen).

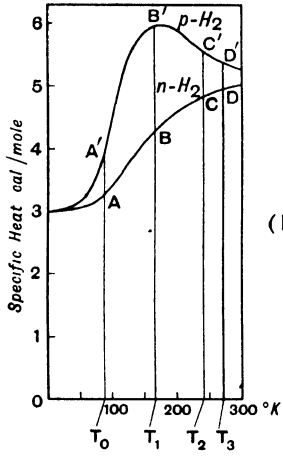
hydrogen to keep a check on any drift that may occur. The conductivity cell must be deeply immersed in liquid air. The conductivity of hydrogen is not quite independent of pressure, and it is therefore necessary to adjust the pressure in the cell to within 0·05 mm. at a total pressure of 20-40 mm. by means of a cathetometer and needle valve. If the nature and dimensions of the wire in the gauge are altered it is, of course, necessary to use such a voltage that the temperature of the wire be brought to

about 180° K. to make full use of the difference in thermal conductivity between the two modifications (cf. Fig. 130).

This method uses a large quantity of gas, and hence cannot usefully be employed in experiments where it is necessary to remove small samples of gas from the reaction vessel during the course of a run. A modification of the method described below, using the micro conductivity gauge described on p. 81, obviates this difficulty.



(a)



(b)

FIG. 133. Analysis of para-hydrogen (A. Farkas).

A. Farkas devised a low pressure method for estimating para-hydrogen (*Z. phys. Chem.*, **B, 22,** 344 (1933)), and solved the difficulty of adjusting the pressure in the following way. The experimental set-up is shown in Fig. 133 (*a*). The resistance and voltage values refer to a 0·01 mm. Pt wire 50 mm. long. The volume of the sample of gas is adjusted so that a pressure of about 0·05 mm. is developed in the cell. The volume of the cell need not exceed 10 c.c., and the volume of the fore-vacuum side of the pump and connections should be kept at a minimum. The pressure in the cell is adjusted so that, with a heating current i_1, the temperature of the wire will attain a value T_1, corresponding to a resistance r_1. Actually the hydrogen is pumped into the cell until this pressure is exceeded. The excess is then carefully withdrawn by means of the needle valve *V*. Next the heating current is increased to i_2, the resistance rising to a value r_2. The normal hydrogen is pumped out, para-hydrogen introduced, and the pressure again adjusted, until the resistance r_1 is reached with a current i_1. If the current

is then increased to i_2 the temperature rises to T_3, corresponding to a resistance r_3. A similar procedure is carried through for an unknown mixture, and a linear interpolation of the resistance values gives the para-hydrogen content directly. The reason for T_3 exceeding T_2 can at once be seen from the following considerations. Assuming that the accommodation of coefficient of hydrogen is independent of temperature, then the heat conducted from the wire by the gas is proportional to

$$P\int_{T_0}^{T_1} C_v dT,$$

where T_0 is the temperature of the liquid air and P the pressure. Since the pressures of normal and para-hydrogen are so adjusted that equal amounts of energy are removed from the wire,

$$P_{\text{p-H}_2} : P_{\text{n-H}_2} = \int_{T_0}^{T_1} C_v(\text{n-H}_2)dT : \int_{T_0}^{T_1} C_v(\text{p-H}_2)dT = T_0T_1BA : T_0'T_1'B^1A^1.$$

Hence if T_2 is the temperature of the wire in n-H_2 with a current i_2, the value of T_3 will be defined by the equation, assuming the resistance of platinum is proportional to its absolute temperature,

$$\frac{\int_{T_0}^{T_1} C_v(\text{n-H}_2)dT}{\int_{T_0}^{T_1} C_v(\text{p-H}_2)dT} = \frac{\int_{T_0}^{T_2} C_v(\text{n-H}_2)dT}{\int_{T_0}^{T_3} C_v(\text{p-H}_2)dT} \cdot \frac{T_3}{T_2}.$$

In one cell used by Farkas the following data were obtained :

$i_1 = 5{\cdot}2$ mA.,	$T_1 = 180°$ K.,	$r_1 = 84{\cdot}50\Omega$;
$i_2 = 5{\cdot}7$ mA.,	$T_2 = 250$-$260°$ K.,	$r_2 = 116{\cdot}12$.

Δr for 43·5 per cent. p-H_2 = 1·74Ω, for 97·3% p-H_2 = 6·79Ω (calc.).

Deuterium and hydrogen deuteride. Since the rotational specific heat of D_2 is greater than that of H_2, a similar principle may be used for the analysis of H_2-D_2 mixtures (A. and L. Farkas, *Proc. Roy. Soc.*, **144A**, 467 (1934)).* In practice, however, mixtures of hydrogen and deuterium may contain the equilibrium percentage of HD molecules. As can be seen from Fig. 131, the HD molecule has very nearly the same specific heat as D_2 above 90° K., and it is therefore apparent that the calibration curve for equilibrium and non-equilibrium mixtures will deviate considerably. This is shown in Fig. 134. The separation is large enough to allow of the estimation of the HD content of non-equilibrated mixtures. The practice adopted by Farkas and Farkas is to introduce the mixture and determine its resistance value, then by means of the mercury pump circulate it over a hot nickel spiral and redetermine its resistance value. The nickel wire

* Cf. also D. D. Eley and J. L. Tuck, *Trans. Faraday Soc.*, **32**, 1425 (1936) ; K. Wirtz, *Z. phys. Chem.*, **B**, **32**, 335 (1936).

must be brought into a catalytically active condition by repeated oxidation and reduction at progressively lower temperatures. There is one precaution to be observed in the analysis of deuterium mixtures by this method. During pressure adjustment, hydrogen escapes more quickly through the needle valve than deuterium, and therefore an enrichment of the D content will occur in the cell. To cut this factor down to a minimum it is advisable to use a doser of small capacity, e.g. of such a volume that five doses are necessary to fill the cell to the requisite pressure. In addition it is also necessary that the complete dose be pumped into the cell in order to avoid separation of the isotopes in pumping.

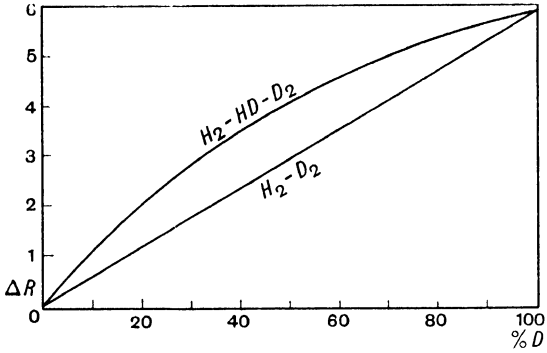


FIG. 134. Calibration curve for deuterium-hydrogen mixtures (low pressure).

It often happens in using the low pressure technique that the value of r_1 drifts. This is probably due to small changes in accommodation coefficient of hydrogen, to drift in the voltage of the bridge battery and to change in level and in composition of the liquid air. When this drift is pronounced each analytical determination must be preceded and followed by a determination of the resistance value of hydrogen. The value of $r_3 - r_2$ does not usually change to a large extent. Frequent checks are, however, easily made by having two reservoirs containing the appropriate gases attached to the main vacuum line (cf. Fig. 133A).

The comparatively simple high pressure technique for the measurement of the para-hydrogen content of hydrogen can obviously be applied to the analysis of hydrogen or deuterium mixtures, or for that matter to any binary mixture, but the quantity of gas required is far too large except in special circumstances. This difficulty has been removed (H. W. Melville and J. L. Bolland, *Proc. Roy. Soc.*, **A, 160,** 384 (1937)) by the development of a conductivity gauge of a volume of only 0·05 c.c. (see Chapter II, p. 81). This is mounted on top of an apparatus exactly resembling a McLeod gauge, the capillary tubes being about 0·2 mm. in diameter and the compression bulb 200 c.c. in volume. The

gauge itself is surrounded by a water jacket and supplied with water from a thermostat. For accurate work the temperature of the bath is kept constant to within 0·01°. Two methods are available for measuring the difference in thermal conductivity. The first is to apply a constant voltage across the bridge in which the gauge wire is placed, and alter the resistance in one arm of the bridge until a balance is obtained. Alternatively the normal Pirani gauge technique may be followed by applying a variable voltage to the bridge until balance is attained. For hydrogen-deuterium mixtures it is essential, on account of the relatively small difference in conductivity, to use a potentiometer for measuring this voltage.

The operation of the gauge is best described by detailing the procedure for calibration using the constant voltage method. First a standard pressure is chosen at which the gauge is to be calibrated. The smallest practical pressure is 50 mm., which means that the minimum quantity of gas required for analysis is 0·0035 c.c. at N.T.P. A sample of approximately this volume is admitted to the apparatus, and the mercury raised until a pressure of about 50 mm. is developed in the closed capillary. This is facilitated by the use of a length of thick wire, 50·0 mm. long, placed alongside the capillary. The difference in height of the mercury levels is then accurately measured by a travelling microscope. (Sticking of the mercury is prevented if a small trace of Apiezon Oil B, thoroughly degassed *in vacuo*, is run on to the surface of the mercury.) The resistance of the wire is then determined to at least 1 part in 10,000. A calibration curve of resistance *v.* pressure is used to obtain the resistance at exactly 50·0 mm. If the voltage of the battery has drifted from a selected standard value, it is also necessary that the resistance value should be corrected for this factor. With good accummulators the drift is generally small. Several samples of gas are treated in the same manner, and thereby a calibration curve is constructed. With hydrogen-deuterium mixtures it is, of course, necessary to plot a separate curve for the equilibrium H_2+HD+D_2 mixtures. Such equilibration is most readily established by an active nickel wire inserted in the tube leading to the analyser. The voltage-resistance and pressure-resistance calibration curves must also be constructed for the other component of the mixture, and a linear interpolation made for mixtures.

The voltage-resistance calibration may be dispensed with by taking "H_2" resistance values from time to time as in the low pressure method, since the difference in resistance values of the two components of the mixture is not appreciably affected by a variation in voltage.

A typical calibration curve is shown in Fig. 135, where it will be observed that the " HD " curve lies *below* the "H_2-D_2" curve. The length of the platinum cell wire was 50 mm. and diameter 0·015 mm., the

temperature about 200° C. with 8 volts across the wire. In this gauge there is an optimum value for the diameter for the analysis for HD. If it is greater than 0·015 mm. the "HD" curve moves towards the "H_2-D_2" curve, coinciding and finally reaching a position a little above it. The accuracy of the analysis of the HD content of the mixture is thereby decreased. On the other hand, with thinner wires the effect of pressure on the resistance becomes larger, and again accuracy is decreased. Similar remarks apply at higher pressures. The reason* for the

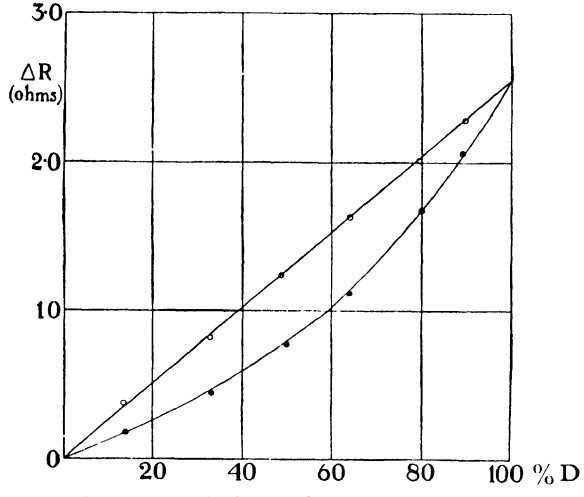


FIG. 135. Calibration curve for hydrogen-deuterium mixtures (high pressure).

HD curve lying below the H_2-D_2 is due to the fact that the accommodation coefficient of HD is almost exactly the same as D_2, and that at 50 mm. the temperature drop at the metal-gas interface plays a large part in the conduction of heat from the wire.

By arranging the gauge to dip into liquid air (Fig. 137), it may be used for the estimation of small volumes of para-hydrogen using similar technique to that described above. The optimum wire temperature for getting the maximum difference in resistance values is about 180° K. when the gauge is immersed in liquid oxygen.

Analysis of Ternary Mixtures by Thermal Conductivity Measurements

Micro-methods for the analysis of hydrogen and deuterium in gas mixtures depend on freeing these components from the other gases present initially. This is easily accomplished with liquid air, if necessary

* For a complete theory of the gauge see J. L. Bolland and H. W. Melville, *Trans. Faraday Soc.*, **33**, 1316 (1937).

boiling at reduced pressure, except when the following are present : N_2, O_2, CO, CH_4 and the inert gases. These can only be removed by means of liquid hydrogen—a refrigerant which is not always available. The following method (J. L. Bolland and H. W. Melville, *Trans. Faraday Soc.*, **33**, 1316 (1937)) enables the analysis of mixtures of hydrogen, deuterium and one non-condensable gas to be carried out without the use of liquid hydrogen.

The method depends on the non-classical variation of the rotational specific heat of hydrogen with temperature. From the data, given by W. F. Giauque and H. L. Johnson and E. A. Long (*J. Amer. Chem. Soc.*, **56**, 1045 (1934)), for the rotational specific heat of hydrogen and deuterium, the relative thermal conductivities for the two isotopes have been calculated, at various temperatures, and are shown in the table below.

T(° K.)	- 50	100	150	200	250	300
K_{H_2}/K_{D_2}	- 1·120	1·147	1·272	1·344	1·384	1·403

The relative conductivities can thus be altered by working at low (*ca.* 100° K.) and at high (*ca.* 300° K.) temperatures. In general, the specific heat of the non-condensable gas will be constant down to at least liquid oxygen temperatures ; the conductivity relative to that of deuterium will vary but little, the actual magnitude depending on the Sutherland constant of the particular gas. Hence, by operating the gauge at two wire temperatures (*ca.* 110° K. and 300° K.) with the wall tempera-

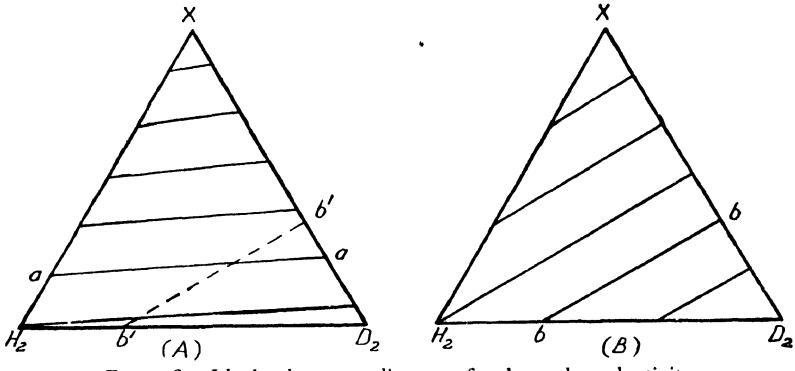


FIG. 136. Idealised ternary diagrams for thermal conductivity of ternary gas mixtures

ture at 95° K., conductivity diagrams of the type indicated in Figs. 136 (A) and 136 (B) are to be expected. At the low temperature, the tie-lines denoting the ternary mixtures of different composition having the same apparent conductivity, are almost parallel to the H_2-D_2 side of the triangle, while at the higher wire temperature they make quite a definite angle with it. Suppose an unknown mixture is passed into the cell and

the apparent conductivity (measured by the " constant resistance-variable voltage " method) is found to correspond to the lines *aa* and *bb* at the low and high wire temperature respectively, then the composition of the mixture is given by the intersection of *aa* and *bb* (as shown by the dotted line in Fig. 136A).

Method of calibration. The form of the gauge used for the analysis is shown in Fig. 137. It consists of a close tungsten spiral—from a 40 watt gas filled lamp *—having a resistance of about 20 ohms at 300° K. It is convenient for calibration purposes to have reservoirs of the three separate gases attached to the apparatus, through capillary pipettes. The voltage values, for the two wire temperatures, for the several gases are determined first ; next, the gauge is calibrated for three series of binary mixtures, and finally a few calibrations for ternary mixtures, in order to determine any curvature of the isovolt lines, are carried out. The mixtures are made up at low pressures with the help of an ordinary Pirani gauge, calibrated for the three gases. For the success of this method of analysis, it is essential that the gauge should give reproducible readings over long periods of time. This is most easily accomplished by using tungsten. Fig. 138 shows a typical calibration for H_2-D_2-N_2 mixtures, plotted on square paper for convenience. The isovolt lines are quoted relative to hydrogen as unity.

In order that the choice of operating conditions for these micro-gauges may readily be made, the following table indicates the most suitable gauge for any specific purpose. It will be seen that the spiral wire gauges have the widest applicability. Incidentally they are the most convenient to use, as the pressure adjustment is not so critical as that with a straight wire gauge. If, however, liquid air is not available and HD analyses are required, then the straight wire must be employed.

Purpose	Type of gauge and operating conditions	Wire temp., ° K.	Bath temp., ° K.
D-content of hydrogen gas, not sensitive to HD molecules	Spiral	350	295
D-content of hydrogen gas, sensitive to HD molecules	Straight	350	295
	Spiral	180	90
Sensitive to HD, insensitive to D_2 molecules	Spiral	115	90
Estimation of para-hydrogen -	Spiral	180	90
Analysis of ternary mixtures -	Spiral	115	90
		340	90

The spiral gauge dipping into liquid air has also the following advantage. If the hydrogen-deuterium ratio is required in a mixture when the gases

* It is preferable to employ unused filaments, since those from a burnt-out lamp are very brittle and therefore difficult to spot-weld.

C_2H_2, C_2H_4, C_2H_6, CO_2, N_2O, PH_3, SbH_3 or SiH_4 are present, it is necessary to free the hydrogen gas from these molecules by means of a pumped-out liquid air trap if the gauge is operated at a bath temperature of 20° C. But with a gauge cooled in liquid air, these gases have a negligible vapour pressure compared with 50 mm., the standard pressure of hydrogen gas used in the gauge, and do not therefore interfere with the analysis.

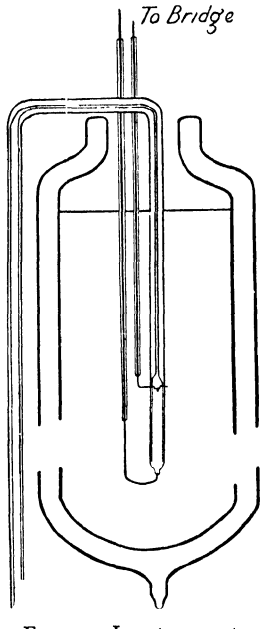


FIG. 137. Low temperature high pressure micro-thermal conductivity gauge.

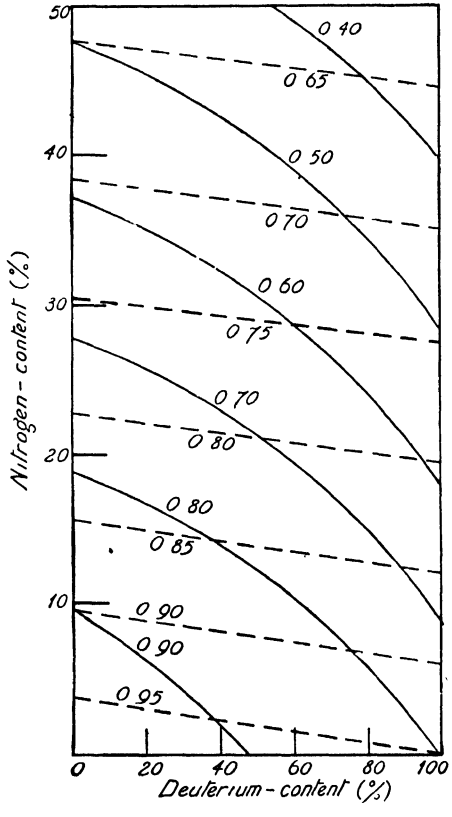


FIG. 138.

The gas density balance. In the preparation and purification of gases it is often necessary to have a rapid method of determining the density. This occurs, for example, in the preparation of the silanes, the boranes and other gases during fractionation. The same problem arises, too, in the preparation of deuterides where, after a complicated series of processes, the D-content of the deuteride must be known before commencing experiments with the gas. The analysis of deuterides can, of course, be carried out by decomposing the latter to deuterium or exchang-

ing in the presence of a catalyst a known amount of hydrogen with the deuterium in the deuteride until equilibrium is attained, and then measuring the D-content of the hydrogen gas. These latter methods, however, are not always applicable.

The gas may be weighed in the usual manner, but the method is not very accurate unless elaborate precautions are taken. The gas density balance (Fig. 139) is just as accurate and much more rapid and convenient in operation. The principle is simple. A sealed bulb B is attached to a beam A, a counterpoise C being attached to the other end

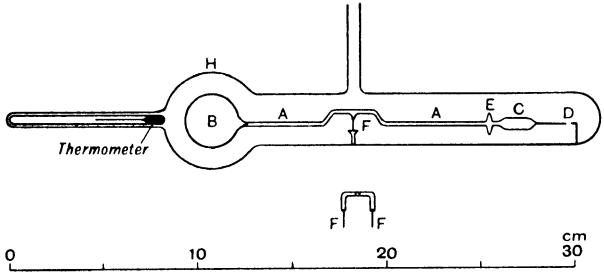


FIG. 139. Gas density balance.

of the beam. The whole is suspended by two pivots at F and enclosed in an envelope, in which the pressure may be adjusted and measured accurately. First, a gas of known density D_A is introduced to such a pressure p_A that the instrument is balanced. Secondly, a gas of unknown density D_B is run into the balance case until the pointer D returns to the zero mark at a pressure p_B. Then $D_B = \frac{p_A}{p_B} \cdot D_A$. The balance is therefore not an absolute density meter.

It has been used for determining the density of radon (R. W. Gray and W. Ramsay, *Proc. Roy. Soc.*, **A, 84,** 536 (1911)), of neon (F. W. Aston, *Proc. Roy. Soc.*, **A, 89,** 440 (1913)), of helium and hydrogen (T. S. Taylor, *Phys. Rev.*, **10,** 653 (1917)), while a very comprehensive paper by A. Stock and G. Ritter (*Z. phys. Chem.*, **119,** 333 (1926)) gives elaborate details for the construction and of the performance of this type of balance.

The following details may be given for the construction of a balance of moderate sensitivity. The bulb, beam and counter-weight are made of glass—preferably of Pyrex. The beam is borne on two steel pivots resting in two jewels such as are used for watch bearings. The beam terminates in a fine pointer D, another pointer or scale being set up in the glass envelope as a reference point. At E there are projections, so that glass may be added or removed from the beam until balance is obtained at pressures of about 500 mm. A thermometer is also enclosed in the glass envelope, which is immersed in a water bath (thermostatically con-

trolled for the most accurate work) resting on a firm foundation. To prevent vibrations reaching the balance, for example, from a boiling mercury diffusion pump, it is best to connect it to the remainder of the apparatus by a long spiral of glass tubing. The additional apparatus required consists of reservoirs of the standard gas and of the gases whose densities are to be determined, an accurate barometer (see p. 72) and a suitable means, e.g. a needle valve, for adjusting the pressure precisely. If large quantities of the gases are not available, the volume may be kept at a minimum by adopting the modification due to Aston, of working at low pressure, e.g. 50 mm., and by extending the period of swing of the suspended system to the maximum practicable value, namely 15 sec. Using a bulb of 13 c.c. and weight about 1 gm. and a period of swing of 7 sec., a change in pressure of 10 mm. changes the position of the pointer about 1 mm. If this latter is read to 0·05 mm. by means of a microscope, the pressure must then be estimated to 0·5 mm. For a period of 15 sec. the sensitivity increases by a factor of 4.

The procedure in operating the balance is briefly as follows. The standard gas is admitted and the pressure adjusted until balance is attained. At least two manometer readings are taken, approaching the balance point from opposite directions. A similar procedure is adopted with the gas of unknown density. Finally another measurement is made with the standard gas. In a typical balance the error in determining the density of CO_2 using air as standard is about $\pm$ 0·2 per cent.

For the most accurate work the moving system is best constructed of quartz. Control of the balance can also be accomplished magnetically by attaching a small permanent magnet to the beam and bringing the instrument to balance by varying the current in an external electromagnet (see A. Stock, *The Hydrides of Boron and Silicon*, Chap. XXX : Cornell University Press; E. Lehrer and E. Kuss, *Z. phys. Chem.*, **A, 163,** 73 (1933)).

D. VAPOUR PRESSURES OF GASES

The vapour pressures of all the gases, whose preparation is described in previous pages, is given in the following tables. For convenience the temperatures are given in ° C. and in ° K. and the pressures in millimetres of mercury. The order is that adopted in the section on preparation. If no reference is given under the table it means that the values were taken from the *International Critical Tables.*

Oxygen

Vapour pressure equation (valid between -182 and -211° C.) :

$$\log_{10} p\,(\text{mm.}) = -\frac{419{\cdot}30}{T} + 8{\cdot}1173 - 0{\cdot}00648T.$$

Ozone

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
80	−193	0·015	130	−143	74·6
90	−183	0·17	140	−133	182·8
100	−173	1·3	150	−123	387·7
110	−163	6·87	160·8	−112·4	760·0
120	−153	25·4			

Chlorine

° K.	° C.	p (mm)	° K.	° C.	p (mm.)
119 3	−153 9	0·0015	193·2	−80	60 0
116·2	−147·0	0·0067	194·6	−78·6	64·4
146·7	−126·5	0·26	197·9	−75·3	76·1
161·2	−112	2·64	198·2	−75·0	82·0
170·1	−103·1	8·9	216·4	−56·8	240·6
173 2	−100·0	12·4	218·2	−55·0	276
176 9	−96 3	16·5	233·9	−39·3	592
177·7	−95·5	17·4	238·7	−34·5	760

F. A. Henglein, G. v. Rosenberg and H. Muchlinski, *Z. Physik*, **11**, 1 (1922); M. Pellaton, *J. chim. Phys.*, **13**, 434, 439 (1915); F. M. G. Johnson and D. McIntosh, *J. Amer. Chem. Soc.*, **31**, 1138 (1909).

Hydrogen chloride

For solid between −158° and −110° C.:

$$\log_{10} p \text{ (mm.)} = -\frac{1023{\cdot}0}{T} + 8{\cdot}443.$$

Deuterium chloride

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
152 6	−120·6	54·4	168·2	−105·0	205·5
157·1	−116·1	84·5	181·0	−92·2	486·5
158·2 (M.P.)	−115·0	92·3	200·9	−72·3	1474·5
159·5	−113·7	104			

G. N. Lewis, R. T. MacDonald and P. W. Schultz, *J. Amer. Chem. Soc.*, **56**, 494 (1934).

Hydrogen bromide

$$\left.\begin{array}{ll} \text{Solid} & \log_{10} p \text{ (mm.)} = -\dfrac{1103}{T} + 8{\cdot}309 \\ \text{Liquid} & \log_{10} p \text{ (mm.)} = -\dfrac{945{\cdot}7}{T} + 7{\cdot}465 \end{array}\right\} \quad 174 - 205° \text{ K.}$$

Deuterium bromide

$$\left.\begin{array}{ll} \text{Solid} & \log_{10} p \text{ (mm.)} = -\dfrac{1103}{T} + 8{\cdot}306 \\ \text{Liquid} & \log_{10} p \text{ (mm.)} = -\dfrac{956{\cdot}3}{T} + 7{\cdot}517 \end{array}\right\} \quad 174 - 205° \text{ K.}$$

J. R. Bates, L. C. Halford and J. O. Anderson, *J. Chem. Physics*, **3**, 531 (1935).

Hydrogen iodide

Solid $\log_{10} p$ (mm.) $= 10{\cdot}493 - 0{\cdot}003167T - 0{\cdot}377 \log_{10} T - 1406/T.$
Liquid $\log_{10} p$ (mm.) $= 26{\cdot}119 + 0{\cdot}002293T - 7{\cdot}111 \log_{10} T - 1636/T.$

Deuterium iodide

Solid $\log_{10} p$ (mm.) $= 10{\cdot}505 - 0{\cdot}003167T - 0{\cdot}337 \log_{10} T - 1406/T.$
Liquid $\log_{10} p$ (mm.) $= 26{\cdot}129 + 0{\cdot}002293T - 7{\cdot}111 \log_{10} T - 1636/T.$

W. F. Giauque and R. Wiebe, *J. Amer. Chem. Soc.*, **51**, 1441 (1929); J. R. Bates, L. C. Halford and J. O. Anderson, *J. Chem. Physics*, **3**, 413 (1935).

Carbon monoxide

$$\log_{10} p \text{ (mm.)} = -\frac{331{\cdot}87}{T} + 6{\cdot}976. \qquad \text{(Range } -290° \text{ to } -206° \text{ C.)}$$

Carbon dioxide

Solid $$\log_{10} p \text{ (mm.)} = -\frac{1275{\cdot}62}{T} + 0{\cdot}00683T + 8{\cdot}3071.$$

Carbon oxysulphide

$$\log_{10} p \text{ (mm.)} = -\frac{1003{\cdot}9}{T} + 7{\cdot}383. \qquad \text{(Range } -80 \text{ to } -50° \text{ C.)}$$

Nitrogen

$$\log_{10} p \text{ (mm.)} = -\frac{334{\cdot}64}{T} + 7{\cdot}5778 - 0{\cdot}00476T \text{ (64 - 84° K.)}.$$

H. v. Siemens, *Ann. d. Physik*, IV, **42**, 871 (1913); P. G. Cath, *Versl. Amst.*, **27**, 656 (1918).

Ammonia

Solid $$\log_{10} p \text{ (mm.)} = -\frac{1641{\cdot}5}{T} + 9\ 9974. \qquad \text{(Range } -127° \text{ to } -78° \text{ C.)}$$

Trideutero-ammonia

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
202·3	−70·9	63	232·1	−41·1	445
213	−60·2	154	238·6	−34·6	628
226·1	−47·1	313			

J. C. Jungers and H. S. Taylor, *J. Chem. Physics*, **2**, 373 (1934).

Nitric oxide

Solid $$\log_{10} p \text{ (mm.)} = -\frac{855{\cdot}78}{T} + 10{\cdot}048. \qquad \text{(Range } -200 \text{ to } -161° \text{ C.)}$$

Liquid $$\log_{10} p \text{ (mm.)} = -\frac{681{\cdot}04}{T} + 8{\cdot}440. \qquad \text{(Range } -163{\cdot}7 \text{ to } -148° \text{ C.)}$$

Nitrous oxide

Solid $$\log_{10} p \text{ (mm.)} = -\frac{1232{\cdot}1}{T} + 9{\cdot}579. \qquad \text{(Range } -144 \text{ to } -90° \text{ C.)}$$

Liquid $$\log_{10} p \text{ (mm.)} = -\frac{858{\cdot}11}{T} + 7{\cdot}535. \qquad \text{(Range } -90{\cdot}1 \text{ to } -88{\cdot}7° \text{ C.)}$$

Nitrogen peroxide

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
183	− 90	0·0051	262·4	− 10·8	146 M.P.
195	− 78	0·040	263	− 10	151·6
228	− 45·2	4·84	273	0	257·5
237	− 36	18	285 1	12·1	483
250	− 23	53	294·5	21 5	752
258	− 15	102			

A. C. G. Egerton, *J.C.S.*, **105**, 647 (1914) ; F. E. C. Scheffer and J. P. Treub, *Z. phys. Chem.*, **81**, 308 (1913) F. Russ, *Z. phys. Chem.*, **82**, 217 (1913).

Methane

$$\log p \text{ (mm.)} = -\frac{472{\cdot}47}{T} + 1{\cdot}75 \log T - 0\ 0096351\,T + 4{\cdot}60175.$$

(Range − 182° to − 150° C.)

A. Stock, F. Henning and E. Kuss, *Ber*, **54**, 1119 (1921).

Ethane

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
165·3	− 107·9	288	179·2	− 94 0	546
170·8	− 102 4	354	180·2	− 93 0	575
172 8	− 100·4	385	181·7	− 91·5	630
175·0	− 98·2	422	183·3	− 89·9	681
176·1	− 97·1	454	183·9	− 89·3	713
178·2	− 95 0	510	184 8	− 88·4	765

O. Maass and D. McIntosh, *J. Amer. Chem. Soc.*, **36**, 737 (1914).

Ethylene

$$\log p \text{ (mm.)} = -\frac{834{\cdot}13}{T} + 1{\cdot}75 \log T - 0{\cdot}008375\,T + 5\ 3234.$$

A. Stock, F. Henning and E. Kuss, *Ber.*, **54**, 1119 (1921).

Cyanogen

Solid $\log p \text{ (mm.)} = -\frac{1694{\cdot}1}{T} + 9\ 653.$ (Range − 72° to − 28° C.)

Liquid $\log p \text{ (mm.)} = -\frac{1240{\cdot}5}{T} + 7{\cdot}808.$ (Range − 32° to − 6° C.)

Acetylene

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
129·9	− 143·3	1	180·8	− 92·4	400
138·5	− 134·7	6	183·6	− 89·6	500
153·2	− 120·0	30	187·2	− 86·0	650
164·9	− 108·3	100	188·0	− 85·2	700
172·5	− 100·7	200	188·6	− 84·6	730
177·3	− 95·9	300	189·1	− 84·1	760

$$\log p \text{ (mm.)} = -\frac{1127{\cdot}1}{T} + 8{\cdot}84.$$

G. A. Burrell and I. W. Robertson, *J. Amer. Chem. Soc.*, **37**, 2188 (1915).

Hydrocyanic acid

$$\log p \text{ (mm.)} = -\frac{1454{\cdot}1}{T} + 7{\cdot}7446. \qquad \text{(Range } -8^\circ \text{ to } 27^\circ \text{ C.)}$$

Deuterocyanic acid

Solid $\log p \text{ (mm.)} = 9{\cdot}476 - \frac{1907}{T}$ (Range -38° to -12° C.)

Liquid $\log p \text{ (mm.)} = 7\,695 - \frac{1440}{T} - \frac{175}{T^2}$ (Range -12° to 20° C.)

G. N. Lewis and P. W. Schultz, *J. Amer. Chem. Soc.*, **56**, 1002 (1934).

Hydrogen sulphide

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
191	−82	172	207	66	535
195	−78	235	211	−62	660
199	−74	339	215	−58	830
203	−70	432			

For solid H_2S from -110° to -83° C.:

$$\log p \text{ (mm.)} = -\frac{1080{\cdot}6}{T} + 7{\cdot}880.$$

Sulphur dioxide

For solid SO_2 from -95° to -75° C.:

$$\log p \text{ (mm)} = -\frac{1871{\cdot}2}{T} + 10{\cdot}591.$$

Phosphine

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
140	−133	29·3	164	−109	209·9
144	−129	43·0	168	−105	274·6
148	−125	61·3	172	−101	354·2
152	−121	85·7	176	−97	450·4
156	−117	117·5	180	−93	564·5
160	−113	158·3	184	−89	699·5

Silanes

	SiH_4			Si_2H_6	
° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
113	−160	11	163	−110	0·2
123	−150	41	183	−90	1·05
133	−140	102	202·1	−71·1	4·45
143	−130	230	223·9	−49·3	15·7
153	−120	470	244·7	−28·5	42
158	−115	630	255·7	−17·5	65
161	−112	750	257·5	−15·7	72·5

A. Stock and C. Somieski, *Ber.*, **50**, 1739 (1917).

Boron Hydride. B_2H_6

° K.	° C.	p (mm.)	° K.	° C.	p (mm.)
143	−130	40	173	−100	400
153	−120	100	183	−90	650
163	−110	250			

A. Stock and K. Friederici, *Ber.*, **46**, 1959 (1913).

Boiling Point of Liquid Air as a Function of Composition

E. C. C. Baly, quoted by M. Travers, *Study of Gases*, p. 224

Vapour Phase

Pressure, 760 mm.

Temp. (hydrogen scale)	% O_2	Temp. (hydrogen scale)	% O_2
77·54	0·00	84·5	40·45
78·00	2·18	85·0	44·25
78·5	4·38	85·5	48·17
79 0	6·80	86·0	52·19
79 5	9·33	86·5	56·30
80·0	12·00	87·0	60·53
80 5	14·78	87·5	64·85
81·0	17·66	88·0	69·58
81·5	21·22	88·5	74·37
82·0	23·60	89·0	79·45
82·5	26·73	90·0	89·80
83·0	29·95	90·5	95·10
83·5	33·35	90·96	100·00
84·0	36·86		

Liquid Phase

Temp. (hydrogen scale)	% O_2	Temp. (hydrogen scale)	% O_2
77·54	0 00	84·5	69·31
78·0	8·10	85·0	72·27
78·5	15·25	85·5	75·10
79·0	21 60	86·0	77·80
79·5	27·67	86·5	80·44
80·0	33·35	87·0	82·95
80·5	38·53	87·5	85·31
81·0	43·38	88·0	87·60
81·5	47·92	88·5	89·82
82·0	52·17	89·0	91·98
82·5	55·94	89·5	94·09
83·0	59·55	90·0	96·15
83·5	62·93	90·5	98·16
84·0	66·20	90·96	100·00

CHAPTER IV

PHOTOCHEMICAL TECHNIQUE

A LARGE part of the technique employed in the study of thermal gas reactions is directly applicable to photo-chemical reactions, such as the methods employed for following the reaction and for controlling the gases undergoing illumination. In this chapter the additional apparatus required in photo-chemistry will be described.

A. ABSORPTION SPECTRA OF GASES

Extinction coefficients are defined by the following equations :

$I = I_0 e^{-\alpha^1 d}$ (α^1 = extinction coefficient),

$I = I_0 10^{-\alpha d}$ (α = decadic extinction coefficient = $0{\cdot}434\alpha^1$),

and $I = I_0 10^{-\epsilon c d}$ (ϵ = molar (decadic extinction coefficient, c = concentrations in moles/litre)).

where I and I_0 are the intensities and transmitted and incident light respectively and d is the thickness of the absorbing layer.

It is unfortunate that accurate values of the extinction coefficients of a large number of gases have not yet been measured. In the following diagrams and tables the extinction coefficients are given over a band of wavelengths, and where no quantitative data exist the approximate wavelength of the onset of absorption is indicated. For these molecules which exhibit well defined vibrational and rotational lines the extinction coefficient will vary very widely in any individual band. For most practical purposes, therefore, an average value of the extinction coefficient is given over a short wavelength range. Where more accurate values are required references are given to the original literature.

It is not in general satisfactory for accurate quantitative work to take the value of the extinction coefficient and calculate the fraction of light absorbed at any given wavelength. A small error in the extinction coefficient will give rise to a large error in the calculation, since the coefficient appears as an exponent in the formula giving the absorbed intensity of the light. Another complication is caused by the fact that transparent gases often affect the value of the extinction coefficient. The following figures are brought together mainly to act as guide to indicate at what

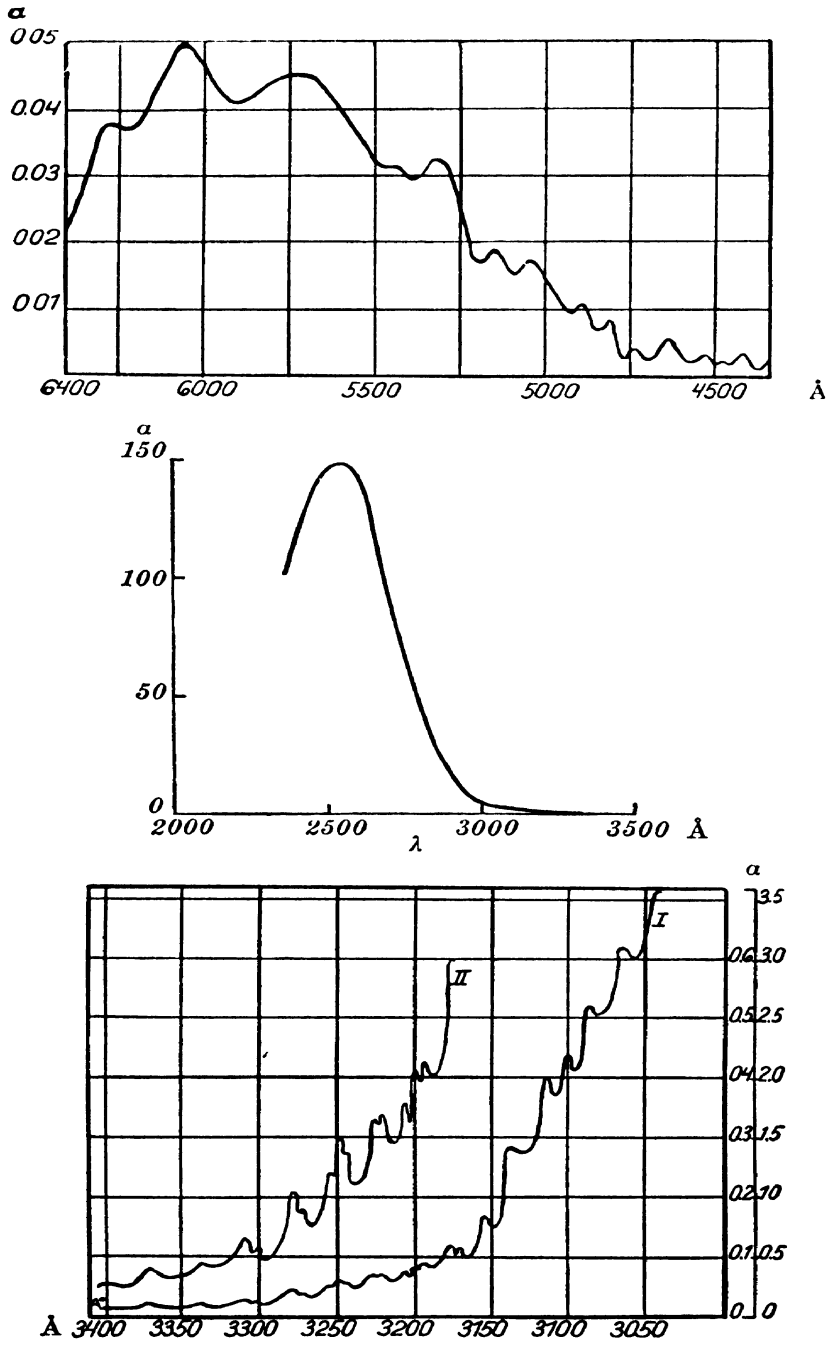


FIG. 140. Extinction coefficients of ozone at 1 atmosphere.

wavelengths photochemical experiments are most conveniently carried out, and to allow for an approximate calculation of the size of reaction vessel required. For example, if 90 per cent. of the radiation is absorbed in a layer of gas 1 cm. thick, there is nothing to be gained by using a reaction vessel 10 cm. thick. Indeed, by using the larger vessel the percentage photo change will be reduced by a factor of about 10.

Oxygen. This molecule absorbs very weakly in the red region of the visible spectrum (R. M. Badger and R. Mecke, *Z. Physik*, **60**, 59 (1930)), and also very weakly between 2400 and 2600 Å (G. Herzberg, *Naturwiss.*, **20**, 577 (1932)). These absorption regions are not of interest for the majority of photochemical purposes. The absorption beginning at 1924·8 Å (the Schumann bands) is of importance photochemically, since ozone is produced in this region. Oxygen in the air between a source and reaction vessel effectively cuts off wavelengths shorter than 1800 Å, if any fused quartz in the apparatus has not already limited the intensity of wavelengths shorter than 2000 Å. For photochemical experiments in this region, the source of light, e.g. a hydrogen tube or mercury lamp, is usually made contiguous with the reaction vessel, the dividing partition being of *crystalline* quartz or of fluorite. The following table gives the wavelengths of O_2 bands observed by S. Leifson (*Astrophysical Jour.*, **63**, 73 (1926)).

1924·8	1846·9	1793·4	1763·8
1903·1	1831·1	1783·9	1759·8
1883·0	1816·8	1775·5	1756·7
1864 2	1804·3	1769·2	—

Ozone. This gas absorbs weakly in the visible and very strongly in the ultra-violet with a maximum at about 2500 Å. The extinction coefficients for these regions are given in Fig. 140.

Nitrogen does not absorb in the quartz ultra-violet.

Halogens. All these molecules exhibit a band spectrum preceding the continuous absorption spectrum. The average value of the extinction coefficients are given in the accompanying figures. Chlorine (H. v. Halban and K. Siedentopf, *Z. phys. Chem.*, **103**, 71 (1923); G. E. Gibson and N. S. Bayliss, *Phys. Rev.*, **44**, 188 (1933)) has a maximum at about 3200 Å. Bromine, Fig. 141 (G. Ribaud, *Ann. de Phys.*, **12**, 107 (1919)), has a peak at 4100 Å. In Fig. 141 the extinction coefficients of iodine along with those of bromine and chlorine are given (E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 544 (1936)). The effect of foreign gases in lowering the extinction coefficient of iodine vapour is also indicated. The absorption spectra of iodine chloride (G. E. Gibson and H. C. Ramsperger, *Phys. Rev.*, **30**, 598 (1927); G. E. Gibson, *Z. Physik*,

50, 692 (1928) ; J. Patkowski and W. E. Curtis, *Trans. Faraday Soc.*, **25** 725 (1929) ; W. E. Curtis and O. Darbyshire, *ibid.*, **27,** 77 (1931)) and bromine chloride (S. Barratt and O. Stein, *Proc. Roy. Soc.*, **122A,** 58 (1929) ; L. T. M. Gray and D. W. G. Style, *ibid.*, **126A,** 603 (1930) W. Jost, *Z. phys. Chem.*, **153A,** 143 (1931)) have also been photographed

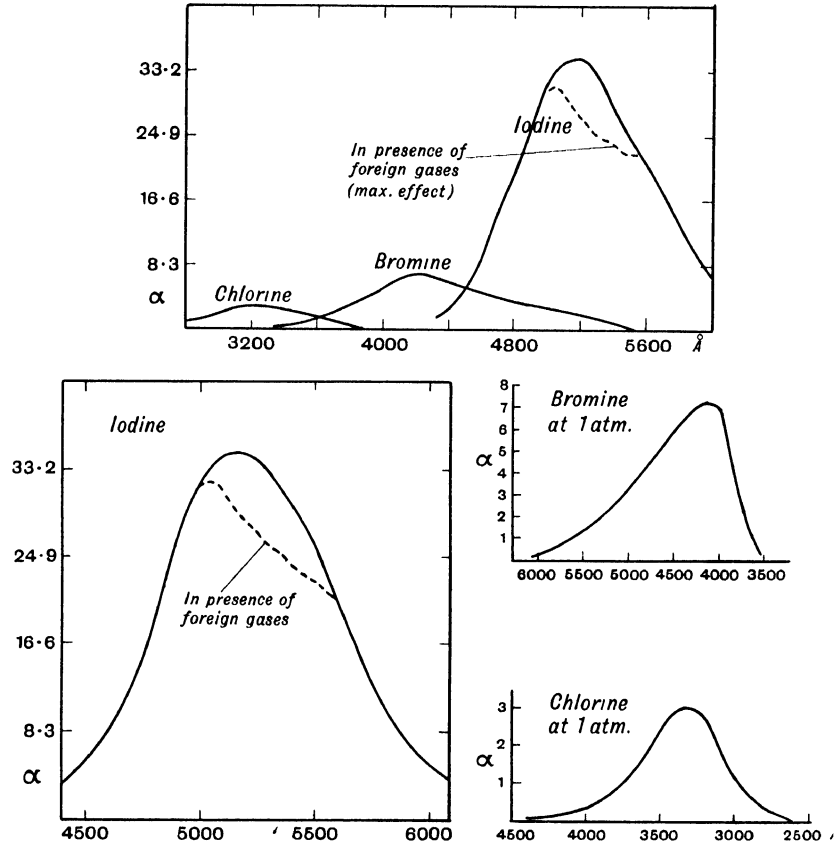


FIG. 141. Extinction coefficients of the halogens.

Halogen hydrides. At atmospheric pressure in a layer of hydrogen chloride 15 mm. thick absorption is complete at wavelengths shorter than 2250 Å (S. Leifson, *Astrophys. J.*, **63,** 73 (1926)). The extinction coefficients of hydrogen and deuterium bromide and hydrogen and deuterium iodide (J. R. Bates, L. C. Halford and J. O. Anderson, *J. Chem. Physics* **3,** 415, 531 (1935)) are given in Fig. 142.

Carbon monoxide, carbon dioxide. There is no appreciable absorption above 1800 Å (S. Leifson, *Astrophys. J.*, **63,** 73 (1926)).

Hydrocarbons. Methane and ethane are both transparent up to the limit of transmission of quartz. There is some slight disagreement about

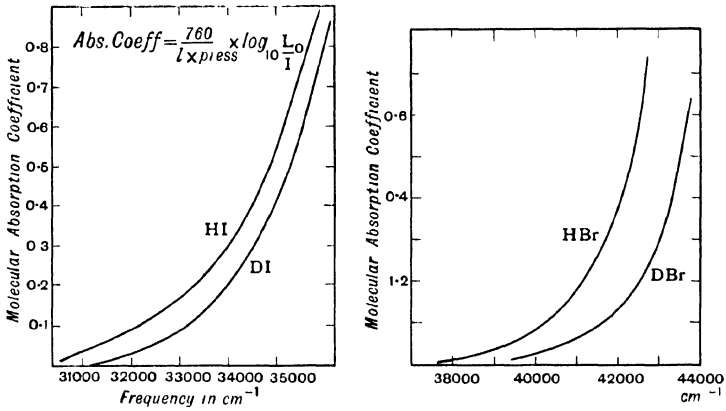


FIG. 142. Extinction coefficients of halogen hydrides and deuterides.

the onset of absorption with acetylene. G. B. Kistiakowsky states that bands become apparent at 2400 Å (*Phys. Rev.*, **37**, 276 (1931)) whereas J. Stark and P. Lipp (*Z. phys. Chem.*, **86**, 36 (1914)) put the limit at 2200 Å, and G. Herzberg says there is no absorption until 2070 Å is reached. S. C. Lind and R. Livingston (*J. Amer. Chem. Soc.*, **54**, 94 (1932)) have measured the extinction coefficient at a wavelength of about 2150 Å, and found in a 4·7 cm. long tube that 6·5 per cent. of the incident light is absorbed at a pressure of 500 mm. Ethylene absorbs at even shorter wavelengths. R. B. Mooney and E. B. Ludlam (*Trans. Faraday Soc.*, **25**, 442 (1929)) estimate that at 2020 Å 75 per cent. of the incident radiation is absorbed in a tube 150 cm. long, at a pressure of 1 atmosphere.

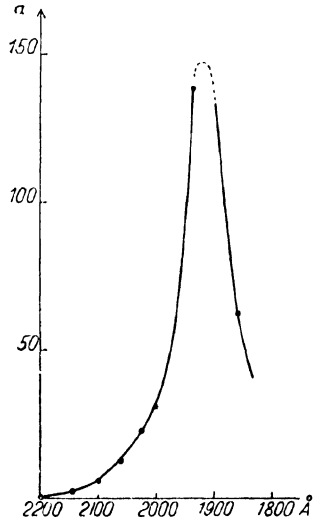


FIG. 143. Extinction coefficient of ammonia.

Ammonia. This molecule exhibits a predissociation band spectrum beginning at about 2300 Å (S. Leifson, *Astrophys. J.*, **63**, 73 (1926)) with a maximum intensity of absorption at about 1900 Å. The extinction coefficient wavelength curve plotted in Fig. 143 (G. Landsberg and A. Predwoditeleff, *Z. Physik.*, **31**, 544 (1925)) is only approximate in order

to indicate the intensity of the extinction. It should have superposed on it a band structure.

Trideutero-ammonia. In common with deuterides the extinction coefficients of ND_3 are higher than those of NH_3 and the position of the bands is altered. Unfortunately in the only spectrogram published no wavelength scale is marked (J. C. Jungers and H. S. Taylor, *J. Chem. Physics*, **2**, 373 (1934)).

Hydrazine exhibits continuous absorption, beginning at about 1990 Å (R. R. Wenner and A. O. Beckmann, *J. Amer. Chem. Soc.*, **54**, 2787 (1932)).

Nitrous oxide exhibits continuous absorption, beginning at about 2000 Å.

Nitric oxide has an absorption spectrum consisting of a number of double bands having the following wavelengths (S. Leifson, *Astrophys. J.*, **63**, 73 (1926)) :

Å	Å
2264·7	1957·4
2150·9	1950·4
2111·1	1910 6
2067·2	1877·2
2048·8	1847·4
1986·7	—

Nitrogen dioxide. The extinction coefficients of the NO_2 and N_2O_4 molecules have been measured by H. H. Holmes and F. Daniels (*J. Amer. Chem. Soc.*, **56**, 630 (1934)), and are given below.

TABLE 27

$\epsilon = \frac{1}{p \cdot l} \cdot \ln I_0/I$, where p is in mm. at 0° C. and l in cm.

λ(Å)	$\epsilon(NO_2)$	$\epsilon(N_2O_4)$	$\epsilon(N_2O_5)$
4360	0·0192	—	—
4050	0·0216	—	—
3660	0·0187	0 00824	—
3340	0·013	0·015	—
3130	0·00773	0·0119	—
3020	0·0055	0 0085	—
2800	0·00263	0 0174	0 0029
2650	0·00136	0·0243	0·0063

Hydrogen sulphide. The extinction coefficients of hydrogen sulphide are given in Fig. 144 (C. F. Goodeve and O. Stein, *Trans. Faraday Soc.*, **27**, 397 (1931)).

Sulphur dioxide. This molecule exhibits two regions of banded absorption, one stretching from 2600 to 3900 Å (W. W. Watson and A. E. Parker, *Phys. Rev.*, **37**, 1013 (1931) ; K. Wieland, *Trans. Faraday Soc.*, **30**,

260 (1934)) and another commencing at 2400 Å (V. Henri, *Leipziger Vortrage*, p. 131 (1931)). The average values of the extinction coefficients have not been measured.

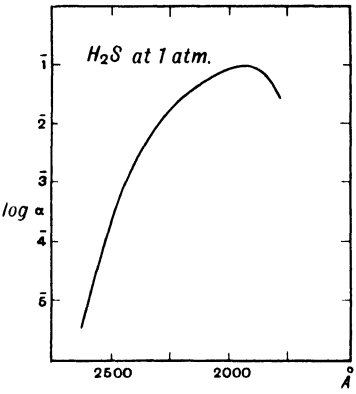


FIG. 144. Extinction coefficient of hydrogen sulphide.

Absorption spectra of hydrides of the fifth group

Phosphine at atmospheric pressure and thickness of 100 cm. absorbs all light below about 2200 Å. There are a few very weak predissociation bands preceding the continuous absorption (H. W. Melville, *Proc. Roy. Soc.*, **A 139**, 542 (1933) ; G. H. Cheesman and H. J. Emeléus, *J. Chem. Soc.* (1932), 2847). Arsine absorbs at somewhat longer wavelengths. Under similar conditions the limit is at about 2390 Å (Cheesman and Emeléus, *loc. cit.*). The limit of absorption by stibine is at 2750 Å. Unfortunately no data are available about the absolute value of the extinction coefficients.

Monosilane is transparent to light down to a wavelength of 1850 Å. Disilane in a thickness of 10 cm. at 65 mm. pressure absorbs at about

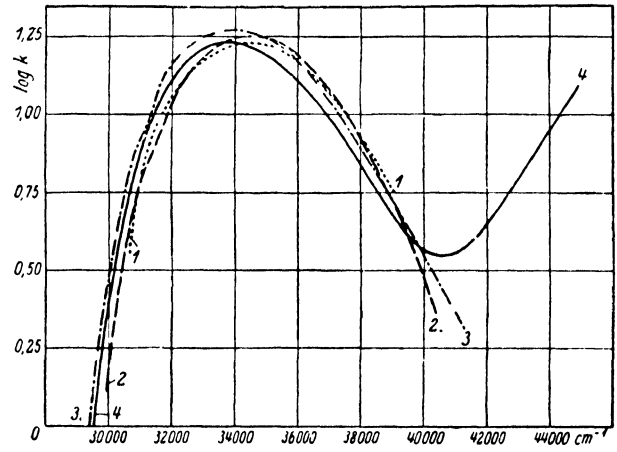


FIG. 145. Extinction coefficients of aldehydes (1) acetaldehyde (2) propionaldehyde (3) *n*-butyroaldehyde (4) isobutyroaldehyde in heptane solution.

2000 Å, whilst trisilane under the same conditions exhibits absorption at about 2200 Å (H. J. Emeléus and J. Stewart, *Trans. Faraday Soc.*, **32**, 1577 (1936)).

Aldehydes. The extinction coefficient-frequency curve for a number

of simple aliphatic aldehydes is shown in Fig. 145 (K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie*, p. 174). The similarity in absolute magnitudes of the extinction coefficients is due, of course, to the presence of the carbonyl group ; these are little altered by increase in the length of the hydrocarbon chain.

Formaldehyde has a banded spectrum which has been measured accurately by G. H. Dieke and G. B. Kistiakowsky (*Proc. Nat. Anad. Sci.*, **18**, 367 (1932)), and its photo-decomposition has been measured by R. G. W. Norrish and F. W. Kirkbride (*J. Chem. Soc.* (1932), 1518).

B. SOURCES OF RADIATION

The mercury lamp. Of all the sources of light employed in photochemical work, the mercury lamp is the most extensively used. Its advantages are numerous. If operated under properly controlled conditions its output is fairly constant ; it emits, if made of quartz, a number of intense lines from 1860 Å to the two yellow lines at 5683 Å and 5688 Å, which may be separated satisfactorily for most purposes by simple filters. One important disadvantage is the comparatively large area from which the light is emitted, though capillary arcs have lately been improved, by operating under very high pressures, up to 150 atmospheres, so that the intrinsic brilliance is much greater than that of the usual type operating at atmospheric pressure or lower. In fact, for nearly all photochemical purposes in which light of wavelength longer than 2000 Å is required, the mercury lamp is the most suitable source to use.

The number of designs of mercury lamps described in the literature and manufactured by commercial undertakings is so large that no attempt can be made here to describe them in detail. Roughly, however, two types may be distinguished, viz. (*a*) low and (*b*) high pressure lamps. In the former class the mercury vapour pressure is kept as low as is practicable, with the result that the intrinsic brilliance is small. This type, however, has one advantage, that much of the energy emitted lies in the first resonance line of the mercury spectrum at 2537 Å ; and secondly, the line (really a group of five closely spaced lines) is unreversed. Such lamps are suitable where a particularly strong source of resonance light is required, as in mercury photosensitised reactions. In the second class are the majority of the commercial lamps. In these the lines in the visible spectrum are intense, as are also a number of useful lines in the near ultra-violet. The 2537 line is now, however, strongly reversed, though still intense. One lamp may be used for both purposes, but it is invariably more satisfactory to design a lamp for one or the other purpose specifically.

Low pressure lamps. R. W. Wood was the first to investigate the excitation of resonance radiation in a cell containing mercury vapour. To prevent self-reversal of the exciting line he cooled the cathode of a vertical quartz mercury arc, having a tungsten anode ; and, by means of an electromagnet, deflected the discharge against the walls of the quartz tube. A convenient lamp of this kind is shown in Fig. 146. It simply consists of an ordinary 200 v. burner, except that the cathode has a small silica water jacket extending a few mm. above the level of the mercury in the cathode chamber. If it is desired to run the arc "hot", then the water is merely run out of the jacket. When running cold the discharge is less steady than when running hot. To avoid frequent extinction of the arc it is advisable to insert an inductance of 0·1-0·3 henry in series with the regulating resistance. The lamp burns at 4-5 amp. and 20-30 volts.

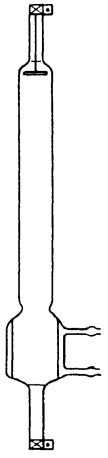


FIG. 146. Tungsten anode mercury lamp.

A lamp may easily be run at low pressure by immersing lamp and reaction vessel in a water bath, but the disadvantage of any arrangement in which the sides of the discharge tube are directly cooled with water is the condensation of mercury to droplets which obscure the radiation.

To obviate the unsteadiness of low pressure lamps operating with a mercury cathode two improvements have been effected. The first is to use a high voltage lamp, the discharge occurring through a mixture of rare gas and mercury vapour. The second is to use a hot cathode and an anode of mercury, tungsten, nickel, etc.

High voltage mercury lamps. In these lamps the discharge occurs at some hundreds of volts in a mixture of rare gas—helium, neon, or argon—and mercury vapour. The current is carried by the inert gas, and the mercury atoms are probably excited by secondary processes. A typical lamp of this type is shown in Fig. 147 (H. W. Melville, *Trans. Faraday Soc.*, **32**, 1525 (1936)). It is entirely constructed of silica, the electrodes are of iron as used in neon signs, and the electrode chambers are water-cooled to prevent the mercury pressure from becoming too high. The lamp need not be bent in the form of a U-tube. For some purposes it would be better straight and surrounded by a chromium-plated reflector to focus the light on the reaction vessel. The electrodes are welded to nickel and then to tungsten, which is sealed into the silica in the usual way with lead. The lamp is excited from a 1000 v. transformer capable of delivering 200 milliamperes. With a lamp of the dimensions shown in

Fig. 147, the secondary voltage required varies from 300-800. Regulation of secondary current is, of course, best made by inserting resistances in the primary circuit of the transformer. Any of the rare gases will function well, but probably neon is the best, as the conditions for optimum output are not too sharply defined. The procedure in filling the lamp is as follows. It is attached to a good vacuum line and baked out in the usual manner by enclosing in a furnace, the electrodes being outside to avoid melting the lead seals. A little liquid mercury is run in, followed by neon, to a pressure of about 10 mm. The lamp is then run for a few hours at as high a current density as the electrodes will stand without

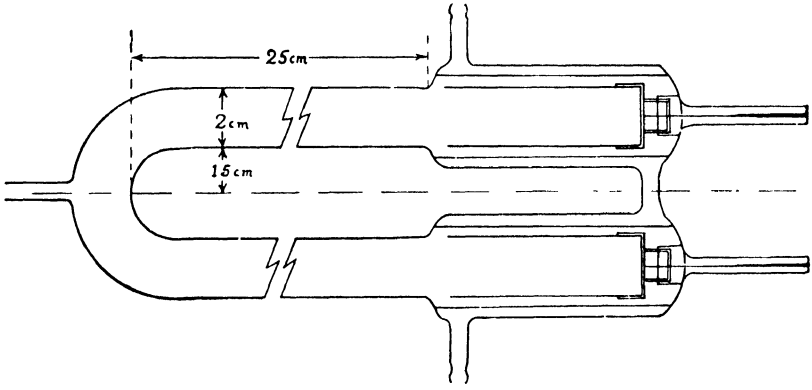


FIG. 147. High voltage cold cathode mercury lamp.

sputtering and the neon pumped out. Fresh neon is added and the lamp sealed off. Fig. 148 shows some characteristic curves of such a lamp, the output in quanta per sec. at 2537 Å per cm. length being plotted against current at a number of different pressures. It will be seen that there is no advantage to be gained in running the lamp above a current of 0·180 amp., since the output is then at a maximum. Within a few minutes of switching on the lamp attains steady working conditions and operates with a blue glow in the space between the electrodes, while the electrodes themselves are covered with the characteristic glow of a neon discharge. At least 90 per cent. of the light emitted is at a wavelength of 2537 Å. The line is particularly free from self-reversal, and has been used as a source of resonance radiation for mercury vapour quenching experiments.

The lamp has another great advantage in that it may be inserted in a furnace for photochemical experiments at high temperatures, thus permitting the intense irradiation of reaction vessels. A suitable arrangement of the lamp, etc., is shown in Fig. 167. In the normal method of placing

the lamp outside a very large proportion of the light is wasted. Moreover, the intensity is independent of temperature up to 600° C. This was tested by following the mercury sensitised conversion of para-hydrogen, and also by observing the temperature coefficient rate of exchange of deuterium with ammonia (cf. A. Farkas and H. W. Melville, *Proc. Roy. Soc.*, **A, 157,** 625 (1936) ; H. W. Melville and J. L. Bolland, *ibid.*, **160,** 384 (1937)) with the apparatus shown in Fig. 167, and with another set-up in which the lamp was outside the furnace. With this particular

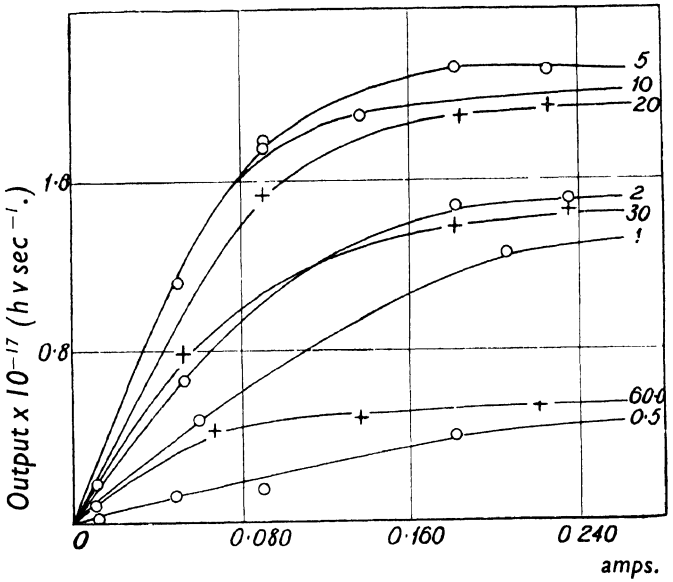


FIG. 148. Neon , effect of current. At 60 mm. the voltage across the lamp was 1000 ; at 30 mm. 700-850 ; at 20 mm. 500-550 ; at 10 mm. 400-470 ; at 5 mm. 400-570 ; at 2 mm. 430-580 ; at 1 mm. 440-530 ; at 0 5 mm. 500-680.

lamp the total output for an input of 70 watts was 10^{19} quanta per sec. at 2537 Å, the luminous efficiency reaching the comparatively good figure of 10 per cent.

Hot cathode low pressure mercury lamp. (G. Kornfeld and F. Müller-Skjold, *Z. phys. Chem.*, **B, 31,** 223 (1936).) The use of high voltages may be dispensed with, if a thermionic cathode is used in the lamp. This leads, however, to some additional complication, as is shown in Fig. 149. The anode consists of a nickel alloy beaker-shaped cup welded to tungsten wire. To prevent water cooling from becoming too efficient an evacuated space is provided between the discharge tube and the water-cooled compartment carrying the tungsten-

silica seals. The cathode, also of nickel alloy sheet, covered with a mixture of barium and strontium oxides, is indirectly heated by a tungsten spiral. The sheet metal is wound zig-zag fashion inside the cup in order to obtain the maximum possible emitting surface. Two leads carry the current for the heater, and the other lead is connected to the cathode. The tungsten-silica seals are water cooled. The cathode is " formed " by covering it with a mixture of barium and strontium carbonates, and gradually heating over a period of several hours until the carbonates are completely decomposed, during which time the lamp is connected to the pumps. The current to the lamp is switched on, and the discharge started by a high frequency current from a Tesla coil. The voltage drop is 16-18 with a current of 14 amperes, the operating temperature being 55-60° C.

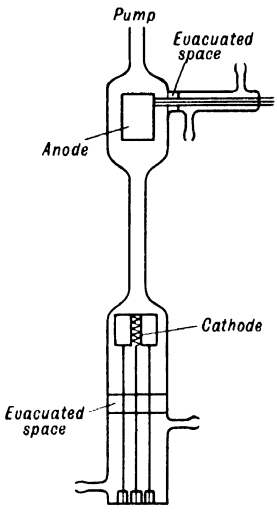


FIG. 149. Hot cathode lamp.

Under these conditions the output is said to be 3-4 times greater than that from an ordinary water-cooled lamp. The voltage on the lamp must not exceed 20, under which conditions the life of the cathode is about 800 hours.

High pressure lamps. As the temperature, and therefore pressure, in a mercury lamp is raised the intensity of light weakens in the far ultra-violet, and becomes greater in the visible and in the near ultra-violet. The individual lines also become broader and the discharge contracts into the middle of the arc tube. Since the light is now transmitted through a layer of non-emitting mercury vapour, the first and second resonance lines at 2537 and 1846 Å. are strongly reversed, and the intensity of the reversed lines is, in general, small. Such lamps usually work at a pressure of the order of one atmosphere. Details of two of the most common laboratory types are given in Table 28, the arc length being about 12 cm. The voltage required is about 160 and the current 3·5 amp. when working temperature is reached. By shortening the arc tube to about 6 cm. these lamps may be operated on a 100 volt supply.

The following table shows the output in quanta of the principal lines in the mercury spectrum from two different horizontal arcs operating under optimum conditions, as observed by A. J. Maddock (*Proc. Phys. Soc.*, **47**, 424 (1935)).

TABLE 28

Arc length, 12 cm. Output in quanta, cm.$^{-2}$ sec.$^{-1}$ at 100 cm.

λ in Å	2·5 amp. type 150 volts	3·5 amp. type 140 volts
7082, 6907	$2{\cdot}02 \times 10^{13}$	$3{\cdot}45 \times 10^{13}$
6234, 6149, 6124	$6{\cdot}9 \times 10^{12}$	$1{\cdot}16 \times 10^{13}$
6073, 5790, 5770	$2{\cdot}65 \times 10^{14}$	$4{\cdot}9 \times 10^{14}$
5461	$2{\cdot}8 \times 10^{14}$	$4{\cdot}6 \times 10^{14}$
4916	$5{\cdot}0 \times 10^{12}$	$8{\cdot}8 \times 10^{12}$
4358, 4329	$1{\cdot}89 \times 10^{14}$	$3{\cdot}0 \times 10^{14}$
4078, 4047, 3984	$9{\cdot}5 \times 10^{13}$	$1{\cdot}48 \times 10^{14}$
3906	$2{\cdot}6 \times 10^{12}$	$9{\cdot}4 \times 10^{12}$
3704, 3663, 3655, 3650	$2{\cdot}5 \times 10^{14}$	$4{\cdot}09 \times 10^{14}$
3342	$1{\cdot}84 \times 10^{13}$	$3{\cdot}00 \times 10^{13}$
3132, 3126	$1{\cdot}46 \times 10^{14}$	$2{\cdot}25 \times 10^{14}$
3022	$6{\cdot}03 \times 10^{13}$	$1{\cdot}06 \times 10^{14}$
2967	$3{\cdot}19 \times 10^{13}$	$4{\cdot}94 \times 10^{13}$
2926	$5{\cdot}4 \times 10^{12}$	$1{\cdot}07 \times 10^{13}$
2894	$1{\cdot}23 \times 10^{13}$	$1{\cdot}68 \times 10^{13}$
2804	$2{\cdot}01 \times 10^{13}$	$3{\cdot}03 \times 10^{13}$
2753	$6{\cdot}4 \times 10^{12}$	$1{\cdot}07 \times 10^{13}$
2699	$8{\cdot}4 \times 10^{12}$	$1{\cdot}86 \times 10^{13}$
2655, 2654, 2652, 2640	$4{\cdot}13 \times 10^{13}$	$7{\cdot}2 \times 10^{13}$
2603	$5{\cdot}8 \times 10^{12}$	$1{\cdot}00 \times 10^{13}$
2576	$9{\cdot}5 \times 10^{12}$	$1{\cdot}84 \times 10^{13}$
2537, 2535	$6{\cdot}58 \times 10^{13}$ (Reversed)	$9{\cdot}9 \times 10^{13}$ (Reversed)
2482	$1{\cdot}64 \times 10^{13}$	$2{\cdot}6 \times 10^{13}$

TABLE 28—*continued*

λ in Å	2·5 amp. type 150 volts	3·5 amp. type 140 volts
2464	$3{\cdot}9 \times 10^{12}$	—
2447	$3{\cdot}8 \times 10^{12}$	—
2399	$9{\cdot}4 \times 10^{12}$	$1{\cdot}44 \times 10^{13}$
2378	$9{\cdot}1 \times 10^{12}$	$1{\cdot}02 \times 10^{13}$
2353	$6{\cdot}2 \times 10^{12}$	$7{\cdot}7 \times 10^{12}$
2323	$2{\cdot}8 \times 10^{12}$	—
2302	$7{\cdot}2 \times 10^{12}$	—
Total (Av. λ3500)	$1{\cdot}44 \times 10^{15}$	$2{\cdot}31 \times 10^{15}$
Total $\lambda < 3132$ (Av. $\lambda = 3000$)	$5{\cdot}05 \times 10^{14}$	$7\ 15 \times 10^{14}$

To indicate the effect of altering voltage, and therefore current, the following results of Maddock may be quoted. Over a voltage range of 80 to 140 it was found empirically that

$$\text{Intensity} = C \,.\, i \,.\, E^n.$$

C and n have the values shown in Table 7 for the lines quoted. The magnitudes are such that the intensity is obtained directly in microwatts per cm.^{2} at 117 cm. when E and i are in volts and amps. As will be seen, n is of the order 2, and therefore to ensure a constant intensity it is essential to exercise strict control over the voltage of the supply to the lamp and to maintain the surroundings at a constant temperature.

TABLE 29

λ (Å)	2·5 amp. arc n	2·5 amp. arc C	3·5 amp. arc n	3·5 amp. arc C
5780	1·93	0·0017	—	—
5461	1·74	0 0049	1·66	0·008
4358	1·75	0·0040	1·57	0·0115
3650	1·99	0·0021	1·86	0·0046
3126	1·77	0·0045	1·42	0·026
3022	1·92	0·0008	2·11	0·0004
2652	2·24	0·00014	1·72	0·00165
2537	1·88	0·00115	1·48	0 0092

Although the output of the above described lamp is large, the area of the discharge tube, which would be selected by a quartz condensing lens so that the beam of light could be conveniently used, is small, and hence this has led to the development of a so-called point source lamp (made by the Thermal Syndicate), illustrated in Fig. 150. Here the discharge occurs between a tungsten anode A and a mercury cathode C through a capillary T, 2 mm. in bore. No output data are available. The lamp

runs at 70-100 v. at 3·4 to 2·6 amp., and hence the output should be comparable with the normal type.

An inconvenient feature of all the above lamps is the heat generated, several hundred watts being dissipated. This is troublesome if a manometer is being used to follow a photochemical reaction. One way out of the difficulty is to enclose the reaction vessel in a water jacket with quartz windows.

Hot cathode lamps. Recently the high pressure lamp has undergone further development on account of its extending use in industrial

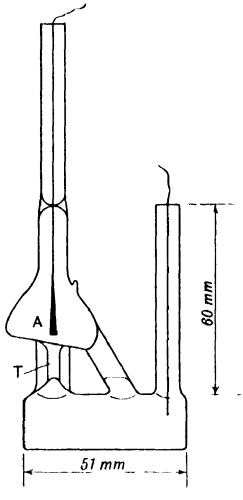


FIG. 150. Capillary mercury arc lamp.

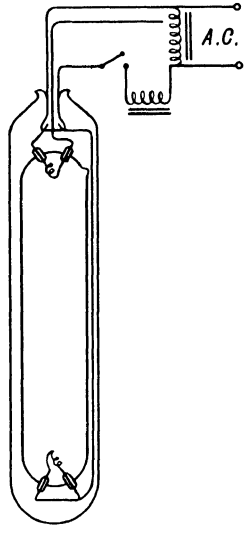


FIG. 151. Hot cathode mercury lamp for A.C. (glass envelope).

and domestic lighting. The mercury anode and cathode are dispensed with, their place being taken by two oxide-coated electrodes, so that the lamp may be run off alternating current and in any position. Only a limited amount of liquid mercury is introduced into the bulb, and the discharge tube itself is mounted in an evacuated tube for temperature control. The discharge tube is filled with neon or argon to a pressure of a few millimetres in order to facilitate starting the discharge. The electrical connections are shown in Fig. 151, an auto-transformer being employed to heat one of the filaments and an inductance, to limit the current passing through the tube. The other cathode is heated by positive ion bombardment once the discharge is started. To prevent damage to the filament, the current required to heat it is switched on for a few seconds before applying the voltage across the tube. As the lamp warms up the

discharge recedes into the middle of the tube, the diameter in a typical 500 watt lamp being a few millimetres. The visible luminous efficiency is about twice that of high power filament lamps, and since the yellow, green, blue and violet lines may be readily separated by filters, such lamps would appear to have useful applications in photochemistry where an intense source of visible light is required. For ultra-violet work both discharge tube and outer envelope require to be made of quartz, thus requiring large graded seals. So far lamps of this type are not available commercially.

The output of two typical hot cathode glass lamps is given in the following Table 30. (B. T. Barnes and W. E. Forsythe, *J. Opt. Soc. Am.*, **27**, 83 (1937).)

TABLE 30

OUTPUT OF HOT CATHODE MERCURY LAMP

Lamp Dimensions	I	II
Inside tube diameter (cm.)	3·5	2·5
Arc length (cm.)	16·0	10 5
Vapour pressure (atm.)	1·4	0·4
Volts	150	67·5
Amps.	2·77	4·06
Lumens	16000	7000

Principal lines	Band of wavelengths	Intensities per cm.^{2} at 100 cm. Microwatts	Quanta sec.$^{-1}$	Microwatts	Quanta sec.$^{-1}$
	7420-6830	—	—	3 3	$1·2 \times 10^{13}$
	6830-6350	5·7	$1·9 \times 10^{13}$	2·3	$7·8 \times 10^{12}$
	6350-5950	5·6	$1·8 \times 10^{13}$	1·9	$5·9 \times 10^{12}$
5791-5770	5950-5615	127	$3·7 \times 10^{14}$	55	$1·6 \times 10^{14}$
5461	5615-5320	131	$3·7 \times 10^{14}$	57·5	$1·6 \times 10^{14}$
	5320-5060	3·5	$9·2 \times 10^{12}$	1·24	$3·3 \times 10^{12}$
	5060-4840	3·02	$7·6 \times 10^{12}$	1·47	$3·7 \times 10^{12}$
	4840-4650	—	—	0·63	$1 5 \times 10^{12}$
	4650-4475,	—	—	0·62	$1·4 \times 10^{12}$
4358	—	92	$2·1 \times 10^{14}$	44·5	$1·0 \times 10^{14}$
4047	—	44·5	$9·2 \times 10^{13}$	23·6	$4·9 \times 10^{13}$
3663-3650	—	41	$7·5 \times 10^{13}$	22·5	$4·2 \times 10^{13}$

Sodium is often used in such discharge lamps. As a monochromatic source of yellow light, and also for some experiments with sodium vapour, this lamp is suitable. The *D* lines are, however, rather broad, and for work requiring very narrow and unreversed lines special precautions have to be taken (see below).

Recently the Thermal Syndicate have put on the market an all-quartz lamp similar in output to the normal hot mercury lamp (see p. 218),

which may be operated from direct or alternating current, and may be placed in any position on account of the fact that both electrodes are thermionic emitters, and only a small amount of liquid mercury is present in the tube when cold. The complication of heating the electrodes before switching on the current to the lamp is eliminated and a very simple starting device is used. The form of construction and the circuit for running the lamp off A.C. are shown in Fig. 152. If run off D.C. the inductance I is replaced by a resistance capable of carrying 3·5 amps. continuously. The high frequency current necessary for starting the lamp is obtained from the auto-transformer of ratio 1 : 4. The switch

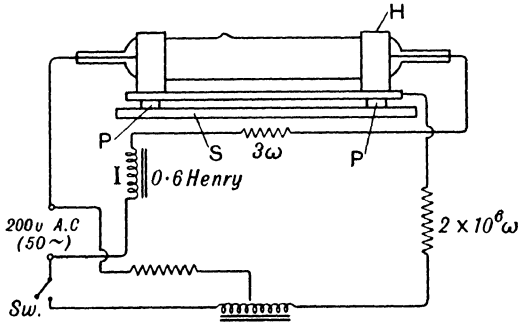


FIG. 152. Hot cathode mercury lamp with quartz discharge tube.

S_w is closed and then rapidly opened, when the arc should immediately strike. The auto-transformer need only be capable of dissipating a few watts. The aluminium holder H for the lamp is insulated from its stand S by two pillars of insulating material P.

S. Sonkin (*J. Opt. Soc. Amer.*, **19**, 65 (1929)) has described a lamp made of Pyrex with a very thin window (cf. p. 328) which is said to transmit wavelengths at 1850 Å.

Capillary mercury lamps. For photochemical experiments in which a high pressure lamp is suitable there is much to be gained by confining the discharge to a capillary tube. By means of a simple reflector and lens nearly all the emitted radiation may be directed into a reaction vessel. Such a lamp is also eminently useful for work with a monochromator ; it may, in fact, replace the slit in the collimator if the utmost intensity is desired at the exit slit. Numerous designs have been described (cf. e.g. G. Harrison and G. S. Forbes, *J. Opt. Soc. Am.*, **10**, 1 (1925), **11**, 99 (1925) ; *J. Amer. Chem. Soc.*, **47**, 2449 (1925) ; P. A. Leighton and G. S. Forbes (*J. Phys. Chem.*, **30**, 1628 (1926) ; R. H. Crist, *J. Amer. Chem. Soc.*, **52**, 4337 (1930), *J. Opt. Soc. Am.*, **21**, 690 (1931)). F. Daniels and L. J. Heidt (*J. Amer. Chem. Soc.*, **54**, 2381 (1932)) describe a very simple and

inexpensive capillary lamp, which consists of a silica tube, inside diameter 1-2 mm. and a wall thickness about 1 mm., with three bulbs, *A*, *B* and *C*, as shown in Fig. 153. This construction localises the arc between *A* and *B*. The distance *AB* may vary from 5 to 30 cm., corresponding to voltages from 50 to 600. Tungsten wire electrodes, 0·5 mm. in diameter, are sealed in with de Khotinsky cement (shellac and pine tar). *E* is sealed in first, the lamp is almost evacuated, filled with mercury, inverted, and finally *D* is sealed in. *C* functions as an expansion bulb, and the level of mercury in *C* then determines the magnitude of the pressure developed during the operation of the arc. Water is played over the arc by the 1 cm. tube shown in Fig. 153. The arc is started by heating *AB* with a fine pointed gas flame or by a small heating coil near *A*. When running the lamp is best immersed in a large tank of water.

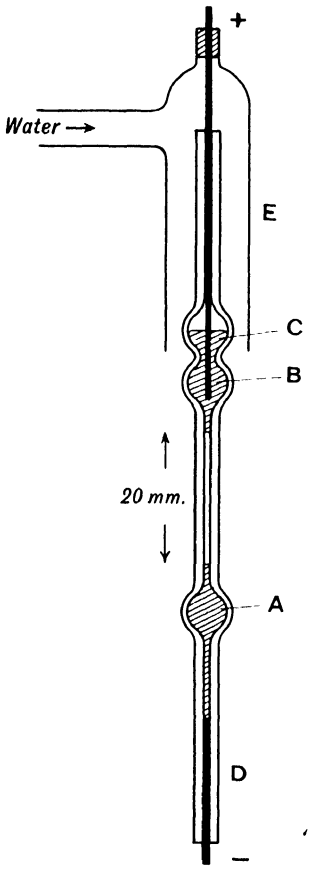


FIG. 153. Capillary mercury lamp.

Such a lamp works at 110 volts at 3-5 amps. A higher voltage gives a more intense discharge. When operated at inputs greater than 500 watts, the lamp has the disadvantage that its life is of the order of 24 hours. Smaller inputs give a longer working life. The near ultra-violet and visible lines are the strongest. Lines at $\lambda < 2650$ Å are weak, and the resonance line at 2536 Å is, of course, strongly reversed. Using the uranyl oxalate actinometer the total output decomposed about 0·3 gm. molecule of oxalate per kilowatt hour of electric power consumed. To indicate the relative intensities of the various lines, the following figures may be quoted, taking the intensity at 3650 Å. as unity: 4358, 0·5; 4047, 0·3; 3650, 1·0; 3130, 0·42; 3020, 0·30. R. H. Crist (*J. Amer. Chem. Soc.*, **54**, 3939 (1932)) recommends deflecting the discharge against the back wall of the capillary arc by means of a magnet. The quartz does not then discolour so quickly.

Capillary lamps containing bismuth, cadmium, lead, thallium and zinc have been constructed by R. M. Hoffman and F. Daniels (*J. Amer. Chem. Soc.*, **54**, 4226 (1932)) in a similar manner to the mercury lamp.

The great disadvantage is that they can only be used once, and though they are of very simple construction, this is not desirable in photochemical experiments.

In this connection the following table shows the wavelengths of the first two resonance lines of mercury, cadmium and zinc, which may be of use for photosensitised experiments (cf. J. R. Bates and H. S. Taylor, *J. Amer. Chem. Soc.*, **50**, 771 (1928)).

	Line	λ (Å)	Cals./mol.	Volts	T (° C.) for vapour press. of 0·012 mm.
Hg	$6^1S_0 - 6^3P_1$	2536·7	112000	4·86	50
	$6^1S_0 - 6^1P_1$	1849·6	152000	6·67	
Cd	$5^1S_0 - 5^3P_1$	3262·1	87000	3·78	240
	$5^1S_0 - 5^1P_1$	2288·8	124000	5·39	
Zn	$4^1S_0 - 4^3P_1$	3076·9	92400	4·01	350
	$4^1S_0 - 4^1P_1$	2139·3	133000	5·77	

Recently capillary lamps have been greatly improved by using oxide-coated cathodes and by introducing a fixed amount of mercury into the tube, such that there is little or no liquid mercury present when the lamp attains working temperature. As developed by W. Elenbaas (*Z. f. Physik*, **78**, 603 (1932) ; *Physica*, **1**, 211, 673 (1934) ; *ibid.*, **2**, 45, 155, 169, 715, 757, 787 (1935) ; *ibid.*, **3**, 12, 219, 859 (1936) ; *Z. f. tech. Physik*, **17**, 61 (1936) ; Elenbaas and de Groot, *Physica*, **2**, 807 (1935) ; Bol, *De Ingenieur*, **50**, 91 (1935)) the working pressure may attain the exceptionally high figure of 150 atmospheres. The lamp consists essentially of a fused silica capillary tube, about 2 mm. internal and 4 mm. external diameter. The electrodes of tungsten wire are sealed into glass, which in turn is fused to the silica by a joint of graded glasses. To obtain the utmost efficiency from such an arrangement, the electrodes are tipped with a mixture of alkaline earth oxides. For high inputs, e.g. 1 K.W. per cm. length, the tube must be water cooled, but air cooling is sufficient if the input is of the order 100 watts per cm. length. The lamp works off alternating current with a suitable stabilising inductance in series with it. This also serves to apply the requisite high voltage for striking the arc. With a lamp of the above dimensions, 1250 volts may be dropped per inch length, the current being approximately 1·4 amp. The intrinsic brilliance may attain the large figure of 260,000 candles per square inch, compared with 110,000 of the carbon arc. The high intrinsic brilliance makes it especially useful for photochemical purposes in the visible and near ultra-violet. All the mercury lines are broadened, and the 2537 line is, of course, strongly reversed.

In some lamps of this kind a graded joint is dispensed with. A strip of molybdenum ribbon is inserted in the silica capillary tube, the lamp is

evacuated and the silica collapsed on to the molybdenum, thus forming a vacuum tight seal capable of standing pressures of several atmospheres. The following figures (B. T. Barnes and W. E. Forsythe, *J. Opt. Soc. Am.*, **27**, 83 (1937)) will give an indication of the output of this type of lamp.

OUTPUT OF HIGH PRESSURE CAPILLARY ARCS

Dimensions and Input	LAMP I			LAMP II		
Inside tube diameter (cm.)	0·4			0 2		
Arc length (cm.)	1·8			1 2		
Vapour pressure (atmospheres)	28·5			110		
Volts	251			505		
Amperes	0·40			1·35		
Lumens	3,400			38,200		
Principal Lines (Å)	Band of Wavelengths (Å)	Intensity per cm.² at 100 cm.		Band of Wavelengths (Å)	Intensity per cm.² at 100 cm.	
		Micro-watts	Quanta sec.$^{-1}$		Micro-watts	Quanta sec.$^{-1}$
—	7420-6830	3·75	$1\,3 \times 10^{13}$	7250-6960	42	$1\,5 \times 10^{14}$
—	6830-6350	3·0	$9{\cdot}9 \times 10^{12}$	6960-6705	41	$1{\cdot}4 \times 10^{14}$
—	6350-5950	3·1	$9\,8 \times 10^{12}$	6705-6470	38	$1\,3 \times 10^{14}$
5791-5770	5950-5615	19·2	$5\,6 \times 10^{13}$	6470-6245	40	$1{\cdot}3 \times 10^{14}$
5461	5615-5320	33·5	$9\,8 \times 10^{13}$	6245-6045	45	$1{\cdot}4 \times 10^{14}$
—	5320-5060	2·2	$5\,8 \times 10^{12}$	6045-5865	67	$2{\cdot}0 \times 10^{14}$
—	5060-4840	2·05	$5{\cdot}1 \times 10^{12}$	5865-5690	125	$3{\cdot}7 \times 10^{14}$
—	4840-4650	2·2	$5{\cdot}3 \times 10^{12}$	5690-5535	114	$3\,2 \times 10^{14}$
—	4650-4475	2·6	$6\,0 \times 10^{12}$	5535-5390	197	$5{\cdot}5 \times 10^{14}$
4358	—	27·1	$6{\cdot}0 \times 10^{13}$	5390-5250	47	$1{\cdot}3 \times 10^{14}$
4047	—	14·5	$3{\cdot}0 \times 10^{13}$	5250-5123	34	$9{\cdot}0 \times 10^{13}$
3663-3650	—	25·7	$4{\cdot}8 \times 10^{13}$	5123-5000	35	$9{\cdot}0 \times 10^{13}$
3341	—	3·2	$5{\cdot}5 \times 10^{13}$	5000-4890	46	$1{\cdot}2 \times 10^{14}$
3129	—	6·9	$1{\cdot}1 \times 10^{13}$	4890-4790	57	$1\,4 \times 10^{14}$
3022	—	1·21	$1{\cdot}9 \times 10^{12}$	4790-4695	56	$1{\cdot}4 \times 10^{14}$
—	—	—	—	4695-4605	52	$1\,2 \times 10^{14}$
—	—	—	—	4605-4515	62	$1{\cdot}4 \times 10^{14}$
—	—	—	—	4515-4430	90	$2{\cdot}1 \times 10^{14}$
—	—	—	—	4395-4320	150	$3{\cdot}3 \times 10^{14}$
—	—	—	—	4280-4210	68	$1{\cdot}5 \times 10^{14}$
—	—	—	—	4210-4140	62	$1{\cdot}3 \times 10^{14}$
—	—	—	—	4080-4020	105	$2{\cdot}1 \times 10^{14}$
—	—	—	—	4020-3960	42	$8{\cdot}5 \times 10^{13}$
—	—	—	—	3960-3900	38	$7{\cdot}5 \times 10^{13}$

Finally mention may be made of one or two unusual designs. For example, the Kromayer lamp (F. Weigert, *Z. phys. Chem.*, **80**, 69 (1912)) is of the high pressure type, but is also water cooled, so that it can be brought close to the object being irradiated without causing any rise in temperature. This is accomplished by having an evacuated silica jacket to surround the arc tube, so that the latter is not cooled by the water circulating in the casing of the lamp. Commercial lamps are made with cadmium lead, zinc, bismuth, etc., dissolved in the mercury. As a source of the arc lines of these elements for photochemical purposes this type of lamp is rather unsatisfactory. A cadmium arc (F. Bates, *Phil. Mag.*, **39**, 353 (1920)) has been employed for cadmium photosensitised reactions (cf. J. R. Bates and H. S. Taylor, *J. Amer. Chem. Soc.*, **50**, 771 (1928)). The liquid alloy of sodium and potassium has also been used in an arc lamp (F. H. Newman, *Phil. Mag.*, **47**, 603 (1924)). A number of early types of mercury lamp are described by Ellis and Wells in *Chemical Action of Ultraviolet Rays* (American Chemical Society Monograph, Chemical Catalog Company).

Condensed sparks. Below 2500 Å. the mercury spectrum is rather deficient in lines of high intensity, and therefore recourse has to be made to condensed sparks between metal electrodes or to the hydrogen lamp (see below). The former is the more intense source and can be made practically monochromatic. The intrinsic brilliance of the spark is high, but it suffers from the disadvantages of being rather unsteady (at best ± 5 per cent.) and extremely noisy. In many experiments this source must be employed, and therefore efforts have been made to improve its characteristics. The electrodes may be of aluminium which emits a few lines in the neighbourhood of 1900 Å, or of zinc, which has a strong group of lines around 2100 Å. Since voltages of the order of 5000 are used, the electrode holders must be adequately insulated. A carbon arc lamp when fitted with extension arms of ebonite forms a suitable device for a spark source. In order to maintain the intensity at a constant value, the current and voltage across the gap are kept constant by continual adjustment of the length of the gap. This is facilitated by projecting an enlarged image of the gap on a screen having ruled divisions upon it (cf. E. Warburg, *Berl. Akad. Ber.*, 747 (1911)). It is also advisable to keep the electrodes cool by means of a strong blast of air. The following figures (H. L. Roxburgh, private communication) will give an indication of the output to be expected :

Zinc spark at $\lambda = 2100$ Å.

Input 5000 volts	0·2 amp.
Capacity of condensers across spark gap	0·01μF.
Output in quanta per minute per cm.^{2} at 10 cm.	2×10^{17}
Total output (assuming spherical polar curve for emission)	$2{\cdot}5 \times 10^{20}$ per min.

When aluminium electrodes are substituted the output is practically the same as with zinc.

To further improve the constancy of the spark A. Hollaender and J. P. Foerst (*Rev. Sci. Instr.*, **4**, 347 (1933) ; cf. also W. T. Bovie, *J. Opt. Soc. Am.*, **7**, 1027 (1923) ; G. R. Harrison and C. E. Hesthal, *ibid.*, **8**, 471 (1924) ; C. Leiss, *Z. f. Physik*, **23**, 333 (1924) ; G. S. Forbes and F. P. Brackett, *J. Amer. Chem. Soc.*, **53**, 3973 (1931)) made the electrodes disc-shaped, 15 cm. in diameter, 0·5 cm. thick, of aluminium or zinc. These were mounted at right angles to each other and rotated by two small synchronous electric motors, as used in electric clocks. Each disc is insulated from the motor spindle by a 3 cm. shaft of bakelite, contact being made by a spring of phosphor bronze. One of the motors is arranged so that it can be moved vertically in order to alter the length of the spark gap.

The speed of rotation should be a few revolutions per minute. The only disadvantage of the rotation disc apparatus is that it is rather difficult to place the spark close to a reaction vessel or to dispose an efficient reflector around it.

Tungsten filament lamps. The larger sizes of tungsten gas-filled lamps are suitable for many purposes requiring a constant source of light in the visible. Recent modifications in filament design have reduced the projected area of the filament to reasonably small dimensions, for example, 1 cm.^{2} for a 1000 watt lamp. The constancy of such lamps run at a fixed current is much superior to that of the mercury lamp. To permit of its use into the ultra-violet, the General Electric Co. of America have introduced a 500 watt lamp (W. E. Forsythe, B. T. Barnes and M. A. Easley, *J. Opt. Soc. Am.*, **24**, 178 (1934)), type CX having a bulb made of glass specially transparent in the near ultra-violet. The output of this lamp is shown in Fig. 154. It will be seen that it is somewhat inferior in intensity to an ordinary mercury vapour lamp (see p. 219).

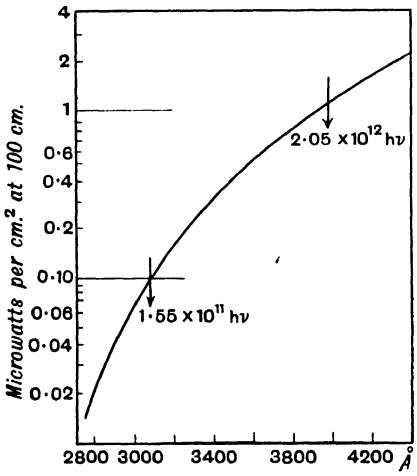


FIG. 154. Output of tungsten filament lamp.

Tungsten arc lamp. The tungsten arc lamp has the advantage over the usual metal filament lamp that the intrinsic brilliance is greater, and is therefore more useful if a complicated filter-lens-reaction-vessel

system is being used. For direct current the lamp consists of a tungsten spiral and a sphere of tungsten a few mm. in diameter spaced at a distance of 1-2 mm. The tungsten spiral is heated white hot electrically, switched off, and simultaneously a positive potential is applied to *S* resulting in an arc discharge between filament and tungsten sphere. Tungsten arc lamps are also made for running off alternating current, in which case two tungsten spheres are used, as shown diagrammatically in Fig. 155. The maximum candle power of the D.C. model is given as 1000, and thus

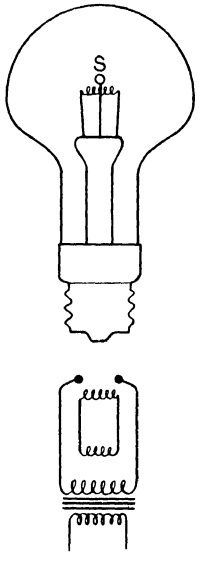


FIG. 155. Tungsten arc lamp.

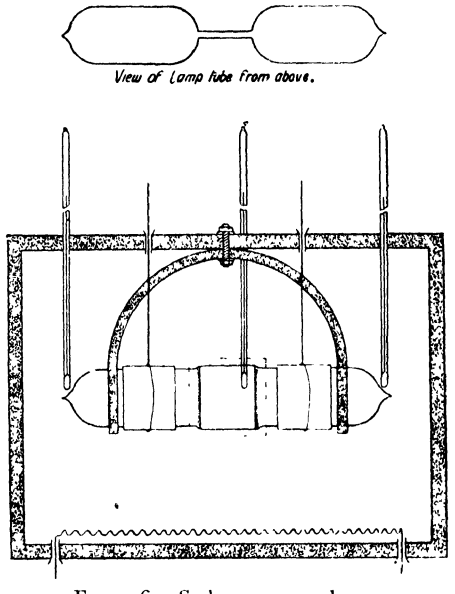


FIG. 156. Sodium vapour lamp.

is comparable in total intensity with a 1000 watt gas-filled metal filament lamp, in so far as energy output is concerned.

Electrodeless metal vapour lamps. (F. Fairbrother and J. L. Tuck, *Trans. Faraday Soc.*, **31**, 520 (1935).) While the commercial sodium lamps are of great use for the majority of purposes, the lines emitted are broad and in most cases slightly reversed. To obtain as pure a line as possible, the vapour must be excited at very low pressures. In this lamp the excitation is by high frequency current, *ca.* 10^8 cycles per second. The form of the lamp, which is of Pyrex, and its containing box, heated with a resistance mat, are shown in Fig. 156. The dotted lines show where the sodium is distilled into the lamp and where exhaustion is effected. The middle portion of the lamp, from which the light is taken, is flattened to an inside thickness of 2 mm. in order to avoid reversal. It is absolutely

necessary to distil the sodium *in vacuo* to get rid of dissolved hydrogen. The lamp, before sealing off from the sodium reservoir, is baked for 2 hours at 300° C., a high frequency discharge being applied until no discharge inside the lamp is apparent. The sodium is then distilled through the flat portion with the discharge still operating. Such lamps may be filled with mercury, cadmium or thallium, while caesium and rubidium may be introduced by heating the respective chlorides with calcium. The lamp is excited by means of a valve oscillator, the wavelength being 3-10 metres. The circuit diagram and values of the

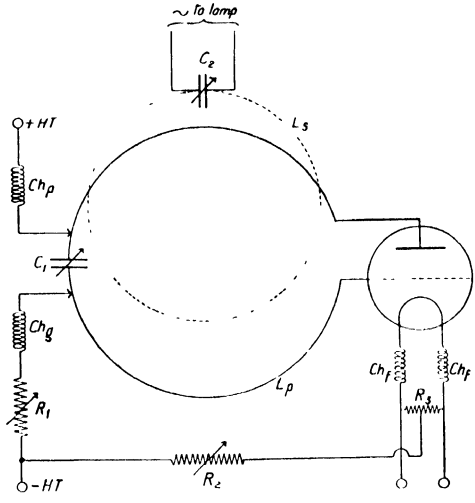


FIG. 157. Thermionic oscillator for sodium vapour lamp. Ch_p, Ch_g 150 turns 36 S.W.G. on 1 cm. diameter former. Ch_f 25 turns 16 S.W.G. on 2·5 cm former R_1 25,000, R_2 5,000, R_3 300 Ω ; C_1, C_2 0·00001 F ; L_s, L_p single turn of 12 S.W.G. copper wire ca. 15 cm. diameter.

associated coils and condensers are given in Fig. 157. The valve actually used was a Mazda PP 5/400, dissipating 25 watts at 400 volts on the anode. If desired the wavelength may easily be measured by setting up a pair of Lecher wires and exploring the potential distribution with a flash-lamp bulb. The frequency may be varied by C_1 and C_2L_s tuned to the altered frequency. The coupling between the coils must not be too tight. The anode current is best supplied by a rectifier system. Fig. 158 shows approximately the output in lumens as a function of temperature.

Hydrogen lamp. At high hydrogen pressures and current densities the spectrum emitted by a hydrogen tube becomes continuous. This type of source is used normally for photographing absorption spectra in

the ultra-violet. By sufficiently increasing the input, the output at wavelengths less than 2500 Å becomes great enough to be of use for photochemical purposes. A high degree of monochromatism must, of course, be sacrificed if high intensity is aimed at. Such a lamp is shown in Fig. 159 (E. O. Lawrence and N. E. Edlefson, *Rev. Sci. Intr.*, **1**, 45 (1930) ; cf. also E. Gehrcke and E. Lau, *Ann. d. Physik*, **76**, 673 (1925) ; Z. Bay and W. Steiner, *Z. f. Physik*, **45**, 337 (1927)). The electrodes consist of aluminium cylinders 6 × 40 cm., open at the bottom, but closed at the top end, which is attached to a tungsten wire passing through the

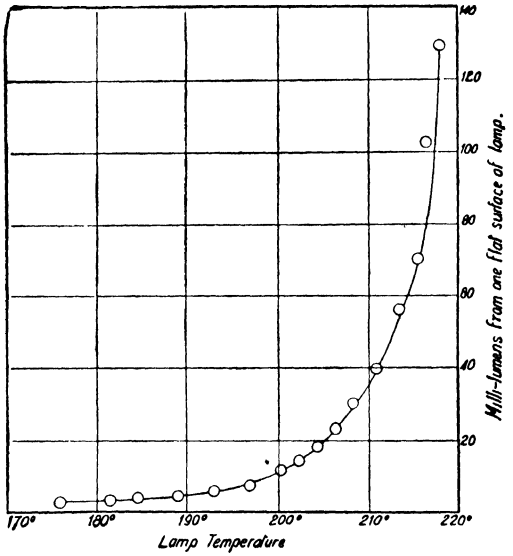


FIG. 158. Output of sodium vapour lamp.

Pyrex glass at the end of the tube. The electrodes fit closely into the glass tubes to facilitate cooling, and are carefully rounded off at the edges to prevent the occurrence of hot spots. The electrode chambers are connected together by a silica tube, 7 mm. in diameter and 60 cm. long. The waxed Pyrex-silica seals are kept cool by directing a stream of water against them, as indicated in the diagram. With this arrangement the tube is stated to stand an input of 6·5 amperes at 3000 volts. Normally the tube is designed to run at 3 amperes. The light emerges from a crystalline quartz window cemented on to the discharge tube. This window may conveniently be waxed to the reaction vessel if absorption of short wavelengths by oxygen of the air is to be avoided. The tube requires to be " flushed " with hydrogen several times to get rid of impurities. The operating pressure is of the order of a few mm. of

mercury. Higher pressures prevent the required current being sent through the tube. Low pressures give rise to the atomic spectrum. The

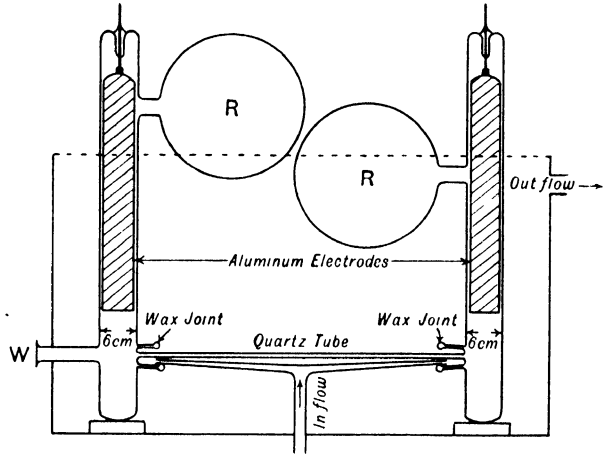


FIG. 159.

bulbs *RR* function as a hydrogen reservoir. It is estimated that the intensity of the light in the region around 2500 Å is not inferior to that of a mercury vapour lamp. The intensity of light is directly proportional to current from 1 to 5 amperes.

C. CONTROL OF RADIATION

Filters

The only satisfactory method of obtaining monochromatic radiation over a wide range of wavelengths is to employ a monochromator. Even with large instruments, however, the intensity available at the exit slit is so small that only those reactions which have large quantum yields or can be followed by sensitive analytical devices may be studied conveniently. It is fortunate that in the spectrum emitted by both high and low pressure mercury lamps there are a number of intense and widely spaced lines. These can be isolated by comparatively simple filter systems.

Table 31 shows a selection of filters suggested by E. J. Bowen (*J. Chem. Soc.*, p. 76 (1935)). The beam of light is obtained by placing the filter in column 2 in a 10 cm. diameter round silica flask, followed by the other filter in plane parallel-sided (silica) cells. The reaction vessel is placed behind a diaphragm about 24 cm. from the lamp. The

nickel and cobalt sulphate must be free from traces of iron salts. This latter filter cuts off the visible, infra-red, and also the strong group of lines at 3650 Å.

TABLE 31

Hg lines (Å)		
2480	145 g. $NiSO_4$, 6·7 H_2O + 41·5 g. $CoSO_4 \cdot 7H_2O$ in 1 litre H_2O, 10 cm. bulb.	Gaseous Cl_2, 1 atm., 3 cm.
2540		0·108 g. I_2†
		0·155 g. KI† in 1 litre H_2O, 1 cm.
2650		CCl_4† 2 mm. ; or
2700		$HgCl_2$* 45 g./l. in H_2O, 1 cm.
2750		
2805		
2896		
2925		
2970		
3030		
3135		Oxalic acid † sol. in water (20 g./l.), 1 cm. ; or $CuSO_4 \cdot 5H_2O$ 15 g./l., 1 cm.
3340		KH Phthalate † 5 g./l., 1 cm. ; Uric acid sat. sol. in water, 1 cm.
3660	4·4 g. $CuSO_4 \cdot 5H_2O$ + 150 c.c. NH_4OH (0·88) in 1 l. H_2O, 10 cm.	2-3 mm. Chance's black " ultra-violet " glass
4050		I_2 in CCl_4 (7·5 g./litre), 1 cm. ; quinine hydrochloride in water (10 g./l.), 2 cm.
4360		75 gm. $NaNO_3$ in 100 c.c. water,* 1 cm.
5460	13 g. $CuSO_4 \cdot 5H_2O$ + 0·449 g. $K_2Cr_2O_7$ + 50 c.c. conc. H_2SO_4 in 1 l. H_2O, 10 cm.	Corning glass 512, 5 mm.
5770		Corning glass 344, 3·4 mm.
5790		

* Renew frequently. † Renew occasionally.

An alternative system of filters due to A. J. Maddock (*J. Sci. Instr.*, **12**, 218 (1935)) is given in Table 32, with the transmission of the combination in the last column.

TABLE 32

Wavelengths transmitted	Filter combination: Cell A, 10 mm.	Cell B, 5 3 mm.	Cell C, 26 mm.	Wratten Filter No.	Transmission (per cent.)
5780	$CuSO_4 . 5H_2O$ 11·1 g./100 c.c.	—	$K_2Cr_2O_7$ sat. soln.	—	36
5461	$CuCl_2 . 2H_2O$ 4 57 g./100 c.c. ethyl alcohol	$CoCl_2 . 6H_2O$ 1·4 g./100 acetone	—	—	12
4358	$KMnO_4$ 0 84 g./1000 c.c.	$CuCl_2 . 2H_2O$ 37·5 g./100 c.c.	—	—	12
4358 | 4047 /	$KMnO_4$ 0·84 g./1000 c.c.	$CuCl_2 . 2H_2O$ 25·9 g./100 c.c.	—	—	20
3650	—	$Cu(NO_3)_2 . 6H_2O$ 167 g./1000 c.c.	—	18	10
3650	$CuSO_4 . 5H_2O$ 11·1 g./100 c.c.	—	—	18	30
3342				—	13
2652 (Mainly)	$NiSO_4 . 7H_2O$ 100 g./100 c.c.	$KMnO_4$ 0 84 g./1000 c.c.	—	—	17

For work in the visible there are the Wratten gelatine filters cemented between glass plates, which transmit the yellow, green, blue and violet lines. Table 33 gives the transmission of these filters.

TABLE 33

No.	Line transmitted	Percentage transmission
22	Yellow	70 per cent. at 5880 Å, and λ's longer than this.
62	Green	16 per cent. at 5461 Å, 0·1 per cent. yellow line.
77	Green	63 per cent. at 5461 Å, 0·16 per cent. yellow line.
50	Blue	2·2 per cent. at 4358 Å.
		0·4 per cent. at 4047 Å.
		0 0 per cent. at 3650 Å.
18	Ultra-violet	25·0 per cent. at 3650 Å.
		0·63 per cent. at 4047 Å.

Variable monochromatic filter for the visible spectrum. F. Weigert and H. Stande (*Z. phys. Chem.*, **130**, 607 (1927)) have described a very ingenious type of monochromatic filter, which, however, is only applicable to the visible portion of the spectrum. It is based on a discovery made by C. Christiansen (*Wied. Ann.*, **23**, 298 (1884); **24**, 439 (1885)), who found that if a powdered isotropic substance, such as NaCl or glass, be suspended in a liquid, a narrow band of wavelengths is transmitted where the refractive indices are identical. In general the refractive

index of a liquid changes more rapidly with wavelength than that of a solid, and if substances are chosen properly the refractive index-wavelength curves intersect (Fig. 160). At all other wavelengths the light is scattered randomly, owing to the irregular nature of the particles of the solid. Weigert and Stande found that crown glass of refractive index $n_D = 1{\cdot}1562$ immersed in methyl benzoate was very suitable. The glass is powdered in a steel mortar until the particles are 0·3-1 mm. in diameter. Cracks in the individual particles are then removed by keeping the powder at 200-300° C. for several days. This is followed by washing with hydrochloric acid to remove metallic powder, and finally with distilled water. The transmission band of the filter is simply changed by altering the temperature of the filter. The following table shows that a temperature range of only 18-50° C. is necessary (see

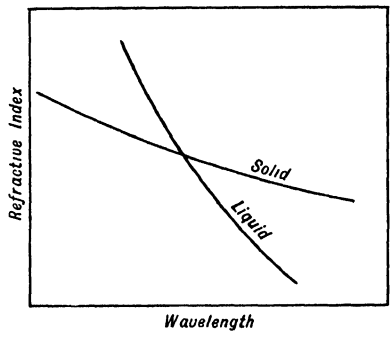


FIG. 160.

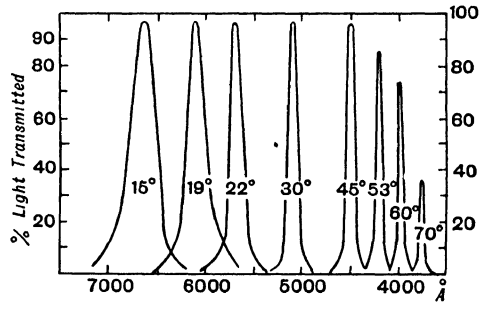


FIG. 161.

also Fig. 161). Since the boiling point of methyl benzoate is 199° C. there is no loss of ester by evaporation.

Temp. ° C.	Transmission band (Å)	Temp. ° C.	Transmission band (Å)
18	6800	35	5040
20	6300	40	4870
25	5700	45	4730
30	5320	50	4630

The construction of a filter is shown in Fig. 162. A plane parallel-sided glass vessel *F* holds the mixture of glass and ester. This is immersed in a larger glass rectangular trough. If the sides of the latter are not plane

they may be improved by fixing on plate glass plates, G_1 and G_2, the space between being filled with water. Two water-air lenses serve to send parallel light through the filter. The cell is now made by Zeiss in a vessel with plain polished windows and sealed so that the methyl benzoate cannot escape. Fig. 161 shows the degree of monochromatism achieved by the filter. The absorption of light by the glass and the benzoate limit its application to the visible spectrum.

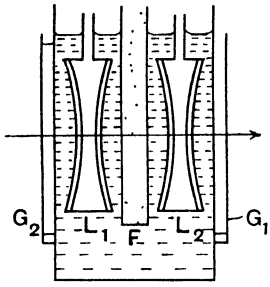


FIG. 162. Construction of filter.

Focal isolation method. This method of producing approximately monochromatic light depends on the chromatic aberration exhibited by single lenses (W. Rubens and R. W. Wood *Phil. Mag.*, **21**, 249 (1911); A. Terenin, *Z. physik*, **31**, 33 (1925); Andrews, *Gen. Elect. Rev.*, p. 817 (1917)). Two lenses L_1 and L_2, and three diaphragms, D_1, D_2 and D_3, and a source of light S, are arranged in the manner shown in Fig. 163. D_2 and D_3 are placed in the image planes of S. Light of longer wave length will follow the path shown by the dotted lines, and thus will not find its way into the reaction vessel *R.V.* Though the degree of mono

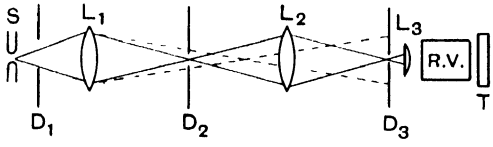


FIG. 163. Focal isolation method for obtaining approximately monochromatic light.

chromatism is not high, this method is useful for isolating the prominent lines in the spark spectra of zinc, aluminium and cadmium, and is much more efficient than a monochromator. The following results obtained by E. O. Wiig and G. B. Kistiakowsky (*J. Amer. Chem. Soc.*, **54**, 1812 (1932)) serve to indicate the intensity available. The degree of monochromatism was estimated at 95 per cent.

Input to spark, 2-3 K.W.		Aperture of L_1 *ca.* f/4 at 2000 Å.
Zinc - - -	2100 Å	5000 erg. sec.$^{-1}$, 5×10^{14} quanta sec.$^{-1}$
Aluminium - -	1960 Å	2000 erg. sec.$^{-1}$, 2×10^{14} quanta sec.$^{-1}$
Cadmium - -	2144 Å	1000 erg. sec.$^{-1}$, 1×10^{14} quanta sec.$^{-1}$

Intensity filter for the mercury resonance line at 2537 Å. In photochemical chain reactions the effect of the intensity of the light immediately indicates how the chains are terminated. If the rate is directly proportional to the intensity the termination collision involves only one

carrier, whereas if the rate is proportional to the square root of the intensity then two carriers are involved. In a given reaction it is often essential to know what fraction of the chains end, say, by self-neutralisation. When a thermopile or photoelectric cell is already being employed, it is easy to determine the rate intensity relationship. When, however, the reaction bulb is in a furnace and the source of light is of considerable area, such as a mercury lamp, the problem is not so readily solved. A filter of known transmissibility must then be used. For mercury sensitised reactions one such filter consists of sulphur-free carbon tetrachloride dissolved in spectroscopically pure *n*-hexane or cyclohexane (H. W. Melville and H. J. Walls, *Trans. Faraday Soc.*, **29**, 1255 (1933)). Such a filter effectively cuts off light of $\lambda<2537$ Å, which might cause direct photo-reaction. The extinction coefficient (ϵ) of carbon tetrachloride in hexane are defined by the equation

$$\log_{10} I_0/I = \epsilon cd,$$

where I_0 and I are the incident and emergent intensities, c is the concentration in moles per litre, and d thickness of the absorbing layer in cm. The value of $\epsilon = 0{\cdot}588$ mole^{-1} cm.^{2} at 2537 Å. To save calculation the following data are computed for a 5 mm. cell :

Composition	Intensity rel. to *n*-hexane
1·2 c.c. in 25 c.c. solution	0 80
2 0 ,, ,,	0·68
3·5 ,, ,,	0·51
10·0 ,, ,,	0·15

Continual exposure of the filter causes some decomposition and the extinction coefficient increases. It is therefore advisable to renew the filter occasionally during exposures of several hours.

Wire gauze screens and perforated plates. The majority of filters employed for altering the intensity of a beam of light suffer from the disadvantage that the extinction coefficient varies with wavelength. This does not matter when the source is already monochromatic, for then it is merely necessary to measure the extinction coefficient at the particular wavelength. This is not always an easy matter if $\lambda<4000$ Å and a quartz monochromatic illuminator and thermopile or photo-electric cell are not available. It is in such circumstances that a wire screen or perforated plate becomes useful, for then transmissibility may be measured in the visible by any photometer available (e.g. photronic cell and galvanometer). They may be used for the ultra-violet, using the same transmission coefficient (Lansberg, *Z. f. Physik*, **46**, 106 (1927)). For relatively small reductions in intensity wire gauze screens suitably blackened (e.g. of copper blackened with ammonium sulphide) are most useful. Two or more screens

cannot be placed in series unless they are continuously rotated with respect to each other—an awkward complication. If a large reduction in intensity is required it is preferable to drill equidistant holes in a plate, the distance between the holes being not more than 1/10th of the linear dimensions of the body being irradiated. If the holes are drilled cleanly the transmission may be calculated, but since this is very difficult to accomplish, it is safer to measure the transmissibility in the usual way.

If the screen is placed between a source focused on the slit of a monochromator diffraction occurs, with the result that the intensity of light entering the monochromator is reduced on this account alone. With a large enough slit this may also be eliminated. Further details will be found in the following papers : Ham, Fehr and Bitner, *J. Frank. Inst.*, **182**, 299 (1914) ; Wenther, *Z. f. wiss. Phot.*, **22**, 125 (1923) : *ibid.*, **25**, 230 (1928) ; Robertson, *J. Opt. Soc. Am.*, **7**, 983 (1923) ; G. R. Harrison and Hesthal, *ibid.*, **8**, 471 (1924) ; W. Wien, *Ann. d. Phys.*, **73**, 499 (1924) ; G. R. Harrison, *J. Opt. Soc. Am.*, **18**, 492 (1929).

Sectors and Allied Devices

Gaseous reactions in general take place through the intermediary of activated atoms and molecules. The concentration of the latter, in fact, controls the rate at which the reaction proceeds. The stationary concentration $[A]$ is determined by the simple equation :

$$\frac{d[A]}{dt} = F - f(D)[A] = 0,$$

or

$$[A] = F/f(D) = F \cdot \tau,$$

where F is the rate of formation, $f(D)[A]$ is the rate of destruction, and τ is the life-time of the activated species. F is usually measurable, e.g. from the quantum input in a photo-reaction, $f(D)$ is often calculable if the mechanism of the reaction is thoroughly elucidated. Lacking this knowledge a direct determination of τ may sometimes be made, and hence conversely provide some evidence about the mechanism of the reaction. Since τ is finite, the stationary concentration of A will not be immediately established, nor will the concentration fall to zero if the source of activation is removed. By adopting suitable devices the decay period of A may then be measured. Such a decay period is termed a photochemical after-effect, if the activation is produced photochemically. It is only in photo-reactions that the method has been used. The extent of a reaction in a single decay period cannot in general be measured accurately, and hence the effect is multiplied by working with intermittent illumination. F. Weigert and K. Kellermann (*Z. phys. Chem.*,

107, 1 (1923)) measured the duration of the after-effect in the photosynthesis of hydrogen chloride by illuminating with an intense spark discharge, and noting the change in refractive index of the mixture due to change in the composition and to the increase in temperature. The lifetime so obtained was of the order of 0·01 sec.

With recent developments in the construction of hot cathode discharge tubes for stroboscopic purposes, this principle of Weigert and Kellermann might well be extended to many other reactions, though the hydrogen-chlorine reaction is an especially favourable example with which to work on account of the very long chain length of 10^5.

In these photochemical chain reactions where the rate of reaction is proportional to the square root of the intensity of the light, the mean life of the chain carrier can be measured in the following way (A. Berthoud and H. Bellenot, *Helv. Chem. Acta.*, **7**, 307 (1924) ; F. Briers, D. L. Chapman and E. Walters, *J.C.S.*, 562 (1926). Cf. also M. Bodenstein, *et al.*, *Z. phys. Chem.*, **B**, **35**, 382 (1937)). A disc is constructed so as to be capable of rotation by an electric motor at a known speed. Out of the disc there are cut a number of equally spaced sectors, so that there are equal periods of illumination and darkness. If I is the intensity without the sector, then $I/2$ is the effective intensity provided the intervals between illumination are short compared with the mean life of the activated species. The rate will then be proportional to $(I/2)^{\frac{1}{2}}$. If now the disc is rotated so slowly that the activated molecule is destroyed before the next period of illumination, then effectively the system will receive light of intensity I but for half the period of the experiment, and hence the rate will be proportional to $I^{\frac{1}{2}}/2$. The rate will therefore be $\sqrt{2}$ times faster at high rates of rotation of the sector. Following Briers, Chapman and Walters, a quantitative relationship between rate of rotation and mean life of the chain carrier may be derived in the following way, the assumption being made that activated molecules mutually destroy each other. If the rate of destruction is $k[A]^2$, then at any time t after the light is switched on

$$\frac{d[A]}{dt} = cI - k[A]^2,$$

where c is a proportionality constant and I the intensity of the light. If $a^2 = c \,.\, k \,.\, I$ and x (the reciprocal of the mean life) $= k[A]$, then

$$\frac{dx}{dt} = a^2 - x^2.$$

If, further, $\tau = at$ and $y = x/a$,

$$\frac{dy}{d\tau} = 1 - y^2,$$

or
$$\left[\ln \frac{1+y}{1-y}\right]_{y_1}^{y_2} = 2\tau_2 - 2\tau_1 ; \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

y is the ratio of $[A]$ at time t to its value in the steady state defined by $d[A]/dt = 0$; τ is the ratio of the time t to the mean life of A. In the dark

$$-\frac{d[A]}{dt} = k[A]^2,$$

or
$$1/y_1 - 1/y_2 = \tau_3 - \tau_2 ; \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

y_1 and y_2 are the final and initial values of y, and τ_1 and τ_2 the corresponding values of τ. If the times of illumination and darkness are equal, $\tau_2 - \tau_1 = \tau_3 - \tau_2$; y must therefore attain the steady value y_3. Hence

$$\ln \frac{1+y_2}{1-y_2} + \frac{2}{y_2} = \ln \frac{1+y_1}{1-y_1} + \frac{2}{y_1}.$$

Then for each value of y_1, the corresponding value of y_2 is obtained from the above equation. If τ is chosen such that when $y = 0$, $\tau = 0$, (1) becomes

$$\ln \frac{1+y}{1-y} = 2\tau. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Hence for each value of y there is a corresponding value of τ. It is now necessary to find the mean value of y for a given rate of rotation of the disc. From (3) during illumination

$$y = \tanh \tau,$$

and during the period of non-illumination,

$$y = 1/(\tau_2 + 1/y_2),$$

where τ_2 is the time (taking the mean life as the unit) during which the system is in the dark and y_2 the value of y when the light is shut off.

The mean value of y during uniform rotation of the disc is given by

$$y = \frac{\ln \cosh \tau_2 - \ln \cosh \tau_1 + \ln [(\tau_2 - \tau_1)y_2 + 1]}{2(\tau_2 - \tau_1)}.$$

The mean value of y when the disc is rotating very rapidly is $(2)^{-\frac{1}{2}}$. Hence, since the mean value of y is proportional to the rate of chemical change :

$$\frac{\ln \cosh \tau_2 - \ln \cosh \tau_1 + \ln [(\tau_2 - \tau_1)y_2 + 1]}{\sqrt{2}(\tau_2 - \tau_1)} = \frac{\text{rate (disc rotating at given speed)}}{\text{rate (disc rotating rapidly)}}.$$

By trial a value of τ_1 is found which satisfies this equation. This can be done, since for every value of τ_1 there are corresponding values of τ_2 and y_2. Further, as $\tau_2 - \tau_1$ is the duration of the exposure in mean life-times,

the value of the mean life can be calculated from the known rate of rotation of the disc. In the iodine-oxalate reaction, for example, the mean life of the activated species was found to be 0·03 sec., the disc being rotated at speeds of 20 and 1000 r.p.m. and having eight sectors.

Some reactions are complicated by an after-effect of longer duration especially if the surface of the vessel plays any part in starting or stopping the reactions. In this case the sector is again useful (H. W. Melville, *Proc. Roy. Soc.*, **A, 146,** 751 (1934)), and is now constructed of two discs mounted on a common spindle and having two sectors of 90° each. These may be rotated with respect to one another, so that angle of the opening may be increased from 0° upwards. It can be shown that if the reaction velocity is directly proportional to the intensity or to the square root of the intensity and if, as before, the interval between the periods of illumination is long compared with the life-time of the activated molecules, the rate of reaction is directly proportional to the angle of the open sector. For example, this happens in the mercury photo-sensitised reaction between hydrogen and nitrous oxide, but the rate-angle line makes a positive intercept on the rate axis, showing therefore that an additional "dark" reaction accompanies the normal photo-reaction. When the sector is speeded up under conditions where the rate is proportional to the square root of the intensity the rate-sector-angle curve follows the square root law, and hence an estimate may be made of the mean life of the activated molecules.

The speed of such rotating sectors may be most easily measured stroboscopically. A disc attached to the sector plates consisting of radial strips of black and white is illuminated with a neon lamp run off frequency-controlled alternating current, and the speed of the disc adjusted until the strips appear stationary. If the frequency of the D.C. is f cycles/sec. and there are n strips in the disc, then at the stationary state the disc is rotating at $120\,f/n$ revolutions per minute. The speed of the disc may then be doubled to obtain a second stationary state at $240\,f/n$, and so on. For high speeds of rotation the disc may be geared up and the speed of the driving motor determined stroboscopically.

Reaction Vessels for Photochemistry

The ideal arrangement for photochemical experiments is shown in Fig. 164, where the light from a suitable source is rendered monochromatic by a monochromator, and passes as a parallel beam through the reaction vessel, through another lens, and finally to a thermopile or photo-electric cell. The reaction vessel is cylindrical with polished silica windows, and for accurate work is immersed in a constant temperature bath. The whole assembly should be erected on a simple type of optical

nch. The reaction vessel cannot conveniently be surrounded by a rnace if a thermopile is being used, though the arrangement is perfectly tisfactory for use with a photo-cell (see, e.g., M. Ritchie, *Proc. Roy. Soc.*, , **146,** 828 (1934)). In these experiments where a thermopile must be ed, a movable furnace made to divide into two half-cylinders has been nployed in some experiments, though the device is rather cumbersome id time-consuming to work in practice.

The only disadvantage of this set-up is the extremely small light inten- y available in the reaction vessel, especially at shorter wavelengths. ie development of efficient filters (cf. p. 233) for the principal lines in e mercury spectrum almost removes the necessity of employing a onochromator, with, of course, a large gain in intensity. Even with

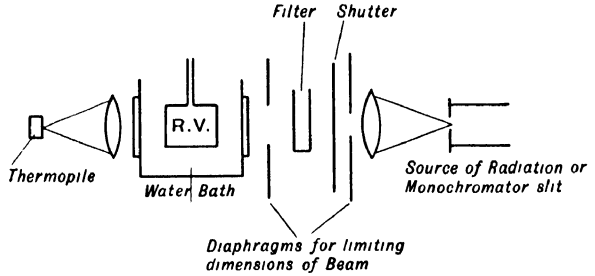


FIG. 164. General arrangement of apparatus for photochemical experiments.

is improvement it is apparent that only a small fraction of the radiation nitted by the lamp is actually transmitted to the reaction vessel. In der to obtain the maximum possible intensity the reaction vessel may : placed parallel to the mercury lamp, and the whole surrounded by ı elliptical reflector of nickel or chromium-plated brass, such that the mp is at one focus and the reaction vessel at the other. The lamp, how- er, radiates so much heat that the reaction vessel must be cooled either r a blast of air or, better, by means of a water jacket. Often another cket is fused on the reaction vessel to act as a container for the filter. ith this arrangement the absolute intensity cannot now be measured r means of a thermopile. Alternatively, however, use may be made of liquid actinometer such as uranyl oxalate (cf. p. 254). The only uncer- inty introduced by this procedure is the fraction of incident light sorbed by the reactants. If this is not at least 0·95 it becomes rather fficult to calculate, say, from the known extinction for the wavelength nployed, the percentage of light absorbed.

A more compact way of achieving the same object is to surround the mp itself with a series of annular vessels containing the cooling water, e filter, and finally the reaction mixture. Such vessels are costly to

manufacture, and it is not easy to introduce a shutter unless the lamp forms a separate unit over which the cooling filter-reaction vessel assembly can slip. A typical lamp of the low pressure type is shown in Fig. 165 (L. Farkas, *Z. phys. Chem.*, **B, 23,** 89 (1933)). With these low pressure lamps the arc length can be made very great, so that large volumes of the reactant may be exposed. Moreover, the fraction of incident light absorbed can easily be measured.

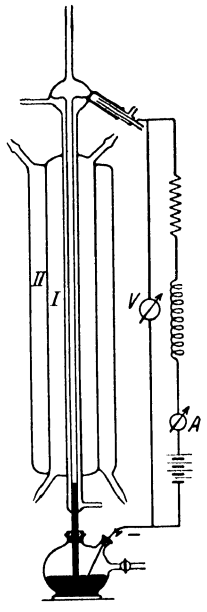


Fig. 165. Combined reaction vessel and mercury lamp.

The set-up may be turned inside out, the lamp surrounding the reaction vessel (Fig. 166) (H. S. Taylor and J. R. Bates, *J. Amer. Chem. Soc.*, **49,** 2438, 1927)); see also p. 331. There is now great economy in silica apparatus, since the lamp of the low pressure variety (a high pressure lamp cannot be worked in this manner) may be constructed of Pyrex. The Pyrex-silica waxed seals are, however, a troublesome part of this type of apparatus.

If photochemical reactions are to be carried out at high temperatures, e.g. up to 1000° C., the reaction vessel is enclosed in a furnace, one end of which is closed by a fused silica lens (see, e.g., Fig. 12). The lamp and filter remain outside: again this leads to much loss of useful light. For reactions requiring light of $\lambda = 2537$ Å, or shorter, however, the low pressure high voltage discharge lamp may be placed directly in the furnace (Fig. 167) (H. W. Melville and A. Farkas, *Proc. Roy. Soc.*, **A, 157,**

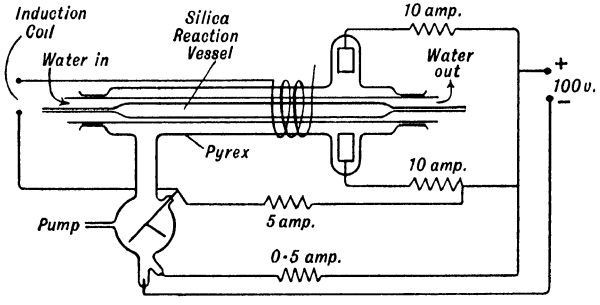


Fig. 166.

625, (1936)) without affecting the intensity, provided the electrode compartments remain outside. Filters cannot, of course, be employed, but intensity filters (*F*) consisting of wire gauze or perforated plate are easily

used. A rotary shutter (S_1, S_2) can also be conveniently incorporated in the apparatus. In order to get an even larger intensity C. K. Ingold and C. L. Wilson (Fig. 168) (*J. Chem. Soc.*, 944 (1936)) have wound such a

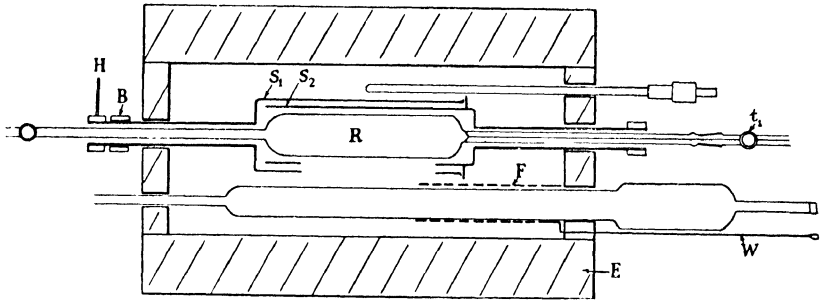


FIG. 167.

high voltage lamp around the insolation vessel. Another arrangement for obtaining very high intensity radiation is shown in Fig. 169 (K. Hilferding and W. Steiner, *Z. phys. Chem.*, **B, 30,** 412 (1935)). This was designed for work on the H_2-Br_2 reaction. The reaction vessel *R* is surrounded by a bath of naphthalene vapour *B*. The vapour jacket in turn is surrounded

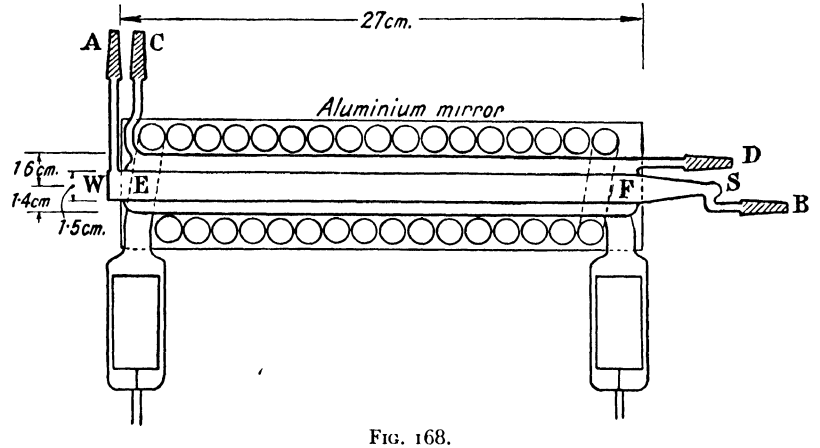


FIG. 168.

by a glass filter *F*. The source of radiation is six 200 watt tungsten lamps *S*. The whole apparatus is enclosed in a polished steel cylinder *T*.

These descriptions will serve to show how a particular problem is to be tackled according to the sensitivity of the system to radiation and the analytical devices available for following the course of the reaction.

Combined reaction vessel and McLeod gauge. (H. W. Melville, *Proc. Roy. Soc.*, **A, 139,** 543 (1933).) A compact form of reaction system

is shown in Fig. 170, in which the bulb of the McLeod gauge is blown out in order that a convex silica lens may be affixed to one hole and a smaller quartz plate to the other. The whole apparatus is easily thermostatted by placing in a brass box through which water is circulated. The light from the exit slit of a monochromator may then be focussed on a thermopile behind the small window. Such an arrangement may be used as a controlling photometer. For example, in one case it was necessary to measure the output of a zinc spark for wavelengths less than 2300 Å. Ammonia to a pressure of several hundred millimetres was allowed into the vessel, and after the requisite period of illumination was condensed out with liquid air and the

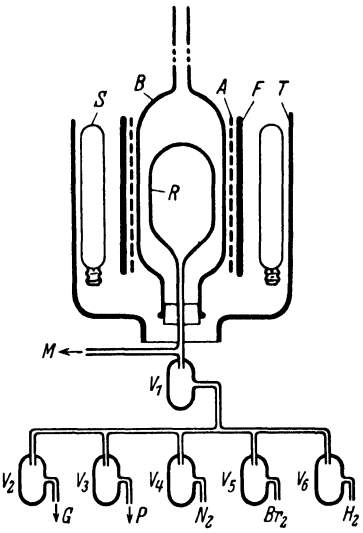


FIG. 169.

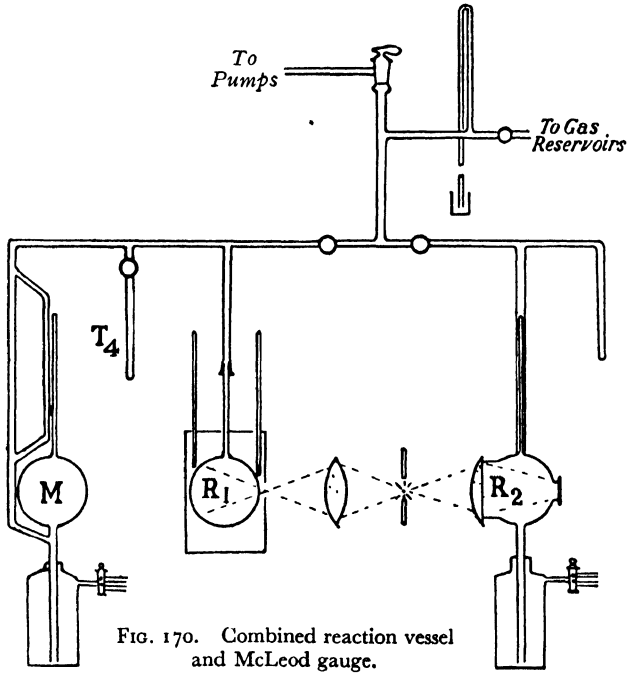


FIG. 170. Combined reaction vessel and McLeod gauge.

pressure of the residual nitrogen and hydrogen measured in the usual way.

Extinction coefficients of glasses. Table 34, calculated from the data in a paper of Kohler (*General Electric Review*, **39**, 232 (1936)), gives an indication of what glass is most suitable for a reaction vessel system at any given wavelength.

TABLE 34

Extinction coefficient (ϵ).

λ (Å)	Corex A	Corex D	Pyrex	Window glass	H_2O (liquid)	Fused silica	Crystalline quartz	Calcite	Rock salt
1860	—	—	—	—	0 688	—	0·39	—	0 36
1930	—	—	—	—	0 166	—	—	—	—
2000	—	—	—	—	0·09	—	—	—	—
2030	—	—	—	—	—	—	0·179	—	—
2100	—	—	—	—	0·061	—	—	—	0·26
2140	—	—	—	—	—	—	0·083	—	—
2200	—	—	—	—	0 057	—	—	—	—
2220	—	—	—	—	—	—	0·051	—	—
2300	—	—	—	—	0·034	—	—	1·25	—
2310	—	—	—	—	—	—	—	—	0·15
2400	—	—	—	—	0·032	0 76	—	0·58	—
2500	2·22	—	—	—	—	0·35	—	0·40	—
2600	1·40	—	—	—	0·025	0 20	—	0·29	—
2800	0·74	8·87	—	—	—	0·177	—	0·16	0·046
3000	0·48	2·44	10 60	—	0 015	—	—	—	—
3100	—	—	5·55	—	—	—	—	—	—
3150	—	—	—	7·6	—	—	—	—	—
3200	0·37	0 76	3·08	5 0	—	—	—	—	—
3300	0·33	—	1·71	—	—	—	—	—	—
3400	—	0·457	1·18	1·29	—	—	—	—	—
3600	—	—	0·64	0·45	—	—	—	—	—

ϵ is defined by the equation $I = I_0 e^{-\epsilon d}$ (d = thickness in cm.).

Reflectivity of polished metals. The reflectivity of well-polished specimens of a number of materials commonly employed as reflectors is

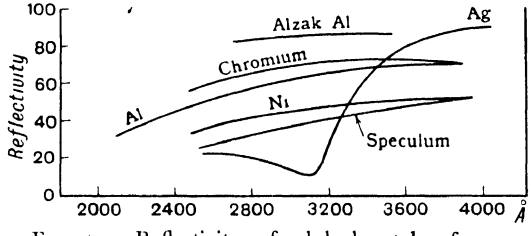


FIG. 171. Reflectivities of polished metal surfaces.

given in Fig. 171 (Kohler, *Gen. Electr. Rev.*, **39**, 232 (1936)). It will be observed that silver is particularly ineffective below 3500 Å.

Corrections for reflection and loss in transmission of light through reaction vessels. If a thermopile or photo-electric cell is being used to measure the absorption of radiation by a gas, it is not simply sufficient to note the photo-electric current with and without the gas and then compute the fraction of the light absorbed. The simplest set-up is shown in Fig. 172. In this the end plate *ab* of the tube reflects and may absorb some of the radiation. The easiest way in which to correct for

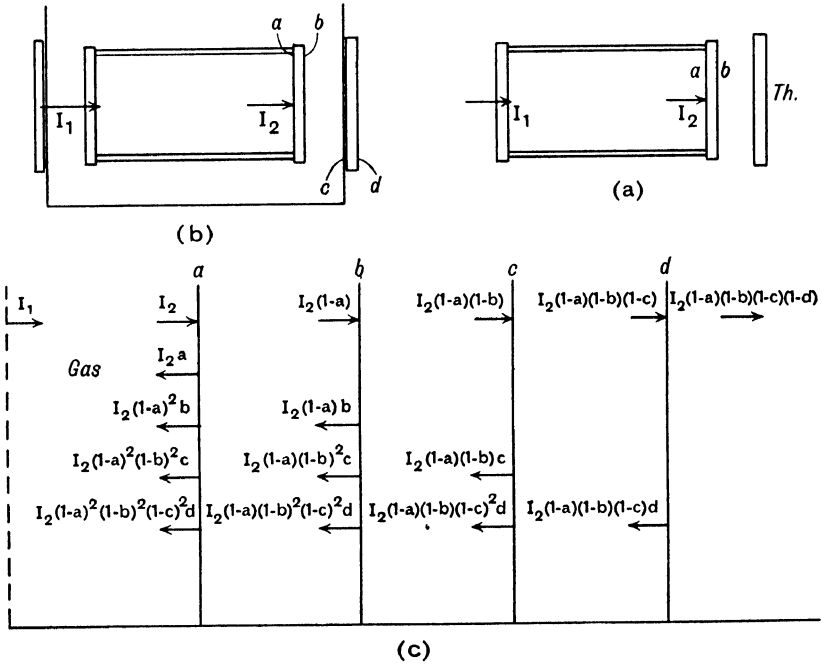


FIG. 172. Reflection losses at interfaces in reaction vessel systems.

these effects is to remove the end plate and allow the beam of light to fall directly on the thermocouple or photo-cell. Once this fraction is determined the intensity I_2 incident on *a* may then be computed in any experiment. When, however, the radiation of intensity I_2 strikes *a*, a fraction $\left(\frac{n_1-n_2}{n_1+n_2}\right)^2$ is reflected back into the gas (n_1 and n_2 are the refractive indices of the media on either side of the interface *a* for the wavelength under consideration). Of this a fraction $1-I_2/I_1$ will be absorbed. Hence the total absorption will be

$$I_1 - I_2 + (1 - I_2/I_1)\, I_2 \left(\frac{n_1-n_2}{n_1+n_2}\right)^2.$$

For example, if $I_2 = 1/2I_1$ and $n_1 = 1$ and $n_2 = 1{\cdot}5$, then the second factor is 1/50 of the first. If there is complete absorption this reflection does not occur.

In general the above simple system becomes more complicated in practice, and it is often practically impossible to measure the reflection losses at the several interfaces. Provided it is certain that there is no appreciable absorption of light by the media it traverses after leaving the reaction vessel, the relationship between incident intensity and the intensity impinging on the measuring device may be calculated by an application of the above formula. For example, consider the practical case where a reaction vessel is immersed in a bath, as shown in Fig. 172 (*a*), a slightly convergent beam striking the thermopile, *Th*. Let I_1 and I_2 be the intensities of the radiation entering and leaving the gas, the fraction of light transmitted (E) is therefore defined by $I_2 = I_1E$. The system is diagrammatically shown in Fig. 172 (*c*), where a, b, c, d represent the fraction of light reflected at the several interfaces, i.e. $\left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$, etc. Then the intensity, I_T, of light reaching the thermopile is given by

$$I_T = I_1 \,.\, E \,.\, (1-a)\,(1-b)\,(1-c)\,(1-d).$$

When the cell is empty the intensity of light reaching the thermopile I_{vac} is given by

$$I_{\text{vac}} = I_1\,(1-a)\,(1-b)\,(1-c)\,(1-d).$$

The fraction of light absorbed by the gas will therefore be given by

$$\frac{I_{\text{abs}}}{I_1} = (1-E) + E\times$$

$$\{a + (1-a)^2 b + (1-a)^2(1-b)^2 c + (1-a)^2(1-b)^2(1-c)^2 d\}$$

$$= \left(1 - \frac{I_T}{I_{\text{vac}}}\right) + \frac{I_1}{I_{\text{vac}}}\times$$

$$\{a + (1-a)^2 b + (1-a)^2(1-b)^2 c + (1-a)^2(1-b)^2(1-c)^2 d\},$$

or

$$I_{\text{abs}} = \frac{1}{(1-a)\,(1-b)\,(1-c)(1-d)}\times$$

$$[I_{\text{vac}} - I_T\{1 - a - (1-a)^2 b - (1-a)^2(1-b)^2 c - (1-a)^2(1-b)^2(1-c)^2 d\}].$$

As before, if there is complete absorption, i.e. $E = 0$, the correction disappears.

Finally if there is a lens focussing, say, a parallel beam of light on to the thermopile or photo-cell, another correction must be applied, since

the light reflected from the side of the lens facing the reaction vessel will not wholly re-enter the gas.

Monochromators. It is outside the scope of this book to describe in detail the construction of monochromators suitable for photochemical purposes. The following figures are quoted to indicate approximately the intensity available with the largest instruments constructed. The lenses and prisms are of fused silica, and hence the monochromators cannot be usefully employed for wavelengths shorter than about 2500 Å. To reach the limit of transmission at 2000 Å., a crystalline quartz optical train must be used. L. J. Heidt and F. Daniels (*J. Amer. Chem. Soc.*, **54**, 2384 (1932)) describe one design in detail, in which the lenses are 15·25 cm. in diameter and 35 cm. focal length at $\lambda = 7950$ Å and the prism 14 cm. high. The source of light is the capillary arc mentioned on p. 224, running with an input of 1000 watts (life of arc only 24 hours); and Table 35 gives the output for two slit widths. The narrower slit gives much better resolution of the individual lines.

TABLE 35

Intensity at exit slit.

	0·6 mm. slit		0·1 mm. slit	
λ (Å)	erg. sec.$^{-1}$	$h\nu$ sec.$^{-1}$	erg. sec.$^{-1}$	$h\nu$ sec.$^{-1}$
5780	$2{\cdot}2 \times 10^{5}$	$6{\cdot}4 \times 10^{16}$	$1{\cdot}25 \times 10^{5}$	$3{\cdot}7 \times 10^{16}$
5461	$2{\cdot}0 \times 10^{5}$	$5\,5 \times 10^{16}$	$6{\cdot}0 \times 10^{4}$	$1{\cdot}7 \times 10^{16}$
4360	$1{\cdot}4 \times 10^{5}$	$3{\cdot}1 \times 10^{16}$	$8{\cdot}5 \times 10^{4}$	$1{\cdot}9 \times 10^{16}$
4047	$7{\cdot}5 \times 10^{4}$	$1{\cdot}54 \times 10^{16}$	$5{\cdot}5 \times 10^{4}$	$1{\cdot}1 \times 10^{16}$
3650	$2{\cdot}3 \times 10^{5}$	$4{\cdot}3 \times 10^{16}$	$1{\cdot}4 \times 10^{5}$	$2{\cdot}6 \times 10^{16}$
3340	$2{\cdot}5 \times 10^{4}$	$4{\cdot}2 \times 10^{15}$	$1{\cdot}5 \times 10^{4}$	$2{\cdot}5 \times 10^{15}$
3130	$1{\cdot}0 \times 10^{5}$	$1{\cdot}6 \times 10^{16}$	$6{\cdot}5 \times 10^{4}$	$1\,0 \times 10^{16}$
3020	7×10^{4}	$1{\cdot}0 \times 10^{16}$	$3{\cdot}5 \times 10^{4}$	$5{\cdot}4 \times 10^{15}$
2800	2×10^{4}	$2{\cdot}9 \times 10^{15}$	1×10^{4}	$1{\cdot}4 \times 10^{15}$
2650	$1{\cdot}5 \times 10^{4}$	$2{\cdot}0 \times 10^{15}$	7×10^{3}	$9{\cdot}5 \times 10^{14}$

In another design by P. A. Leighton and G. S. Forbes (*J. Amer. Chem. Soc.*, **51**, 3550 (1929)), with a capillary arc burning at a much lower input, namely 60 volts and 3 amps., the following intensities were obtained at the exit slit.

λ (Å)		5780	4350	4060	3660	3130
Intensity	erg. sec.$^{-1}$	1900	1030	750	1880	1270
	$h\nu$ sec.$^{-1}$	$5{\cdot}6 \times 10^{14}$	$2{\cdot}3 \times 10^{14}$	$1{\cdot}5 \times 10^{14}$	$3{\cdot}5 \times 10^{14}$	$2{\cdot}0 \times 10^{14}$

λ (Å)		3020	2800	2700	2540
Intensity	erg. sec.$^{-1}$	870	210	310	208
	$h\nu$ sec.$^{-1}$	$1{\cdot}4 \times 10^{14}$	$3{\cdot}0 \times 10^{13}$	$4{\cdot}3 \times 10^{13}$	$2{\cdot}7 \times 10^{13}$

The performance of a third type of monochromator, constructed of fused silica optical parts, is given below (Benford, *Gen. Electr. Rev.*, **39**, 181 (1936)).

1 mm. slit. Hg. lamp burning at 150 v. 3·3 amp.

Dispersion 2652-3650 Å, 2·5 cm.

λ (Å)		3650	3125	3021	2967	2894
Intensity	erg. sec.$^{-1}$	$3{\cdot}4 \times 10^{4}$	$1{\cdot}4 \times 10^{4}$	7×10^{3}	4×10^{3}	2×10^{3}
	$h\nu$ sec.$^{-1}$	$6{\cdot}2 \times 10^{15}$	$2{\cdot}7 \times 10^{15}$	$1{\cdot}1 \times 10^{15}$	6×10^{14}	$2{\cdot}9 \times 10^{14}$

λ (Å)		2804	2652
Intensity	erg. sec.$^{-1}$	3×10^{3}	1×10^{3}
	$h\nu$ sec.$^{-1}$	$4{\cdot}2 \times 10^{14}$	$1{\cdot}4 \times 10^{14}$

Finally the output of a large crystalline quartz monochromator may be quoted (E. K. Rideal and J. S. Mitchell, *Proc. Roy. Soc.*, **A, 159,** 211 (1936)). The 60° prism was $11{\cdot}5 \times 10{\cdot}2$ cm., the lenses 11·5 cm. in diameter, and the aperture of the collimator was $f/2{\cdot}2$. Using a hydrogen tube of the following dimensions—$1{\cdot}8 \times 20$ cm. nickel electrodes, capillary $20 \times 0{\cdot}4$ cm. and input 1 amp. at 2000 v., the capillary constituting the slit of the collimator—the total output in the region 2350-2400° Å. was $3{\cdot}0 \times 10^{14}$ quanta per sec.

For setting monochromators to the desired wavelength a small portable quartz spectroscope fitted with a fluorescent screen is extremely useful. Failing this a small spectrograph with a piece of uranium glass or translucent screen of fluorescent material will suffice. A fluorescent screen itself, e.g. of willemite or calcium tungstate, will serve for adjusting the instrument for maximum intensity.

D. THE MEASUREMENT OF RADIATION INTENSITY

The only absolute method of measuring radiation intensity is to use a calibrated thermopile, bolometer or radiometer. For the majority of photochemical purposes the thermopile is most suitable. Calibration is now easily effected by means of the carbon filament lamp, which may be standardised by the National Physical Laboratory or the Bureau of Standards. Many types of thermopile have been described, and the following models manufactured by the Cambridge Instrument Co. to designs of W. J. H. Moll (*Proc. Kon. Akad. Wetensch. Amsterdam*, **16,** 568 (1913) ; *Proc. Phys. Soc.*, **35,** 257 (1923) ; *Phil. Mag.* v. **50,** 618 (1925)) will indicate the sensitivity obtainable.

TABLE 36

Sensitivity of Thermopiles.

Type	Resistance (Ω)	Area of receiving surface	E.M.F. in microvolts	Radiation Intensity Cals./sec.	$h\nu$ sec.$^{-1}$ at 2000 Å	$h\nu$ sec.$^{-1}$ at 4000 Å
Large surface pattern	50	2 cm. diameter circle (3·14 cm.^{2})	330	$3{\cdot}85 \times 10^{-4}$	$1{\cdot}7 \times 10^{15}$	$3{\cdot}3 \times 10^{15}$
Linear	22	$2 \times 0{\cdot}1$ cm.	22	$0{\cdot}24 \times 10^{-4}$	$1{\cdot}0 \times 10^{14}$	$2{\cdot}1 \times 10^{14}$
Small surface	10	1 cm. diameter circle (0·78 cm.^{2})	85	$0{\cdot}98 \times 10^{-4}$	$4{\cdot}2 \times 10^{14}$	$8{\cdot}4 \times 10^{14}$
Micro-thermopile	30	0·1 cm. diameter circle (0·008 cm.^{2})	47	$0{\cdot}35 \times 10^{-4}$	$1{\cdot}5 \times 10^{14}$	$3{\cdot}0 \times 10^{14}$
		Fluorite window	75			
		With 1 mm. slit	8			
		Fluorite window	13	$7{\cdot}3 \times 10^{-6}$	$3{\cdot}1 \times 10^{13}$	$6{\cdot}2 \times 10^{13}$
Vacuum thermopile	30	$0{\cdot}8 \times 0{\cdot}01$ cm. (single element)	100	10^{-6}	$4{\cdot}3 \times 10^{12}$	$8{\cdot}6 \times 10^{12}$

The galvanometer required depends, of course, on the intensity available for measurement. The less sensitive the galvanometer the easier it is to obtain stable working conditions. The performance of three typical galvanometers specially designed for use in conjunction with thermopiles are given below. These are Cambridge instruments.

Type	Resistance (Ω)	Sensitivity at 1 metre	Period (sec.)
Moll (moving coil) - - -	50	4 mm./microvolt	1·3
Paschen (moving magnet) - -	12	1220 mm./microvolt	6
		135 mm./microvolt	2 sec.
Modified Broca (moving magnet)	20	60 mm./microvolt	6
	100	22·6 mm./microvolt	6

The limit of sensitivity, that is 1 mm. deflection, employing the Paschen galvanometer with the vacuum thermopile under the most favourable conditions, is thus about 10^8 quanta/sec. at 4000 Å falling on an area of about 0·01 cm.^{2}. The lowest measurable (i.e. to 1 per cent.) intensity may therefore be put at 10^{12} quanta/sec./cm.^{2}. This is considerably below the intensity furnished by the monochromators described on p. 249.

Photo-electric relays for moving coil galvanometers. Though the moving magnet galvanometer can be made more sensitive than a moving coil instrument, the former is subject to external disturbances. The

moving coil galvanometer has now been made so sensitive by the addition of a photo-electric relay that it is replacing the moving magnet instrument. Originally a thermo-electric relay was used (W. J. H. Moll and H. J. Burger, *Phil. Mag.*, **50**, 624 (1925)), but with the rapid development of the copper oxide and selenium photo-electric cells this method of amplification has been superceded (A. V. Hill, *J. Sci. Instr.*, **8**, 262 (1931); *ibid.*, **11**, 281 (1934)). The principle of the method is shown in Fig. 173 (*a*). *F* is a tungsten filament, an image of which is projected on to a photo-electric cell *C* by means of a lens *L* from the galvanometer mirror *M*.

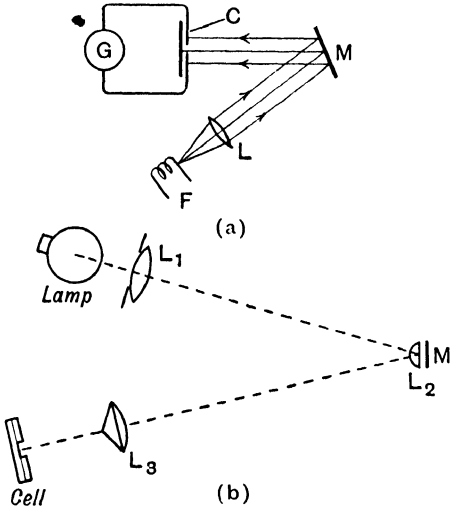


FIG. 173. Photo-electric amplifier for a galvanometer.

The cell is divided into two parts with a common electrode. When the image of the filament is symmetrically disposed with respect to the two halves, the galvanometer will not be deflected, since the e.m.f.'s of the two halves exactly neutralise each other. If the mirror *M* is deflected the symmetry of the system is destroyed and *G* in turn will be deflected. *G* need not be specially sensitive, as the current generated by the cell is comparatively large if *F* is, say, a 36 watt motor head lamp bulb. R. V. Jones (*J. Sci. Instr.*, **11**, 302 (1934)) has described a method of attaching such a relay to a Cambridge Moll galvanometer. The amplification factor is of the order of several hundred so that the whole device can detect a current of the order of 10^{-11} amp. To achieve the maximum sensitivity the 'primary' galvanometer must be mounted on substantial foundations, and is placed in a well-lagged box for temperature control.

It is evident that in order to obtain linear amplification the image of an illuminated rectangular aperture should be thrown upon the divided cell and the surface sensitivity of the cell should be absolutely uniform. This latter trouble may be completely avoided (E. B. Moss, *J. Sci. Instr.*, **12**, 144 (1935)) by means of a bi-prism-lens system (Fig. 173 (*b*)), which projects two images of the galvanometer mirror on each of the photo-cells (or halves of the divided cell). The illuminated patch thus remains in a fixed position on the cell surface.

It may be of interest to quote some figures (G. K. T. Conn, private communication) to indicate the maximum usable sensitivity of this method of amplifying galvanometer deflection. With a Zernicke (Kipp and Zonen) primary galvanometer a current of 4×10^{-12} amp. gave a deflection of 1 cm. at 1 metre on the secondary galvanometer through a resistance of 15 Ω. Using a sensitive vacuum thermopile 10^{-4} ergs/cm.^{2}/sec. gave a deflection of 1 cm. This corresponds to about 10^7 quanta per sec. at 3000 Å. Electro-cells were employed in the amplifier.

Calibration of thermopiles. The set-up for calibrating the thermopile as recommended by the National Physical Laboratory is shown in Fig. 174. The lamp *L* itself is disposed in exactly the same position in

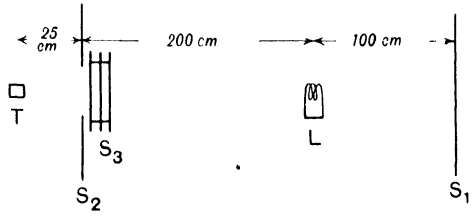


FIG. 174. Calibration of thermopiles.

which it was originally calibrated.* Behind the lamp a black velvet screen S_1 is erected; in front there is a blackened cardboard screen S_2 with an aperture 10 × 15 cm. The shutter (S_3) consists of three thin sheets of aluminium 20 cm. square separated by 1 cm. Before starting calibration the lamp is run for at least ten minutes to obtain steady conditions. With 100 volt carbon filament lamps the energy received by the thermopile under these conditions is of the order 10^{-6} watts per square millimetre. The current flowing through the lamp may be measured by a standard resistance and potentiometer.

In principle the thermopile-galvanometer system is the most satisfactory combination for the determination of intensities. To obtain reasonably accurate results, however, the most stringent precautions must be taken. The galvanometer must be mounted on a very rigid pillar or sus-

* Precise directions are given with the N.P.L. report.

pended by a shock-proof assembly. If of the moving magnet type it must be carefully shielded. In so far as the thermopile is concerned, care must be taken that all the light incident on the reaction vessel falls on the thermo-junctions. If this cannot be accomplished the thermopile must be moved from point to point in the beam of light in order to integrate over the whole field.

Chemical Actinometers

These difficulties have therefore led a number of experimenters to develop chemical actinometers which have been accurately calibrated against absolute standards. Three such actinometers have been developed: (*a*) uranyl oxalate, (*b*) monochloracetic acid, (*c*) malachite green. The first is very sensitive and, moreover, practically uniformly sensitive from 2000 to 4500 Å; the second has a much more restricted range—2000-2600 Å– and is less sensitive than the uranyl oxalate; while the third has been investigated from 2537 to 3342 Å.

The Uranyl Oxalate Actinometer. (P. A. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, **52**, 3139 (1930); **52**, 5309 (1930). L. J. Heidt and F. Daniels, *ibid.*, **54**, 2384 (1932). G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).) The working of this actinometer depends on the fact that the UO_2^{++} ion photosensitises the decomposition of oxalate ion into CO, CO_2 and HCOOH. It possesses the following practical advantages: (1) the actinometer may be used from 2000 to 4500 Å, (2) the reciprocity law holds over a wide range of intensity, (3) the temperature coefficient is only 1·03 per 10° at 20° C., (4) the analytical method of determining oxalate by titration with permanganate is simple and accurate, (5) the quantum yield does not vary much with changing wavelength, which renders the actinometer especially useful if the source of radiation is rendered monochromatic by employing filters instead of a monochromator.

Materials. Uranyl oxalate is prepared by mixing hot solutions of recrystallised oxalic acid and uranyl sulphate or uranyl nitrate. The oxalate is thoroughly washed, dried *in vacuo* and then in air at 110° C. for three hours. The oxalate has the composition $UO_2(C_2O_4) \cdot H_2O$ (M.W. 376·2). If the uranyl nitrate is of doubtful purity it may be treated in the following way. Uranyl nitrate is ignited in a platinum crucible, 20 per cent. sulphuric acid added, and the whole evaporated until fumes of SO_3 appear. This is repeated several times, and finally an aqueous extract made, evaporated and the crystals washed. These are again recrystallised. The uranium content may be checked by the method of Lundell and Knowles (*J. Amer. Chem. Soc.*, **47**, 2637 (1925)) and the sulphate by precipitation as $BaSO_4$.

Procedure. A 0·005 M solution of uranyl oxalate is suitable except below 2500 Å, where such a solution absorbs 77 per cent. of the incident light 0·01 mm. from the entrance window, thus setting up concentration gradients which might cause irregular working. A 0·001 M solution obviates these difficulties. Up to 4500 Å absorption is for the present purpose complete in a cell 2 cm. thick. A weighed quantity of

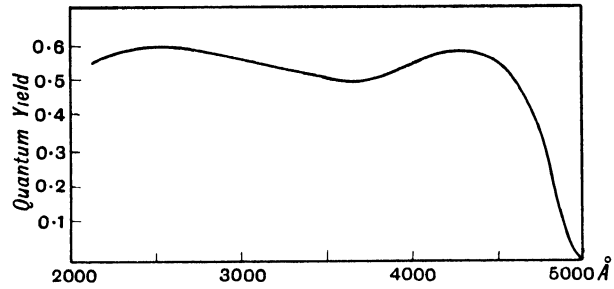


FIG. 175. Quantum yield wavelength curve for uranyl oxalate actinometer.

actinometric solution is placed in a suitable cell and exposed for a given time. A flattened platinum wire spiral serves as a stirrer. A portion of the solution is transferred to a small beaker and the cell reweighed. This procedure eliminates washing of the cell and consequent dilution of the solution to be titrated. 1 c.c. of 96 per cent. sulphuric acid is added for every 10 c.c. of solution, and titrated at 85° C. with permanganate or

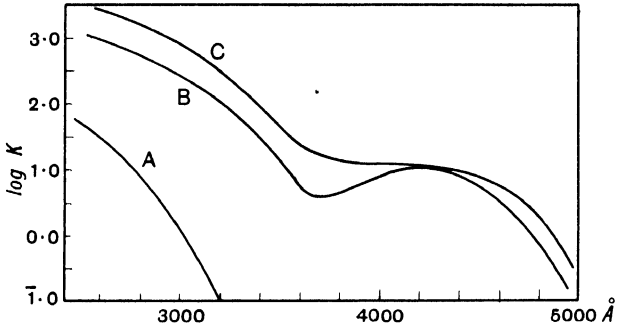


FIG. 176. Extinction coefficients of components of uranyl oxalate actinometer.
A = 0·05 M $H_2C_2O_4$; B = 0·01 M UO_2SO_4; C = UO_2SO_4 + 0·05 M $H_2C_2O_4$.

electrometrically with ceric sulphate. A portion of the unexposed standard solution is also titrated in a similar manner. The titration should, of course, be carried out in absence of strong light of wavelength shorter than 5000 Å.

In Fig. 175 the values of the quantum yields are plotted against the wavelength, and in Fig. 176 the extinction coefficients of the substances used in the actinometer. It will be observed that at the shorter wavelengths the oxalate ion exerts an inner filter effect.

If photolysis is allowed to go too far, the U^{++++} ion is produced. This would interfere with the determination of the oxalate. E. C. Pitzer, N. E. Gordon and D. A. Wilson (*J. Amer. Chem. Soc.*, **58**, 67 (1936)) have estimated the extent of reduction, using cupferron as reagent, and obtained these results :

Per cent. $H_2C_2O_4$ decomposed -	- 42·5	71·0	85·8	90·5	94·0
Per cent. UO_2^{++} reduced -	- 0·0	1·8	3·3	13·0	43·4

The monochloracetic acid actinometer. (E. Rudberg, *Z. Physik*, **24**, 247 (1924).) This actinometer depends for its action on the photochemical hydrolysis of monochloracetic acid at wavelengths shorter than about 2600 Å. The quantum yield of the reaction in aqueous solution is unity, and hence the actinometer is most useful for shorter wavelengths only. This is an advantage, for it is easy to filter off wavelengths shorter than a given value, e.g. 2537 Å by 2 cm. of 25 per cent. aqueous acetic acid, provided longer wavelengths do not affect the actinometer. In order to obtain complete absorption of impinging radiation, say at 2537 Å, it is necessary to employ a rather concentrated solution, namely one gram-mole per litre. A 1 cm. layer of N-acid transmits 14·5 per cent. of light of $\lambda = 2537$ Å. The slight absorption by water cannot be neglected. Rudberg, using 0·5 N-acid 2·0 cm. thick, found that water absorbed 12·5 per cent. of the incident radiation and the acid 74·8 per cent. One disadvantage is that the solution hydrolyses on standing, and must be made up freshly each day. Even then a blank experiment must always be done simultaneously with the photochemical run, which in turn requires that a considerable fraction of the acid must be photochemically hydrolysed. With quite powerful sources of 2537 Å radiation the exposure times are therefore of the order of hours.

The chloride is precipitated in the usual way with excess silver nitrate, filtered off and the excess silver estimated by back titration with potassium thiocyanate. If, however, the p_H value of the solution after exposure is adjusted to 4 a direct titration with silver nitrate would appear to be feasible, using as adsorption indicator—dichloro fluorescein (private communication from Prof. K. Fajans). The procedure recommended by I. M. Kolthoff, W. M. Lauer and C. J. Sunde (*J. Amer. Chem. Soc.*, **51**, 3273 (1929)) is as follows. An acetate buffer is added to the solution to bring the p_H value to approximately 4. For every 10 c.c. solution, 2 drops of indicator are added (the indicator is made as follows : 0·1 gm. dichlorofluorescein is dissolved in 60 c.c. alcohol, 2·5 c.c. 0·1 N NaOH added, and the volume made up to 100 c.c. with water) and the titration started with silver nitrate. The colloidal silver chloride thus formed is yellowish-orange, and 0·5 per cent. before the end point it flocculates. At the end

point the AgCl turns dark red. A 0·01 N solution can be titrated with an accuracy of 0·5 per cent. If too much silver nitrate is added, back titration with chloride *immediately* after will give the correct end point.

Malachite green actinometer. (L. Harris, J. Kaminsky and R. G. Simard, *J. Amer. Chem. Soc.*, **57**, 1151, 1154 (1935).) The operation of this actinometer depends on the fact that an alcoholic solution of leuco-cyanide of malachite green (*pp'*-di-dimethyl aminotriphenyl acetonitrile) is coloured on exposure to ultra-violet light. The quantum yield is, within 1 per cent., unity over the range 2480-3340 Å. The reciprocity law is obeyed. The temperature coefficient for the reaction at 2537 Å is 1·007 per 10°. The malachite green is determined colorimetrically. A layer 1 cm. thick and concentration 10^{-3} gm. mole per litre (solubility $3{\cdot}1 \times 10^{-3}$ at 24·5° C.) absorbs 99 per cent. of the incident light. The leuco-cyanide prepared, according to the directions of F. Lifschitz and C. L. Joffé, *Z. phys. Chem.*, **97**, 426 (1921) and A. Hantzsch and G. Osswald, *Ber.*, **33**, 307 (1900), is dissolved in 95 per cent. ethyl alcohol to the required concentration, and one or two drops of 3NHCl added to eliminate the dark reaction. The solution is stirred by bubbling nitrogen through it. The solution, after exposure, is then compared with a malachite green solution of known concentration containing an amount of acid equivalent to that of the solution to be analysed.

The reaction is probably

$$[(CH_3)_2NC_6H_4]_2[C_6H_5] : C-CN \xrightarrow{\text{Light}}$$
$$[(CH_3)_2NC_6H_4]_2[C_6H_5] : C\,.\,CN \text{ (excited)}$$
$$\downarrow$$
$$\{[(CH_3)_2NC_6H_4]_2[C_6H_5] : C\}\ CN$$
$$\downarrow$$
$$\{[(CH_3)_2NC_6H_4]_2[C_6H_5] : C\}\ Cl.$$

Determination of quantum yields of gas reactions by actinometry. In reactions where it is not convenient to use the same reaction vessel for irradiation of the gas mixture, and subsequently for the actinometric liquid, G. S. Forbes, G. B. Kistiakowski and L. J. Heidt (*J. Amer. Chem. Soc.*, **54**, 3246 (1932)) have described an apparatus to facilitate the comparison between reaction vessel and the actinometer cells. The arrangement of the monochromator *M*, the source *O* (capillary arc) and condensing lens is shown in Fig. 177. There are three similar cells of trapezoidal shape (the exit slit of the monochromator is furnished with a cylindrical lens to diminish the divergence of the emergent beam), two for the actinometric liquid and one for the gas mixture. If necessary the latter may be surrounded by a water jacket if a sensitive differential manometer is being used to measure pressure changes. Since in general

it is not easy to alter the position of the gas cell, the whole monochromator is arranged to rotate round an axis at *O*, so that the exit slit may be brought in turn opposite the three cells. If very accurate work is being done, it

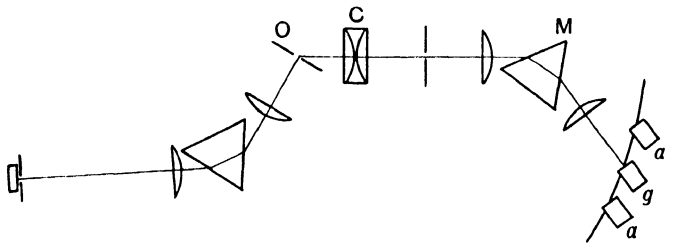


FIG. 177. Measurement of quantum yield of a reaction by liquid actinometer.

is advantageous to add a second monochromator fitted with a thermopile and adjusted to transmit the same line as the first monochromator. A continuous check may then be kept on the output of the mercury lamp.

Photo-electric quantum counters. In photochemistry it is usually found that the methods of measurement of the intensity of the radiation are somewhat more sensitive than the devices, such as manometers, available for measuring the amount of chemical change. From this point of view there is therefore no need to further extend the sensitivity of thermopiles, photo-electric cells, etc. On some occasions it may be necessary to measure the intensity of fluorescent light, maybe after resolution in a monochromator, or the intensity of a feeble chemi-luminescence. Photographic measurement may solve the difficulty, but with the added complication of translating the density on the photographic plate to intensity of incident radiation, especially if the density is not very large. By far the most sensitive detector of visible or ultra-violet radiation is the photo-electric quantum counter, which may achieve a sensitivity of 0·05 quanta per sec. under the most favourable conditions (G. L. Locker *Phys. Rev.*, **42**, 525 (1932)). Unfortunately little use has been made of such counters for photochemical purposes, and hence only a brief description can be given of their capabilities in this direction, though they would seem to have a wider application, for special problems, e.g. the investigation o

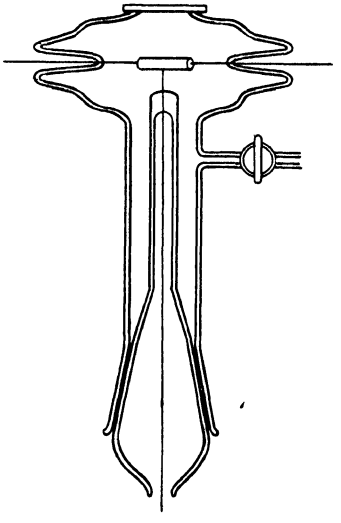


FIG. 178. Photo-electric quantum counter.

the glow of phosphorus (C. Ouellet, *Trans. Faraday Soc.*, **29**, 486 (1933)). Essentially the counter consists of a cylindrical cathode with an axial wire anode, the whole being enclosed within a bulb, having a suitable window to admit light to the cathode, and containing gas at a few cm. pressure. A potential of the order of 1000 volts is applied between cathode and anode. When a photo-electron is emitted from the cathode and the voltage on the anode is of the optimum value, a burst of ionisation is brought about by collision of the electron with gas molecules. The potential of the anode is thus suddenly altered. The 'burst' is complete within 10^{-3} sec., and the counter returns to its normal state within this interval. If the voltage is too low, the necessary burst does not occur ; on the other hand, if the voltage is too high an ordinary discharge takes place in the gas which is useless for the present purpose. The sudden change in the anode potential is magnified by a valve amplifier fitted with a mechanical counting device. B. Rajewski (*Phys. Z.*, **32**, 121 (1931)) was the first to show that the familiar Geiger-Müller counter could be adapted for measuring ultra-violet radiation. G. L. Locker (*loc. cit.*) has given many practical details for the construction of such counters. The counting tube itself is shown in Fig. 178. The whole is made of Pyrex, such that the anode and cathode leads are as far apart as possible to avoid leakage troubles. The cathode is mounted on a ground joint for interchangeability, and the anode wire, of rouge polished platinum or tungsten 0·03-0·1 mm. in diameter, is mounted on the axis of the cathode cylinder and kept taut by a steel spring. Sharp points on anode and cathode must be avoided in order to prevent spontaneous discharges. A suitable two-stage amplifier followed by a mercury vapour triode is shown in Fig. 179. The valves V_1 and V_2 are of the ordinary 'general purpose' type, and have automatic bias resistances. The mercury valve V_3 must have a separate bias battery, so that it can be adjusted to prevent the arc striking unless a discharge occurs in the counter. The device for stopping the discharge in V_3 is due to R. Jaeger and I. Kluge (*Z. f. Instr.*, **52**, 229 (1932)). The condenser C_4 is charged through the resistance R_8; when an impulse causes an arc to strike in V_3, C_4 discharges through the tube and recording device, after which the arc stops. R_8 is made just large enough to keep the arc from being maintained directly from the battery.

The voltage for the counter is best supplied by a number of high tension batteries in series, and provided with tappings so that the voltage may be adjusted to the requisite value. The range of permissible voltage is quite narrow—10-100 volts—and the sensitivity of the counter may alter in this small range, hence it is essential to keep a check on the voltage, say, by means of an electrostatic voltmeter. For ultra-violet light, e.g.,

$\lambda < 3000$ Å, the cathodes may be of tin, zinc, copper, silver, mercury or cadmium. Ag, Sn and Hg were found to be the most sensitive, since 'dark' rate of the counters was a minimum. The 'dark' rate always present is due partly to cosmic rays and to other electrical disturbances. To prevent oxidation, such cathodes are kept in an atmosphere of nitrogen. Alkali metal cathodes are made by dipping a well amalgamated copper cathode in the appropriate amalgam preserved under xylene. The cathode is then placed in the counter, which is thoroughly pumped out and filled with hydrogen. A discharge of a few microamperes is passed

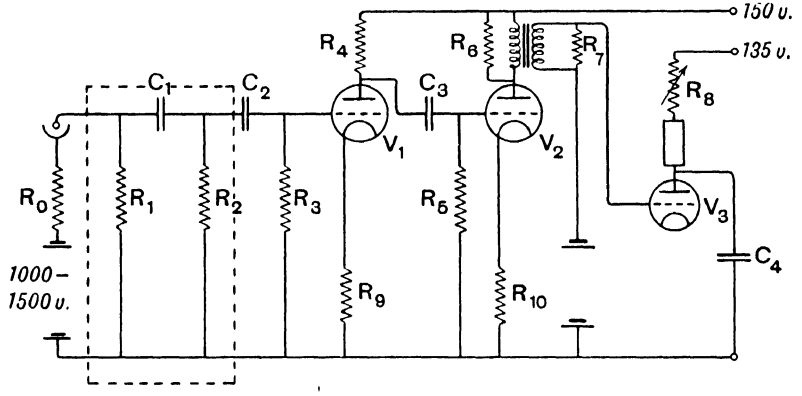


FIG. 179. Circuit for quantum counter. Resistances in megohms, capacities (C) in microfarads. R_0 1000 (*see* N. R. Campbell, *Phil. Mag.*, **22**, 301 (1911)). R_1 30, R_2 0·5, R_3 10, R_4 5, R_5 1, R_6 0·5, R_7 2, R_8 0·1; C_1, C_2 and C_3, 0·01, C_4 1. Transformer ratio 1 : 3.

through the tube, and the alkali metal which has collected on the anode removed by heating the latter red hot. The threshold for Na is 6000 Å for K 6500 and for Cs 7500 Å.

The following are the limitations of such counters (Locker, *loc. cit.*) :

(*a*) Maximum sensitivity 300-400 electrons per sec. This correspond to 5×10^{-7} amp. Higher sensitivity may be obtained by decreasing effective area of cathode.

(*b*) Constant high voltage must be applied to counter tube.

(*c*) Small intensities corresponding to a minimum of 0·05 electron/sec need long periods of observation.

(*d*) Spectral sensitivity of cathode may alter.

Photo-electric Cells

Photo-electric cells suffer from the same disability as chemical actinometers in so far as measurement of radiation intensity is concerned. Since the sensitivity varies rapidly with wavelength, the cell must be ultimatel

calibrated by comparison with a thermopile. Photo-cells are of two types : (*a*) those with metallic cathodes mounted in a vacuum, or in presence of a small pressure of one of the inert gases ; (*b*) those of the surface type, in which the electrons are supplied by cuprous oxide or selenium.

Since the first type are normally made with glass bulbs their use is restricted to the visible region of the spectrum. Such cells are, however, sometimes fitted with quartz windows, and may then be used in the ultra-violet, though sensitivity falls off rapidly with decreasing wavelength. For accurate work the vacuum type is essential, since the photo-current is only then strictly proportional to the intensity. The point of maximum sensitivity varies among the alkali metals from sodium with a peak about 3800 Å to caesium at about 7000 Å. Two typical curves are given for a potassium and caesium cell in Fig. 180. The current generated by the

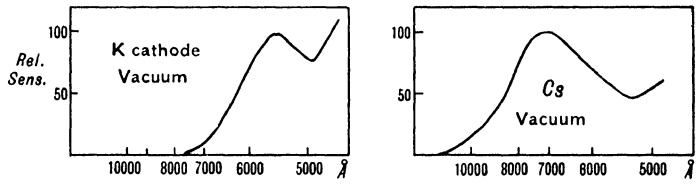


FIG. 180. Spectral sensitivity of potassium and caesium cells.

vacuum cell is small and is normally not easy to amplify. To overcome this difficulty the General Electric Company have sealed a vacuum cell and an electrometer triode valve into one glass envelope. Gas-filled cells are much more sensitive, but on account of the mechanism of the amplification of the primary photo-current, by ionisation, are less steady. They require accurate calibration, as at high applied voltages the relationship between photo-current and intensity of illumination is non-linear. Amplification of the photo-current by a single triode valve dispenses with the need for a sensitive galvanometer. Further details of the amplification circuits will be found in N. R. Campbell and D. Ritchie's book, *Photo-electric Cells* (Pitman).

Weston photronic cell. This is of the dry copper oxide type, having an effective diameter about 1·75 inches. Its internal resistance is about 7000 Ω at zero illumination intensity, falling to 1000 at 210 foot-candles from a tungsten filament at 3000° K. Owing to the resistance decreasing on increasing the intensity of the light, the current-intensity curve is not linear unless the external resistance is low. For example, the percentage deviation from linearity at an intensity of 5 foot-candles is about 15 per cent. with an external resistance of 1000 Ω, the photo current being 7·5 microamps. With an internal resistance of 100 Ω the intensity may be in-

creased to 250 foot-candles, and the deviation is only 6 per cent., at which intensity the current is 337 microamps. The cell is normally fitted with a glass window, but can be fitted with a quartz window, when the sensitivity curve is as shown in Fig. 181. It is usable down to 2500 Å. No figures

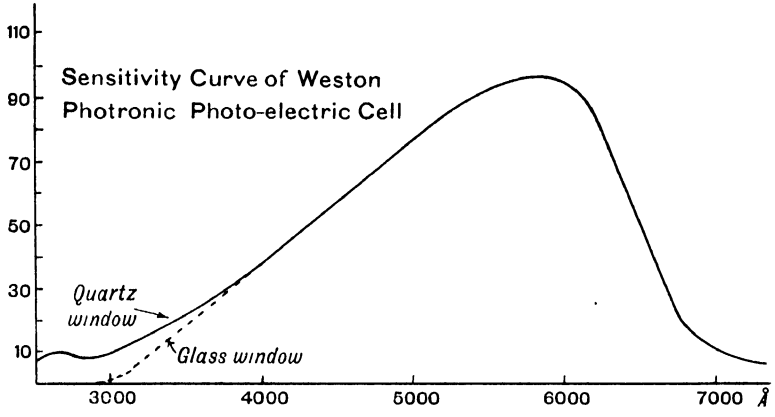


FIG. 181. Spectral sensitivity of copper oxide cell.

of the absolute sensitivity are available, and hence the cell must be calibrated at any given wavelength with a thermopile.

Electro-cell. This is probably of the iron-selenium type, the cell elements being covered by a suitable transparent varnish. The dark

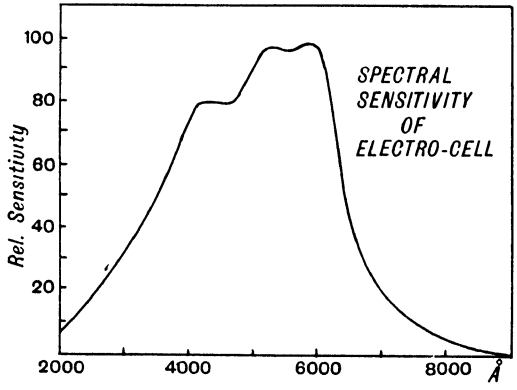


FIG. 182.

resistance is 500-1000 Ω for a 1·75 inch diameter cell. The current in an external resistance of 500 Ω is linear up to 40 foot-candles, and at 5 foot-candles has a value of 20 microamps. The response of the cell falls off in the ultra-violet, but it is still sufficiently sensitive to be useful. The drop is probably due to absorption by the film of protective varnish (Fig. 182).

Bowen's photo-electric photometer. The use of photo-electric cells for measuring radiation intensity is practically confined to the visible region of the spectrum. Cells have been constructed with a fused quartz window with cadmium and sodium cathodes, and a silica cell with a platinum cathode has been described for the measurement of radiation at 2537 Å (M. Zemanski, *Phys. Rev.*, **36**, 919 (1930)). The great disadvantage is that the sensitivity varies rapidly with wavelength, thus making the instrument inconvenient for photochemical purposes. E. J. Bowen (*Proc. Roy. Soc.*, **A, 154,** 349 (1936)) has therefore set up a transparent fluorescent substance in front of the cell, so that ultra-violet and visible light yield a fluorescent radiation which lies in the most sensitive wavelength region of the photo-cell. In order that such an arrangement be satisfactory it is essential that the intensity of the fluorescent radiation should be independent of the magnitude of the quantum exciting fluorescence. Bowen has tried a number of substances, and found that for wavelengths between 2500 and 4360 Å a layer, 1 mm. thick, of crystals of uranyl ammonium sulphate or uranyl potassium sulphate held together with paraffin wax was most suitable. If the crystals are grown in the form of small plates, the paraffin wax may be dispensed with. Table 37 shows the variation of sensitivity with wavelength. The decrease at 3665 Å and 4360 Å is due to incomplete absorption, but a thicker layer would seriously diminish the intensity of fluorescent light owing to scattering. A 1 cm. layer of a solution of 1 gm. of aesculin in 1 litre of water is more satisfactory between 2000 and 3665 Å.

TABLE 37

Sensitivity relative to 3150 Å.

λ (Å)	Uranyl ammonium sulphate	Aesculin
2520	0·98	1 00
2600	1·01	1·00
2670	0·99	0·98
3150	1 00	1·00
3665	0·94	0·98
4050	1 01	—
4360	0·94	—

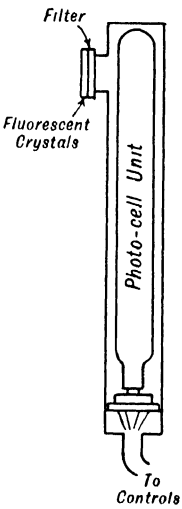


FIG. 183. Photo-cell unit.

Such an arrangement will also be suitable for heterochromatic light if only an approximate estimate of the number of quanta is required. The set-up is shown in Fig. 183, in which a General Electric photo-cell photometer unit (Winch and Machin, *G.E.C. Journal*, **6**, No. 4 (1935)) is employed to measure the intensity of

the fluorescence (Bowen, private communication). This combined unit has the great advantage that the grid current circuit of the electrometer valve and the connecting leads to the photo-cell are *in vacuo*, and there-

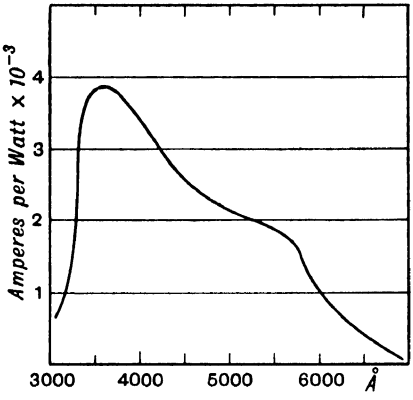


FIG. 184. Spectral sensitivity of cell.

fore troubles due to electrical leakage are obviated. Behind the cell containing the fluorescent crystals is a gelatine filter cutting off wavelengths of $\lambda < 4700$ Å, so that the exciting light shall not affect the photo-cell. In the G.E.C. unit a vacuum potassium cell is employed, the

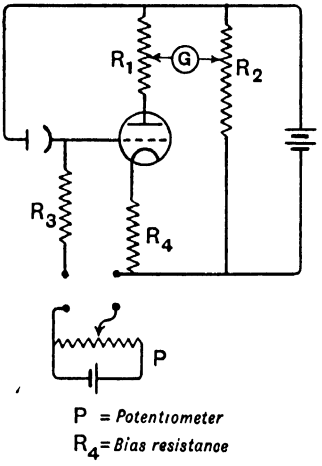


FIG. 185. Simplified circuit diagram.

spectral sensitivity of which is shown in Fig. 184, though gas-filled cells can be fitted with an increase in sensitivity, but with a loss in stability.

The electrometer valve is used as a null instrument, the simplified circuit being shown in Fig. 185. With the cell in the dark and the potentiometer set at zero volts, the galvanometer tappings on R_1 and R_2

are altered until equipotential points are obtained. The cell is then illuminated and the tapping on the potentiometer adjusted until the galvanometer current is brought back to zero.

The complete circuit diagram is shown in Fig. 186. To shield it from electrical disturbances, the whole unit is enclosed in a metal case, but in

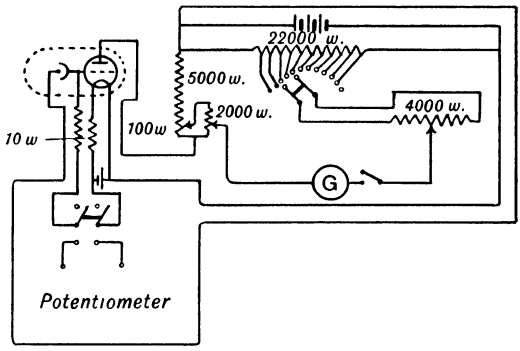


FIG. 186. Theoretical circuit diagram

order to make the unit more convenient to use, the photo-cell and valve may be enclosed in a tube, the necessary connecting wires being enclosed in a flexible metal tube. Bowen estimates that the photometer will just measure an intensity of 5×10^{-2} ergs cm.$^{-2}$ sec.$^{-1}$ This corresponds to $3{\cdot}0 \times 10^{8}$ and $1{\cdot}5 \times 10^{8}$ quanta cm.$^{-2}$ sec.$^{-1}$ at 4500 and 2250 Å respectively.

CHAPTER V

EXPERIMENTAL METHODS FOR THE INVESTIGATION OF CHEMICAL REACTIONS

A. REACTION VESSELS

THE following factors have to be considered when choosing a suitable material for a reaction vessel : (*a*) temperature, (*b*) pressure, (*c*) chemical resistance, and (*d*) in photochemical experiments, light transmission.

1. Vessels of Glass and Silica

The most commonly used material for constructing reaction vessels is glass. Some characteristics of common glasses are summarised in Table 38.

TABLE 38

	Composition	Maximum temperature at which usable, ° C.	Coefficient of expansion, $\times 10^6$
Soda glass - - -	Sodium calcium silicate	350-400	9
Lead glass - - -	Lead silicate	350	9
Jena Combustion glass No. 20 (Schott and Gen.)	Alumo-borosilicate	450-500	5
Pyrex (Corning Glass Works)	Borosilicate	550-600	3
Duran (Schott and Gen.)	Borosilicate	550-600	3
Supremax (Schott and Gen.)	Alumo-borosilicate	700	3
Silica - - - -	SiO_2	1100-1200	0·5

Soda glass is used for ordinary glass apparatus which is not exposed to very high temperature. Lead glass is suitable for sealing in platinum wires : it also joins to soda glass. In the reducing atmosphere of the blow torch it becomes black owing to the reduction of the lead oxide. If oxidised, the black colour disappears. Pyrex, Duran and Supremax glass can only be blown in the oxygen-coal gas blow torch, and silica in the oxygen-hydrogen or oxygen-acetylene flame.

Silica vessels are liable to devitrify if used for long periods at 1100-1200° C., especially if they come in contact with metals in a reducing

atmosphere. The devitrification becomes visible only if the silica is cooled below 300° C. Since crystalline and amorphous silica have different expansion coefficients, devitrified silica becomes brittle.

The expansion coefficient of a glass is of importance if the vessel has to stand sudden changes of temperature or if wires have to be sealed into it. Soda glass is rather sensitive to sudden changes from room temperature to higher temperatures, but a well-blown vessel, even if it contains internal seals, should stand a sudden change to the temperature of liquid air from room temperature without any serious danger of cracking.

Vessels of Pyrex are very much more resistant towards sudden changes of temperature, and can be heated with a blow torch without much preheating. A curious property of silica is its occasional breaking when heated with the oxygen-gas flame instead of the oxygen-hydrogen flame.

Soda glass and Pyrex or Pyrex and silica can only be sealed together through a graded seal made up from 4-10 glass rings of gradually changing composition.

A " home made " joint between soda glass and Pyrex (or Jena) glass can be prepared in the following way. Soda and Pyrex (or Jena) glass are pulverized and mixed in proportions of 4 : 1, 3 : 2, 2 : 3, and 1 : 4. Then the glass mixtures are melted to rods and the rods applied in form of consecutive rings to the tube to be joined.

Crystalline quartz cannot be sealed to fused silica vessels on account of their different coefficients of expansion.

Only tungsten wire can be sealed into Pyrex. Before sealing in, the tungsten wire is heated and rubbed by a rod of potassium nitrite in order to remove superficial oxidation. The wire is then washed and dried with filter paper. Before being sealed in the vessel a thin glass tube, one to two cm. long, is sealed on the wire.

The different kinds of glasses or silica are not attacked by any of the common gases, except by hydrogen fluoride at room temperature. Vapours of alkali metals attack soda glass at temperatures above 200° C. and give it a brownish colour. Such discoloured glass becomes brittle, and therefore it is preferable to use resistance glass when working with alkali vapours. M. Bodenstein (*Z. physik. Chem.*, **13**, 56 (1894) ; **22**, 1 (1897) ; **29**, 295 (1899)) found that at 300° C. and upwards some hydrogen iodide disappears in soft glass, due to a reaction between hydrogen iodide and the glass. Atomic hydrogen as produced by electric discharge at low pressures attacks glass according to E. Heidemann (*Z. physik. Chem.*, **A, 164**, 20 (1933)), and certain volatile silico-hydrogen compounds are formed. Such silanes were occasionally mistaken for triatomic hydrogen, or for NH_3 alleged to have been formed from activated hydrogen and molecular N_2. H. J. Schumacher and G. Stieger (*Z. physik. Chem.*, **B, 7**, 369

(1930)) observed that the chlorine atoms formed in the photochemical reactions of chlorine with hydrogen can react with glass. The nature of the compound thus formed was not ascertained, but it had a marked inhibiting effect on the reaction studied. The same effect was shown with silica. Similarly, iodine atoms, produced in the photochemical dissociation of hydrogen iodide or iodine, might react with silica (G. Brauer, *Z. physik. Chem.*, **B, 174**, 435 (1935)). According to H. J. Schumacher and Frisch (*Z. physik. Chem.*, **B, 37**, 1 (1937)) fluorine oxide attacks glass even at low temperatures, but silica is unaffected.

At ordinary room temperatures glasses and silica are practically impermeable to all gases except helium. With increasing temperatures more and more hydrogen diffuses through the glasses, and especially through silica (W. D. Urry, *J. Am. Chem. Soc.*, **54**, 3887 (1932)). Even oxygen can penetrate silica at higher temperatures.

R. M. Barrer (*J. Chem. Soc.*, 378 (1934)) found the following figures for the diffusion of different gases through silica at atmospheric pressure, the rate (p) being expressed in cm. of Hg pressure increase per minute. For air, the diffusing surface was 120 cm.^{2}; for other gases 80 cm.^{2}, the wall thickness 1·25 mm., and the volume 500 c.c.

TABLE 39

H_2 - - -	193	290	378	496	580	676	800	940° C.
p(cm./mins.) × 10^4	0·013	0·062	0·185	0·50	0·92	1·58	3·17	5·75
Air - - -	422	566	678	796	884° C.			
p(cm./mins.) × 10^5	0·028	0·010	0·184	0·712	1·18			
He - - -	17	281	516	613	756	849	936° C.	
p(cm./mins.) × 10^4	0·0035	0·318	1·55	2·36	3·82	4·54	5·20	

Oxygen and nitrogen diffuse at the same rate as air; argon diffuses much more slowly. The rate of diffusion depends on the pretreatment of the silica. For more data on the passage of gases through glass and silica, cf. Lord Rayleigh (*Proc. Roy. Soc.*, **A, 156**, 351 (1936)) and D. L. Chapman and P. W. Reynolds (*Proc. Roy. Soc.*, **A, 156**, 287 (1936)).

The strong absorption of light by glass which occurs in the region below 3500 Å (see p. 246) makes this material unsuitable for work with ultra-violet radiation. H. Klumb and Th. Haase (*Z. Physik*, **76**, 323 (1932)), S. Sonkin (*Journ. Optical Soc. Am.*, **19**, 65 (1926)) and C. M. Slack (*Journ. Optical Soc. Am.*, **18**, 123 (1929)) have shown that very thin glass windows transmit sufficient ultra-violet light to permit the use of glass vessels. To withstand atmospheric pressure, if the vessel is under vacuum, the windows are constructed as shown in the Fig. 187. This type of window can be made by sucking instead of blowing, and if it is 0·03 mm. thick transmits 80 per cent. of the light at wavelength 2537 Å.

Glass tubes can stand rather higher pressures than is generally assumed. Table 40 shows some data on bursting tests with glass tubes (*Chemical Engineer's Handbook*, McGraw Hill Book Company, New York and London (1934), p. 1794).

TABLE 40

Outside diameter (d_o) in mm.	Inside diameter (d_i) in mm.	Ratio d_o/d_i	Bursting pressure in atmospheres
5·8	0·46	12·60	1200
6·7	0 24	27·90	1100
9·2	3 00	3·06	380
10·4	4·00	2 60	240
3·8	2·42	1·57	283
6·4	4·78	1·34	221

Glass, however, is not a very reliable material for work with high pressure, owing to its occasional breaking without any obvious reason. This might be due to certain strains in the glass arising from the heat treatment while it was being blown.

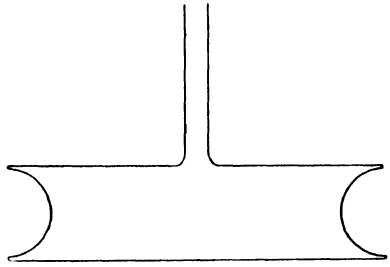


FIG. 187. Glass vessel with thin window.

The use of glass cannot be avoided, since metals usually exert a catalytic effect on the reaction under investigation or are chemically attacked. G. B. Kistiakowsky (*J. Amer. Chem. Soc.*, **50**, 2315 (1928)) investigated the decomposition of HI up to concentration of 7 moles/litre in fused quartz vessels. This concentration corresponds to a pressure of about 300 atmospheres at 300° C. The vessels used for the highest concentrations had a volume of 0·7 c.c., a length of 20 cm. and an internal diameter of 2 mm. The walls of the vessel were 4 mm. thick. Wider vessels with the same internal diameter : wall thickness ratio were unreliable and exploded on account of their thick walls (10 mm.) at considerably lower pressures.

A more elaborate apparatus was used for the investigation of the thermal decomposition of N_2O (cf. p. 324) at pressures up to 10 atmospheres in silica vessels by N. Nagasako and M. Volmer (*Z. physik. Chem.*, **B**, **10**, 414 (1930)). Ten atmospheres is about the highest pressure that can be safely attained using non-capillary reaction vessels of glass or silica, which are connected to storage vessels, valves and the like. If the pressures inside and outside a glass vessel are equal, rather higher pressures can be maintained in the vessel without the danger of its being broken. The experimental arrangement for

this method of pressure compensation is described on p. 325. According to W. A. Bone and L. Outridge (*Proc. Roy. Soc.*, **A, 157**, 234 (1936)) explosions can be carried out safely in 'red-line' Jena glass at 130 mm. pressure in C_2H_4—O_2 or C_2H_2—O_2 mixtures or at 760 mm. if the explosive mixtures are diluted with He, A or N_2.

2. Vessels of Refractory Materials

For temperatures above 1200° C. reaction vessels of refractory material must be used. These materials contain different amounts of Al_2O_3, CaO and SiO_2. The disadvantage of vessels of such materials is that their form cannot be changed by blowing. It is possible, however, to close or join thin tubes of porcelain in the oxygen-hydrogen blow torch. Good refractory materials stay sufficiently gas-tight up to the highest temperature, but they are not suitable for high vacuum work. The softening point of hard porcelain at 2 atmospheres pressure is 1400-1500° C. It is gas-tight up to 1200° C. Pythagorasmass (Haldenwanger, Berlin-Spandau) is gas-tight to 1600° C.; its softening point is 1700° C. Sinter-Korund (H. Gerdien, *Z. Elektrochem.*, **39**, 130 (1933))—Al_2O_3—is gas-tight to 1700° C. and softens at 2030° C.

3. Metal Vessels for High Pressures

Most of the kinetic measurements at high pressures, and especially at elevated temperatures, are made in metal vessels. Mild steel is a common material for pressures up to several hundred atmospheres and 500° C. At elevated temperatures steel is attacked by CO, iron carbonyl being formed. It is also weakened by hydrogen, since at high pressures and temperatures this gas is soluble in steel and removes carbon from the steel. These effects can be counteracted by making a lining of a suitable material, such as enamel, copper or aluminium, or by using chromium steel.

(*a*) *The wall thickness* for cylindrical reaction vessels may be calculated from the Barlow formula,

$$P = \frac{S}{1}\left(1 - \frac{1}{R}\right), \qquad \text{.....(1)}$$

where S = maximum allowable fibre stress, P = internal pressure, $R = \frac{r_i}{r_0}$ = ratio of inner radius to outer radius ($t = r_0 - r_i$ = wall thickness). The fibre stress allowed depends on the tensile strength of the material to be used. For a safety factor of 5 it is taken as one-fifth of the tensile strength.

The tensile strength and maximum allowable fibre stress of some materials at 20° C. are listed in Table 41.

TABLE 41

	Tensile strength		Maximum allowable fibre stress	
	lb./sq. in.	kg./cm.²	lb./sq. in.	kg./cm.²
Brass (60 per cent. Cu, 39 per cent. Zn, 1 per cent. Sn)	57000	4000	11400	800
Copper	4600	3240	9200	648
Steel, 0·24 per cent. C.	88500	6230	17700	1246
Steel, 0·45 per. cent C.	104000	7320	20800	1464

The dimensions of reaction vessels of mild steel with 0·24 per cent. C. suitable for use at different pressures are listed in Table 42.

TABLE 42

Pressure in atmospheres (kg./cm.²)	100	200	400	1000
$R = r_i/r_0$	0 93	0·86	0·72	0·30
For $r_i = 12·5$ mm. :				
Outer radius (r_0)	13·5	14·5	17·5	42
Wall thickness (t)	1	2	5	29 5
For $r_i = 25·0$ mm. :				
Outer radius (r_0)	24	29	35	84
Wall thickness (t)	2	4	10	59
For $r_i = 50$ mm. :				
Outer radius (r_0)	54	58	70	167
Wall thickness (t)	4	8	20	117

Copper tubes will stand pressures up to 1000 atmospheres if the ratio of internal and external diameter is 1 : 4.

Working with high pressure equipment requires the utmost care. All apparatus should be tested before use at a pressure 50 per cent. higher than the operating pressure. If the equipment is to be used at higher temperatures, the testing pressure should be correspondingly higher. (For further information cf. E. B. Maxted, *Chem. and Ind.*, **45**, 366 (1926).)

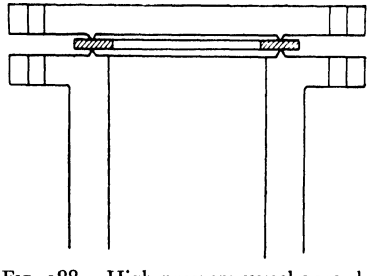


FIG. 188. High pressure vessel according to Ipatieff.

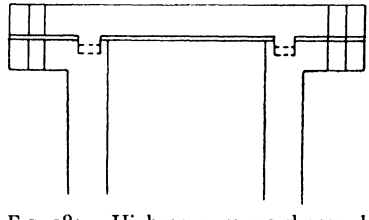


FIG. 189. High pressure vessel according to Willstatter and Ungar.

(*b*) *Gas-tight joints between the cover and the vessel* can be constructed by different methods, shown in Figs. 188-190.

V. N. Ipatieff's method. The knife edges of the cover and of the vessel (slightly exaggerated on the drawing) are exactly opposite each other, and the soft copper gasket is placed each time in the same position to assure tight closure in successive experiments.

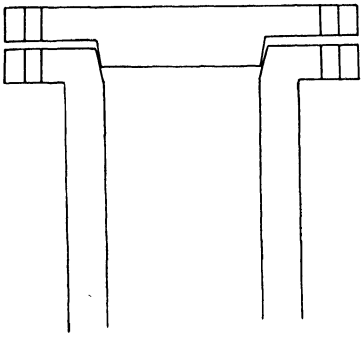


FIG. 190. High pressure vessel according to Haber and Le Rossignol.

Method of Willstatter and Ungar. The washer of lead, copper or aluminium, or, at low temperature, of vulcanised fibre, is arranged in the recess in order to prevent its being pushed aside by the gas. A number of concentric grooves machined in the recess on top of the vessel and in the projection of the cover ensure specially tight closure.

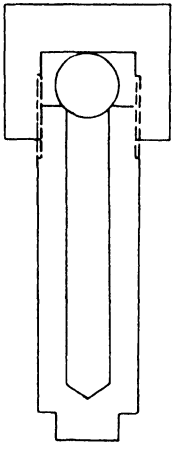


FIG. 191. Small pressure vessel.

Method of F. Haber and R. Le Rossignol (*Z. f. Elektrochemie*, **19**, 57 (1913)). The cone of the cover has an angle of about 7°. The angle of the aperture is two or three degrees larger. A tight closure is obtained without washers, since under the pressure of the bolts, cone and aperture touch along a line. Instead of using bolts and nuts the cover can be pressed on the vessel in each case by means of thread and nut, as shown in Fig. 191.

A very simple method of closing a high pressure vessel is shown in Fig. 191. This may be used with small vessels if no valves or other fittings are required. Closure is obtained by pressing a ball-bearing of suitable diameter in the opening of the vessel.

(*c*) *Fittings.* Demountable connections between the reaction vessel and its fittings, such as valves and manometers, and between tubes are made according to the same methods as those described for the closure of vessels. The arrangement for connecting tubes by means of a cone and

nut (Fig. 192) are self-explanatory. Another type of connection is shown in Figs. 193 and 194, and P. W. Bridgman's connection, capable of with-

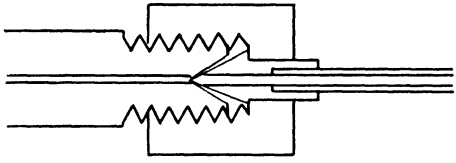


FIG. 192. High pressure connection of tubes.

standing pressures even above 1000 atmospheres, in Fig. 195 (*Proc. Amer. Acad.*, **49**, 627 (1914)).

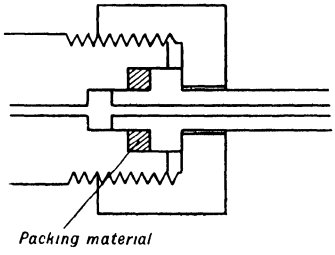


FIG. 193. High pressure connection of tubes according to Amagat.

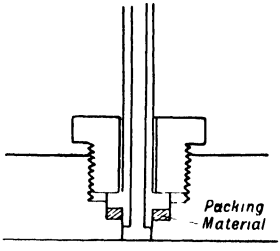


FIG. 194. Connection between a tube and the reaction vessel according to Amagat.

A convenient valve for high pressure work is described by R. Le Rossignol (*Chemiker Zeitung*, **32**, 820 (1908)), and is shown in a somewhat modified

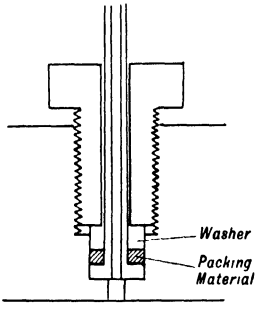


FIG. 195. Bridgman's connection.

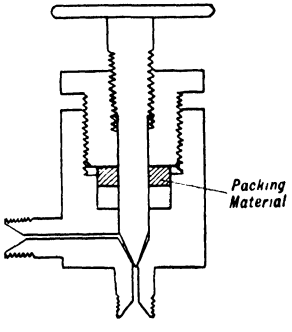


FIG. 196. High pressure valve.

form in Fig. 196. The needle of the valve is made of hardened steel and its body of mild steel. The method of packing in the valve is the same as that of the connection shown in Fig. 195. Again the angle of the needle is smaller than that of the hole. A long and slim needle ensures fine adjustment of pressure.

It is often necessary to have electric connections in the pressure vessel. According to F. Haber and R. Le Rossignol these can be made by soldering the wire to a copper or brass disc (8 mm. in diameter and 3 mm. thick), and insulating the disc from the reaction vessel by vulcanised fibre or rubber washers as shown in Fig. 197. To prevent the wire touching the screw or the wall of the vessel, short glass or ebonite tubes are fitted into the hole between the screw and the wall. This type of connection will not stand elevated temperatures. H. J. Welbergen (*J. Sci. Instr.*, **10**, 247 (1933)) describes a type of insulation which can be used to 200° C., and

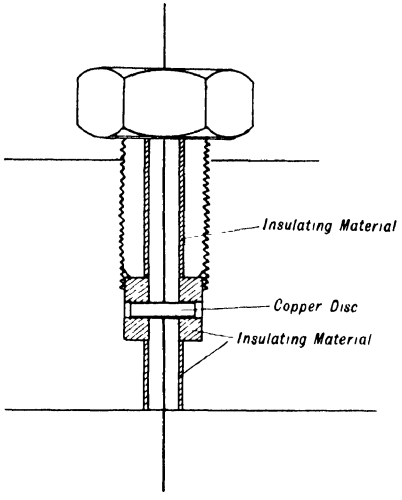


FIG. 197. Electric connection.

up to pressures as high as 3000 atmospheres. The insulation is secured by a conical ground joint of Pyrex glass sealed between material made from a special chromium steel (24 per cent. Cr). Occasionally a motor car sparking plug can be used as an insulated connection for pressure vessels.

High pressure vessels are either heated from outside or from inside. The latter method is especially suitable for the investigation of catalytic reactions. The heating is then arranged so as to heat the catalyst only, whereas the walls of the high pressure vessel may be cooled. A typical high pressure vessel of Messrs. A. Hofer, Muhlheim, Ruhr, with inner heating, is shown in Fig. 198. The gas passes over the catalyst in the inside tube, which is heated electrically, the temperature being measured by a thermocouple. The space between the inner tube and the wall of the pressure vessel is filled with inert gas at the same pressure as that in the reaction vessel, and the insulation of lead-in wires is carried out by the method of F. Haber and R. Le Rossignol.

4. Wall Reactions

A homogeneous gas reaction involves only particles (atoms, molecules and ions) in the free gaseous state ; any reaction with particles adsorbed on or absorbed and dissolved in solids or liquids or with particles of solids or liquids is termed a heterogeneous reaction. Even in the absence of an added liquid or solid, the possibility of a heterogeneous reaction occurring on the walls of the reaction vessel remains. It is of great importance to determine what part is played by the heterogeneous wall reaction in any gas reaction under investigation, and no further experiments should be made until this question is settled definitely. If the main interest is in the homogeneous reaction, it is necessary to find experimental conditions under which the rate of the wall reaction is small compared with that of the homogeneous reaction.

The usual method employed to determine the part played by a heterogeneous reaction is the variation of the surface : volume ratio of the reaction vessel. The (relative) velocity of a homogeneous reaction is independent of the volume or surface of the vessel ; that of a heterogeneous reaction is directly proportional to surface and inversely proportional to the volume. Consequently with increasing surface : volume ratio the influence of the heterogeneous reaction will be increased. The surface : volume ratio of a reaction vessel can be changed by changing the dimensions of the vessel, by changing the shape of the vessel, or by packing the vessel with the same material as that of the vessel itself. According

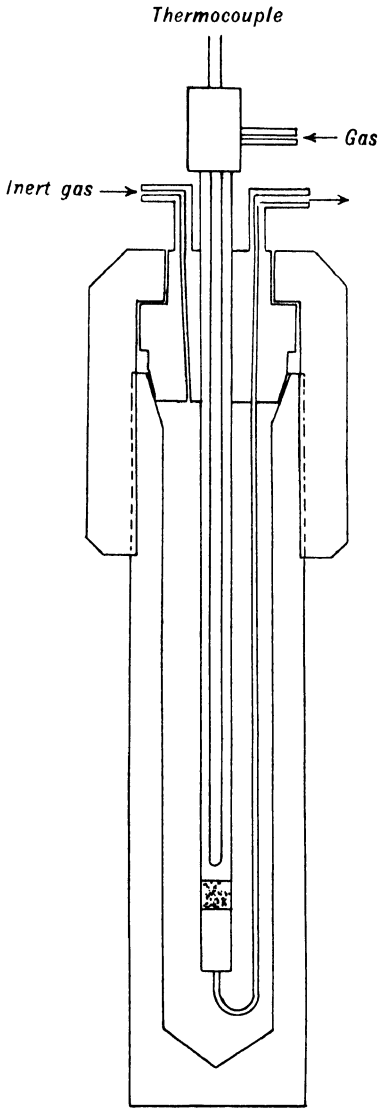


FIG. 198. High pressure reaction vessel with internal heating.

to the first two methods the surface : volume ratio (s/v) cannot be easily changed by a factor of more than ten, as is shown by the following examples. The s/v for a sphere is 3/radius and the value s/v can only be increased in the same proportion as the radius is decreased. s/v for a cylinder is 2/radius. Therefore if a spherical vessel of the radius r_1 is replaced by a spiral tube with a radius r_2 of the same volume, s/v changes by the factor $2r_1/3r_2$. A much higher variation of s/v is possible by packing the vessel with coarse powder, irregular pieces or tubes of the same material as the vessel. Packing the vessel with coarse powder is a rather unreliable method. If the vessel is half filled with powder only the surface of those powder particles is effective which are in the top layer, and the heterogeneous reaction occurring on the surface of the particles in the bulk may not become apparent owing to slow diffusion. It is then difficult to compute the fraction of heterogeneous reaction occurring in the empty vessel.

The velocity of a homogeneous reaction is not always increased by a concurrent heterogeneous reaction, but may also be reduced by a wall reaction. In certain essentially homogeneous chain reactions the chains are initiated and branch in the gas phase, and are broken by the wall. The velocity of such reactions decreases as the surface : volume ratio increases. In other chain reactions the chains are both initiated and broken by the walls, and it might happen that these two effects occur simultaneously and give an apparently paradoxical result. This is well illustrated in the combination of hydrogen and oxygen (W. Garstrang and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A**, **134**, 2 (1931)). If the reaction vessel is packed with powdered material an increase in the reaction velocity is observed, whereas on packing the vessel with tubes the velocity is diminished. The explanation is that the tubular packing reduces the homogeneous chain reaction by stopping the chains on the walls, while on the largely increased surface of the powdered material a fast heterogeneous reaction sets in, though the homogeneous reaction has been completely stopped. If broken glass is used to increase the surface, it must be remembered that the surface of broken glass is of a different nature from the surface of fire-polished glass. For example, according to R. W. Wood (*Proc. Roy. Soc.*, **A**, **102**, 1 (1922)), the recombination of the hydrogen atoms produced in electric discharges is strongly catalysed by the surface of broken or ground glass, but is unaffected by fire-polished glass.

The most convenient way of packing a reaction vessel is to use thin tubing of the same length as the vessel. The tubes are introduced one after the other through the inlet tube and placed parallel to the axis of the vessel. In order to prevent catalysis on the sharp edges of [illegible] to smooth the edges in a flame. In calculating the

surface : volume ratio, account must be taken of the fact that both the inner and outer surfaces of the tubes are available, and that the volume is reduced by that of the tubes themselves. The velocity of the homogeneous reaction is then found by plotting velocity of the whole reaction against surface : volume ratio and extrapolating to $s/v = 0$. This method is only reliable if it is ascertained that the packing material has had the same history as the reaction vessel regarding heat treatment, cleaning and the like. It is often found that glass or silica showing signs of divitrification induces a heterogeneous reaction more readily than faultless material.

In order to obtain the homogeneous reaction unaccompanied by the heterogeneous reaction, a thorough cleaning of the reaction vessel will help. Grease, dust of any organic material is effectively removed by chromic acid from glass, silica or porcelain vessels. Chromic acid is prepared by saturating concentrated sulphuric acid with potassium bichromate. The solution is rather slow, but the chromic acid thus prepared is more effective than a mixture of sulphuric acid and a concentrated aqueous solution of potassium bichromate. Chromic acid is only effective as long as its colour is red or brown. A greenish colour shows that most of the chromate has been reduced. It is advisable to remove all impurities, grease, etc., from the vessel to be cleaned as far as possible before using chromic acid. If hot chromic acid is applied, the vessels can be emptied after an hour. The vessel is then rinsed several times with distilled water and dried. It is not advisable to remove the water, before drying, with alcohol or ether, since these liquids nearly always contain traces of organic matter which might char and give rise to a heterogeneous reaction. The same trouble might arise if the chromic acid is not completely removed by washing and traces of chromate are left in the reaction vessel. For this reason fuming nitric acid is to be preferred to chromic acid.

Fused silica vessels can be further cleaned by etching with 5 per cent. hydrofluoric acid.

If cleaning has not eliminated the heterogeneous reaction the walls may be poisoned. Hydrogen atoms produced in an electric discharge recombine to molecules almost exclusively on the walls as a heterogeneous reaction. This wall reaction can be eliminated by addition of water vapour (K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924); R. W. Wood, *Proc. Roy. Soc.*, **A, 102**, 1 (1923)), or by covering the walls with phosphoric acid (H. v. Wartenberg and G. R. Schultze, *Z. physik. Chem.*, **B, 2**, 1 (1929)) or KCl (K. H. Geib and E. W. R. Steacie, *Z. physik. Chem.*, **B, 29**, 215 (1935)).

The wall reaction is often diminished by changing the material of the reaction vessel. According to H. S. Taylor (*J. Phys. Chem.*, **28**, 984 (1924))

there is a heterogeneous decomposition of HI in Pyrex vessels, but not in silica vessels.

Since a heterogeneous reaction has often a smaller temperature coefficient and is less dependent on the pressure than the corresponding homogeneous reaction, the homogeneous reaction may be predominant at higher temperatures and pressures. Unfortunately the rate of the reaction is often so fast under these conditions that no accurate measurements can be made.

Silica reaction vessels should not be heated to high temperatures when in contact with metals. Metals such as iron or nickel will diffuse into the quartz and give rise to heterogeneous reactions, even when present in minute quantities. It is practically impossible to remove such impurities. For this reason, if silica vessels are heated in electric furnaces made of iron tubes, a tube of clay, porcelain or other refractory material should be placed round the vessel to avoid direct contact with the iron.

A similar contamination of silica vessels can happen if impure hydrogen has been used in the blow-pipe flame. Commercial hydrogen, unless prepared by electrolysis, may contain carbon monoxide, which can form iron carbonyl with the material of the cylinder. These compounds are decomposed during the process of blowing, traces of iron being deposited in the silica.

B. PROGRESS OF THE REACTION WITH TIME

The procedure for investigating the progress of the reaction with time is different for static and flow systems, but in both cases it is necessary to measure a certain parameter which changes as the reaction proceeds. In static systems this parameter is measured after the reaction has proceeded for a certain time. This can be done either while the reaction is still in progress or after it has been stopped by suitable means. The former is the more desirable way, since it is possible to make more measurements in a given time than by the latter method. In flow systems the progress of the reaction is followed by measuring some parameter of the products leaving the reaction space at different velocities of flow, or by measuring the parameter at different places of the reaction space at constant velocity of flow.

The parameter which is chosen to characterise the progress of the reaction may be connected, in principle, with any physical or chemical property of the substances involved in or produced during the reaction. Thus a great variety of methods is available for kinetical investigation. The most direct, but not the simplest, method, however, is always the actual chemical analysis of the reaction mixture, and chemical analysis

should in every case supplement any other method. In the following, some typical methods will be discussed with examples of their application.

1. Manometric Methods

The most used method for following reactions is the measurement of pressure. It is applicable in static experiments to reactions in which the number of molecules is changing, and to those reactions not involving a

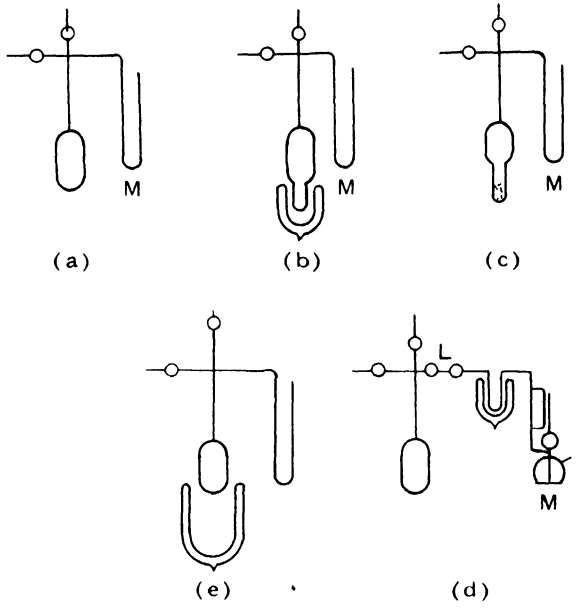


FIG. 199. Manometric methods.
M = manometer.

(*a*) Direct measurement of pressure.
(*b*) Reaction product continuously removed by condensation.
(*c*) Reaction product continuously removed by absorption.
(*d*) Capillary lock method.
(*e*) Condensable reaction partners removed intermittently.

change of the number of the molecules in which one of the reaction products can be removed easily (e.g. by condensation or absorption). In both cases the pressure measurement can be made while the reaction is in progress, as shown schematically in Figs. 199 (*a*)-(*e*). The disadvantage of the arrangements (*b*) and (*c*) is that the whole of the reaction vessel cannot always be kept at a uniform temperature (the absorbent, e.g. P_2O_5 for H_2O, must be kept cool even if the vessel is heated), and therefore these methods should not be used for investigating homogeneous gas reactions. Both methods can, however, be used for catalytic reactions (especially on

heated filaments) and for photochemical reactions if the reaction vessel is kept at constant temperature. If water is removed continuously from the reaction vessel by P_2O_5, it is necessary to take into account the fact that it takes some time for the water vapour to diffuse from the reaction vessel to the P_2O_5, and that thus there is always a stationary residual pressure of water in the reaction vessel (H.W. Melville, *Proc. Roy. Soc.*, **A, 142,** 524 (1933)). This pressure (p) is equal to the product of the reaction rate and diffusion time, if the reaction rate is expressed by increase of water pressure per second and the diffusion time (t) is calculated from the equation (45), p. 15,

$$x^2 = 2Dt,$$

with x as the distance between reaction vessel and the drying agent. On the basis of these considerations it is possible to design the apparatus in such a way as to keep the stationary pressure of water sufficiently low. Another method for removing continuously the reaction product is the absorption of the HCl formed in the reaction $H_2 + Cl_2 = 2HCl$ by water (D. L. Chapman, *Journ. Chem. Soc.*, **123,** 3002 (1923)).

According to method (*d*) the pressure in the reaction vessel is not measured directly, but the pressure in a certain volume exerted by known small samples of gas extracted from the reaction vessel (e.g. L. and A. Farkas, *Naturwiss*, **22,** 218 (1934)). Since the capillary lock L can be made very small compared with the volume of the reaction vessel, the change of pressure in the vessel caused by the extraction of the samples can be regarded as negligible. (In accurate measurements naturally this change in pressure can be taken into account.) This method is applicable to the above-mentioned types of reactions, and to those in which no change occurs in the number of molecules but one of the reactants is condensable. The following figures may serve to illustrate the dimensions of the actual apparatus and the pressure range in which it can be used. Volume of reaction vessel, 50 c.c. ; volume of capillary lock, 0·1 c.c. ; volume of McLeod manometer, including connections to tap L, 100 c.c. : ratio of pressure in vessel to pressure measured 1000 : 1 ; minimum pressure required in the reaction vessel, 1 mm.

Fig. 199 (*e*) shows an arrangement in which the reaction is stopped and the condensable reactants and products are removed before each pressure measurement. After the pressure measurement the reaction is continued. An example of this method is the investigation of M. Bodenstein and W. Dux (*Z. physik. Chem.*, **85,** 297 (1913)) on the photo-reaction of hydrogen and chlorine. After the reaction had proceeded for some time, illumination was stopped and chlorine and hydrochloride removed by dipping the reaction vessel in liquid air ; the residual pressure of hydrogen was then measured.

For the arrangements shown in Figs. 199 (*a*), (*b*), (*c*) and (*e*) manometers of small volume must be employed to reduce dead space : i.e. capillary manometers filled with Hg or oil, Bourdon-, membrane-, or Pirani-gauges, etc., depending on the pressure range and on the nature of gases involved. Care must be taken that diffusion should establish uniformity of gas composition throughout the system before analysis is attempted. The dead space should in general be ' flushed out ' to reduce the time required for analysis.

Using the method of pressure measurement, it should be always borne in mind that the pressure changes alone do not always give reliable information about the chemical changes during the reaction if complicated molecules are involved. M. W. Travers has pointed out (*Trans. Faraday Soc.*, **33**, 1342 (1937)) that it is not sufficient to supplement the pressure measurements by a few analyses, since in the more complicated reactions intermediate compounds are formed in measurable quantities which, however, disappear as the reaction proceeds further. Some excellent examples of complete chemical analysis performed during different phases of the reaction may be found in the investigations of W. A. Bone and collaborators on oxidation reactions (cf. e.g. W. A. Bone, A. E. Haffner and H. F. Rance, *Proc. Roy. Soc.*, **A**, **143**, 16 (1933)).

2. Thermal Conductivity Methods

(*a*) *General.* Table 6 shows that the heat conductivities of the various gases are sufficiently different to allow the measurement of this property to be used as a means of following the course of certain reactions. This method is especially suitable for reactions involving the production or consumption of hydrogen, since the heat conductivity of hydrogen is 5-10 times larger than that of any other gas (except the inert gases). At low pressures, when the thermal conductivity depends on pressure, the heat conductivities are no longer in the ratio shown in Table 6. At very low pressures, when the mean path is commensurable with the dimensions of the vessel in which the thermal conductivity is measured, the thermal conductivity is given by formula (51), p. 18,

$$k = \frac{aC_v}{\sqrt{2\pi M\mathbf{R}T}}\, p. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In this pressure region the large difference between the thermal conductivities of hydrogen and the other gases disappears, since the accommodation coefficient (a) for H_2 is of the order 0·2-0·3 (for Pt, Ni, etc.), whereas that of the heavier gases is near unity.

The experimental technique for the determination of thermal conductivity is modified in several respects if applied to kinetic measurements. No absolute values are required, since the gauge is calibrated empirically. Thus exact determinations of end losses, losses by radiation, can be neglected. It is often desirable to reduce the amount of gas necessary for one determination as much as possible. Consequently small vessels are used.

The general principle of constructing vessels for thermal conductivity cells is the same as that for designing Pirani gauges (p. 77). There are some additional features. Wide vessels and pressures above 50-100 mm. Hg may cause convection currents. A horizontal arrangement of the vessels helps to eliminate convection, though this arrangement is not always practical, especially if the vessel has to be kept at low temperatures in Dewar flasks.

Platinum is generally used for wires of thermal conductivity cells. Nickel or tungsten are just as suitable, except when these metals are attacked chemically. In certain cases their higher temperature coefficient of resistance is of advantage. The thickness of the wire in the cell depends on the pressure range to be employed. If the cell is to work under conditions in which the heat conductivity is independent of the pressure, the diameter of the wire has to be made larger, about 10 times, than the mean free path. Thus, for example, with H_2 at 50 mm. pressure the mean free path is about 0·002 mm., and a wire of 0·02 mm. thick can be used. Wires thicker than 0·1 mm. should not be used, since the resistance of a wire is inversely proportional to the square of its diameter, and the measurement of low resistances is inaccurate unless special equipment for this purpose is available. The resistance of the filament can be considerably increased by using ' coiled-coiled ' tungsten wire as in incandescent lamps (J. L. Bolland and H. W. Melville, *Trans. Faraday Soc.*, **33**, 1316 (1937)). If the cell is worked at low pressures thin wires are required, in order to keep the heat capacity of the wire down to a minimum. At low pressures, owing to the poor heat conductivity, relatively low currents are used to maintain a given temperature difference. At pressures around several hundredths of a millimetre the diameter of the wire should not exceed 0·01-0·02 mm., in the pressure range of 0·001 mm. of Hg, 0·005 mm. The lengths of the cells may vary from a few centimetres to 10 or 20 centimetres. It is not advisable to use cells with very short wires, since through the end losses the temperature distribution along the wire might cease to be uniform, and thus the temperature of the middle portion of the wire might become very much higher than the ' average ' temperature calculated from the total resistance (cf. p. 345).

(*b*) *Some examples of application.* What has been said about the electric circuit for Pirani gauges (p. 79) holds good also for thermal conductivity cells. The 'constant voltage-variable resistance' and the 'constant resistance-variable voltage' method are shown diagrammatically in Figs. 200 and 201.

According to the first of these methods a certain constant voltage is applied to the filament, and its resistance is measured as a function of the conductivity of the gas (Fig. 200). In practice the voltage across the cell does not remain constant if the thermal conductivity and the temperature

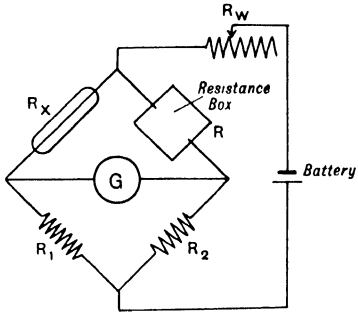


FIG. 200. Constant voltage-variable resistance method.
G = galvanometer.

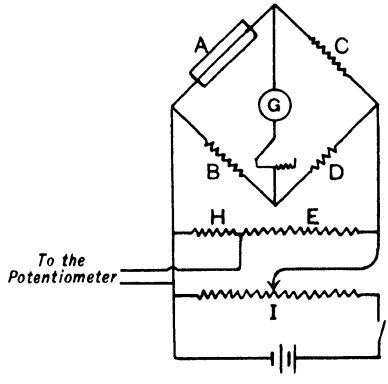


FIG. 201. Constant resistance-variable voltage method.
G = galvanometer.

of the filament changes, since a resistance (R_w) is used to control the heating current, and hence the voltage across the cell is given by

$$R_x E_1 (R_x + R_1 + R_w).$$

The sensitivity of the arrangement is somewhat increased by taking R_w larger than R_x. The resistance of the filament is measured by the Wheatstone bridge. The ratio of the resistances R_1 and R_2 is chosen in such a way as to prevent high currents from flowing through the resistance box (R). The highest sensitivity of the Wheatstone bridge is obtained if all the resistances are of the same order of magnitude. Therefore the resistance should be about the same as that of the thermal conductivity cell, and the ratio not larger than necessary.

The wiring diagram of the constant resistance-variable voltage method is shown in Fig. 201. The Wheatstone bridge (*ACBD*) is used to check the resistance of the filament (*A*), while the heating current is being adjusted by the variable resistance (*I*). The voltage across the bridge is measured by the potentiometer. The resistances *H* and *E* are large compared

with *A*, *B*, *C*, *D*. Occasionally it is found that this method is of advantage when compared with the variable resistance-constant voltage method, although it requires more electrical apparatus.

A good example of the use of the thermal conductivity method is the analysis of ortho- and parahydrogen mixtures, according to K. F. Bonhoeffer and P. Harteck (cf. p. 190). A thermal conductivity gauge suitable for the analysis of mixtures of light and heavy hydrogen and of certain deuterised hydrocarbons is described by N. R. Trenner (*J. Chem. Phys.*, **5**, 382 (1937)), Fig. 202. The gauge consists of a 0·02 mm. platinum filament (*A*) stretched axially in a 3·2 mm. hole bored through the axis of a 13 mm. brass rod (*B*). One end of the gauge is closed by a brass plug (*E*), the other by a Pyrex ground joint (*G*). The filament is kept taut by a small tungsten spring (*F*), and held in the axial position by means of a bakelite bushing (*C*), through which the upper lead-in wire passes. The cell is surrounded by a frame of insulating material with platinum wire (No. 28, B. and S.) wound on it. This coil serves as the compensator wire *B* (Fig. 201), and has the same resistance and temperature coefficient as the wire of the gauge *A*. The resistance of *A* is 65 ohm at 26° C. *C* and *D* (Fig. 201) are two manganin resistance coils, to match the resistance of the gauge at 46° C. (=69·5 ohms) and that of coil *B* respectively. The gauge and all three resistances are immersed in a thermostat. The bridge is balanced if the filament of the gauge is heated to a temperature 20° higher than that of the thermostat. The heating voltage is adjusted by the voltage divider *I*, which consists of 33 metres of manganin wire (resistance = 100 ohms) wound on a grooved drum of insulating material and provided with a suitable sliding contact. The procedure for analysis is as follows :

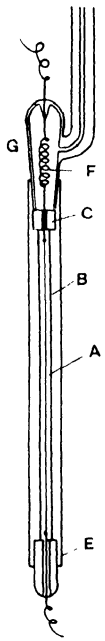


FIG. 202. Heat conductivity cell according to Trenner.

The gauge is filled with gas to be analysed, to a pressure between 200 and 230 mm., adjusted with an accuracy of 0·2 mm. Then the voltage is adjusted to balance the bridge, and the voltage measured across the bridge by a sensitive potentiometer. The calibration is done empirically, and is expressed by the ratio $R = E'/E_1$, where E' and E_1 is the voltage necessary to balance the bridge if the gauge is filled with a gas of known composition and with one component respectively. The calibration curves are shown for mixtures of light

and heavy hydrogen on Fig. 203; and for mixtures of some pure and deuterised hydrocarbons on Fig. 204.

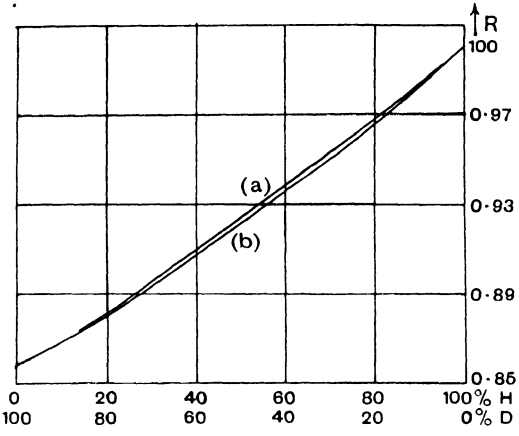


FIG. 203. Calibration curve for
(*a*) equilibrium mixture $H_2 + D_2 + 2HD$
(*b*) mechanical mixture $H_2 + D_2$

An interesting application of the thermal conductivity method is the measurement of the velocity of recombination of hydrogen atoms as described by H. Senftleben and O. Riechemeier (*Ann. der Physik* [**5**], **6**, 105 (1930); *Physik. Z.*, **30**, 745 (1929)). If a mixture of hydrogen and mercury vapour is illuminated with the light of wavelength 2537Å from a mercury lamp, hydrogen atoms are produced from molecules by collisions with excited mercury atoms. The atoms recombine to molecules, but in the stationary state a certain concentration of atoms is maintained. The gas containing atoms has a different thermal conductivity than undissociated hydrogen, and thus the change in the thermal conductivity can be used as a measure of the concentration of atoms. Recombination of the atoms is followed by determining the change in the atom concentration after the mercury light is cut off. The electric circuit is shown in Fig. 205. W_d is the thermal conductivity cell, W_v a fixed resistance corresponding to the resistance of the filament in the thermal conductivity cell; $W_v = 1{\cdot}25 \times$ resistance of the filament of the thermal conductivity cell at the temperature of the wall(W_0). W_1 and W_2 are two equal resis-

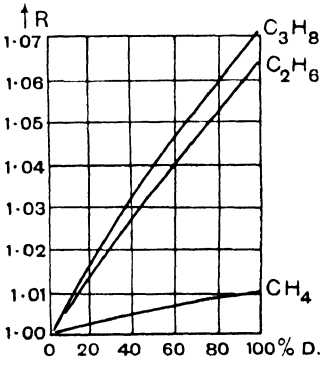


FIG. 204 Calibration curves for methane, ethane and propane.

tance boxes. The bridge is balanced by varying the resistance W_h, the exact value of which is determined in a separate bridge B_2. Through change of thermal conductivity the bridge B_1 is thrown out of balance, and the deviation of the sensitive ' Saiten ' galvanometer S (sensitivity 10^{-6} volt) registered photographically, is a measure of the change in the thermal conductivity, as is shown by the following considerations.

If i_d is the heating current through the filament in the thermal conductivity cell, β the temperature coefficient of its resistance, ΔT the

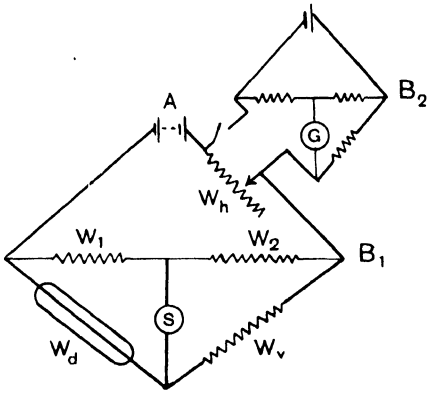


FIG. 205. Electric circuit for measuring the concentration of atomic hydrogen according to the heat conductivity method.

temperature difference between the temperature of the filament and the wall, and λ the thermal conductivity in arbitrary units, then

$$i^2_d W_d = \lambda dT = \lambda (W_d - W_0)/W_0\beta. \quad \ldots\ldots (3)$$

If λ changes by $d\lambda$, W_d can be kept constant by varying W_h. Then i_d changes by di_d, and we obtain by differentiating (3),

$$\frac{d\lambda}{\lambda} = \frac{2di_d}{i_d}. \quad \ldots\ldots (4)$$

Since i_d is proportional to the total current i,

$$i = E/W + W_h \quad \ldots\ldots (5)$$

$$\left(E = \text{voltage of battery } A,\ \frac{1}{W} = \frac{1}{W_1 + W_2} + \frac{1}{W_d + W_h}\right),$$

$$\frac{di_d}{i_d} = \frac{di}{i} = -\frac{dW_h}{W + W_h}. \quad \ldots\ldots (6)$$

The deflection of the galvanometer is found empirically to be proportional to a small variation of W_h, consequently the relative change in the

thermal conductivity is, in fact, proportional to the deflection of the galvanometer.

For small concentrations of atoms,

$$\frac{d\lambda}{\lambda} = 2\alpha\left(\frac{\lambda_a}{\lambda} - 1\right), \quad \ldots\ldots(7)$$

where α is the degree of dissociation (α = molecules dissociated : molecules undissociated), and λ_a the thermal conductivity of the atoms. The theoretical calculation of this quality and the dependence of the thermal conductivity on pressure will not be described here. It may suffice to say that according to the final formula the number of atoms present is directly proportional to the change of the thermal conductivity.

These experiments are carried out at pressures around 6-30 mm. Hg. Since the changes in the thermal conductivity are only very small, the slightest variations of the accommodation coefficient on the wire, and even on the wall, must be eliminated. Such changes are connected with changes in the adsorption layer on the surface which occur under the influence of atomic hydrogen. The original papers may be consulted about the treatment necessary to provide the wire and wall with a stable adsorption layer. This layer must be of such a nature as to exclude heterogeneous recombination of atoms on the surface of the filament or wire.

By using two gauges instead of one it is possible to compensate for slight variations in the heating current in the temperature of the wall of the gauge. The two gauges, one filled with the reference gas and the other containing the gas to be analysed, are in branches of the Wheatstone bridge. Either the resistance of the filament heated in the gas of unknown composition is measured as shown in Fig. 200, or the bridge is balanced by suitably changing the resistances R_1 and R_2, while both cells contain the reference gas and the current determined when the composition of gas in cell 1 is changed (Fig. 206). (Concerning sensitivity and other details of gauges of this type, cf. p. 178 and H. A. Daynes, *Proc. Roy. Soc.*, **97**, 273 (1920)). A double gauge suitable for the analysis of mixtures of light and heavy hydrogen is described by H. Sachsse and K. Bratzler (*Z. physik. Chem.*, **A, 117**, 332 (1934)).

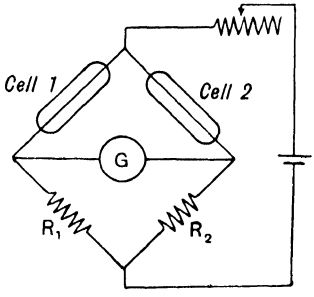


FIG. 206. Double gauge system.

(*c*) *Ternary gas mixtures.* With two double gauge systems two components of a gas with three or more components can be determined if one

of them can be removed by some suitable method. Fig. 207 shows this principle applied to the analysis of mixtures of H_2O, CO, CO_2 and H_2. In the first system the mixture of CO, CO_2, H_2 is compared with that of $CO + H_2$, remaining after removal of CO_2 by KOH. In the second system the mixture $CO + H_2$ is compared with pure H_2 (or CO) as reference gas.

Ternary gas mixtures of light and heavy hydrogen with another gas like CO, N_2, etc., can be analysed by making use of the variation of the thermal conductivity with temperature (see Chap. III).

(*d*) *Low pressure gauges.* The difficulty in using low pressure gauges for analytical purposes lies in the large variation of thermal conductivity

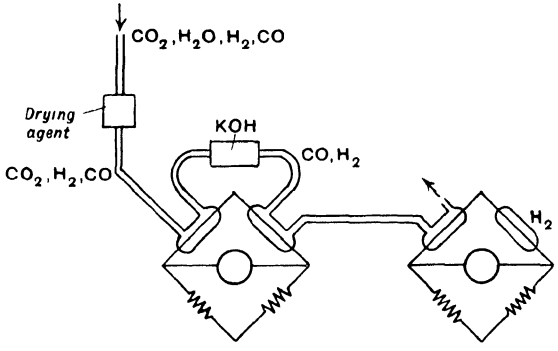


FIG. 207. Two double gauge systems for analysing ternary mixtures.

with pressure. According to K. H. Geib and P. Harteck (*Z. physik. Chem.*, Bodenstein Band, 849 (1931)), at pressures of 0·5 mm. this difficulty can be eliminated for gauges used to analyse ortho-parahydrogen mixtures by using two gauges, one of which is immersed in liquid air and the other in ice water. Both gauges are filled with the gas to be analysed, and are connected up as shown in Fig. 206. Since the heat conductivities of ortho- and parahydrogen are very much less different at 0° C. than at low temperatures, it is possible to compensate variations in the pressure if the dimensions of the filaments of the two gauges are suitably chosen. Farkas' gauge for measuring the concentrations of the different modifications and mixtures of light and heavy hydrogen is described on p. 192.

C. OPTICAL METHODS

The great variety of optical methods which can be used to follow gaseous reactions include interferometry, polarimetry, spectroscopy and photometry. It is outside the scope of this book to describe these methods in detail, since they are adequately treated in text-books or in the instruc-

tions supplied with the instruments by the manufacturers. In the following, examples of typical applications are given.

1. Interferometry

The principle of the gas interferometer (F. Haber and F. Löwe, *Z. f. anorg. Chem.*, **23**, 1393 (1910)) is shown schematically in Fig. 208 (Lord Rayleigh, *Proc. Roy. Soc.*, **59**, 203 (1896)). White light coming from slit S_1 (Fig. (*a*)) produce the interference pattern P_1 after traversing the system of lenses L_1, L_1', and the slit S_1'. The pattern consists of a series of coloured strips, and its centre is indicated by a white strip between two black ones. If the rays 1 and 2 traverse two cells containing gases of

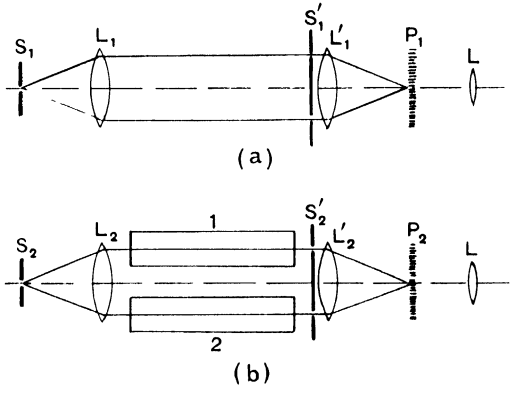


FIG. 208. Principle of the interferometer.

different refractive indices (Fig. *b*), the interference pattern P_2 will be shifted relatively to pattern P_1. By arranging the light paths represented in Figs. 208 (*a*) and (*b*) in such a way that the pattern P_2 is produced directly below P_1, it is possible to estimate the relative shift of the two patterns through the magnifying lens L. This shift is larger the larger the difference in the refractive indices of the gases in the cells 1 and 2, and can be measured exactly by compensating the optical paths of rays 1 and 2 through a plane-parallel glass plate inserted in one of the beams. This glass plate can be rotated around an axis perpendicular to the beam by means of a very sensitive micrometer screw and the reading taken on the drum of this screw when the middle portions of both patterns are brought into coincidence.

The interferometer is suitable for estimating minute amounts of a component in a gas or for comparing two gases, the composition of which differ slightly. Usually the interferometer is calibrated empirically. For absolute measurements of refractive indices monochromatic light has to

be used. The ratio of the refractive indices of the gases in cells 1 and 2 is then given by $n=m(l+\lambda)l$, where m is the relative shift expressed in distances between two consecutive strips, l the length of the cell and λ the wavelength. The accuracy of a portable instrument manufactured by Messrs. Zeiss, with gas cells of 10, 20 and 50 cm. length respectively is : $\pm 0{\cdot}10$, $0{\cdot}04$ and $0{\cdot}02$ per cent. for CO_2, CH_4 or H_2 in air.

It is not possible to follow gas reactions in stationary systems with interferometers of the above type, since the composition in the cell will always differ considerably from the composition of the gas in the reaction vessel, owing to slow intermixing by diffusion. The interferometric method, however, is applicable to reactions in flow or circulatory systems. For example, A. Magnus and A. Krauss (*Z. physik. Chem.*, **A, 158**, 183 (1932)) used the interferometer for analysing mixtures of acetylene and dimethyl-ether.

2. Polarimetry

The methods of polarimetry merit no description here. They have not been applied sufficiently to gaseous reactions, since not many racemisation reactions have yet been investigated. As an example of application, R. L. Burwell's (*J. Am. Chem. Soc.*, **59**, 1609 (1937)) experiments on the catalytic racemisation of *l*-butanol may be mentioned.

3. Spectroscopic Methods

(*a*) *Concentration measurements of H, O and N atoms* in electrically activated gases (cf. pp. 153, 157, 358) may be carried out according to Z. Bay and W. Steiner (*Z. phys. Chem.*, **B, 3**, 149 (1929)) by exciting the atomic lines through an auxiliary discharge and measuring the intensity of these lines by spectrographic methods. The gas to be analysed streams through a wide tube, which is provided with outside electrodes consisting of metal foil wound around neighbouring sections of the tube. The auxiliary discharge is produced by connecting the electrodes to a transformer coil in which high frequency oscillations are induced by a triode valve oscillator. The total energy input is about 5 watts. With a given auxiliary discharge circuit the intensity of the atomic lines depends only on the concentration of the atoms, since there is no difficulty in producing with this type of generator oscillations of a high degree of constancy and purity. Owing to the absence of metallic electrodes in the gas stream and to the small energy input in the auxiliary discharge the composition of the gas in the reaction tube is not altered.

(*b*) *Ultra-violet and infra-red spectroscopy.* It was shown by H. S. Taylor and J. C. Jungers (*J. Chem. Phys.*, **2**, 373 (1934)) and by F. Bowman, W. S. Benedict and H. S. Taylor (*J. Am. Chem. Soc.*, **57**, 960 (1635)) that

the replacement of light hydrogen atoms by heavy hydrogen atoms in compounds like ammonia and benzene can be followed in a semi-quantitative manner by absorption spectroscopy, since the ultra-violet absorption spectra of the deuterium compounds differ appreciably from those of the hydrogen compounds.

This type of analysis is far more complicated for compounds like methane and ethane, which have no absorption bands in the visible or ultra-violet region, since their absorption spectra have to be investigated in the infra-red region. The spectra of the gases enclosed in a Pyrex absorption cell with rock-salt window were analysed by a rock-salt prism spectrometer (R. B. Barnes, R. R. Brattain and F. Seitz, *Phys. Rev.*, **48**, 582 (1935)). For each sample the extinction coefficient

$$K = (-\log I/I_0)/pl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

(I = transmitted intensity, I_0 = incident intensity, p = pressure in mm. Hg. and l = length of the cell in cm.) was determined as a function of wavelength. For calibration purposes the following gases were analysed : methanes with 9·5, 18·1, 46, 79·8, 88·6 and 98·2 per cent. D ; and the compounds CH_4, CH_3D, CH_2D_2 and CHD_3. Each sample of methane in the first group represented equilibrium mixtures of the compounds in the second group and of CD_4 in a ratio corresponding to its D-content. If the sample contains x per cent. D, the distribution of the components is given by :

$$\left.\begin{array}{ll} CD_4 & x^4/10^8, \\ CD_3H & 4x^3(100-x)/10^8 \\ CD_2H_2 & 6x^2(100-x)^2/10^8 \\ CDH_3 & 4x(100-x)^3/10^8, \\ CH_4 & (100-x)^4/10^8. \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

From these data the contribution of each molecular species to the extinction coefficient at any wavelength could be calculated in two independent ways, and it was found to be sufficient to measure the extinction coefficient K_H and K_D of the sample to be analysed at 3020 cm.$^{-1}$ and 2250 cm.$^{-1}$, which are the two wavelengths characteristic of the C-H and C-D bands respectively. This method was used for following the exchange of hydrogen atoms between methane and heavy hydrogen on metallic catalysts and under the influence of excited mercury atoms. A complete analysis had to be carried out if the sample in question did not contain the five molecular species in equilibrium. Such mixtures are obtained, for example, in the catalytic exchange of hydrogen and deuterium atoms between CH_4 and CD_4 molecules, and were successfully analysed by Morikawa, W. S. Benedict and H. S. Taylor (*J. Am. Chem.*

Soc., **58**, 1445, 1705 (1936)). The analysis of the different deuteroethanes may be carried out in a similar manner.

4. Photometry

The concentration C of an absorbent medium, its molecular coefficient of extinction ϵ_λ at the wavelength, λ, and the thickness of the absorbent layer d are connected with the ratio of the intensities of the incident and transmitted light (I_0/I) by the equation

$$I_0/I = e^{\epsilon_\lambda C d}. \quad \text{.....(10)}$$

Thus it is possible to follow chemical reactions involving the production or consumption of one component, the absorption of which is easily measurable. This method has the advantage that the measurements can be carried out continuously while the reaction is in progress, requires small amounts of substance and is relatively simple, using modern photo-elements or similar devices. An example of the application of this method is given in the investigation of the photo-synthesis of hydrogen chloride from its elements by M. Ritchie and R. G. W. Norrish (*Proc. Roy. Soc.*, **A, 140**, 99 (1933)), in which the decrease of the chlorine concentration was measured. The experimental arrangement is shown on Fig. 209

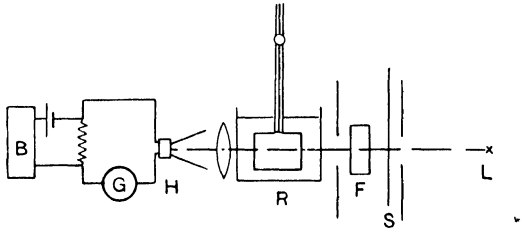


FIG. 209. Concentration measurement by photometry with a thermopile.
S = Shutter, G = Galvanometer, R = Resistance box.

R is the reaction vessel placed in a thermostat and L the light source, a quartz mercury vapour lamp run at 150 volts and 4 amps. Its light is made parallel by a system of lenses and circular stops and monochromatic by a suitable light filter F. The intensity of the transmitted light is measured by a Moll thermopile H in the same way as described on p. 250. At the beginning and end of each experiment the intensity I transmitted through the empty cell is determined. The concentration of the chlorine is calculated from the ratio I/I_0 by an empirical calibration. Working with the wavelength 3650 Å the concentration of chlorine may be determined every 2 to 3 minutes. If, however, the reaction proceeds too rapidly or if wavelengths other than 3650 Å have been used, only the final chlorine concentration is measured after the gaseous mixture has been made

insensitive towards the light by adding an excess of oxygen. This determination is followed by measuring I_0 after the cell has been evacuated.

Another arrangement is that used by O. Reitz (*Z. physik. Chem.*, **B, 179,** 119 (1937)). It is of general applicability, although originally it was used for investigating the bromination of acetone in solution (Fig. 210). A mercury high-pressure arc (p. 218) is used as a light source. The arc is run at 180 mA. by using a barretter resistance R_1 (p. 150). The filter F transmits the wavelength $\lambda = 5461$ Å, and by means of the lenses L_0 and L_1 two beams are formed, one of which passes through the micro-cuvette containing bromine (K), and the other serves to determine the intensity of the incident light. By means of the prisms P_0 and P_1 both beams are directed on a photo-element (Z), and the photo current is measured by a

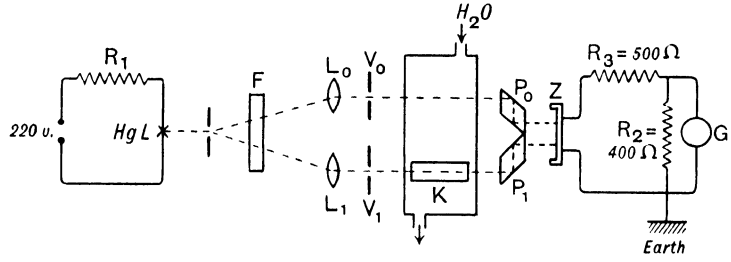


FIG. 210 Concentration measurement by photometry with a photo-element.

sensitive galvanometer (G). The resistance R_2 serves to damp the oscillations of the galvanometer. By a suitable arrangement of the shutters V_0 and V_1 it is possible to expose the photo-element alternatively to the unabsorbed light and to that passed through the absorption cell. The deflection of the galvanometer for the unabsorbed light amounts to 700-800 mm. on a scale at a distance of 2·5 metres. If g_0/g and g_0'/g' denote the intensity ratios of the unabsorbed light and that passed through the absorption cell for the concentrations c and c' respectively, then the change in the concentration is

$$\Delta c = (1/\epsilon d)\,(\log g_0/g_1 - \log g_0'/g'), \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

since the difference in the two light paths (that is, loss of intensity through reflection from the windows of the absorption cell) cancel. This relation naturally holds even if the intensity of the arc changes from one concentration determination to the next, i.e. if $g_0 \neq g_0'$. Additional arrangements for absorption measurements will be found in the papers of E. J. B. Willey and S. G. Foord (*Proc. Roy. Soc.*, **A, 135,** 166 (1932)) and of F. Bach, K. F. Bonhoeffer and E. A. Moelwyn-Hughes (*Z. physik. Chem.*, **B, 27,** 71 (1934)).

According to E. Rabinowitch and H. L. Lehmann (*Trans. Faraday Soc.*,

31, 689 (1935)) it is possible to measure the change in extinction coefficient of bromine due to the dissociation of the molecules when the gas is under strong illumination. The same method is also applicable to other halogens

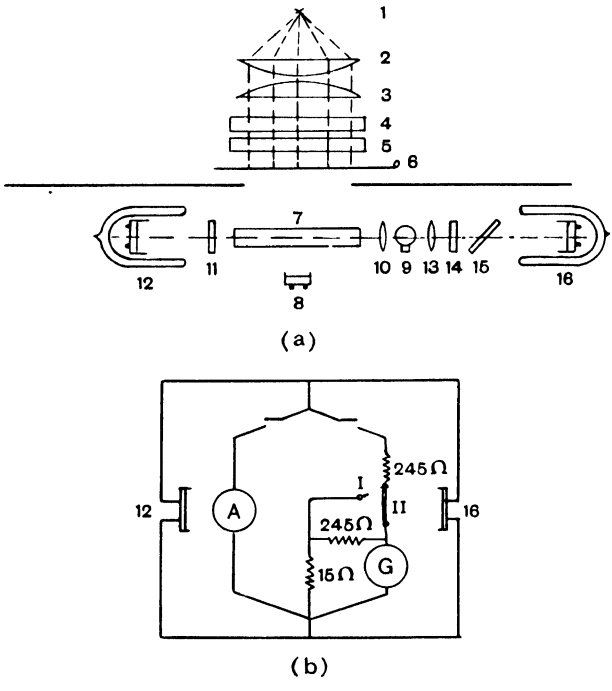


FIG. 211. Concentration measurement by photometry with two photo-cells.
(*a*) optical set-up. (*b*) electric circuit.

1. Carbon arc, 25 amps., 1500 watts.
2-3. Glass lenses, 120 mm. in diameter.
4. Water filter, 4 cm.
5. Saturated $CuSO_4$ filter, 3 cm.
6. Shutter.
7. Absorption vessel, rectangular, 20 × 20 × 120 mm. of optically flat quartz.
8. Moll thermopile.
9. Straight coil tungsten lamp, 6 volts, 24 watts.
10, 13. Telescope lenses, 10 mm.
11, 14. Light filters (Schott BG 12 glass).
15. Clear glass mirror rotatable on a horizontal axis.
12, 16. Selenium photo-cells in Dewar flasks, internal resistance 10 ohms.
A. Microammeter, 260 ohms.
G. Zernicke galvanometer, 15 ohms.

(E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 907, (1936), and *J. Chem. Phys.*, **4**, 497 (1936)). The experimental arrangement is shown in Fig. 211, and is, moreover, a good example of the high accuracy obtainable in absorption measurements with relatively simple apparatus.

The whole absorption set-up Fig. 211 (*a*) is arranged on an optical bench. The photo-electric circuit Fig. 211 (*b*) has three different ranges of sensitivity: over the microammeter (*A*) 1×10^{-6} amps./div., over the galvanometer (*G*) with key in position I 4×10^{-9} amps./mm. (on a scale 3 metres away), and with key in position II $2{\cdot}3 \times 10^{-10}$ amps./mm. The light beams coming from the lamp (9) and falling on the two photo-cells are compensated by moving lens (13) and turning the mirror (15), using the three different sensitivity ranges one after the other. Although special precautions have been taken to ensure the absence of any mechanical vibrations and the constancy of the voltage for lamp (9), the highest accuracy in this compensation corresponds to a variation of the photo current in the bridge of $\pm 4 \times 10^{-10}$ amps. Since the intensity of each beam produces a photo current of $2{\cdot}4 \times 10^{-4}$ amps., the accuracy attained is high enough to detect changes in intensity of the beam of 0·02 per cent.

A typical experiment requires the following measurements:

(1) The total intensity (I_0) of the incident beam of the lamp (9) is measured with vessel (7) evacuated and photo-cell (16) covered.

(2) The total absorption of 5 mm. bromine vapour is determined. With the light filter (11) this is 55 per cent.

(3) Photo-cell (17) is uncovered and the light beams compensated.

(4) Vessel (7) is illuminated with the carbon arc, and the change in the intensity of the transmitted beam is measured by the deflection of the galvanometer at intermittent opening and closing of the shutter (6).

(5) The same measurement is repeated with increasing amounts of different foreign gases. The observed value of $\Delta I/I_0$ is of the order of 0·1 per cent. If the light beams are monochromatic, the relative change of the transmitted light $\Delta I/I_0$ is proportional to the change of the concentration of the bromine molecules. With the arrangement described this is true also for a beam of wavelength 4000-5000 Å if the absorption is about 60 per cent.

The curves obtained representing the dependence of ΔI on the pressure of the foreign gas are of a rather complicated structure, and a detailed calculation shows that this is due partly to thermal effects causing changes in temperature and concentration along the absorption vessel. This effect is larger the lower the conductivity of the gas in the vessel, i.e. the lower the foreign gas pressure. The bromine atoms will recombine at low foreign gas pressures mainly on the wall, where they arrive very quickly by diffusion. Thus the atom concentration and corresponding value of $\Delta I/I_0$ will be low. At higher pressures this heterogeneous recombination is eliminated, and the concentration of bromine atoms and $\Delta I/I_0$ rise. At still higher pressures of foreign gas the homogeneous

recombination sets in and [Br] and $\Delta I/I_0$ fall. It is possible—as is shown by detailed calculation in the original paper—to allow for the thermal effect and for the heterogeneous recombination, and actually to estimate the recombination constant. A more elaborate photo-electric photometer for reaction kinetic work is described by G. Brauer (*Z. physik. Chem.*, **B, 26,** 71 (1936)).

5. Gas Density Methods

If the density of the gas mixture changes during the reaction the progress of the reaction may be followed by a gas density balance, described in Chap. III, and requires less than one c.c. of gas (N.T.P.) for each determination.

Such density balances have been used for investigating exchange reactions of light and heavy hydrogen (M. Calvin, *Trans. Faraday Soc.*, **32,** 1428 (1936)), and might prove of great importance for following exchange reactions of hydrogen and deuterium compounds of the type

$$XH + YD = XD + YH,$$

especially if one of the reaction partners is easily condensable.

D. FLOW METHODS

In a flow method the reacting gas mixture streams through the reaction space at a known velocity, and the change in its composition is measured when leaving the reaction space. The time of reaction is connected with the velocity of flow and the reaction space, but the theoretical treatment of reactions in flow systems is complicated by the fact that owing to diffusion and convection the gases entering the reaction space are more or less completely mixed with the gases present in the reaction space which have already partially reacted.

1. Theoretical

(*a*) *General*: Simple formulae are only available for the limiting cases: (1) mixing complete (M. Bodenstein and K. Wolgast, *Z. physik. Chem.*, **61,** 422 (1908)), and (2) mixing negligible (A. F. Benton, *J. Am. Chem. Soc.*, **53,** 2984 (1931)). According to T. Forster and K. H. Geib (*Ann. Physik.*, **20,** 250 (1934)) the general equation for a unimolecular reaction $A \rightarrow B$ is

$$\frac{c}{c_0} = \frac{2}{(1+\alpha)e^{(\sqrt{1+k'}-1)/x} + (1-\alpha)e^{-(\sqrt{1+k'}+1)/x}}, \quad \ldots\ldots\ldots\ldots (12)$$

where

$$\alpha = \frac{1+\frac{k'}{2}}{\sqrt{1+k'}}, \quad k' = \frac{4D}{v^2}k \quad \text{and} \quad x = \frac{2D}{av} \quad \ldots\ldots\ldots\ldots (13)$$

c_0 and c is the concentration of the gas entering and leaving the reaction vessel respectively, k is the velocity constant, D the diffusion coefficient in cm.²/sec., v the velocity of flow in c.c./sec., both measured at the temperature and pressure prevailing in the reaction vessel, and a the volume of the reaction vessel. This equation is valid for reactions which do not involve a change of volume.

For the limiting cases : diffusion negligible ($D=0$) and diffusion very large ($D=\infty$), formula (12) reduces to

$$D=0,\quad c/c_0=e^{-ka/v} \quad \text{or} \quad k=\frac{v}{a}\ln\frac{c_0}{c}, \qquad (14)$$

$$D=\infty,\quad c/c_0=\frac{1}{1+\frac{ka}{v}} \quad \text{or} \quad k=\frac{v}{a}\left(\frac{c_0}{c}-1\right). \qquad (15)$$

Bodenstein and Wolgast proved experimentally the validity of formulae of the type (15). Such formulae apply when the linear velocity of flow is small compared with the diffusion velocity, that is, where the displacement of any particle in unit time due to the flow is small compared with its displacement due to diffusion (see formula 45, p. 15) :

$$\frac{v}{q} \ll \sqrt{2D}, \qquad (16)$$

where v and D have the same meaning as above and q is the cross-section of the reaction vessel in cm.². Condition (16) is more likely to be fulfilled in wide vessels and at high temperatures, since the diffusion coefficient increases rapidly with temperature (cf. p. 15). If the velocity of flow, measured in c.c./sec. at N.T.P., is kept constant, the ratio $\frac{v}{q\sqrt{2D}}$ is independent of pressure, since both v and D are inversely proportional to the pressure.

If mixing is complete the composition of the gas in the reaction vessel is equal to that of the gas leaving the vessel. Then for a reaction of the type $A \rightarrow \nu X$ the velocity constant k is given by

$$C_X = k\tau C_A \quad \text{or} \quad k = C_X/\tau C_A, \qquad (17)$$

where C_X and C_A are the concentrations of the reaction product and the original reactant in the gas leaving the reaction vessel respectively, and τ the time the gases have spent in the reaction vessel. If v_R is the volume of the reaction vessel and v' the velocity of flow for the outcoming gas at the temperature and pressure of the reaction vessel,

$$\tau = \frac{v_R}{v'}. \qquad (18)$$

For reactions of the type $A+B\rightarrow\nu X$, the velocity constant is given by

$$k=\frac{1}{t}\frac{C_X}{C_A C_B}. \quad \text{.....(19).}$$

Equations (17) and (19) are distinctly different from equations (20) and (21) [cf. formulae (91) and (93), p. 34] :

$$k=\frac{\nu}{t}\,ln\frac{C_{A0}}{C_{A0}-\frac{1}{\nu}C_X}, \quad \text{.....(20)}$$

$$k=\frac{\nu}{t}\frac{1}{C_{A0}-C_{B0}}\,ln\frac{C_{B0}(C_{A0}-\frac{1}{\nu}C_X)}{C_{A0}(C_{B0}-\frac{1}{\nu}C_X)}, \quad \text{.....(21)}$$

which are valid for stationary systems (C_{A0} and C_{B0} initial concentrations). For small values of C_X, (20) and (21) become equivalent to (17) and (18) respectively.

If diffusion is small and mixing negligible, the following formula is valid for reactions of the type $A\rightarrow\nu B$, according to H. F. Benton (*J. Am. Chem. Soc.*, **53**, 2984 (1931)).

$$k=\frac{v_0}{v_R}\nu\,ln\frac{n_{A0}}{n_A}-(\nu-1)\left(1+\frac{n_A}{n_{A0}}\right), \quad \text{.....(22)}$$

where v_0 is the velocity of flow of the gas entering the reaction vessel, n_{A0} and n_A the number of moles of A entering and leaving the reaction vessel per second respectively, and v_R the volume of the reaction vessel.

For bimolecular reactions of the type $A+B\rightarrow\nu X$ an equation similar to (22) may be deduced. For small relative reaction rates the velocity constant of a bimolecular reaction may be calculated with sufficient degree of accuracy from the formula

$$k=\frac{\Delta n_A}{\Delta\tau}\bar{v}\,\bar{C}_A, \quad \text{.....(23)}$$

where $\bar{v}$ is the average rate of flow calculated from v_0 and v', $\bar{C}_A$ the average concentration, Δn_A the amount changed in moles, and $\Delta\tau=v/\bar{v}$.

When using flow methods it is customary to measure the amount of reaction partners in mols or litres (N.T.P.) passing through the reaction vessel per unit of time rather than in concentrations. [See equation (22).] This is done if the reaction mixture is passed through the reaction vessel at a known speed and the gases leaving the vessel in a given

time are collected and analysed. Thus we obtain, instead of equations (17) and (18),

$$k = \frac{V}{v}\frac{1}{t}\frac{X}{A}, \quad \ldots\ldots(24)$$

$$k = \frac{V^2}{v}\frac{1}{t^2}\frac{X}{AB}, \quad \ldots\ldots(25)$$

where V denotes the volume of the gas leaving the vessel in the time t; X, A and B are the amounts of reaction partners or products found in volume V and v is the velocity of flow of the outcoming gas.

(*b*) *Space-time-yield.* In technical catalytic reactions the 'Space-time-yield' (S.T.Y.) is used to characterise the activity of the catalyst. The 'space-time-yield' is the amount of reaction product formed per unit of time and unit of volume of catalyst. It is usually expressed in units of gms./hour/c.c., and is proportional to the product of the fraction changed and the space velocity (S.V.), which is the velocity of flow per unit volume of catalyst expressed in litres/hour. At low space velocities the S.T.Y. is proportional to the S.V. while the fractional change is unity, i.e. when the composition of the gas leaving the reaction vessel corresponds to equilibrium. With increasing S.V. the S.T.Y. increases less rapidly and tends toward a maximum value, which is reached for large values of S.V. when the fractional change is very small.

2. Production and Measurement of Flow

If the flow of gas is produced by employing compressed gases in cylinders, it is advisable to use proper reducing valves by which the rate of flow is easily regulated, and a mercury safety valve (as shown in Fig. 212) in order to permit the gas to escape should the reaction tube get blocked. At reduced pressures the flow is produced by suction, as indicated by Fig. 212, which also shows schematically the distribution of pressure in the apparatus. The gas enters the apparatus from the left, its pressure being kept at atmospheric by the valve (1). The velocity of flow is measured by the calibrated flow meter (2) (see p. 102), and controlled by the needle valve (3) (see p. 64), which also serves to reduce the pressure from atmospheric. The pressure in the reaction vessel (5) is adjusted by the valve (6) controlling the speed of pumping, and can be read on the manometer (4).. Since the flow meter is most conveniently calibrated at atmospheric pressure, it is essential to admit enough gas to the system through the valve (0) controlling the gas flow from the cylinder or the gasometer. It is a good practice to employ a slight excess of gas, which bubbles slowly out through valve (1). Tap (7) can be used to calibrate the flow meter.

The velocity of flow can also be measured by gas meters (especially if larger amounts of gas are used (cf. Fig. 221) by the deflection of a

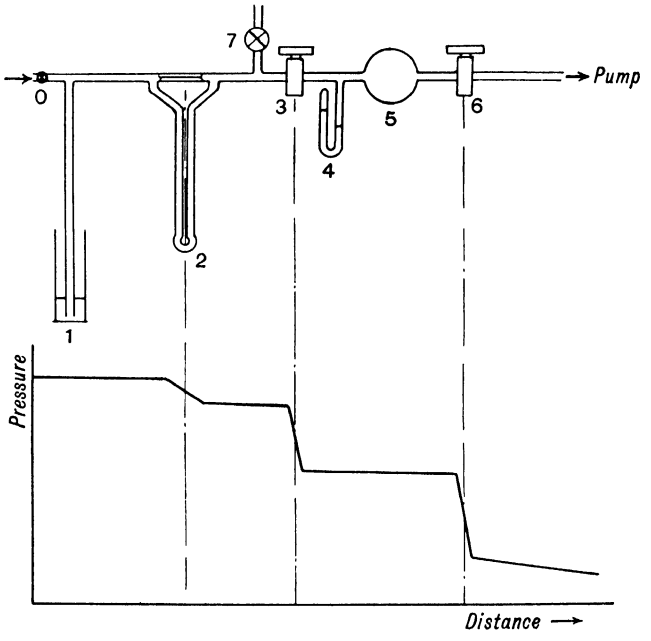


FIG. 212 Production of flow at reduced pressure.

suspended disc under the influence of the gas stream flowing out from a jet (A. V. Sagulin, A. Kowalsky, D. Kopp and N. Semenoff, *Z. physik. Chem.*, **B, 6**, 307 (1930)), or electrically if electrolytic hydrogen and oxygen are used. In this latter case the current flowing through the electrolytic cell is a measure of the rate of flow. This method can also be used for flow experiments at reduced pressure (see Fig. 213). Valve 3 corresponds to valve 3 in Fig. 212. If the gas evolution is too fast the level of the electrolyte in the right limb sinks and the electrolysis is stopped. The total amount of gas evolved in a given time is equal to that evolved in the coulometer *C*.

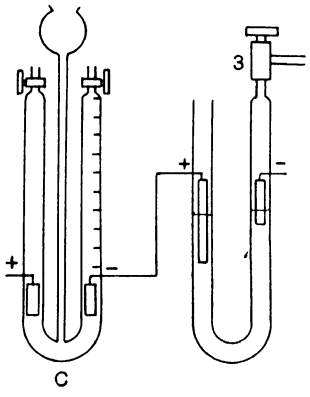


FIG. 213. Electrically controlled flow of gas.

If gaseous mixtures of various compositions are to be used it is preferable to measure the velocity of flow of each component before mixing, since the calibration of the flow meter

depends on the composition. If the vapour of a liquid with a considerable vapour pressure is to be mixed with a gas, the gas stream is saturated by bubbling through the liquid kept at suitable temperature. To ensure good contact between gas and liquid the gas can be admitted through a porous glass filter plate (cf. p. 63).

A simple way of adding a certain amount of liquid to a gas stream is shown in Fig. 214. The rate of flow is regulated by the width of the

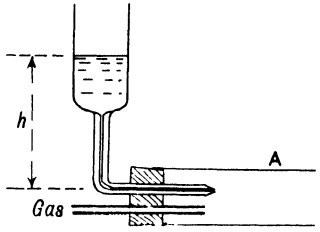


FIG. 214. Addition of liquid to a gas stream.

capillary and the height of the liquid column (h). The drops of liquid are then evaporated in the heated tube A. A. A. Balandin (*Z. physik. Chem.*, **B, 19**, 451 (1932)) describes a more elaborate arrangement, in which the reservoir of the liquid is closed and the rate of flow is controlled by varying the rate of admission of air to the reservoir.

Pumps for circulating gases are described on p. 53. At low pressures, mercury condensation pumps may also be used (p. 48). According to R. Spence and G. B. Kistiakowsky (*J. Am. Chem. Soc.*, **52**, 4837 (1930)), special care must be taken in constructing circulation pumps for mixtures of oxygen and acetylene. Such mixtures are liable to explode under the influence of small electric discharges which develop through friction. Explosions

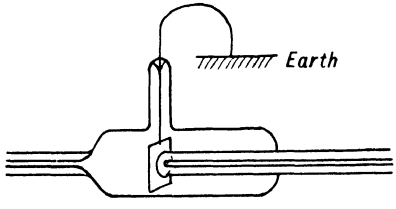


FIG. 215. Earthed valve for circulation pump.

may also occur by using mercury non-return valves or all-glass valves. A satisfactory valve is shown in Fig. 215. The tip of the capillary is platinised (see p. 324), and closed by platinum foil welded to a tungsten wire which keeps it in position. The tungsten wire is earthed, and thus the accumulation of any electric charge is avoided. Earthed vertical mercury columns are used as pistons for pumping the gas, and are kept moving by the oscillating motion of a piston in a steel barrel.

If thermal reactions are investigated by flow methods it is convenient to use reaction vessels of the form shown in Fig. 216, in order to eliminate the effect of a non-uniform temperature distribution in an electric

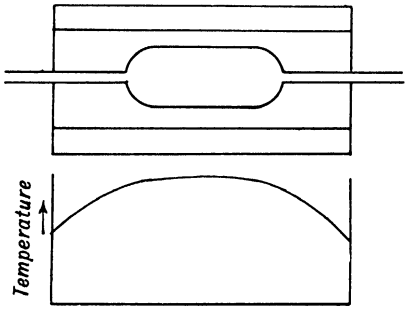


FIG. 216. Reaction vessel and temperature distribution.

furnace. The contact time is then given by the time the gas spends in the zone of uniform temperature, since the linear velocity of flow in the narrow tube is very much larger than in the wide part of the reaction vessel.

3. Examples of the Application of Flow Methods

Flow methods may be used in the following instances :

(1) Very fast reactions. In flow systems reactions occurring very rapidly may be investigated by using narrow reaction vessels and high velocities of flow. In exact investigations it is necessary to ascertain whether the gas has actually attained the temperature of the reaction vessel, and whether the mixing effect due to diffusion is negligible.

(2) The amount of reaction products formed is small. If larger quantities of the reaction products are wanted when the yield is small, it is found more convenient to treat a large volume of gas according to the flow method than to use the static method, which necessitates larger vessels. It is also possible to separate the reaction products from the gas stream, and circulate the same volume of gas until the reaction products have accumulated to a measurable extent.

(3) The reaction involves unstable reaction partners. All reactions of atoms produced in the electric discharge or of radicals produced according to Paneth's method belong to this type. The instability of H, O, N-atoms, of CH_3, and other radicals is due to their recombination to saturated molecules, which usually takes place mainly on the walls of the reaction vessel. Thus the reaction of a substance can be most conveniently investigated by exposing it to a stream of atoms or radicals of known velocity and composition.

(4) In the course of the reaction, unstable products may be formed which are liable to further change. Using flow methods such products can easily be removed from the reaction vessel at a suitable stage of the reaction.

(5) Testing the activity of catalysts.

(6) The intermittent filling and emptying of the reaction vessel, customary in static experiments, is to be avoided. With flow methods it is possible to vary the experimental conditions (reaction time, pressure, temperature) continuously while the reaction vessel is continuously in contact with the reacting gas. This is necessary if repeated evacuation of the reaction vessel may affect the rate of reaction by changing the surface of the reaction vessel itself (in chain reactions) or by altering the catalyst therein (in catalytic reactions).

(7) Using flow methods it is possible to investigate the stage of the reaction after different times of reaction simultaneously. If the mixing effect is negligible, i.e. the velocity of flow is larger than the velocity of diffusion, the composition of the reactive mixture at different places of the reaction tube corresponds to different times of reaction.

In the following pages some typical examples are given of the application of the flow method.

(1) H. Tropsch and G. Egloff (*Ind. Eng. Chem.*, **27**, 1063 (1935)) have used the flow method for the investigation of the high temperature pyrolysis of gaseous paraffin hydrocarbons. A Pythagoras tube (3 mm. inside diameter), the reaction vessel, suspended in the centre of a protecting porcelain tube, 37·5 mm. in diameter and 65 cm. long, has been heated to 1100-1400° C. in an electric 'glow-bar' furnace. The contact times have been calculated by dividing the heated volume of the Pythagoras tube by the average volume of the in- and out-going gases per second at the temperature and pressure of the experiment. These ranged between $0{\cdot}2\text{-}50 \times 10^{-3}$ seconds. There is some uncertainty regarding the volume of the reaction tube heated, since the temperature is only uniform along a length of 15 cm., and in this case it is not possible to employ reaction vessels similar to those shown in Fig. 216 on account of the high velocity of flow employed (cf. also p. 308).

(2) This method has been used by W. E. Vaughan and W. A. Noyes (*J. Am. Chem. Soc.*, **52**, 559 (1930)) for the determination of the quantum efficiency of the photo-chemical formation of ozone in the short wave ultra-violet. The oxygen is streamed through the reaction vessel at such a speed that the absolute amount of ozone formed in a given time is independent of the rate of flow. The amount of ozone is determined by allowing the gas leaving the reaction vessel to bubble through a suitable solution.

H. A. Smith and G. B. Kistiakowsky (*J. Am. Chem. Soc.*, **57**, 835 (1935)) have investigated the photo-chemical reaction between hydrogen and oxygen by a similar method. Use is made of an all-glass circulating pump. Water, hydrogen, peroxide and ozone are continually removed from the gases by absorption and condensation. (Other examples, cf. : at low pressures, T. G. Pearson, *J. Chem. Soc.*, 1718 (1934) ; L. Belchetz and E. K. Rideal, *J. Am. Chem. Soc.*, **57**, 1168, 2466 (1935) : for large amounts of gas, S. Lenher, *J. Am. Chem. Soc.*, **53**, 3752 (1931).)

(3) See pp. 307 ff.

(4) The arrangement shown in Fig. 217 has been used by D. M. Newitt and J. B. Gardner (*Proc. Roy. Soc.*, **A**, **154**, 333 (1936)) to investigate the

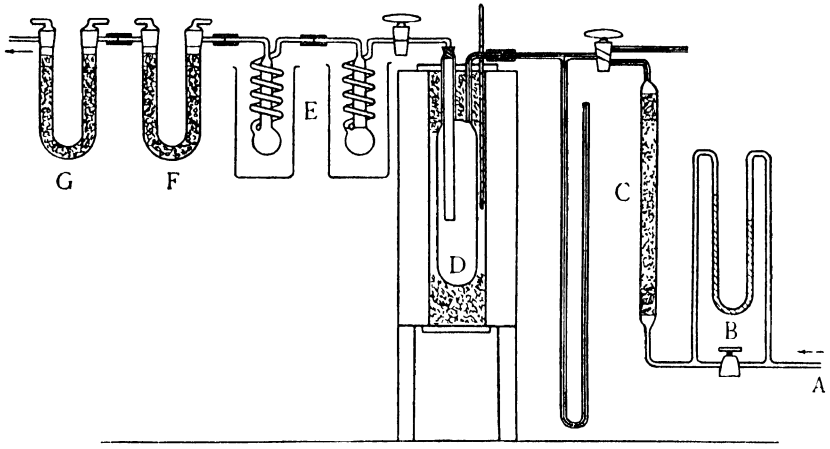


FIG. 217. Experimental arrangement using the flow method.

nature of the products formed in the initial stages of the reaction between methane and oxygen. The velocity of the gas mixture entering from the right side is measured by a flow meter *B*. The silica reaction vessel (*D*) is kept in an electric furnace at the required temperature. The gas leaves *D* through a closed unglazed porcelain tube. To force the gas through this tube suction is applied. Thus back diffusion of the reaction products in the reaction vessel is eliminated. The vessels *E*, *F* and *G* serve to remove condensable products, water and CO_2 respectively ; the residual gas is collected and analysed separately.

J. R. Bates and D. J. Salley (*J. Am. Chem. Soc.*, **55**, 110 (1934)), H. S. Taylor and J. R. Bates (*J. Am. Chem. Soc.*, **49**, 2438 (1927)), and W. Frankenburger and H. Klinkhardt (*Z. physik. Chem.*, **B**, **15**, 421 (1932)) used flow methods for mercury sensitised photo-chemical experiments in order to remove the unstable products quickly from the reaction tube (H_2O_2, formaldehyde, etc.). The reaction vessel is a silica tube, in which

the streaming reaction mixture (e.g. H_2+O_2 saturated with Hg) is exposed to the light of a mercury arc. Water cooling prevents the reaction mixture from being heated by the mercury arc. Three alternative arrangements are shown in Fig. 218 (*a-c*). A fourth arrangement

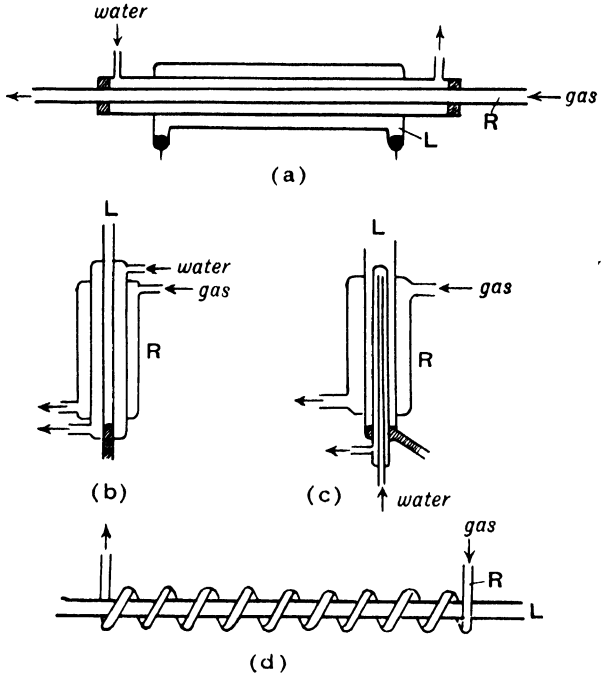


FIG. 218. Reaction vessels for photo-chemical experiments in flow systems.
R = Reaction vessel. L = Light source.

(Fig. 218 (*d*)) consists of a reaction tube wound in form of a spiral round the mercury arc and immersed in water.

(5) The activity of catalysts can be conveniently tested by using a vessel shown in Fig. 219, which allows a quick interchange of the

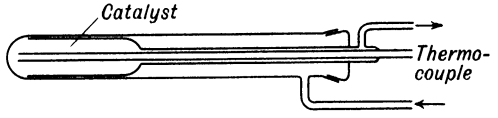


FIG. 219. Vessel for testing catalysts according to the flow method.

catalysts. An experimental arrangement for testing hydrogenation catalysts, for example, is shown schematically in Fig. 220. A hydrogen stream, the speed of which is measured, is saturated with the vapour of the substance to be hydrogenated. The vapour pressure of the liquid is

adjusted by the temperature bath B. The tube A is slightly heated in order to prevent condensation. After leaving the reaction tube R the condensable reaction products are removed from the gas stream, and the

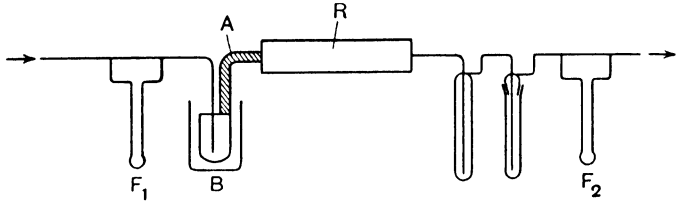


FIG. 220. Measurement of activity of hydrogenation catalysts according to the flow method.

velocity of flow of the residual hydrogen measured by flow meter F_2. The difference between the readings on the flow meters F_1 and F_2 is a measure of the activity of the catalyst.

Fig. 221 shows an arrangement used by V. N. Ipatieff and B. B. Corson (*Ind. Eng. Chem.*, **27**, 1070 (1935)) for the investigation of the

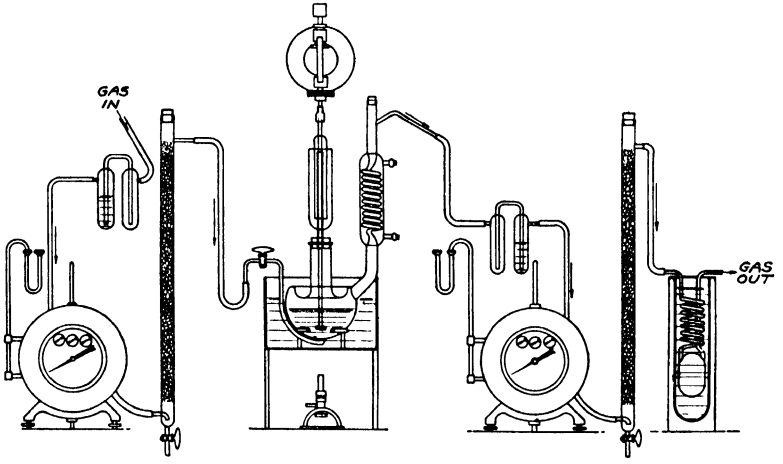


FIG. 221. Arrangement for investigating the polymerisation of olefines according to the flow method.

catalytic polymerisation of olefines by phosphoric acid. The phosphoric acid is kept in the vessel, and is brought into intimate contact with the gas by stirring. The shoulders of this vessel serve to prevent splashing. Part of the polymerisation products remain in the vessel, part is condensed in the gasometer, and the amount of residual gas is measured.

(6) Cf. pp. 323, 352, 363, 365.

(7) W. Steiner and F. W. Wicke (*Z. physik. Chem.*, Bodenstein Bd., 817.

(1931)) used the method described on p. 290 for the determination of the hydrogen atom concentration at different places of the reaction tube. For this purpose the ring electrodes were in rigid but insulated connection with the spectrograph, the whole being moved along the reaction tube. Thus by measuring the intensity of the Balmer spectrum the concentration of hydrogen atoms could be determined at any place in the reaction tube. (For a detailed calculation see W. Steiner, *Trans. Faraday Soc.*, **31**, 623 (1935).)

4. Reaction of Atoms

The investigation of the reaction of H or O atoms by the flow method is based on the following principle (Fig. 222) (K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924); E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1925); K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **A, 139**, 64 (1928); P. Harteck and U. Kopsch, *Z. physik. Chem.*, **B, 12**, 327 (1931)).

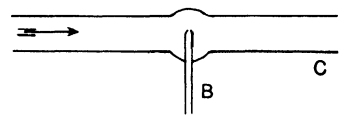


FIG. 222.

The gas containing a known percentage of atoms streams with a given velocity in the direction of the arrow. At point *B* a stream of the reaction partner is admixed. At point *C* the atoms are destroyed by suitable means in order to stop the reaction after a definite period; thereafter the reaction products are separated and analysed. The time of reaction is the time during which the gas streams from *B* to *C*.

The pressure in the reaction tube is determined by the pressure prevailing in the discharge tube in which the atoms are produced. The optimum pressure is of the order of a few tenths of a millimetre (for higher pressures, cf. P. Harteck and E. Roeder, *Z. physik. Chem.*, **A, 178**, 389 (1937)). The linear velocity of flow is given by the speed of the pumps and the cross-section of the tubing. It is desirable to obtain as large linear velocities of flow as possible when a given amount of gas (measured at N.T.P.) is passed through the tube. Narrower tubing will only increase the velocity of flow as long as the tubing offers no considerable resistance to the pumping, since this resistance is inversely proportional to the third or fourth power of the diameter (see p. 19), whereas the velocity of flow is inversely proportional to the square of the diameter. Using steel diffusion pumps it is possible to attain linear velocities of a few metres/sec. in tubes of 18-20 mm. diameter at a few tenths of a millimetre pressure. These figures correspond to a passage of a few litres of gas (N.T.P.) per hour.

Another important point is the admixing of the reaction partner. Since the atomic gas is produced by an electric discharge, it is essential

to design the apparatus in such a way as to prevent the reaction partner diffusing back into the discharge tube against the gas stream and undergoing a chemical reaction in the discharge. According to a formula given by Hertz (*Z. Physik*, **19**, 35 (1923)) the concentration of an admixed gas x cm. upstream is given by

$$C_X = C_0 e^{-vx/D} = C_0 10^{-vx/2 \cdot 3D}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (26)$$

where C_0 is the concentration at the point of admixture, v the velocity of flow in cm./sec., and D the coefficient of diffusion at the temperature and pressure prevailing in the reaction tube. For example, with $v = 300$ cm./sec. and $D = 300$ cm.^{2}/sec., the ratio C_X/C_0 is 10^{-8} 18 cm. upstream or 10^{-4} 9 cm. upstream. This calculation shows that hardly any back diffusion takes place if the reaction partners are added at a distance of about 20 cm. from the discharge. This distance can be shortened by increasing the velocity of flow through a constriction between the discharge tube and the position at which the reactants are added. This restriction, however, must not be too narrow, otherwise it will offer an appreciable resistance to pumping.

5. Dilute Flames

The 'dilute flames' method is essentially a flow method which was developed by Polanyi and collaborators for the investigation of very fast atomic reactions.

The principle of this method (H. Beutler and M. Polanyi, *Z. physik. Chem.*, **B, 11** (1928)) is as follows. Two gases, say sodium and chlorine,

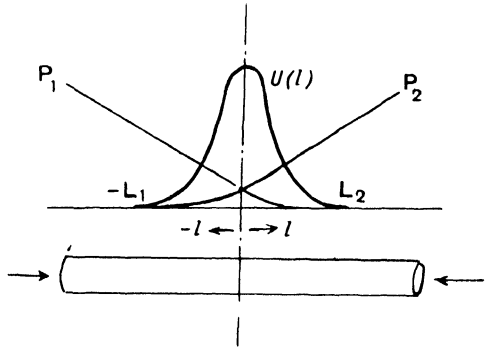


FIG. 223. Principle of the method of 'dilute flames.'

enter the reaction tube from different sides at low pressures. The reaction between these two gases yields a solid precipitate on the walls of the reaction tube (see Fig. 223). If $U(l)$ is the amount of reaction products formed at a distance l from the middle of the reaction tube, p the

pressure of the reactants, and K the resistance of the reaction tube per unit of length $= \frac{3\sqrt{2MRT}}{d^3\pi}$ (cf. formula (56), p. 19),

$$\frac{d^2p_{Na}}{dl^2} \cdot \frac{1}{K_{Na}} = 0U(l). \quad \ldots\ldots(27)$$

Since $U(l)$ is known, the pressure is given by

$$p_{Na} = K_{Na} \iint U(l)\, dl\, dl. \quad \ldots\ldots(28)$$

The solid deposit covers the tube only between $-L_1$ and L_2. Consequently,

$$\left.\begin{aligned} p_{Na} &= 0 \\ \frac{dp_{Na}}{dl} &= 0 \end{aligned}\right\} \text{ for } l \geqq L_2. \quad \ldots\ldots(29)$$

Under these conditions p_{Na} can be determined by graphical integration of formula (28). The pressure of chlorine is similarly given by

$$p_{Cl_2} = K_{Cl_2} \iint \frac{U}{2}\, dl\, dl, \quad \ldots\ldots(30)$$

where the factor $\frac{1}{2}$ allows for the fact that two molecules of NaCl are formed from each chlorine molecule. The velocity constant of the reaction k is then

$$k = \frac{U}{2q\, p_{Na}\, p_{Cl_2}}, \quad \ldots\ldots(31)$$

where q is the cross-section of the tube. Another way of expressing k is

$$k = \frac{27}{B^3} \frac{1}{2qUK_1K_2}, \quad \ldots\ldots(32)$$

where B is half-breadth of the precipitate curve.

The experimental arrangement is shown in Fig. 224. The stream of sodium is produced by heating sodium in the left side of the apparatus

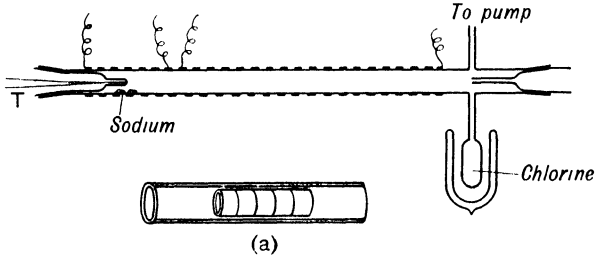


FIG. 224. Dilute flames. Precipitate method.

to a certain temperature which is measured by the thermocouple T. The pressure of halogen is adjusted by a suitable temperature bath at

the other end of the tube. The initial pressure of sodium and chlorine is about 0·01 mm. The middle part of the tube is kept at a higher temperature—about 300° C.—in order to avoid condensation of sodium

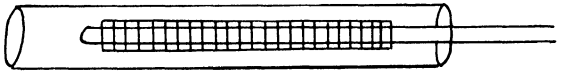


FIG. 225. Precipitate method.

vapour. Nichrome strips wound round the tube serve as a heating resistance and permit observation from the outside. The tube is about 1 metre long and 3 cm. wide. In the inside of the tube 20 mm. long glass rings are placed adjoining one another (Fig. 224 *a*). After the experiment has run for some time the reaction is stopped, the rings are taken out, and the precipitate on each of them is determined by titration. Another way of introducing these glass rings is shown in Fig. 225. The thickness of the precipitate can also be determined by measuring optically the opacity of the deposit.

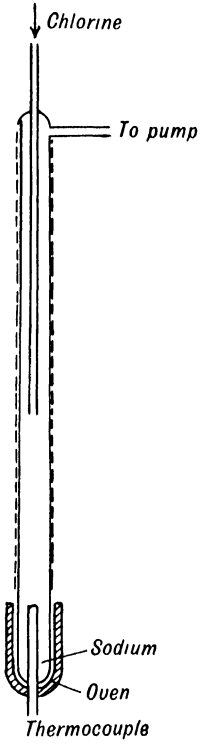


FIG. 226. Dilute flame method.

Simultaneously with the formation of the deposit there is an emission of light, which is strongly intensified (S. v. Bogdandy and M. Polanyi, *Z. physik. Chem.*, **B, 1**, 21 (1928)) if the chlorine is introduced by means of a jet into an excess of sodium, as indicated in Fig. 226. The intensity of the light emission is measured by means of a photometer (M. Polanyi and G. Schay, *Z. physik. Chem.*, **B, 1**, 30 (1928)). The emission of light is connected with the reaction

$$Cl + Na_2 = NaCl + Na, \quad \ldots\ldots\ldots\ldots(33)$$

the Cl atoms being formed by

$$Na + Cl_2 = NaCl + Cl. \quad \ldots\ldots\ldots\ldots(34)$$

For the derivation of the velocity constant of the reaction (33) from the distribution of the intensity of the emitted light, the original papers should be consulted. Similar reactions occur between other halogens and alkali metals and between Na and $HgCl_2$ (M. Polanyi and G. Schay, *loc. cit.* ; H. Ootuka and G. Schay, *Z. physik. Chem.*, **B, 1**, 62, 68 (1928)). All these reactions, and those between alkali metal molecules and hydrogen halides (G. Schay, *Z. physik. Chem.*, **B, 11**, 291 (1931)), proceed at practically every collision.

A different kind of technique was developed by H. v. Hartel and M. Polanyi (*Z. physik. Chem.*, **B, 11**, 97 (1930)) for investigating reactions of the type

$$Na + R\,Hal \rightarrow NaHal + R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (35)$$

(R = organic radical), which do not proceed at every collision. In this 'diffusion' method again the principle of dilute flames is applied, in that the distance is measured into which one component can penetrate into the other. Owing to the relative slowness of these reactions this distance would be large; for experimental reasons it is shortened by increasing the diffusion resistance by the addition of a foreign gas.

The principle of the experimental arrangement is shown schematically in Fig. 227. The foreign or 'carrier' gas streams over the surface of

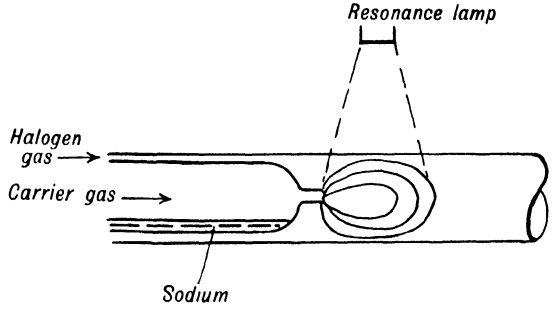


FIG. 227. The principle of the diffusion method.

sodium kept at a fixed temperature (about 250° C.), and is thereby saturated with sodium vapour. The pressure of the carrier gas (usually H_2 or N_2) is about 2 to 10 mm., and the partial pressure of sodium 2×10^{-3} mm. The carrier gas enters the reaction tube through a jet, and reacts there with the halide gas at a pressure of a tenth of a millimetre. The distribution of the sodium vapour in the reaction zone is made visible by illumination with a sodium resonance lamp. The luminous cloud of sodium emerging from the jet is larger the more slowly the sodium is used up by the reaction with the halogen gas. Thus the diameter of this sodium 'flame' is a measure of the velocity constant. If d is the diameter of a spherical flame, D the diffusion coefficient of the gas mixture and p_0 the limiting pressure under which the sodium cloud is no longer detectable, the velocity constant k is given by

$$k = \frac{4\,(ln\, p_{Na}/p_0)^2 D}{d^2 p_{Hal}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (36)$$

(p_0 is less than 10^{-5} mm.). This equation holds, provided the flow of the carrier gas at the jet is fast enough to prevent diffusion of an appreciable

amount of halogen gas through the jet against the gas stream. On the other hand the velocity of flow of the carrier gas in the reaction tube must be sufficiently slow so that the distribution of reactants should be effected only by diffusion, otherwise the halogen gas is blown away from the neighbourhood of the jet by the gas stream, and the flame becomes long instead of spherical.

The experimental arrangement is shown in Fig. 228, according to H. v. Hartel, N. Meer and M. Polanyi (*Z. physik. Chem.*, **B, 19**, 139

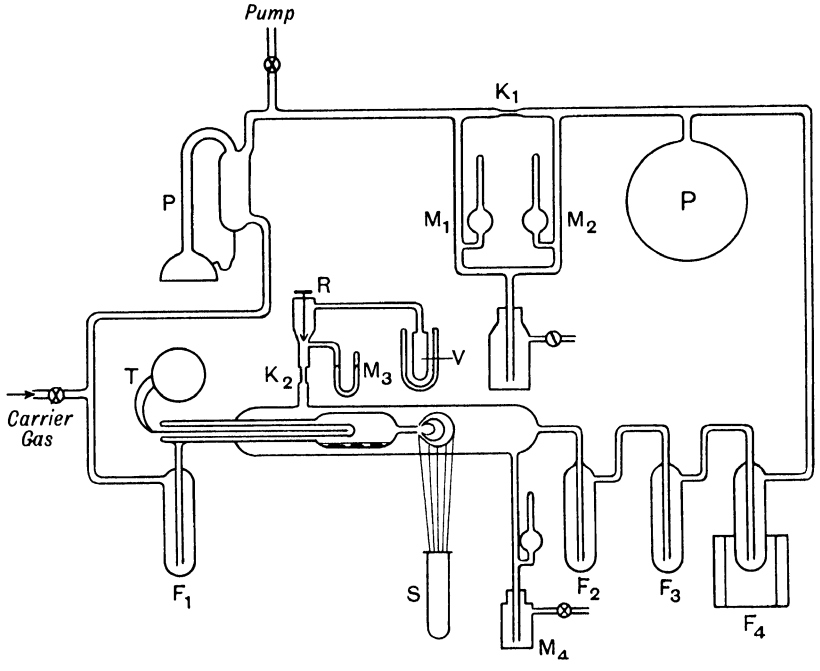


FIG. 228. Experimental arrangement for the diffusion method.

(1932)). The carrier gas, H_2 or N_2, is kept in circulation by the mercury pump P. The velocity of circulation is controlled by the capillary K_1, which can be altered if smaller velocities of flow are required for slower reactions. The velocity of circulation is determined from the pressure difference (a few tenths of a mm.) on both ends of the capillary as measured by the double McLeod gauge M_1M_2 (cf. p. 102). Reaction products are removed from the carrier gas in the liquid air traps F_2 and F_3. In trap F_4 the carrier gas is brought into contact with hot sodium in order to remove traces of hydrochloric acid and cyanogen which are not trapped in F_2 and F_3. The partial pressure of sodium in the carrier gas

corresponds to its temperature as measured by the thermocouple T. The other reaction partner, (Hl), 10-20 gr. alkyl halides or the like, is kept in vessel V at a suitable temperature in order to produce a vapour pressure of about 1/20 to one millimetre. The vapour is then admitted through the valve R and the capillary K_2 into the reaction vessel. The partial pressure of Hl in the reaction vessel is calculated from the pressure read on manometer M_3 by means of an empirical calibration. The buffer volume P (15 litres) serves to reduce the pressure increase caused by the admission of the halogen gas. The pressure inside the reaction vessel is measured by manometer M_4. In order to illuminate the sodium cloud, a sodium arc lamp (S) of the Cario-Lochte-Holtgreven type (G. Cario, and W. Lochte-Holtgreven, *Z. Physik*, **72**, 22 (1927), and W. Zehden, *Z. Physik*, **86**, 555 (1933)) is used, in which self-absorption of the resonance line is prevented by circulation of inert gas.

The experimental procedure is: first to establish the carrier gas circulation, then to adjust the pressure of the halogen gas, and finally to determine the diameter of the flame (N. Meer and M. Polanyi, *Z. physik. Chem.*, **B**, **19**, 164 (1932)).

E. FACTORS INFLUENCING THE PROGRESS OF THE REACTION

1. Time

In kinetic experiments the time is usually measured by stop watches and stop clocks. It is advisable to compare the time-keeping of the stop watches at frequent intervals with that of a reliable ordinary watch or clock. It is also good practice to note the time (hours and minutes) at the beginning of each experiment of long duration. The experiment will not then become useless should the stop watch fail or run down in the middle of an experiment. If the readings are to be taken at certain time intervals an ordinary alarm clock, which can be set to ring after a definite period, is very useful. It must be used in conjunction with the stop watch, and the alarm must be set somewhat earlier than the required time in order to give ample time to get ready for taking a reading.

It is often necessary to stop or start a stop watch automatically. For example, in photo-chemical reactions of long duration, it is of great advantage if the stop watch is arrested when the light source goes out accidentally. If electric clocks are used, this can be easily attained by employing a magnetic relay which breaks the circuit of the clock as soon as the main circuit is interrupted. It is rather difficult to operate a stop

clock mechanically, because quite considerable pressure must be applied to the push button. A stop clock, which is operated by an easily movable lever, can be controlled by a magnetic relay quite conveniently. Fig. 229 shows the arrangement used by A. Eucken (*Handbuch der Experimental-*

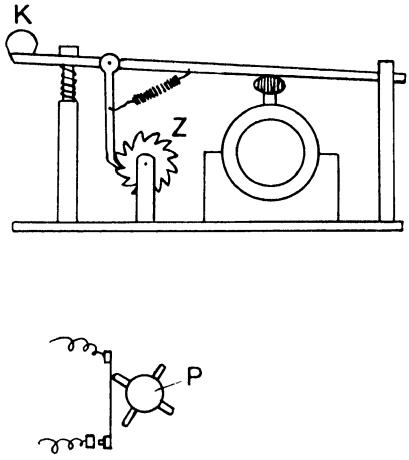


FIG. 229. Arrangement for starting stop-watch and switching on an electric current simultaneously.

Physik, Bd. VIII, 1, 77, Leipzig (1929); A. Eucken and E. Donath, *Z. physik. Chem.*, **124**, 191 (1928)) for switching on one or more electric circuits simultaneously with the starting of the stop watch. By pressing down button *K*, the stop watch is started. At the same time cogwheel *Z* is turned through an angle corresponding to one tooth. The cogwheel has twelve teeth and is coupled with cylinder *P* carrying four projecting cams, which make contact at every third pressing of button *K*.

Very short-time periods are registered photographically on a fast-moving film, the vibrations of a tuning fork being used as time marks (cf. pp. 335, 366).

2. Temperature and Pressure

I. Temperature

There is little more to be said about producing and measuring temperatures than is found on pp. 103-140. Some special types of apparatus are referred to in pp. 326 and 343.

II. Pressure

(*a*) *Adjustment of pressure.* A convenient way of obtaining any required pressure is shown in Fig. 230. The reaction vessel is evacuated, taps 1

and 2 are closed, tap 3 is opened, and the pressure adjusted at leisure in the auxiliary volume V by admitting gas from the storage vessel S and

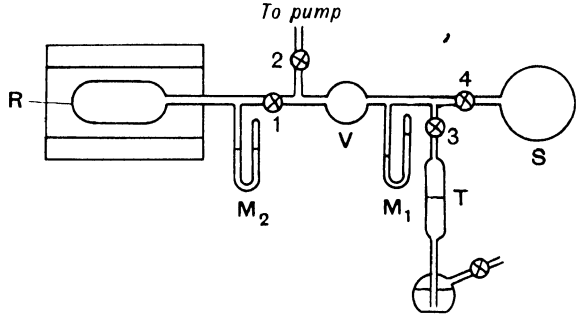


FIG. 230. Adjustment of pressure.

varying the volume of T. If the required pressure, which is easily calculated from the volume ratio of V and R, is reached, tap 3 is closed, and by opening tap 1 once or twice at close intervals for a short time gas is admitted to the reaction vessel. The initial pressure is read on manometer M_1. Manometer M_2 shows the pressure in the reaction vessel, which might be different from that shown by M_1 after a relatively short period of time if the reaction is proceeding very rapidly. If manometer M_2 is read, the error in determining the initial pressure is larger the higher the pressure. Such systematic errors might give the illusion of a decreasing reaction order (cf. C. N. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford (1933), p. 211).

Working with gaseous mixtures at low pressures care must be taken to avoid separation of the components when they are being pumped or admitted through small openings. The separation is greater the greater the difference in the molecular weights of the components (cf. formula 53, p. 18). It was shown by E. O. Wiig (*J. Am. Chem. Soc.*, **55**, 2173 (1933)) that the alleged disappearance of more oxygen than corresponded to the $O_2 : 2H_2$ ratio in the catalytic formation of water on a platinum wire was due to this effect (cf. also E. O. Wiig and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **54**, 1806 (1932)). Such a separation also occurs when working with mixtures of light and heavy hydrogen (A. and L. Farkas, *Proc. Roy. Soc.*, **A, 144**, 467 (1934)).

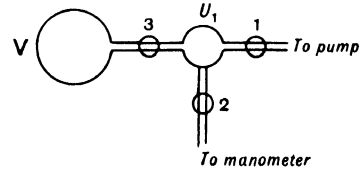


FIG. 231. Separation of gas mixtures.

How this effect can be avoided is best illustrated by the following example. Pressure p_0 in vessel V has to be reduced to p Fig. 231. The pressure is so low that the mean free path is larger than the opening in

tap 3. If the pressure is reduced by pumping through tap 3, the separation is given by

$$\left(\frac{A_0}{A}\right)\left(\frac{B}{B_0}\right)^s = \left(\frac{p_0}{p}\right)^{s-1} \text{ with } s = \sqrt{M_B/M_A}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (37)$$

where A_0, B_0, A and B are the initial and final concentrations of the components and M_A and M_B their molecular weights. No separation occurs, however, if the pressure is reduced by letting the gas expand to volume U_1, closing tap 3 and evacuating volume U_1 completely, and repeating this operation until the required pressure is reached.

Another kind of separation, due to thermal diffusion, occurs if two communicating vessels are kept at different temperatures. (For details cf. T. L. Ibbs and K. E. Grew (*Proc. Roy. Soc.*, **A, 41**, 456 (1929) ; **A, 43**, 142 (1931).)

(*b*) *Mixing of gases.* If one gas is condensable, a mixture of two gases can be made in the following way. First the condensable gas is admitted and the pressure read. Then the gas is condensed in a side tube, the second component added, and the pressure read again after the first component has been evaporated. If the mixture is made up by admitting the second component into a vessel which already contains the first, there is always the risk that some of the first component will leave the vessel while the second is being admitted, except if the initial pressure difference inside and outside of the vessel is large. If gaseous mixtures are made, it is necessary to remember that mixing is not instantaneous. Often it is necessary to add small amounts of a certain gas to another, or to a mixture of other gases. This can be done by preparing, say, a 10 per cent. mixture and combining this with the pure component in the required proportion (cf., for example, S. G. Foord and R. G. W. Norrish, *Proc. Roy. Soc.*, **A, 152**, 196 (1935)). Another method involves the use of capillary locks, as mentioned on p. 146. The tap shown on Fig. 232 (designed by A. and L. Farkas), has the advantage in that it allows both the adding of small amounts of gas to, or extracting them from, a mixture, and connecting tubes 1 and 2 directly through a sufficiently wide hole.

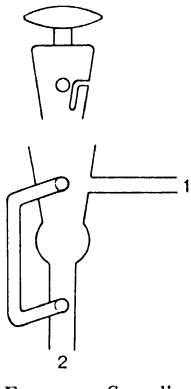


FIG. 232. Sampling tap.

(*c*) At *low pressures* special attention must be paid to the absence of leaks in an apparatus. A convenient way of testing for leaks is to use the Farkas low pressure thermal conductivity gauge, according to the arrangement shown in Fig. 133 (p. 192). The cell is evacuated, the filament slightly heated and the bridge balanced. If the tap to the lower

pump is closed, all gas from the apparatus is pumped into a cell. The bridge is thrown out of balance and the galvanometer is deflected if gas is set free in the apparatus. By this method leakage can be detected within a few seconds, even if the gas is accumulating in the apparatus so slowly that some minutes elapse before it could be measured by a sensitive McLeod gauge or other manometer.

Porous materials, such as powdery catalysts and charcoal, contain considerable amounts of gases. This has to be taken into consideration if an apparatus containing these kinds of materials has to be evacuated. Conversely, the establishment of the pressure equilibrium in vessels containing such substances takes time, because at low pressures diffusion into fine pores is a relatively slow process (G. Damköhler, *Z. physik. Chem.*, **A**, **174**, 222 (1935)). Similarly temperature equilibrium is slowly attained at low pressures, owing to poor heat transfer from one particle to another. If such materials have been outgassed at high temperatures, the inside of the powder will remain hot long after the walls of the vessel have attained room temperature.

(*d*) *The order of the reaction* can be determined from (1) the progress of the reaction with time, (2) the variation of the velocity with concentration, (3) the time of equal fractional change, and (4) the variation of the initial velocity with concentration.

According to the first method, the progress of the reaction is followed at certain intervals, and from each reading of the indicating instrument a set of velocity constants is calculated, assuming different orders for the reaction. The correct order is one in which these constants show no drift during the progress. This method is not very exact, since the progress of the reaction, especially in the initial steps, can usually be equally well represented by constants calculated on the basis of the order 1 or 2, or even 3. The second method is far more satisfactory, that is, the concentration is varied and the constants calculated assuming different orders. In this case the correct order is that one for which the constants are independent of the pressure. As an illustration of these two methods some data on the thermal parahydrogen conversion (A. Farkas, *Dissert.*, Frankfurt (1930)) may be mentioned. The velocity constants k_1, k_2 and k_3 in Table 43 are calculated according to the mechanisms :

$$(1)\quad H + p\text{-}H_2 \rightleftharpoons o\text{-}H_2 + H, \quad \ldots\ldots(38)$$

$$(2)\quad 2p\text{-}H_2 \rightleftharpoons 2o\text{-}H_2, \quad \ldots\ldots(39)$$

$$(3)\quad 3p\text{-}H_2 \rightleftharpoons 2o\text{-}H_2 + p\text{-}H_2. \quad \ldots\ldots(40)$$

The order of the first reaction is 1·5 with respect to the concentration of hydrogen, since the concentration of atomic hydrogen is proportional to the square root of the hydrogen concentration. The second and third

reactions are of the second and third order respectively. It will be recognised that any set of constants is compatible with the progress of the reaction. The dependence of the reaction rate on pressure can only be represented by the constants calculated on the basis of the first mechanism, the order of which is 1·5. The other two sets of constants vary systematically as the pressures changes.

TABLE 43

Pressure, mm. Hg	Time, mins.	% p-H_2	Temperature = 600° C. k_1	k_2	k_3
400	0	48 0	—	—	—
	3	44·3	1 66	0·101	0·015
	5	43·5	1·25	0·076	0·011
	8	41·5	1·19	0·075	0·011
	10	40·8	1·08	0·067	0·010
	13	38·9	1·11	0·071	0 011
	16	36·8	1·19	0 078	0·013
	29	32·9	1 06	0·070	0·012
		Average -	1·22	0 077	0 012
200	0	48·0	—	—	—
	5	44·8	1·21	0·108	0 031
	6	44 3	1·16	0·106	0 030
	9	42·2	1·22	0·115	0 035
	10	42·0	1 20	0·108	0 033
	13	41·4	1·03	0·093	0·029
	20	37·2	1·26	0·134	0 039
	35	32·8	1·22	0·118	0 045
		Average -	1·19	0·112	0·034
100	0	48·0	—	—	—
	3·25	46·4	1·29	0·154	0·101
	4	46·0	1·31	0·157	0·099
	7	44·7	1 27	0·159	0 090
	9	44·8	0 95	0·115	0·068
	12	43·5	1·04	0·130	0·075
	15	42·0	1·15	0·143	0 087
	30	39·1	0 94	0·118	0·064
		Average -	1·13	0 138	0·083
50	0	47·5	—	—	—
	7	45 4	1·59	0·202	0 239
	11	45 0	1·16	0·147	0·190
	12	44·5	1·25	0·167	0·212
	17	44·0	0·99	0·142	0·176
	23	42·4	1·04	0·156	0·197
	36	40·0	0·99	0·163	0·195
		Average -	1·17	0·163	0·202

According to the third method, no velocity constants need be calculated, but the time of equal fractional change measured at different initial concentration or pressures. The order (n) is then given by

$$\left(\frac{\tau_1}{\tau_2}\right)=\left(\frac{p_2}{p_1}\right)^{n-1}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(41)$$

where τ_1 and τ_2 are the times of equal fractional change at the initial pressures p_1 and p_2 respectively. Any fractional change can be chosen to determine τ_1 and τ_2, but very often the reaction is followed until it has taken place to an extent of 50 per cent., and the times are then referred to as times of half-change or half-periods. If the fourth method is used, the reaction is only followed during the initial stages. Then the plot chemical change against time is practically linear, since the initial concentration changes only little. If Δc_1 and Δc_2 are the changes in the concentration in given time at the initial concentration c_1 and c_2 respectively, the order (n) is given by

$$\frac{\Delta c_1}{\Delta c_2}=\left(\frac{c_1}{c_2}\right)^n. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(42)$$

An equation of the same form is valid if the concentration c is replaced by the pressure p. This method should be used very cautiously, since the initial stages of the reaction are often somewhat indefinite, owing to experimental conditions. The gases take some time to become thoroughly mixed or to attain the temperature of the reaction vessel. Slight impurities or other effects can cause induction periods (cf. p. 366).

If two or more reactants are involved, the order of the reaction has to be determined with respect to each. This can be done conveniently according to the above methods if all of the other reaction partners are present in great excess.

For heterogeneous catalytic reactions the order of the reaction can refer to the dependence of the reaction velocity on the concentration in the gaseous phase or on the concentration in the adsorption layer. It is obvious that the order referring to the concentration in the adsorption layer, the true order, is more characteristic of the catalytic reaction than the apparent order referring to the concentration in the gaseous phase. (True and apparent order are used here in a different sense than by C. N. Hinshelwood, *Kinetics of Chemical Change*, p. 326). The true order can only be determined if the dependence of the concentration in the gaseous phase, i.e. the adsorption isotherm, is known (cf. p. 351). For catalysts with a small surface area (wires, strips, etc.) the adsorption isotherm cannot usually be determined, owing to the small amount of gas present in the adsorption layer. A further complication arises in certain cases owing to the mutual displacement of the reaction partners

by each other or by the reaction products from the adsorption layer (cf. p. 37). For these reasons the apparent order is usually determined according to the same principles as those employed for homogeneous reactions.

Working at pressures of about one atmosphere it is necessary to ascertain whether the diffusion is fast enough to transport gas to and from the catalyst in order to cope with the chemical change on the surface of the catalyst. This is of special importance if the catalyst does not fill the whole of the reaction vessel uniformly. If by increasing the temperature of the catalyst the velocity of the reaction increases according to the temperature coefficient at lower pressures and much faster than corresponding to the variation of the diffusion coefficient with temperature (p. 15), it is certain that the diffusion is fast enough. Another way to assess the rôle of diffusion in the heterogeneous reaction is to vary the dimensions of the reaction vessel and the distribution of the catalyst.

(*e*) *High pressures.* If cylinders containing compressed gases at 100 to 200 atmospheres are used as a source of gas, no further apparatus is necessary to obtain high pressures. Otherwise, compressors or hand-pumps have to be applied. An example of the use of the latter in

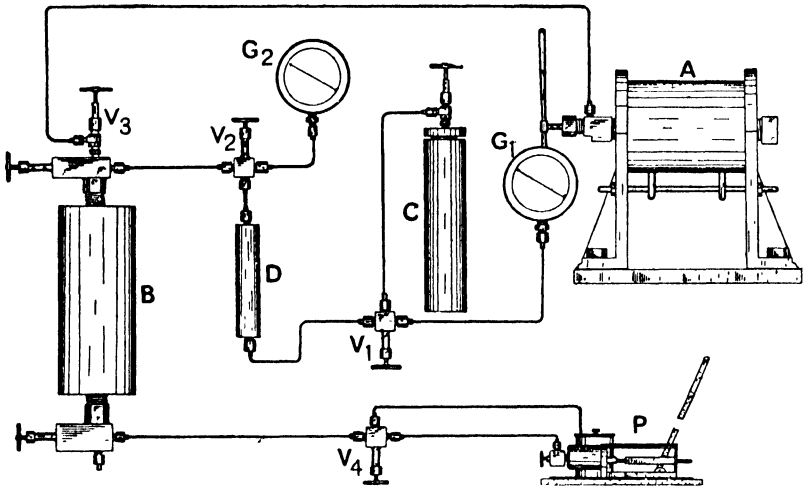


FIG. 233. Experimental arrangement for obtaining high pressures.

producing pressures up to 1000 atmospheres is shown in Fig. 233 (W. A. Bone, D. M. Newitt and D. T. A. Townend, *Proc. Roy. Soc.*, **A**, **139**, 62 (1933)). From cylinder *C* the compression cylinder *B* and reaction vessel *A* are filled to 100 atmospheres (vessel *D* serves to clean the gases). Then valve V_1 is closed. By means of hydraulic pump *P*, mercury is

pumped into *B*, and the gases thus compressed to the desired pressure. For producing the highest pressure the hydraulic pressure is increased by an intensifier, i.e. a hydraulic press with two pistons of different cross-section mounted together in a single cylinder (cf. P. W. Bridgman, *Physics of High Pressure*, G. Bell & Sons, London (1931), p. 56; and D. T. A. Townend and L. A. Bhatt, *Proc. Roy. Soc.*, **A, 134**, 502 (1931)).

Condensable gases like O_2, N_2 and NH_3 can be compressed through condensation by immersing a small steel cylinder in liquid air while the

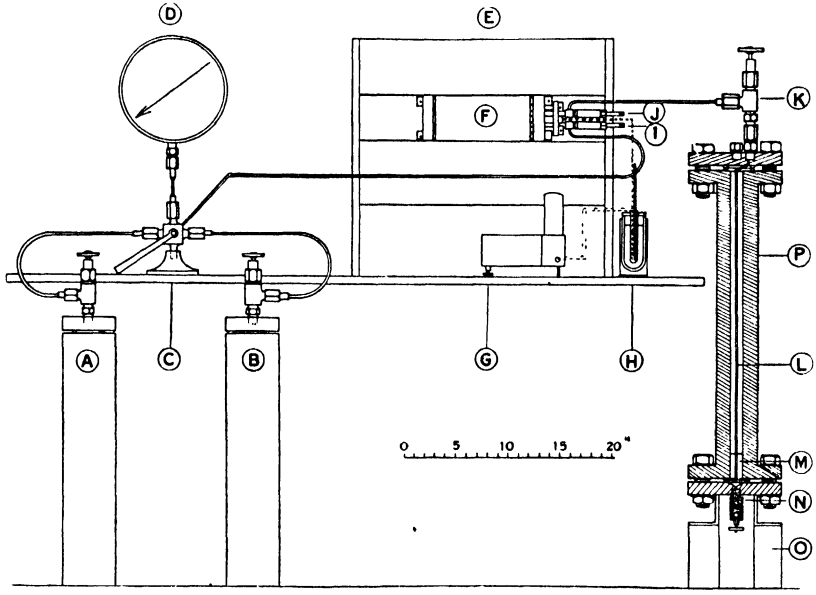


FIG. 234. Experimental arrangement for investigating reactions at high pressures.

cylinder is in connection with a low pressure gas reservoir. This operation should be done very carefully and the amount of gas condensed exactly determined, since the cylinder is liable to burst if too much gas has been condensed in it and is thereafter brought to room temperature. When working with gases like NH_3 and SO_2, which become liquid at room temperature at relatively low pressures, the amount of gas condensed does not matter, provided that the cylinder has not been filled completely; otherwise the cylinder might burst by the thermal expansion of the liquid.

A simple experimental arrangement used by D. M. Newitt and A. E. Haffner (*Proc. Roy. Soc.*, **A, 134**, 591 (1931)) is shown in Fig. 234. The reaction vessel *F* is made of nickel-chromium-molybdenum steel, and

withstands pressures up to 300 atmospheres at a temperature of 500° C. The cylinders *A* and *B* contain the reaction mixture in the desired proportions at high pressure. The gases are introduced into the reaction vessel through the inlet valve *I* and the control valve *C*, the pressure

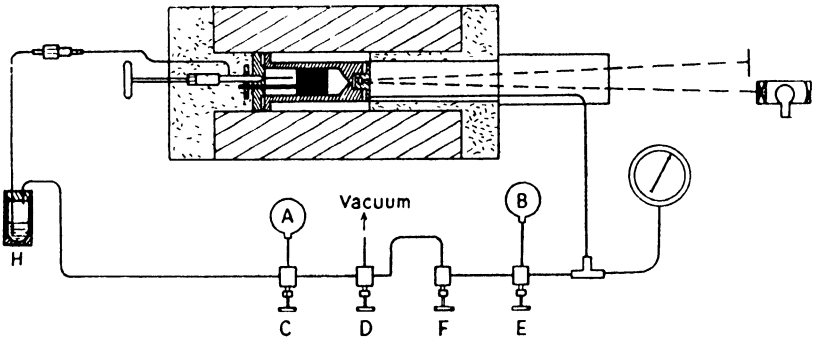


FIG. 235. Experimental arrangement for investigating reactions at high pressures.

being read on Bourdon gauge *D*. The reaction vessel is heated in the furnace *E* and the temperature measured by thermocouple and millivoltmeter (*H* and *G*). The reaction is stopped by opening valves *J* and *K* and discharging the contents of the reaction vessel into expansion chamber *P*. The products in *P* are subsequently analysed.

Another experimental arrangement allowing pressure measurements during the course of the reaction $CO + 2H_2 = CH_3OH$ is shown in Fig. 235 (D. M. Newitt, B. J. Byrne and H. W. Strong, *Proc. Roy. Soc.*, **A**, **123**, 240 (1929)). The reaction vessel containing the catalyst is heated in an electric furnace. The pressure is measured by a high pressure 'neutral disc' manometer, which is very useful if large dead spaces are to be avoided or there is risk of condensation of liquids in the cold parts of a manometer. Its design is shown in Fig. 236 (*Proc. Roy. Soc.*, **A**, **123**, 239 (1929)). The pressure measuring element consists of a thin corrugated metal disc *A*, clamped between reaction vessel *B* and a steel plate *C*. An unsupported area communicates with the reaction vessel and the compensation chamber *D*, and bulges toward the side at the lower pressure. Its movements are transmitted by a fine steel rod to a mirror pivoted on plate *C* and magnified by a beam of light passing through quartz window

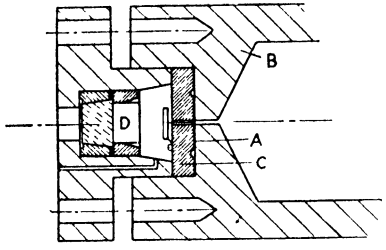


FIG. 236. High pressure 'neutral disc' manometer.

E, which is a truncated cone with slight taper, well ground into the steel shell and kept in position by a washer and a steel collar (W. A. Bone and D. M. Newitt, *Proc. Roy. Soc.*, **A, 115**, 45 (1927)). The pressure inside the vessel is measured by altering the pressure in the compensation chamber until the beam of light returns to its zero position. By using thin discs the sensitivity of the manometer is high enough to measure fractions of one atmosphere at pressures around 100 atmospheres without the danger of permanent distortion or rupture of the disc. The reaction vessel (Fig. 235) can be charged either with a liquid which is forced into the reaction vessel from cylinder *H* by the pressure in cylinder *A*, or with the gas mixture $CO + 2H_2$ from *A* if *H* is empty, or with a mixture of $CH_3OH + CO + H_2$ of known composition if a certain measured amount of CH_3OH is placed in *H*. Cylinder *B* contains nitrogen, which is used to fill the compensation chamber of the neutral disc manometer. By opening valve *F* the reaction vessel and compensation chamber can be filled simultaneously. The apparatus shown in Fig. 237 is used by the

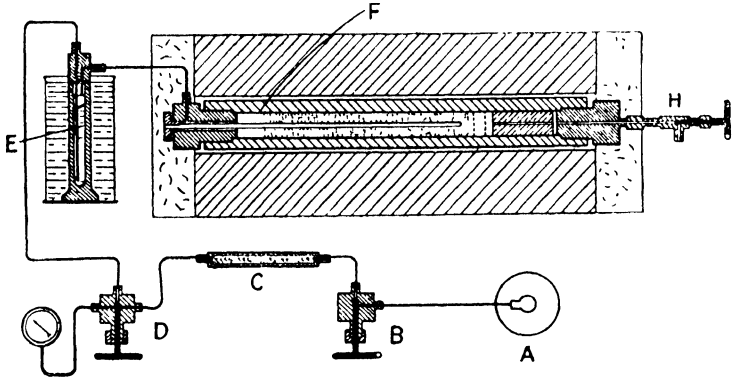


FIG. 237. Experimental arrangement for investigating reactions at high pressures.

same authors for an investigation of the reaction $CO + 2H_2 = CH_3OH$ according to the flow method. The gas mixture $CO + 2H_2$ is contained in cylinder *A*, dried in the $CaCl_2$ tube *C*, and mixed with a certain amount of CH_3OH in vessel *E*, which is kept at constant temperature. The velocity of flow is determined after the gas leaves the reaction vessel through expansion valve *H* (cf. also D. M. Newitt and G. Semerano, *Proc. Roy. Soc.*, **A, 157**, 348 (1936)).

If metal vessels are liable to catalyse the reaction in question, glass or silica vessels have to be used even at higher pressures. The use of glass or silica vessels can be extended to very high pressures if the pressures inside and outside the reaction vessel are kept equal.

Some difficulty is encountered if glass vessels have to be connected with valves, storage vessels, pumps and the like made of metal. Glass or silica can be joined to metal by cementing with sealing wax, as shown in Fig. 238. Another method is to platinise the glass or silica, or to electro-plate it with copper and to solder it to the metal. Platinum coating can be applied to glass or quartz, according to F. Daniels and E. H. Johnston (*J. Am. Chem. Soc.*, **43**, 53 (1921)), in the following way. The glass to be platinised is dipped into absolute alcohol containing 1·5 g. anhydrous platinic chloride and an equal weight of oil of lavender per 100 c.c. It is then held over a piece of sheet copper heated by a blast lamp. The platinum is burnt in with an alcohol flame, overheating being thereby avoided. Two or more coats are applied. Good coating cannot be scraped off with a knife. The layer of cement or of solder joining the metal and the glass has to be kept as thin and long as possible, since this layer is mainly exposed to shearing stress. Glass and metal tubes can also be joined by sealing a thin platinum or copper tube into the glass, which is then soldered to the metal.

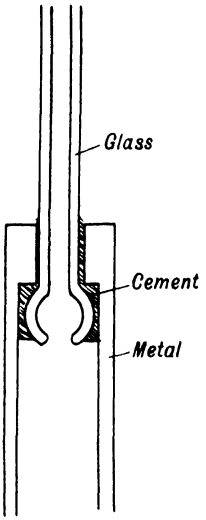


FIG. 238. Metal-glass pressure joint.

The apparatus used by N. Nagasako and M. Volmer (*Z. physik. Chem.*, **B, 10**, 414 (1931)) for investigating the decomposition of N_2O in a quartz vessel at pressures up to ten atmospheres is shown in Fig. 239. The reaction vessel is joined to the glass apparatus by cementing at *W*, and the joint is water-cooled. Trap *F* serves to eliminate impurities and is kept at −25° C. Cylinder *P* contains mercury, and is provided with spindle *S* by which the level of the mercury can be lowered and raised. At the beginning of the experiment the mercury is lowered below mark *M* and the apparatus is exhausted. A certain amount of N_2O is condensed into the reaction vessel from the storage vessel *R* and valve *V* is closed. The amount of gas admitted is calculated from the decrease of

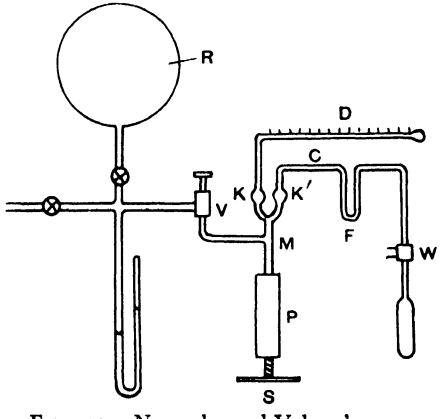


FIG. 239. Nagasako and Volmer's arrangement for investigating reactions in quartz vessels at pressures up to 10 atm.

pressure in R and the volume of R. The N_2O is evaporated by dipping the reaction vessel into water at 45° C., and spindle S is raised until the mercury enters the horizontal portion of the capillary tubes above the bulbs K and K'. Then the reaction vessel is immersed in a lead bath, and the reaction is followed by observing the movement of the mercury in the capillary D, while the level of the mercury is kept at a certain mark in tube C by adjusting spindle S from time to time. At each

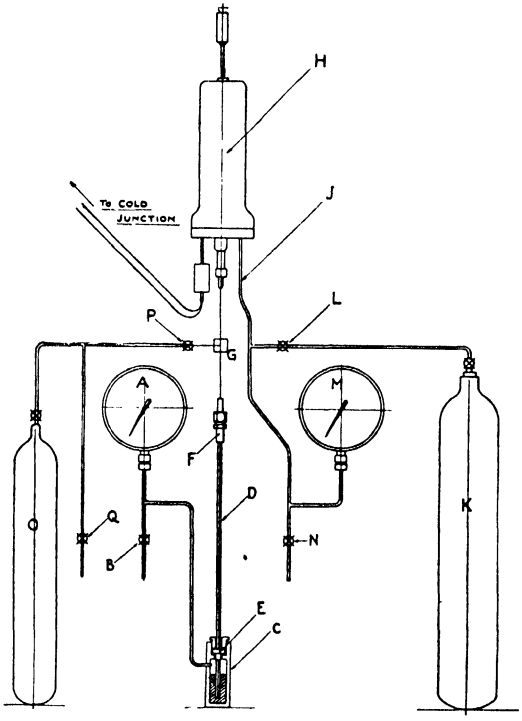


FIG. 240. Method of pressure compensation.

temperature a blank experiment is made with air in order to ascertain the expansion of the gas due to heating.

In using the method of pressure compensation at higher pressures the two pressures cannot be kept exactly equal. It is advisable to keep the outside pressure slightly higher, since glass vessels stand much higher pressure differences from the outside than from the inside. The experimental arrangement used by E. Hunter (*Proc. Roy. Soc.*, **A, 144**, 386 (1934)) illustrates the method of pressure compensation (Fig. 240). Bomb H is fitted with an inner electric heating coil which surrounds the silica reaction vessel. The wires for heating and for the thermocouple

are led into the vessel according to the method of Welbergen (cf. p. 274). The capillary tube of the reaction vessel is soldered to the steel tube leading out of the bomb. By opening needle valves P and L simultaneously, the N_2O is admitted from the high pressure cylinder to the inner reaction vessel, while the bomb is filled from cylinder K with nitrogen at such speed that manometers M and A show equal pressures. Since during the course of the reaction the pressure increases inside the reaction vessel because of the decomposition of N_2O, the pressure outside the vessel is correspondingly adjusted.

3. Photo-chemical Reactions

The general apparatus and methods used in photo-chemical reactions have been discussed in Chapter IV. In the following pages some further special features are given.

(*a*) *Thermostats.* The arrangements for keeping the temperature of the reactive mixture constant during the illumination have been referred to on p. 242. V. A. Plotnikow (*Allgemeine Photochemie*, Walter de Gruyter Co., Berlin (1936), p. 311 ff.) has described a number of ' light-thermostats ' for this purpose. The principle of all these thermostats is the same as that described on pp. 242 ff., i.e. the reaction vessel is surrounded by a suitable cooling material, and the illumination is done through the cooling vessel. Another form of thermostat has been described by M. Bodenstein and P. W. Schenk (*Z. physik. Chem.*, **B, 20,** 420 (1933)), in which the reaction vessel can be illuminated directly. L. Farkas and H. Sachsse (*Z. physik. Chem.*, **B, 27,** 111 (1934)) have inserted an evacuated space in the path of the radiation. The reaction vessel is thus efficiently thermally insulated, and the light is prevented from passing through the liquid in the thermostat.

For photo-chemical reactions at higher temperatures H. J. Schumacher and G. Stieger (*Z. physik. Chem.*, **B, 13,** 157 (1931)) use an aluminium block furnace to keep the temperature constant. The furnace has a form of an inverted cup, and the reaction vessel can be illuminated directly from below.

(*b*) *Reaction cells with plane-parallel windows.* A glass sealing furnace for making adsorption and reaction cells with plane-parallel windows (J. R. Dilley, *Rev. Sci. Instruments*, **8,** 394 (1937)) is shown in Fig. 241. To affix the windows the glass cylinder with the window in position is placed on table A and the furnace B is heated to or near the fusing temperature of the glass. Then a sealing flame is introduced through the flared opening C, and directed against the joint as the table is slowly revolved. To seal the upper window the length of spindle D sliding in the hollow shaft E is adjusted until the window to be

joined is at the same height as that of one of the openings admitting the sealing flames.

(*c*) *Vessels for short wave ultra-violet.* Very thin (0·01 mm.) silica is sufficiently transparent for ultra-violet light down to 1720 Å to permit of its being used as windows for reaction vessels in the short wave range. Thus the use of fluorite windows may be avoided. The construction of thin silica windows is carried out in a similar manner to that of thin glass

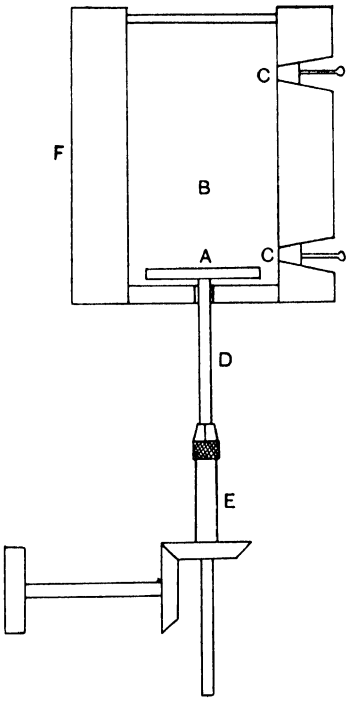


FIG. 241. Glass sealing furnace for making cells with plane-parallel windows.

windows (see p. 268). Such windows have been used by G. B. Kistiakowsky (*J. Am. Chem. Soc.*, **52**, 1868 (1930)) and H. A. Smith and G. B. Kistiakowsky (*J. Am. Chem. Soc.*, **57**, 835 (1935)) with a spark burning between two slowly revolving aluminium discs (E. O. Wiig and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **54**, 1807 (1932)) as a light source. The distance between light source and reaction vessel was 1·5 cm. A layer of air of this thickness completely absorbs radiation in the neighbourhood of 1720 Å, but partially transmits light in the neighbourhood of 1860 Å. Nitrogen does not absorb at either wavelength. A rough filter may therefore be improvised by using air and then oxygen-free nitrogen between source and reaction vessel.

Combinations of light source and reaction vessel incorporating quartz windows are shown in Fig. 242 (H. Neujmin and B. Popov, *Z. physik. Chem.*, **B, 27**, 15 (1934)) and in Fig. 243 (A. Eucken and F. Patat, *Z. physik. Chem.*, **B, 33**, 459 (1936)). In Fig. 242 a quartz hydrogen tube (see p. 230) is used as light source, and is cooled by running water. Since the trap is also made of quartz and is cooled with liquid air, any contamination of the reaction vessel with vapours of grease or picein and the like is avoided (cf. also B. Popov, *Acta Physicochemica*, 3, 223 (1935)). In Fig. 243 an aluminium spark is the light source. The spark burns between two aluminium electrodes (*E*) fastened to copper bars, which are insulated by glass tubes and kept in a fixed position in a silica tube. The silica tube (3·2 cm. wide and 27 cm. long) has a double bottom with a hole in the inner tube. From tube 1 nitrogen streams through the space between the two bottoms and into the inside of the silica tube, in order to cool the electrodes and to prevent condensation of sputtered aluminium. The outer bottom is blown exceedingly thin, so that more than half of the radiation of the wavelength of 1720 Å is transmitted. The reaction zone (*R*) is formed by the space between the silica tube and an outer glass tube into which the former is cemented.

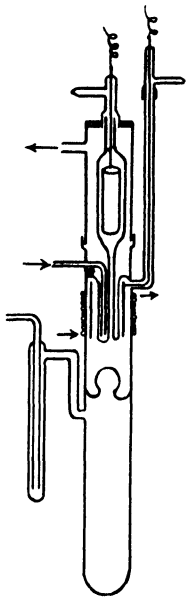


FIG. 242. Combination light source and reaction vessel for short wave ultra-violet.

Another combination of reaction vessel and light source is described by W. Kuhn and H. Martin (*Z. physik. Chem.*, **B, 21**, 93 (1933)) for the photo-chemical separation of the chlorine isotopes.

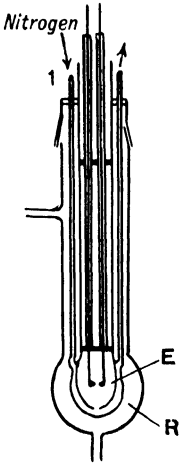


FIG. 243. Combination light source and reaction vessel for short wave ultra-violet.

(*d*) *Special windows.* Corex-glass (Corning) is a phosphate glass used for long wave ultra-violet (for transmission, see p. 246). It is attacked by the atmosphere. W. Zeigler and M. Zeigler-Wellmann (*Z. technische Physik.*, **14**, 288 (1933)) describe a glass made from 76 per cent. boric acid, 18 per cent. lithium carbonate and 6 per cent. barium carbonate, which is stable and transmits

light down to 1900 Å. Artificially prepared sodium and lithium fluoride crystals (E. H. Melvin, *Phys. Rev.*, **37**, 1230 (1931)) are better than natural fluorite, since they transmit light down to 1300 and 1100 Å respectively.

(*e*) *Light sources for short wave radiation.* For the wavelength region 1900-1720Å, W. E. Vaughan and W. A. Noyes (*J. Am. Chem. Soc.*, **52**, 559 (1930)) used a hydrogen discharge tube of the following dimensions as a light source : length 150 cm., width 2 cm., iron electrodes 95 cm. apart in side tubes which are 50 cm. long. The ends of the tube are carefully ground, and closed by fluorite windows cemented on with picein. Hydrogen flows continually through the tube at a pressure of 0·1 mm. Current is supplied by a 1 kw. transformer with a peak voltage of 30,000. The number of short wave quanta emitted is about 10^{17} sec.$^{-1}$.

For the region below 1500 Å the xenon lamp of P. Harteck and F. Oppenheimer (*Z. physik. Chem.*, **B, 16**, 77 (1932)) can be used for investigating photo-chemical reactions. It is a low tension discharge tube filled with a mixture of argon or neon with xenon. The electrodes are oxide-coated filaments heated to 1000° C. The intensity of the emitted group of lines near 1469 Å and 1295 Å is considerably increased according to W. Groth (*Z. Elektrochem.*, **42**, 533 (1936) ; *Z. physik. Chem.*, **37**, 307, 315 (1937)) by applying a magnetic field of about 1000 Gauss. At a current of 60 amps. the number of quanta emitted is about 4×10^{16} sec.$^{-1}$. The light leaves the lamp through a fluorite window, which separates the lamp from the reaction vessel adjoining it. To avoid contamination of the xenon in the discharge lamp by impurities, the gas is kept in circulation by a pump and continuously purified.

In this wavelength region special care must be taken in choosing fluorite windows. According to E. G. Schneider (*Phys. Rev.*, **45**, 152 (1934)) the decadic extinction coefficient of pure fluorite is 1·37 and 2·21 for the wavelengths 1470 and 1295 Å respectively. Slight impurities in the fluorite, which are hardly detectable by chemical means, change the extinction coefficient considerably.

Another xenon discharge tube is described by H. R. Calvert (*Z. Physik*, **78**, 479 (1932)). The tube is filled with 1 mm. helium and 0·01 mm. xenon, the voltage being 1500-1700 volts and the current 70-100 milliamps. The cylindrical electrodes are made of gas-free aluminium. In order to avoid any absorption of the resonance radiation by the gas in the discharge tube, the electrodes are arranged in such a way that the discharge surrounds the fluorite window, through which the radiation enters the adjoining reaction space. One disadvantage of this arrangement is that the xenon is gradually used up in the discharge tube and the radiation emitted is relatively weak. For example, in the reaction space containing

2·5 mm. hydrogen and 0·077 mm. xenon only 2×10^{13} hydrogen molecules are dissociated per second by collisions of the second kind.

(*f*) *Bodenstein's apparatus.* The apparatus used by M. Bodenstein and W. Unger (*Z. physik. Chem.*, **B, 11**, 253 (1931)) for the investigation of the photo-chemical union of hydrogen and chlorine is shown in Fig. 244. *Rf* = reflector, *L* = 1500 watt lamp, *Schr* = light-tight box, S_1 and S_2 = shutters, *M* = matt glass, *B* = screen, *F* = blue filter, *Wk* = water tank, *K* = 3·5 cm. saturated $FeSO_4$ solution, *St* = vapour pressure thermometer.

Hydrogen and chlorine are introduced into reaction vessel *R* through platinum valves V_1 and V_2 (M. Bodenstein and W. Dux, *Z. physik. Chem.*, **85**, 297 (1913)) ; the pressure is measured by a quartz spiral manometer *QM*. The light intensity is varied by aluminium plates *B* provided with

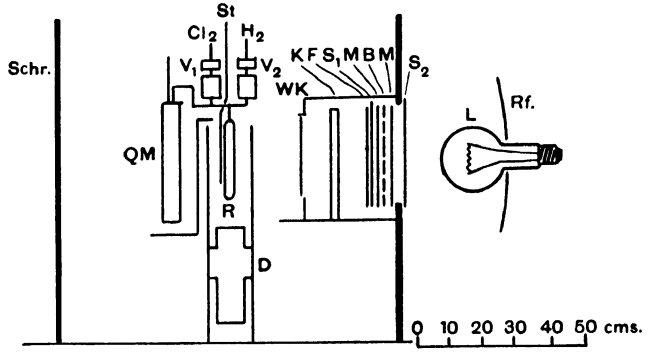


FIG. 244. Bodenstein's arrangement for investigating the photo-chemical formation of hydrogen chloride.

holes, with openings in the ratio 1 : 1/2 : 1/4. The filter combination *F*, *K*, *WK* serves to separate the spectral range near 4360 Å. After the required period of illumination HCl and Cl_2 are frozen out by raising the Dewar vessel (*D*) filled with liquid air, and the pressure of hydrogen is measured.

This type of experimental arrangement was used by the Bodenstein school in a great many investigations on the photo-chemical reactions of the chlorine, phosgene, ozone, etc., that is with gases which are liable to attack mercury or tap grease. In some experiments the platinum or silver valves were replaced by glass or quartz valves (see p. 62) (E. Hertel, *Z. physik. Chem.*, **B, 15**, 325 (1932) ; M. Bodenstein and P. W. Schenk, *Z. physik. Chem.*, **B, 20**, 420 (1933) ; M. Bodenstein and F. Bernreuther, *Sitz. Ber. Preuss. Akad. Wiss.* (1933) ; M. Bodenstein, W. Brenschede and H. J. Schumacher, *Z. physik. Chem.*, **B, 28**, 81, 35, 382 (1937) ; H. J. Schumacher and G. Steiger, *Z. physik. Chem.*, **B, 13**, 157 (1931) ; U. Beretta and H. J. Schumacher, *Z. physik. Chem.*, **B, 17**, 417

(1932) ; H. J. Schumacher and P. Bergmann, *Z. physik. Chem.*, **B, 13,** 269 (1931)).

(*g*) *Mercury sensitised Reactions.* Mercury atoms excited by mercury resonance radiation can activate other molecules which do not absorb this radiation by transferring their energy by collision. Thus hydrogen is dissociated into atoms ; water, ammonia and hydrocarbons are decomposed ; mixtures of hydrogen with oxygen, ethylene or acetylene are induced to react. In all these reactions the essential step is the excitation of the mercury atom, which will only occur if the resonance line of the light source is un-reversed, i.e. if the radiation corresponding to the resonance line 2537 Å is not already absorbed by mercury vapour in the lamp itself. This might happen if the mercury arc used as light source runs hot. Mercury lamps which give un-reversed resonance radiation are described on p. 215. If mercury is replaced by zinc, cadmium (P. Bender, *Phys. Rev.*, **36**, 1535, 1543 (1930)), neon (H. Beutler and W. Eisenschimmel, *Z. Elektrochem.*, **37**, 583 (1931)) or xenon (H. R. Calvert, *Z. Physik*, **78**, 479 (1932)), hydrogen atoms can also be produced from molecules using the corresponding resonance radiation from zinc, cadmium, neon or xenon lamps respectively. The chemical reactions of hydrogen atoms produced in this way have not yet been investigated in great detail. The decomposition of molecules like CO can also be sensitised by excited xenon atoms (W. Groth, *loc. cit.*, p. 329).

The simple arrangement used by K. Morikawa, W. S. Benedict and H. S. Taylor (*J. Chem. Phys.*, **5**, 212 (1937)) for investigating the mercury sensitised exchange reactions of methane and the hydrogen isotopes is shown in Fig. 245. *S* is the light source, *F* filter containing 25 per cent. acetic acid to remove the short wave radiation below 2537 Å, *L* a quartz lens, and *P* a quartz plate closing one end of the furnace *E*. Mercury vapour was added to the reaction vessel from the side tube *M*, its vapour pressure being regulated by adjusting the temperature of *M*. *T* is a capillary for admitting the reaction partners.

If the reaction mixture contains oxygen, then oxygen reacts with excited mercury and the oxide formed may cover the window of the reaction vessel and the surface of the mercury, thus reducing the intensity of incident light and also the evaporation of mercury. This can be counteracted by using flow methods (A. L. Marshall, *J. Am. Chem. Soc.*, **49**, 2763 (1927) ; W. Frankenburger and H. Klinkhardt, *Z. physik. Chem.*, **B, 15,** 421 (1931) ; H. S. Taylor and D. J. Salley, *J. Am. Chem. Soc.*, **55**, 96 (1933) ; J. R. Bates and D. J. Salley, *J. Am. Chem. Soc.*, **55**, 110 (1933)), or by injecting a fine spray of mercury into the reaction vessel if a static method is being used (L. Farkas and H. Sachsse, *Z. physik. Chem.*, **B, 27,** 111 (1934)).

A very convenient method of checking the light intensity in mercury sensitised reactions involves the use of para-hydrogen (L. Farkas and H. Sachsse, *loc. cit.* ; A. Farkas and H. W. Melville, *Proc. Roy. Soc.*, **A, 137**, 625 (1936)). The mercury photo-sensitised conversion of para-hydrogen proceeds according to the equations :

$$(1) \quad Hg + h\nu = Hg^*, \quad \ldots\ldots (43)$$

$$(2) \quad Hg^* + H_2 = 2H + Hg^*, \quad \ldots\ldots (44)$$

$$(3) \quad 2H = H_2, \quad \ldots\ldots (45)$$

$$(4) \quad H + p\text{-}H_2 = o\text{-}H_2 + H. \quad \ldots\ldots (46)$$

At temperatures above 50° C., when the reaction (4) is fast compared with (3), the rate of the para-hydrogen conversion is proportional to the

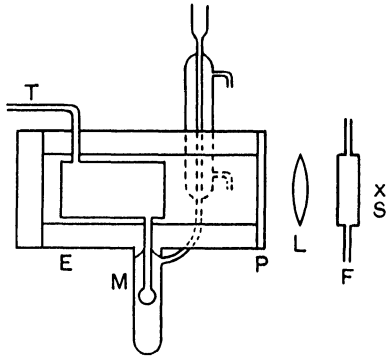


FIG. 245. Arrangement for investigating mercury sensitised reactions.

stationary H-atom concentration, which in turn is directly proportional to the square root of the intensity of the absorbed resonance radiation. At low temperatures, however, when the collision efficiency of reaction (4) is small and the H-atoms recombine before they undergo reaction (4), the para-hydrogen conversion will proceed by sensitised dissociation (2) followed by recombination (3). In this case the quantum efficiency of the conversion is unity (provided the dissociation of H_2 molecules proceeds according to the above scheme and does not involve the formation of HgH molecules). For a given reaction vessel, hydrogen and mercury pressure, the rate of conversion will depend only on the light intensity, whatever may be the mechanism of the conversion. This method of checking the light intensity is convenient, since it can be done in a short time without the necessity of introducing gaseous or liquid actinometers into the reaction vessel.

(*h*) *The experimental arrangement for the short wave region* 1900-1700 Å as used by W. E. Vaughan and W. A. Noyes (*J. Am. Chem. Soc.*, **52**, 559

(1930)) is shown in Fig. 246. Light source (*C*) (p. 329), thermopile (*A*) and reaction vessel (*E*), each provided with a fluorite window, are enclosed in a box (*L*) in which the air has been replaced by oxygen-free nitrogen in order to avoid light absorption by oxygen. This box is not vacuum-tight, but a slight pressure inside prevents the air from entering. First the absolute energy emitted by the lamp is determined with the thermopile in the position indicated in Fig. 246. The energy corresponding to the short wave radiation is determined by the difference of the readings of the thermopile for the full radiation and of that for the radiation from which the short wave radiation has been removed by a

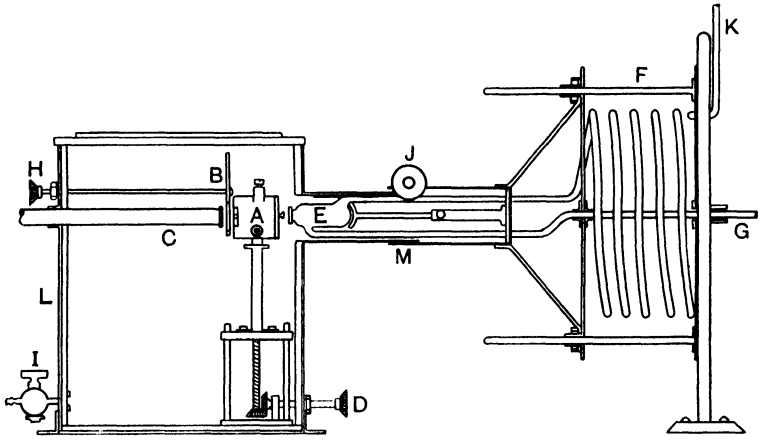


FIG. 246. Arrangement for photo-chemical experiments in the short wave ultra-violet.

layer of oxygen between light source and thermopile. Then the thermopile is lowered and the reaction vessel pushed forward in exactly the same position as that occupied formerly by the thermopile. The reaction vessel is connected with the rest of the apparatus by a large flexible coil of glass tubing (*F*). In these experiments the formation of ozone from oxygen has been determined by means of a flow method (pp. 296 ff.). The oxygen streams through the reaction vessel at flow velocities at which the absolute amount of ozone formed in a given time is independent of the rate of flow.

In the region below 1500 Å photo-chemical experiments have been carried out by W. Groth (*Z. physik. Chem.*, **B, 37**, 307, 315 (1937)) using P. Harteck's xenon lamp. In this region absolute energy measurements are practically impossible, and so the quantum yield for the formation of ozone and the decomposition of ammonia have been determined, assuming a quantum yield for the decomposition of carbon dioxide of unity.

This value follows from the kinetics of the reaction, which, however, cannot be dealt with here. The measurements were made on the same principle as those of W. E. Vaughan and W. A. Noyes, except that the light source and the reaction vessel, each provided with a fluorite window, were joined together. The space between the two windows was used to introduce oxygen to weaken and absorb the radiation for light intensity measurements.

(*i*) *Budde and Draper effect.* The Budde effect is the increase of pressure exhibited by chlorine or by bromine when illuminated (Budde, *J. prakt. Chem.*, **7**, 376 (1873)). It appears that this expansion is due to a slight increase in temperature produced by the heat of recombination of photo-

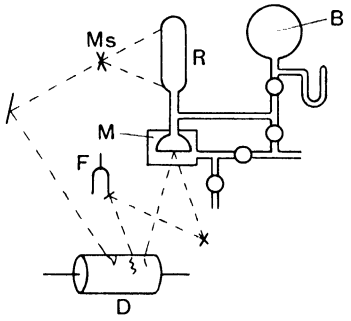


FIG. 247. Magnesium flash light as light source for photo-chemical experiments.

B. Storage vessel for the gas mixture $H_2 + Cl_2$.
M. Membrane manometer with compensation chamber.
R. Reaction vessel.
F. Tuning fork.
D. Drum with photographic film.
Ms. Magnesium flash light.

chemically produced chlorine or bromine atoms. Although a great number of experiments have been made on this question (cf., for example, T. S. Narayana, *Ind. Jour. of Physics*, **9**, 91 (1934) ; W. Smith, M. Ritchie and E. B. Ludlam, *J. Chem. Soc.*, 1680 (1937), where many references are given), many contradictory results have been obtained regarding the influence of water vapour, the pretreatment of the reaction vessel and of impurities in the gas on the Budde effect. According to the most recent experiments of W. Smith, M. Ritchie and E. B. Ludlam (*loc. cit.*), the addition of foreign gases increases the Budde effect by facilitating the homogeneous recombination of the atoms. If, however, the atoms have a chance to diffuse to the walls, they recombine there and no Budde effect appears, since the heat of recombination is dissipated at the wall. The following data may serve to illustrate the magnitude of the effect. Reaction vessel 1500 c.c., light source 500 watt projector lamp (filtered by

14 cm. of 20 per cent. $CuSO_4$), bromine pressure 50 mm. without foreign gas : $\Delta p = 0{\cdot}336$ mm. ; with 538·5 mm. A : $\Delta p = 1{\cdot}105$ mm.

The Draper effect is the increase of pressure which occurs if a thermostatted mixture of hydrogen and chlorine is illuminated. It is caused by the increase of temperature due to the heat set free by the reaction $H_2 + Cl_2 = 2HCl$. The Draper effect appears at the beginning of the reaction, even if the hydrogen chloride formed is removed by absorption in water. The Draper effect causes non-uniform temperature distribution, which can be made visible in the form of ' Schlieren ' by lateral illumination owing to the difference in the refractive indices of layers at different temperatures. This effect can be investigated by Töpler's method (cf. F. Weigert and K. Kellermann, *Z. physik. Chem.*, **107**, 1 (1923)).

(*j*) In order to produce very *large light intensities* V. Kokotschaschwili (*Z. physik. Chem.*, **B, 23**, 431 (1933)) used magnesium flash-light powder ignited by an electrically heated wire. The duration and intensity of the light flash and the pressure change occurring during the photo-chemical reaction are recorded photographically as shown in Fig. 247.

4. Catalysts

Among the catalysts of gaseous reactions representatives of practically every kind of chemical substance may be found. Some of these substances are always active if of reasonable purity, and their activity is independent of their method of preparation. Other substances are only active after being subjected to special treatment or if prepared according to certain methods. In the following pages these latter types of catalysts will be dealt with, and some general methods of the application of catalysts will be described.

(a) Metallic Catalysts

(α) *Compact form.* A great many metals can be used as catalysts in the form of wire, strip, tubing or foil. (Examples of application : C. N. Hinshelwood, *Proc. Roy. Soc.*, **A, 106**, 292 (1924) ; H. zur Strassen, *Z. physik. Chem.*, **A, 169**, 83 (1934) ; E. Fajans, *Z. physik. Chem.*, **B, 28**, 239 (1935) ; and D. L. Chapman and G. Gregory, *Proc. Roy. Soc.*, **A, 147**, 68 (1935)). These have the advantage that they contain far less gas, water and oxide as impurities than the powdery material obtained by reduction of the oxides. They are, however, usually less active than ' bulk ' catalysts. Materials such as platinum, palladium, iron, nickel, copper, silver, gold or tungsten are available in a high state of purity, but it is usually necessary to subject them to a pretreatment before they attain their maximum catalytic activity. Mechanical impurities (grease,

oil, etc.) can be removed from the surface by washing with solvents or by abrasives. The solvents used must be very pure, and must not contain any dissolved solid or other non-volatile matter. Material intended for use as a catalyst should be handled with tweezers ; touching with bare fingers should be avoided.

Superficial gas layers and gases dissolved in the metal can be removed by heating *in vacuo* to high temperatures. If the binding forces between the metal and the gas are very strong, the removal of gas only becomes possible at very high temperatures or by chemical reaction. For example, the superficial oxidation of tungsten, which occurs as soon as the minute traces of oxygen come into contact with tungsten, may be cited (I. Langmuir, *Chem. Rev.*, 147 (1933)). Such oxygen-covered tungsten wires do not catalyse the interconversion of ortho- and para-hydrogen, which proceeds, however, with great speed if the oxygen has been removed from the surface of the wires by flashing them at 2400° K. (A. Farkas *Z. physik. Chem.*, **B, 14,** 371 (1931)).

Recently D. L. Chapman and P. W. Reynolds (*Proc. Roy. Soc.*, **A, 156,** 284 (1936)) observed that a platinum wire loses most of its activity in catalysing the union of hydrogen and oxygen if heated to 1000° C., and regains its activity after etching with acids. At first sight this result seems to contradict the above considerations, but a closer investigation has shown that this effect is due to traces of copper present even in platinum of very high purity. At elevated temperatures the copper diffuses from the interior of the wire to its surface, thus destroying the activity of the platinum. When the copper is removed from the surface by etching, the catalytic activity is restored.

If the vapour pressure of the metal constituting the catalyst reaches $10^{-5} - 10^{-4}$ mm. at temperatures below its melting point, the surface of the catalyst can be conveniently cleaned by evaporating several layers of atoms, especially if the catalyst is used in form of wire. It is then often found that both the original catalyst and the (sometimes invisible) layer of metal deposited on the wall of the reaction vessel catalyse the reaction in question (cf. A. Farkas, *loc. cit.* ; D. L. Chapman and P. W. Reynolds, *loc. cit.*). The action of these two catalysts can be distinguished by keeping them at different temperatures or by poisoning one of them. This can be done, for example, by cooling the walls of the vessel as the catalyst is heated electrically, or by admitting oxygen if oxidisable metal is used as a catalyst. The layer of oxygen can subsequently be removed from the wire by reduction with hydrogen.

In certain cases a considerable increase in activity is observed if the catalyst is alternately oxidised and reduced. According to E. K. Rideal (*J. Chem. Soc.*, **121,** 309 (1922)) nickel foil will catalyse the addition of

hydrogen to ethylene after the following treatment. The nickel foil is immersed in dilute nitric acid, touched with the end of a platinum wire and withdrawn after a contact time of a few minutes. The foil is then dried, and the thin film of nickel nitrate formed on the surface of the foil carefully decomposed over a hydrogen flame. Then the catalyst is introduced into the reaction vessel and reduced *in situ* in a slow stream of hydrogen at 270-340° C.

For catalysing the same reaction a nickel wire 15 cm. long and 0·1 mm. in diameter can be rendered active by oxidation at 600° C. and reducing below 300° C. several times, according to A. Farkas, L. Farkas and E. K. Rideal (*Proc. Roy. Soc.*, **A, 146,** 630 (1934)).

The activation is probably connected with an increase of the available surface of the catalyst. Sintering may destroy the increased activity of the catalyst if it is heated to high temperatures. This effect must be borne in mind when working with electrically heated wires for the following reason. The accommodation coefficient of hydrogen on oxidised nickel or copper (D. L. Chapman and W. K. Hall, *Proc. Roy. Soc.*, **A, 124,** 478 (1929) ; D. R. Hughes and R. C. Bevan, *Proc. Roy. Soc.*, **A, 117,** 102 (1928)) is higher than on the metal itself. Thus considerably more electrical energy is required to heat an oxidised wire in hydrogen to a given temperature than a bare wire, and at constant heating current the temperature of the wire will suddenly increase as soon as the layer of oxide is completely removed. If care is not taken to keep the temperature of the wire constant by adjusting the heating current as the reduction proceeds, the sudden rise in temperature might annul the activating effect of the oxidation and reduction.

The best results are obtained if the oxidation and reduction are carried out at successively lower temperatures (cf. below). The progress of the oxidation can be observed by the appearance of interference colours. After several reductions the wire appears dull, having lost its metallic lustre.

When platinum foil or wire is used as a catalyst, its catalytic activity can be increased many-fold by platinising. The catalyst thus obtained accelerates the ortho- para-hydrogen conversion, the exchange of hydrogen and deuterium atoms between molecular hydrogen and water, alcohol, benzene, ethylene and the hydrogenation of benzene, ethylene and acetone (A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33,** 678, 837 (1937) ; *J. Am. Chem. Soc.* **60,** 22 (1938)).

The platinising solution is prepared by dissolving 2 g. chloplatinic acid in 50 c.c. distilled water and adding 8 c.c. of a 0·2 per cent. solution of lead acetate. The catalyst is cleaned by connecting it to the positive pole of a battery for 2 to 5 minutes, oxygen being evolved (current density

30 ma./cm.^{2}); then the current is reversed and the wire platinised for five minutes. The current density is conveniently adjusted by varying the depth of immersion of the second electrode. Catalysts prepared in this way are very active and stable.

Palladium foil or wire can be activated in the presence of air by heating to dull-red heat (600° C.), for example, in a Pyrex test tube. The palladium then shows bluish interference colours, which disappear as soon as the palladium comes into contact with hydrogen (H. W. Melville and E. K. Rideal, *Proc. Roy. Soc.*, **A**, **153**, 89 (1935); A. Farkas, *Trans. Faraday Soc.*, **32**, 1667 (1936), and **33**, 552 (1937)).

(β) *Metals in form of powder.* Most metallic catalysts are not used in their compact form, but as powders. The classical example of this kind of catalyst is finely divided nickel introduced by Sabatier and Senderens. The metals of the platinum group are usually obtained in powder form by precipitation from solution by suitable reducing agents, whereas other metals are prepared by reducing the oxides or hydroxides with hydrogen.

Platinum black. (O. Loew, *Ber.*, **23**, 289 (1890); R. Willstatter and E. Waldschmidt-Leitz, *Ber.*, **54**, 122 (1921)). Two g. of chloroplatinic acid are dissolved in 8 c.c. of H_2O. Some HCl and 15 c.c. of 33 per cent. formaldehyde are added. The solution is cooled to −10° C., and 42 g. of 50 per cent. KOH added drop by drop while mixing thoroughly. The temperature must not rise above 3° C. The liquid is then warmed to 55-60° C. for half an hour, mixing being continued. When the precipitate has settled, it is washed by decantation until the washings contain neither alkali nor chlorine. The platinum black is conveniently kept under water and dried immediately before use.

Palladium black (R. Willstatter and E. Waldschmidt-Leitz, *loc. cit.*) can be prepared in the same way as platinum black, using the following quantities of reagents: 4·25 g. palladium or equivalent in 100-150 c.c. distilled water with some HCl, 50 c.c. 33 per cent. formaldehyde, and 100 g. 50 per cent. KOH.

Nickel (A. F. Benton and P. H. Emmett, *J. Am. Chem. Soc.*, **46**, 2728 (1924)) in finely divided form is obtained by reducing nickel oxide in a stream of hydrogen at 200-300° C. Nickel oxide in turn is prepared by drying and then calcining crystalline nickel nitrate, basic carbonate or hydroxide at 400° C. in a current of air. Reduction of the oxide takes place less readily the higher the temperature at which the oxide was prepared (cf. also F. Thorén, *Z. anorg. Chem.*, **163**, 367 (1927)).

Copper (R. N. Pease and R. B. Purdum, *J. Am. Chem. Soc.*, **47**, 1437 (1925)). A very active copper catalyst suitable for hydrogenation of benzene is obtained from 80 g. 4-16 mesh copper oxide granules by reduction in a stream (25 c.c./minute) of electrolytic hydrogen for about

50 hours at 150 and 200° C., and for several hours at 300° C. (cf. also R. N. Pease and H. S. Taylor, *J. Am. Chem. Soc.*, **43**, 2179 (1921)).

Iron in a finely divided state can be prepared in a similar way to nickel, but reduction of the oxide is carried out at higher temperatures. For example, N. M. Morozov (*Trans. Faraday Soc.*, **31**, 660 (1935)) reduced the oxide, which was prepared by precipitating iron nitrate with ammonia, in a stream of hydrogen for 100 hours at 200-300° C., then for 280 hours at 400° C., and finally for 70 hours at 460° C. (cf. G. B. Taylor and H. W. Starkweather, *J. Am. Chem. Soc.*, **52**, 2314 (1930)). Another method of preparing finely divided iron is by the decomposition of ferrous oxalate (A. Magnus and R. Klar, *Z. physik. Chem.*, **A, 161**, 241 (1932)) at 300° C. *in vacuo*. At the beginning of the decomposition there is a strong dusting, and it is therefore not advisable to lower the pressure below 15 mm. The decomposition is complete after 14 days, the product obtained is pyrophoric, and contains some oxide, which can be removed by repeated treatment with hydrogen at 300° C.

(γ) *Colloidal metals.* (E. Huckel, ' Katalyse mit Kolloiden Metallen ', Vol. 6 of *Kolloid Forschung in Einzeldarstellung, Akad. Verlagsges. m.b.H.*, Leipzig (1927).) Colloidal platinum metals are often used in organic chemistry as hydrogenation catalysts. Colloid metal solutions can be prepared according to Bredig by disintegrating the metals by means of an electric arc under water, or according to Paal and Skita by reducing a metal salt solution in the presence of protective colloids. C. Paal uses sodium protalbate or lysalbate prepared from egg albumen (*Ber.*, **35**, 2195 (1902)) as protective colloids. A. Skita uses gum arabic.

Colloidal platinum is prepared (C. Paal, *Ber.*, **37**, 126 (1904)) in the following manner. One g. sodium lysalbate is dissolved in 30 c.c. water, and enough sodium hydroxide added to keep the solution alkaline when 2 g. chloroplatinic acid dissolved in some water are added. The platinum salt is reduced with hydrazine-hydrate, adding it drop by drop to slight excess. After allowing the solution to stand for a few hours, the sodium chloride and hydrazine are separated by dialysis and the colloidal solution concentrated, first by evaporation at 60° C. then by drying in a vacuum desiccator.

Colloidal palladium can be prepared in a similar way, or alternatively by reducing an alkaline solution of palladium chloride in the presence of sodium protalbate with molecular hydrogen at 60° C. (C. Paal, *Ber.*, **38**, 1401 (1905)). A. Skita's method is as follows (*Ann. d. Chem.*, **427**, 268 (1922) ; and **431**, 1 (1923)) : 1 g. platinum dissolved as chloroplatinic acid in 50 c.c. water, 8 g. gum arabic in 50 c.c. water, and 25 c.c. of 0·5 per cent. hydrazine-hydrate solution are mixed. The mixture is heated to the boiling point, cooled to 0°, made alkaline by adding

13-15 c.c. of a 10 per cent. soda solution, and warmed very slowly (1°/min.) to 60°. When the solution becomes brown, it is heated more quickly, and kept boiling for five minutes. Most of the platinum is then reduced ; the remainder can be reduced by shaking for 10-20 minutes with hydrogen. Another method is the inoculation method, according to which the platinum solution is reduced by molecular hydrogen in the presence of small amounts of colloidal platinum.

(b) Oxide Catalysts

(α) *Platinum oxide.* According to Adams and collaborators (V. Voorhees and R. Adams, *J. Am. Chem. Soc.*, **44**, 1397 (1922) ; R. Adams and R. L. Shriner, *J. Am. Chem. Soc.*, **45**, 2171 (1923)) platinum oxide is prepared as follows. A solution of chloroplatinic acid containing 1 g. platinum in 5 c.c. of water and 20 g. of sodium nitrate are mixed in a crucible and heated to 500° C. The mass is then dissolved in water and the platinum oxide washed well. The same method is suitable also for the preparation of palladium oxide (R. L. Shriner and R. Adams, *J. Am. Chem. Soc.*, **46**, 1683 (1924)).

(β) *Chromium oxide.* An active preparation can be obtained (W. A. Lazier and J. V. Vaughen, *J. Am. Chem. Soc.*, **54**, 3080 (1932)) by igniting ammonium bichromate in thin layers below 400° C. If the decomposition is too violent, the ' glow ' phenomenon may appear and the products are inactive. Chromium oxide gels are prepared by reducing chromic acid with alcohol, followed by precipitation with ammonium hydroxide or from trivalent salts and ammonium hydroxide. R. L. Burwell and H. S. Taylor (*J. Am. Chem. Soc.*, **58**, 697 (1936)) prepared active chromic oxide gels by slowly adding 0·1 N. ammonium hydroxide to an electrically stirred 0·1 N. solution of chromic nitrate in stoichiometrical quantity. The precipitate settled out if the addition of ammonia was interrupted for some hours, during which stirring was continued.

(γ) *Zinc oxide.* (H. S. Taylor and D. V. Sickman, *J. Am. Chem. Soc.*, **54**, 602 (1932).) Zinc oxalate is heated gradually to 400° C. When gas evolution stops, the temperature is raised to 450° C. and maintained there for ten hours. W. E. Garner and F. E. T. Kingman (*Trans. Faraday Soc.*, **27**, 322 (1931)) precipitate 40 per cent. $ZnSO_4$ solution with slight excess of ammonia ($d = 0{\cdot}880$) in the cold, wash the precipitate and ignite it at 450° C.

(δ) *Manganous oxide* (H. S. Taylor and A. T. Williamson, *J. Am. Chem. Soc.*, **53**, 2170 (1931)) is prepared by igniting at 300° C. manganous oxalate, which has been made by the interaction of concentrated solutions of potassium permanganate and oxalic acid in the presence of acetic acid.

(ε) *Copper chromite.* (H. Adkins and R. Connor, *J. Am. Chem. Soc.*, **53**, 1091 (1931).) .Ammonium hydroxide is added to 500 c.c. of a molar solution of ammonium dichromate until the colour changes from orange to yellow. The solution is cooled to room temperature and 1 mol $Cu(NO_3)_2.3H_2O$ dissolved in 3000 c.c. of water added while stirring. The red-brown precipitate is filtered and dried at 110-120° C. It is then powdered, and heated in a crucible by an open flame. When the decomposition has started, the heat generated is sufficient to decompose almost all of the chromate. When decomposition has ceased, the material is heated again, and stirred until fumes stop being evolved. The finely-powdered black product is cooled, washed with 10 per cent. acetic acid, then with water, and finally dried. (Cf. also R. Connor, K. Folkers and H. Adkins, *J. Am. Chem. Soc.*, **54**, 1138 (1932) with regard to copper chromites with different additions.)

(ζ) *Manganous chromite* (H. S. Taylor and A. T. Williamson, *loc. cit.*) is obtained in a similar way to copper chromite from manganous nitrate and ammonium chromate in the presence of ammonia. The filtered precipitate is washed with an ammonium nitrate solution, dried and decomposed at 400° C.

(η) *Silica gel* is prepared from solutions of sodium silicate by precipitation with diluted acid (cf. A. Magnus and L. Cahn, *Z. anorg. Chem.*, **155**, 205 (1926) ; E. Sauter and H. Kratz, *ibid.*, **174**, 142 (1928) ; A. Magnus and W. Kälberer, *ibid.*, **164**, 357 (1927) ; E. Berl and H. Burkhardt, *ibid.*, **171**, 102 (1928) ; and R. Schwarz and H. Richter, *Ber.*, **62**, 31 (1929)).

(ν) *Zinc chromite* (cf. H. S. Taylor and C. O. Strother, *J. Am. Chem. Soc.*, **56**, 586 (1934) ; Garner and Kingman, *Trans. Faraday Soc.*, **27**, 332 (1931).) Zinc ammonium chromate, precipitated by mixing zinc nitrate and neutral ammonium chromate in stoichiometrical proportions, is heated to 400° C., reduced by hydrogen for five hours at 450° C. until water is no longer produced.

(c) Charcoal

A great variety of charcoals is prepared from the most diverse materials, such as bones, blood, coconut, peach stones and wood. All these charcoals contain larger or smaller amounts of metals and oxides. A. Magnus and H. Kratz (*Z. anorg. Chem.*, **184**, 241 (1929)) worked out the following methods of purification by which ash-free charcoals may be prepared. The charcoal is boiled several times in concentrated hydrochloric acid, and washed with water until the acid is removed. The charcoal is then heated repeatedly with hydrofluoric acid and some sulphuric acid in a platinum dish, the acids evaporated, and finally again boiled in hydrochloric acid and washed with water. By means of these operations the ash content

of the charcoal can be reduced to 0·01 per cent. and less. Another method of preparation of ash-free charcoal is due to B. Bruns and A. Frumkin (*Z. physik. Chem.*, **A, 141**, 141 (1929)). The purest sucrose is dissolved in conductivity water, filtered and precipitated by alcohol. This operation is repeated twice and the product, with an ash-content of 0·001-0·002 per cent., charred in a silica dish. The resulting charcoal is activated by heating for 4-5 hours at 1100° C. in current of CO_2. In order to obtain a uniform product the porcelain tube in which the activation is done is rotated around its axis. During the activation about 40 per cent. of the charcoal is burnt. The final product has an ash-content of 0·01-0·02 per cent., resulting mainly from contact with silica and porcelain ; it is autoxidisable in air.

(d) Supported and Composite Catalysts

The variety of catalysts is greatly increased by mixing two or more together, by adding small amounts of otherwise inactive substances (promoters) to the catalyst, or by depositing the catalyst on inert supports or carriers. Among these methods only the last appears to have general applicability. By depositing the catalyst on inert supports, i.e. on porous materials like clay and pumice, it becomes less susceptible to poisoning, less liable to sintering and more economical in use, since relatively less active material is required to produce a given acceleration of the reaction. The following examples may serve to illustrate the preparation of supported catalysts.

(α) *Kieselgur*, impregnated with nickel, was used by H. S. Taylor and A. Sherman (*Trans. Faraday Soc.*, **28**, 249 (1932)) ; cf. p. 155.

(β) *Clay.* (E. Winter, *Z. physik. Chem.*, **B, 13**, 401 (1931).) Pieces of clay (1-3 mm.) are cleaned with nitric acid soaked in an iron nitrate solution (1 millimol of iron to 10 g. clay) and reduced at 500-600° C.

(γ) *Asbestos* impregnated with platinum or palladium. (N. D. Zelinsky and P. P. Borisoff, *Ber.*, **57**, 150 (1924).) Pure asbestos, washed with acid and glowed, is soaked first in a concentrated solution of chloroplatinic acid (or in an acidified solution of palladium chloride), then in a 35-40 per cent. formaldehyde solution (3 c.c. per gram Pt or 5 c.c. per g. Pd). The asbestos is cooled and 40-50 per cent. sodium hydroxide solution is added slowly (4 g. per g. Pt or 7 g. per g. Pd). Then the asbestos is warmed on the water bath, washed first with water, then with diluted acetic acid, and again with water, and finally dried at 110° C.

(δ) *Diatomite bricks* have been used as support by R. N. Pease and L. Stewart (*J. Am. Chem. Soc.*, **49**, 2784 (1927)) for iron, cobalt, nickel, copper or silver catalysts. The bricks are broken, screened to 5-10 mesh, boiled with 15 per cent. HNO_3, washed with water and dried at dull-red

heat. Then 15 c.c. of a nitrate solution containing 0·02 gram-atom metal are added for each 20 g. of brick granules. This amount of solution is absorbed without wetting the support. The catalyst is dried in a current of warm air, then heated gradually to 350-400° C., and finally reduced at the following temperatures : Fe, 450° ; Co, 370° ; Ni, 300° (to 420° at the end) ; Cu, 200° ; and Ag, 150° (to 250° at the end). (For copper catalysts, cf. C. W. Griffin, *J. Am. Chem. Soc.*, **57**, 1206 (1935).)

(ε) *Charcoal* impregnated with palladium is obtained according to O. Diels and W. Gädke (*Ber.*, **58**, 1232 (1925)) in the following way. Palladium chloride solution is added to the charcoal suspended in water ; after allowing the mixture to stand for two hours it is heated to 50° C., and a strong current of pure hydrogen passed through the liquid. The charcoal is washed, and finally dried in the desiccator. B. Bruns and A. Frumkin (*Z. physik. Chem.*, **A, 141**, 141 (1929)) prepare platinised charcoal by adding the charcoal to the platinum solution, evaporating the solution and reducing the charcoal in a current of hydrogen at 1000° C.

(ζ) *Various supports.* Silica gel has been used as support for palladium, platinum and copper by V. N. Morris and L. H. Reyerson (*J. Phys. Chem.*, **31**, 1220 (1927)) ; pumice for copper chromium oxide catalysts has been used by R. E. Dunbar, D. Cooper and R. Cooper (*J. Am. Chem. Soc.*, **58**, 1053 (1936)) ; and infusorial earth for nickel by H. Adkins and H. I. Cramer (*J. Am. Chem. Soc.*, **52**, 4349 (1930)).

As an example of the method of preparation of more complicated catalysts the method for synthetic ammonia catalysts described by A. T. Larson and C. N. Richardson (*Ind. Eng. Chem.*, **17**, 971 (1925) and A. Mittasch and E. Kuenecke (*Z. physik. Chem.*, Bodenstein vol., 574 (1931)) may be cited. Other methods for preparing various catalysts may be found in E. K. Rideal and H. S. Taylor's *Catalysis in Theory and Practice*, Macmillan & Co., London (1926) ; and in E. B. Maxted's *Catalysis and its Industrial Applications*, Churchill, London (1933).

(e) Arrangement and Temperature Control of Filaments

Wires or strips, when used as catalysts, are often arranged in a way which permits of electric heating. The most common types of arrangement are shown in Fig. 248. Spiral springs or weights serve to keep the filament taut. Longer wires are either used in form of a spiral or are arranged in zigzag form as in vacuum incandescent lamps. The pinch-seal (*b*) is preferable to the simple seal (*a*), owing to its higher mechanical stability. The best connection between the lead-in wire and the filament is made by spot welding. With copper or platinum lead-in wires a good connection can be obtained by folding the lead-in wire over the filament.

Above 600° C. the temperature of the filament can be determined by means of an optical pyrometer. In such measurements the emissivity of the filament has to be taken into account, since it is usually much less than that of the black body for which the pyrometer was calibrated (cf. p. 112).

Reflected light from the filament and light absorption by the walls of the reaction vessel might (especially if partially covered with evaporated metal) cause errors in measurement of temperature. It is good practice to determine the resistance of the filament in use at different temperatures measured by the pyrometer. Thus it is possible to reproduce any temperature on the basis of the resistance, even if pyrometer temperature measurements are not possible.

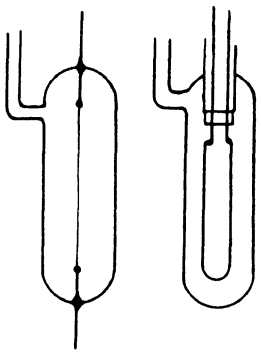


FIG. 248. Arrangement of wires.

At lower temperatures the temperature of the filament is usually calculated from its electrical resistance. It is customary to make the filament one branch of a Wheatstone bridge in a manner similar to that used for Pirani gauges. Since the resistance and its temperature coefficient may be considerably altered by small amounts of impurities and may depend on the mechanical and thermal treatment of the wire, it is good practice to anneal the wire at the highest temperature at which it will be used during the experiments as long as its resistance changes, and determine its resistance as a function of the temperature. The lead-in wire is made much thicker than the filament, and is thus not heated by the electric current. Therefore the ends of the filament are always colder than its middle portion, and the average temperature of the filament as calculated from its resistance is always lower than the temperature of the (hottest) middle portion. The end losses, i.e. the heat flowing from the filament to each lead, increase with the thermal conductivity and thickness of the filament, and are larger for short filaments at low pressures than for long wires at high pressures (cf. p. 123). If the end losses are small (1 per cent.) compared with the total heat consumption of the filament, they can be neglected, otherwise a suitable correction must be made.

Another method of obtaining the real filament temperature is based upon using two wires (Fig. 249). The two wires, one longer, the other shorter, of the same diameter and material, are mounted in similar positions and heated with the same current in the same atmosphere. The end losses are eliminated if the temperature is calculated from the

ratio $(R_1 - R_2)_t / (R_1 - R_2)_0$, where $R_1 - R_2$ denote the difference of the resistance of the long and short wire, i.e. the resistance of the centre portion of the longer wire at an approximately uniform temperature (cf. D. L. Chapman and W. K. Hall, *Proc. Roy. Soc.*, **A**, **124**, 482 (1929)).

It was shown by Busch (*Ann. Physik.*, [4], **64**, 401 (1921)) that under certain conditions a uniform temperature distribution along an electrically heated wire suddenly becomes unstable, and two or more regions of distinctly different temperature are formed.

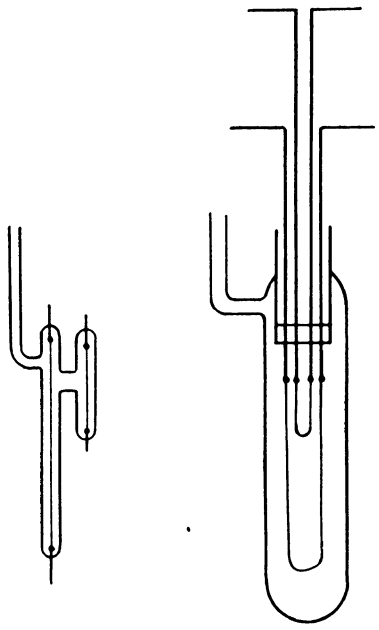


FIG. 249. Compensation for end losses.

A uniform distribution of temperature along an electrically heated wire is maintained as long as the relative temperature coefficient of the heat dissipated (A) is larger than the relative temperature coefficient of the electrical resistance (R), i.e. if

$$\frac{d \log A}{dT} > \frac{d \log R}{dT}, \quad \ldots\ldots(47)$$

or

$$\frac{1}{A}\frac{dA}{dT} > \frac{1}{R}\frac{dR}{dT}. \quad \ldots\ldots(48)$$

When this condition is fulfilled a uniform temperature distribution is re-established, even if it is upset by a temporary perturbation (e.g. local

cooling at a certain part of the wire). Under conditions, however, when this relation no longer holds, the slightest disturbance upsets the uniformity of the temperature, and the distribution of temperature becomes stable only if different regions of the wire have different temperatures. Since the temperature differences between neighbouring regions of the wire may amount to several hundred degrees, and the phenomenon may remain unnoticed unless the hotter regions attain glowing temperatures, it is of importance to know exactly the experimental conditions under which these phenomena occur (A. Farkas and H. Rowley, *Z. physik. Chem.*, **B, 22,** 335 (1933)). Since $A = Ri^2$ (i = current), formula (48) is equivalent to

$$\frac{d \log (Ri^2)}{dT} > \frac{d \log R}{dT}, \quad \ldots\ldots (49)$$

or

$$\frac{d \log i}{dT} > 0, \quad \ldots\ldots (50)$$

or

$$\frac{di}{dT} > 0. \quad \ldots\ldots (51)$$

This means that the condition for uniform temperature distribution is guaranteed as long as the current increases with the (apparent) temperature of the wire or with the voltage, since experimentally the temperature of a wire is varied by varying the voltage across it. This is a simple experimental criterion for the maintenance of uniform temperature distribution, and can easily be checked by determining the voltage-current characteristic of the wire in question.

The condition for the stability of uniform temperature may not always be fulfilled, especially under the following experimental conditions :

(1) Wires having high temperature coefficient of resistance (Ni, Fe).

(2) With vessels, the walls of which are kept at low temperatures (e.g. at the temperature of liquid air).

(3) In a pressure region where the heat conductivity is dependent on pressure.

(4) With gas mixtures containing hydrogen.

It is evident that the temperature of the wire cannot even be approximately determined from its total resistance if the stability condition is not fulfilled, and that wires under such conditions are not suitable for catalytic investigations. In such cases the above-mentioned experimental conditions have to be altered until the conditions for uniform distribution of temperature are fulfilled.

As the composition of a reaction mixture changes during the reaction, its heat conductivity will correspondingly change, and therefore it is necessary to readjust the heating current in order to keep the temperature

of the filament constant. This can be conveniently done if the filament is connected in a Wheatstone bridge, as shown in Fig. 200, p. 283. If the resistance R_1 and the ratio R_1/R_2 are chosen sufficiently low, the heating current for the filament will not damage any of the resistances. By adjusting the resistance R to a value R_2/R_1 times that of the resistance of the filament at the given temperature, the filament can be kept at the required temperature by varying the resistance R_W until the galvanometer reads zero.

Another method of temperature control is described by G. M. Schwab and H. Schmidt (*Z. physik. Chem.*, **B, 3**, 337 (1929)), and is shown in Fig. 250. The resistance of the filament is constant if the ratio voltage/current is constant. For a given sensitivity of the voltmeter V, this ratio

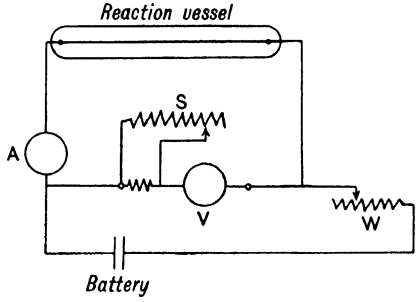


FIG. 250. Temperature control of electrically heated filament.

is constant whenever the angles of deflection of the needles of the voltmeter V and ammeter A are equal. A convenient way of comparison is obtained if one instrument is provided with a glass scale and is arranged above the other. The resistance W is then varied until both instruments show the same angle of deflection. In order to set the instruments for another temperature, the sensitivity of the voltmeter is varied by the shunt S, which is provided with an empirical temperature scale. The calibration of the filament temperature is done by an optical pyrometer, when shunt S is varied until voltmeter and ammeter show the same deflection. This position of the shunt is marked as the temperature measured by the pyrometer.

If very long wires are used (D. L. Chapman and P. W. Reynolds, *Proc. Roy. Soc.*, **A, 156**, 284 (1936), employed 109 metres of platinum wire as catalyst) or absolutely uniform temperature is required, the filaments can be heated from outside the reaction vessel by an electric furnace. Even then it is convenient to arrange the wire (if not too long) in a way which permits of its electrical heating in order to allow outgassing and glowing at higher temperatures.

(f) Catalytically Active Metal Films

Catalytically active metal films can be prepared by evaporation by direct electrical heating of a wire, or by heating the metal to be evaporated indirectly by means of a tungsten spiral. Although these methods appear to be rather simple, the catalysts so produced are not very reproducible in activity, nor stable, and according to some investigators, not even active (A. W. Gauger, *J. Am. Chem. Soc.*, **47**, 2287 (1925)). One complication which arises in connection with this type of catalyst is due to the circumstance that both the deposited film and the wire evaporating surface might be catalytically active, and it is not simple to assess the activity of each (cf. p. 336). Recently it was pointed out by K. S. Ablesowa and S. Roginsky (*Z. physik. Chem.*, **174**, 449 (1935)) that the activity of such films depends largely on the amount of gas content of the film. According to these authors, layers containing no gas and large amounts of gas are inactive.

According to W. Frankenburger and K. Mayrhofer (*Z. Elektrochem.*, **35**, 590 (1929) ; W. Frankenburger, K. Mayrhofer and E. Schwamberger (*Z. Elektrochem.*, **37**, 772 (1931)), evaporated iron layers can be prevented from sintering by dilution with simultaneously evaporated sodium chloride.

Another method of preparing metallic layers is based on the sputtering which occurs by the impact of high speed ions with the cathode in an electric discharge (G. Bredig and R. Allolio, *Z. physik. Chem.*, **126**, 41 (1927)) ; G. Käb, *Z. physik. Chem.*, **115**, 224 (1925)) ; G. I. Finch, C. A. Murison, N. Stuart and G. P. Thomson, *Proc. Roy. Soc.*, **A**, **140**, 414 (1933)).

(g) Poisoning and Sintering

It has long been noticed that the activity of a catalyst is greatly reduced if the catalyst comes into contact with relatively small amounts of certain substances. This effect is called poisoning. Poisoning can be reversible or irreversible, depending upon whether original activity does or does not return on removing the poison (cf. E. K. Rideal and H. S. Taylor, *loc. cit.*, p. 343). The poisoning effect depends also on the nature of the catalyst, some catalysts being more sensitive than others. Poisons may be present in the apparatus itself or introduced with the reactants.

The poisoning effect of vapours of tap grease and of mercury on certain catalysts has long been known (A. Berliner, *Wied. Ann.*, **35**, 903 (1888) ; L. Mond, W. Ramsay and J. Shields, *Z. physik. Chem.*, **25**, 657 (1898)), but even now no precautions are taken to avoid poisoning by these

substances. The poisoning effect is larger the lower the pressure at which the experiments are performed. If the catalyst is always in contact with gas (e.g. to the vapour of a liquid), poisoning by mercury and vapours of tap grease is often negligible (L. and A. Farkas, *Trans. Faraday Soc.*, **33**, 678, 837 (1937)). According to D. L. Chapman and W. K. Hall (*Proc. Roy. Soc.*, **A**, **124**, 478 (1929)), mercury poisons the catalytic activity of silver for the union of hydrogen and oxygen. It is not possible to obtain platinum or nickel catalysts (K. F. Bonhoeffer and A. Farkas, *Z. physik. Chem.*, **B**, **12**, 231 (1931) ; A. Farkas, *Z. physik. Chem.*, **B**, **14**, 371 (1931)) of reproducible and constant activity for the ortho- para-hydrogen conversion unless vapours of mercury and grease are kept out of contact with the catalyst by a trap cooled with liquid air or solid carbon dioxide. The catalysis of the same reaction by nickel or tungsten is very much reduced by air or oxygen. Tungsten is even so sensitive that it becomes poisoned by the gases (air or water) given off by the walls of the reaction vessel. This poisoning can be eliminated by immersing the reaction vessel in liquid air.

Vapours of cements like picein or sealing wax may exert a poisoning effect. In experiments at very low pressures, it is advisable to use Apiezon grease (cf. p. 67) instead of rubber tap grease, or better still, to replace all traps by mercury cut-offs. It is important to remember that mercury in fresh taps only partially condenses even at the temperature of liquid air. If a layer of mercury has already been formed in the trap the condensation is complete at $-80°$ C. This effect is due to critical condensation phenomena (M. Knudsen, *Ann. Physik.*, **50**, 472 (1916) ; R. W. Wood, *Phil. Mag.*, **32**, 364 (1916)). Mercury can also be removed by gold foil, by sodium or potassium (A. L. Hughes and F. E. Poindexter, *Phil. Mag.*, **50**, 423 (1925) ; *Nature*, **115**, 975 (1925)), or by liquid sodium potassium alloy (G. I. Finch, *Nature*, **119**, 856 (1927)) if low temperature traps cannot be used. Table 44 shows the approximate pressures of mercury, water and carbon dioxide in mm. Hg at -80 and $-185°$ C.

TABLE 44

	Hg	H_2O	CO_2
$-80°$ C.	10^{-9}	4×10^{-4}	672
$-185°$ C.	—	—	10^{-6}

It is important to notice that water has a measurable vapour pressure at $-80°$ C.

Poisoning effects may also have their origin in impurities contained in the reactants.

The catalytic activity of some catalysts is reduced by heat treatment

(e.g. G. Tammann, *Z. anorg. Chem.*, **224**, 25 (1935) ; E. B. Maxted and C. H. Moon, *J. Chem. Soc.*, 393 (1935) ; E. Fajans, *Z. physik. Chem.*, **B, 28,** 252 (1935)). For this reason it is preferable to start the experiments at the lowest temperatures and to check the activity of the catalyst frequently at standard conditions. The effect of sintering is greatly reduced by using supported catalysts.

(h) Shaking

If the catalytic reaction investigated involves the interaction of a gas and a liquid, it is necessary to bring the gas and liquid into intimate contact by stirring, shaking and dividing the gas into fine bubbles or the liquid into drops, since the diffusion of gases into liquids is much slower than gaseous diffusion. The diffusion coefficients of gases into water, for example, are of the order of one cm.^{2}/day, which is about 10^5 times smaller than the coefficients of gaseous diffusion, which are of the order of one cm.^{2}/sec. In each experiment it is essential to ascertain whether the experimental arrangement for stirring, shaking, etc., is sufficiently thorough, and that there is no delay in the reaction due to insufficient mixing, by varying the form and dimensions of the reaction vessel, the frequency and amplitude of shaking, etc. If the reaction velocity varies exponentially with temperature it is probable that mixing is efficient, since the rate of diffusion is proportional to the 3/2 power of the absolute temperature in the majority.

The experimental arrangements for shaking and mixing are well known, and need not be discussed here in detail. The reaction vessel can be shaken without detaching it from the apparatus if it is connected

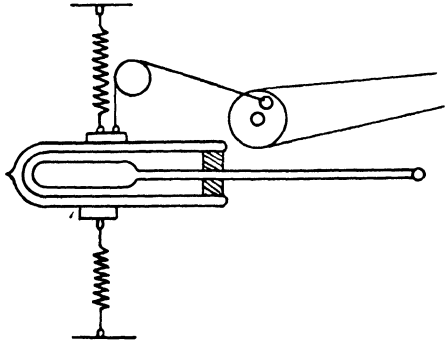


FIG. 251. Shaking device.

to it by a flexible glass spiral or tube bent into zigzag form. Fig. 251 shows the arrangement used by D. Eley and M. Polanyi (*Trans. Faraday Soc.*, **32**, 1388 (1936)). The shaking is done by the pull of a string from

a motor-driven eccentric, and the frequency of the vibration (15-20 per sec.) is controlled by the two springs. The temperature inside the Dewar flask is regulated by the heating (or cooling) coil and measured by a thermocouple. The vessel is attached to the apparatus by a ground joint which serves as bearing. The vibration caused by the shaking is taken up by a glass spiral.

For small amounts of liquid a shaking device described by A. Stock (*Ber.*, **53**, 751 (1920)) is useful. It consists of a light induction coil, movable core and interrupter. It can be clamped directly to the vessel, which is kept in strong vibration if the connecting tube is narrow enough.

(i) Reactions in the Adsorbed Layer

If the adsorptive power of the catalyst is sufficiently large, it may happen that the amount of the reactants in the gaseous phase is small compared with the amount in the adsorption layer. Under such conditions the investigation of catalytic reactions is specially favourable, since the amount of the reactants present in the adsorption layer can be determined directly by adsorption measurements,* and the rate of the catalytic reaction is not influenced by transport phenomena from the gaseous to the adsorption layer.

Examples of this kind of experiment are as follows. The decomposition of alcohols on bauxite has been investigated by H. Dohse and W. Kalberer (*Z. physik. Chem.*, **B, 5**, 144 (1929) ; H. Dohse, *ibid.*, **B, 6**, 343 (1929), and **B, 8**, 159 (1930)) in an apparatus provided with storage bulb, manometer and reaction vessel containing the catalyst. The amount of alcohol adsorbed is calçulated from the pressures in the storage vessel before and after adding the alcohol to the catalyst. The decomposition is followed by measuring the pressure of the olefines formed, since the catalysts only absorb the alcohol and water strongly.

In the hydrogenation experiments of C. Schuster (*Z. physik. Chem.*, **B, 14**, 249 (1931) ; *Trans. Faraday Soc.*, **28**, 406 (1932)) the charcoal catalyst (containing small amounts of iron and copper) adsorbs both ethylene and ethane strongly, but not hydrogen, and thus it is possible to use the decrease in the hydrogen pressure as a measure for the reaction. For example, the amount of ethylene adsorbed by 1 g. charcoal at 0° C. is 1·7 c.c. at a pressure of 0·4 mm., whereas only 0·13 c.c. of hydrogen are adsorbed at a pressure of 78·6 mm. (cf. also B. Bruns and K. S. Ablesowa, *Acta Physicochemica*, **1**, 20 (1934)). The conversion of ortho- para-hydro-

* It is outside the scope of this book to discuss the methods of adsorption measurements. The General Discussion on Adsorption held by the Faraday Society in 1932 (*Trans. Faraday Soc.*, **28**, 131 ff., 1932), and especially E. K. Rideal's paper on 'Experimental Methods' (*ibid.*, page 139), gives ample information on this subject.

gen at low temperatures or charcoal has also been investigated by this method (K. W. Rummel, *Z. physik. Chem.*, **A, 167**, 221 (1933)).

(j) Some Typical Arrangements

(α) *Wire catalysts.* The experimental arrangement of I. Langmuir (*Trans. Faraday Soc.*, **17**, 621 (1922) ; *J. Am. Chem. Soc.*, **37**, 1162 (1915)), used in his classical experiments on the oxidation of hydrogen and carbon monoxide, consisted of the reaction vessel, Töpler pump, McLeod gauge and mercury pump. Mercury seals were used, and a trap cooled by liquid air prevented mercury from entering the reaction vessel, which was in the form of a tube or a bulb 20 cm. in diameter. A platinum wire, 0·077 mm. in diameter and about 10 cm. long, bent into a **U**-shape was used as catalyst. The experiments were performed at about 10^{-3} mm. pressure, and the progress of the reaction was followed by pressure measurements.

Electrically heated wires were used as catalysts also by C. N. Hinshelwood and C. R. Prichard (*J. Chem. Soc.*, **127**, 327 (1925)) and R. E. Burk (*ibid.* 1105) at pressures around 100 mm., for investigating the decomposition of N_2O and NH_3. In some experiments the pressure readings were taken after the heating current of the filament had been switched off, and the gas had cooled to the temperature of the water or ice bath surrounding the reaction vessel.

Exchange reactions between ethylene (L. Farkas, A. Farkas and E. K. Rideal, *Proc. Roy. Soc.*, **A, 146**, 630 (1934)), water (A. Farkas, *Trans. Faraday Soc.*, **32**, 922 (1936)), ammonia (K. Wirtz, *Z. physik. Chem.*, **B, 30**, 289 (1935) ; A. Farkas, *ibid.*, **32**, 416 (1936)), hydrogen chloride, hydrogen bromide (K. Wirtz, *Z. physik. Chem.*, **B, 31**, 309 (1936)) and deuterium have also been studied on electrically-heated wires.

The apparatus of D. L. Chapman and P. W. Reynolds (*Proc. Roy. Soc.*, **A, 156**, 284 (1936)) used for the investigation of the catalytic hydrogen-oxygen reaction is shown in Fig. 252. The quartz reaction vessel contains a platinum wire, which is protected from poisoning by traps *A* and *B* cooled by liquid air. The gases used in these experiments were kept in the tubes closed by mercury cut-offs. The pressure (about 0·1 mm.) was adjusted by the method described on p. 315, and its change during the reaction followed by a McLeod gauge.

(β) With *bulk catalysts* flow methods are customarily used. Investigating the catalytic dehydrogenation of alcohols on copper, F. H. Constable (*Proc. Camb. Phil. Soc.*, **22**, 738 (1925) ; **23**, 593 (1927) ; *Proc. Roy. Soc.*, **A, 113**, 254 (1927)) and W. G. Palmer and F. H. Constable (*ibid.*, **A, 106**, 250 (1924)) regulated the flow of alcohol vapour by varying the current through a heating coil placed in the liquid. The amount of hydrogen

developed in a given time was independent of the rate of flow in a certain range, and was therefore taken as a measure of the velocity of dehydrogenation. A. A. Balandin and A. Bork (*Z. physik. Chem.*, **B**, **33**, 54, 73, 435, 443 (1936)) used a similar method in their dehydrogenation

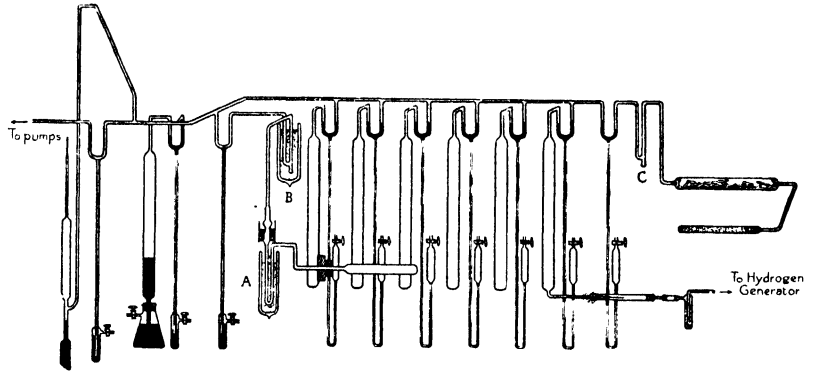


FIG. 252. Chapman and Reynolds' apparatus used for the investigation of the catalytic hydrogenation.

experiments. The liquid mixture of reactants was added to the catalyst as described on p. 301, and the cooled gases collected in a burette with a constant lower level. G. I. Hoover and E. K. Rideal (*J. Am. Chem. Soc.*, **49**, 106 (1927)) employed the apparatus shown in Fig. 253 for

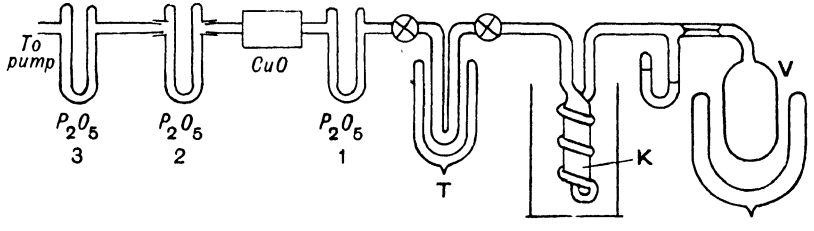


FIG. 253. Arrangement for investigating catalytic reactions at low pressures.

investigating the same reaction at a pressure of 1 mm. on thorium oxide. The rate of flow was regulated by varying the temperature of the alcohol in vessel *V*. The catalyst was kept in tube *K* in a bath of molten potassium and sodium nitrate. Alcohol and ethylene were frozen out in trap *T*. The hydrogen formed was burnt in the CuO tube and its amount determined from the increase in the weight of the P_2O_5 tube 2.

5. Electric Initiation of Reactions

All reactions which are initiated directly or indirectly by electrically charged particles are considered under this heading. Activation can be

brought about by collisions with electrons or ions of controlled speed or by α-particles. From the theoretical point of view the reactions initiated by low speed electrons are simplest, whereas reactions in the electric discharge involve such a great variety of processes between electrons, molecules, atoms, ions and radicals that the disentanglement of such processes from each other is only possible in special cases. The state of affairs becomes very much simpler if one or each of the reactants is separately subjected to the discharge. The production of atoms by electric discharge belongs to this type of reaction and will be discussed in some detail.

(*a*) *Electrons and ions of controlled speed.* The experimental set-up used by A. Caress and E. K. Rideal (*Proc. Roy. Soc.*, **120**, 370 (1928)) for investigating the initiation of chemical reactions by impact of electrons consists of reaction vessel, manometer, storage vessels for gases and pumps (cf. also A. Caress and E. K. Rideal, *Proc. Roy. Soc.*, **115**, 684 (1927) ; O. H. Wansbrough-Jones, *Proc. Roy. Soc.*, **127**, 511 (1930) ; G. F. Brett, *Proc. Roy. Soc.*, **129**, 319 (1930)). The reaction vessel is equipped with three electrodes, comprising the electron emitter, i.e. a barium oxide-coated platinum filament, a helical grid and a cylindrical anode. The electrons emitted by the filament are accelerated by a potential applied between grid and filament in a manner similar to that shown in circuit diagram in Fig. 254 (*b*). In designing this kind of apparatus the dimensions and the pressure have to be chosen in such a way as to give the electrons ample chance of colliding with the gas atoms. The general procedure is to expose the gas mixture under investigation at a pressure of about a tenth of a millimetre to the impacts of a current of electrons of known intensity and speed, and to observe the progress of the reaction. If the progress of the reaction is followed manometrically special precautions must be taken to allow for the disappearance of gases by 'clean-up', i.e. by adsorption of atoms on the walls or by related phenomena. For this reason it is advisable to ascertain the nature of the reaction products formed by chemical analysis.

For effects of high speed electrons see J. C. McLennan, M. W. Perrin and H. J. C. Ireton (*Proc. Roy. Soc.*, **125** (1929)).

Fig. 254 shows the experimental arrangement used by I. Motschan, S. Roginsky, A. Schechter and P. Theodoroff (*Acta Physicochemica*, **4**, 757 (1936)) for studying the formation of ammonia from the elements under the influence of positive ions (cf. also A. I. Leipunsky and A. Schechter, *Z. Physik*, **59**, 857 (1930)). The anode (*H*) consists of a platinum strip coated with a synthetic aluminosilicate (E. J. Jones, *Phys. Rev.*, **44**, 707 (1933)), which serves as a source of positive ions. (Mixture of Fe_2O_3 and alkali salts as sources for positive ions are described by

C. H. Kunsman, *J. Phys. Chem.*, **30**, 525 (1926)). The ion current is 10^{-6}-10^{-5} amps. The ions are accelerated by the voltage between the anode and the grid *S*. The apparatus is thoroughly baked out before each experiment. It is immersed in liquid during the experiments. The pressure is about 0·01-0·1 mm., and is measured by a McLeod manometer.

(*b*) *α-rays.* The methods used in investigating chemical reactions proceeding under the influence of α-rays include methods for the measurement of the intensity of the α-ray radiation and of the intensity of ionisation produced. It is outside the scope of the book to discuss these methods,

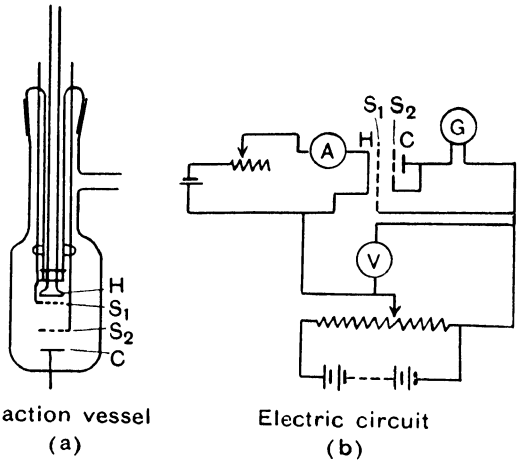


FIG. 254. Arrangement for production of ions of controlled speed.
S_1; S_2 = grids. C = cathode. V = voltmeter.
A = amperemeter. G = galvanometer.

which are dealt with in detail in the monograph : S. C. Lind, *The Chemical Effects of Alpha-particles and Electrons*, the Chemical Catalog Company, New York (1928). As an example of this kind of investigation the recent experiments on the radio-chemical synthesis and decomposition of hydrogen bromide (S. C. Lind and R. Livingston, *J. Am. Chem. Soc.*, **58**, 612 (1936)) may be cited. Radon was used as source of α-rays sealed up in small fragile glass bulbs. The bromine was kept in similar bulbs, and was introduced into the reaction vessel simultaneously with the radon by breaking the bulbs in a side tube by a magnetically controlled plunger. While the radon and the bromine were frozen out by liquid air a known amount of hydrogen was admitted, and the liquid air was only removed after waiting a few hours in order to allow RaA and RaC, produced by the decay of radon, to accumulate. The progress of the reaction was followed by measuring the pressure of hydrogen with a

quartz spiral manometer after the radon, bromine and hydrogen bromide were frozen out by dipping the reaction vessel into liquid air.

(*c*) *Glow discharge.* The glow discharge has been extensively used for the production of hydrogen and oxygen atoms since R. W. Wood's (*Proc. Roy. Soc.*, **A, 97**, 455 (1920) ; **102**, 1 (1922)) discovery (K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924) ; **116**, 391 (1925) ; E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926) ; K. F. Bonhoeffer, *Z. physik. Chem.*, **A, 139**, Haberband 64 (1928) ; P. Harteck and U. Kopsch, *Z. physik. Chem.*, **B, 12**, 327 (1931) ; K. H. Geib and P. Harteck, *Z. physik. Chem.*, Bodenstein Band, **6**, 849 (1931)). The discharge tube is usually 2-3 metres long, bent in U or ∩ shape, and has a diameter of 18-20 mm. The electrodes are cylindrical, made of 0·5 mm. aluminium foil, and have a surface area of about 100 cm.^{2} (100 mm. long and 35 mm. diameter). The aluminium cylinders are fastened to copper or platinum lead-in wires, which are kept as short as possible and are sealed into the glass in the usual way. It is most essential for the successful production of atoms by glow discharge to have the discharge tube absolutely free of any impurities like dust, grease and organic matter, which efficiently destroy the atoms. For this reason the electrodes are arranged in such a way as to prevent any material, which might be dislodged from the electrodes by the discharge, from falling into the discharge tube. The discharge tube takes a form which makes its cleaning by washing with nitric or chromic acid possible without the necessity of detaching it from the apparatus. Some of the usual forms of discharge tube are shown in Fig. 255.

Side tubes are attached near the electrodes and at the highest and lowest points of the discharge tube to facilitate the filling with acid or water. The third electrode (Fig. 255 (*c*)) can be used occasionally to clean the reaction tube, since according to K. F. Bonhoeffer (*Z. physik. Chem.*, **116**, 391 (1925)) certain kinds of impurities, which destroy atoms, are removed by the action of the discharge. Special care must be taken in cleaning the discharge tube. Clamps must not be placed where the discharge passes, in order to prevent puncturing of the glass by sparks from the tube to the clamp.

The pressure in the discharge tube is maintained between 0·1 and 1 mm., usually 0·3 mm. Hg. The voltage required for working the discharge is around 3000-5000, depending on the dimensions of the discharge tube. Direct or alternating current may be used. Usually the latter is most convenient, the current being applied from a suitable transformer, and controlled by a resistance in the primary circuit. The normal current through the discharge tube varies between 50 and 200 ma., about 400 ma. being the maximum current for discharge

tubes and electrodes for the dimensions given above. With too high currents the discharge tubes and electrodes may become overheated. It is advisable to cool the discharge tube with a current of air by means of an electric fan, since it is found that on hot glass surfaces the atoms disappear more easily by recombination than on cold walls. This type of discharge tube is suitable for the preparation of atomic hydrogen or

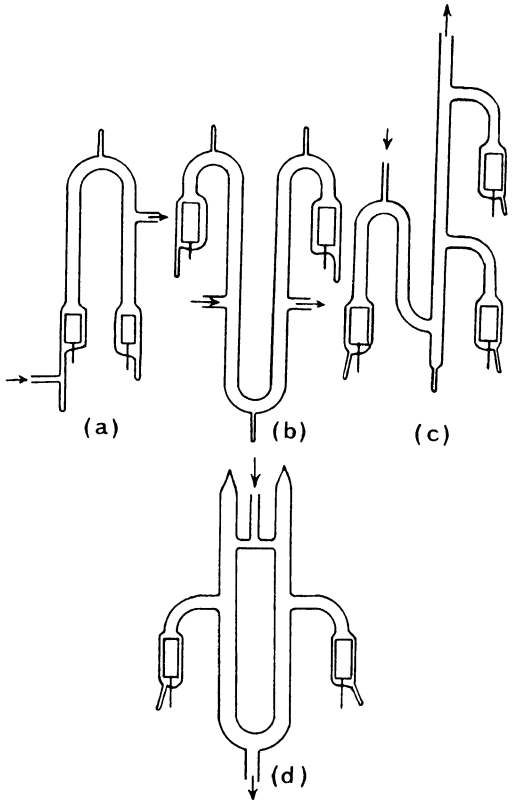


FIG. 255. Discharge tubes for production of atoms.

oxygen at a rate of 3-4 litres (N.T.P.) per hour, corresponding to a linear velocity of flow of 3-8 metres/second. High concentrations of atomic hydrogen are only obtained if the walls of the discharge tube are 'poisoned', since otherwise the atoms disappear by catalytic recombination on the walls. This poisoning can be accomplished according to Wood by mixing about 1 per cent. water vapour with the hydrogen, e.g. by letting it bubble through a dilute solution of potassium hydroxide, or by coating the walls of the discharge tube with meta-phosphoric acid or potassium chloride (cf. p. 277).

According to P. Harteck and E. Roeder (*Z. physik. Chem.*, **A, 178,** 389 (1937)), atomic hydrogen or oxygen can be prepared at pressures up to 20 mm. by adding neon to the gas to be activated, the partial pressure of which is about 0·1-0·3 mm. The general set-up of this apparatus is similar to that used without the addition of neon. In order to prevent waste of neon the gas is circulated, the reaction products being separated, and the hydrogen used replaced.

(*d*) *Impulse discharge.* The ordinary glow discharge is not suitable for activating nitrogen. According to E. Wrede (*Z. Physik*, **54,** 53 (1929)) and W. Steiner (*Z. Elektrochem.*, **35,** 733 (1929); *Z. physik. Chem.*, **B, 9,** 93 (1930)), atomic nitrogen of high concentration can be produced by condensed impulse discharges. The circuit diagram for this method is shown in Fig. 256. High tension direct current of 5000-10,000 volts charges a condenser of 0·5-2·5 μF. capacity through a high resistance of 50,000-100,000 ohms. The condenser is discharged across the spark gap and the discharge tube in pulses as soon as the condenser has reached a high enough voltage, the so-called breakdown voltage. If the resistance (*R*) condenser and the spark gap are suitably chosen, several impulse discharges of short duration but very high intensity can be obtained per second, which yielded about 30-40 per cent. of atomic nitrogen at a pressure of 0·5 mm. The duration of the impulse discharges is of the order of 10^{-5} seconds, and the current flowing may amount to one hundred amperes (cf. also E. J. B. Willey, *Proc. Roy. Soc.*, **A, 152,** 158 (1935)). If the resistance *R* is too small the potential of the condenser will never fall below the breakdown voltage, and discharge then becomes continuous.

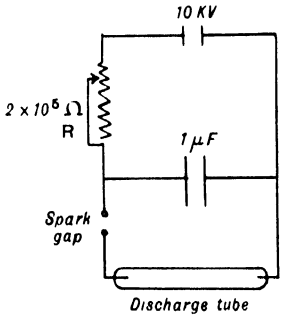


FIG. 256. Electric circuit for impulse discharge.

(*e*) *The electrodeless ring discharge* has been used by W. H. Rodebush and W. C. Klingelhoeffer (*J. Am. Chem. Soc.*, **55,** 130 (1933) for the production of chlorine atoms (see p. 158).

Other examples of different forms of discharges are the following: glow discharge: K. Peters and O. H. Wagner (*Z. physik. Chem.*, **A, 153,** 161 (1931)); K. G. Emeléus, R. W. Lunt and C. A. Meek (*Proc. Roy. Soc.*, **A, 156,** 394 (1936)). Electrodeless discharge: W. D. Harkins and D. M. Gans (*J. Am. Chem. Soc.*, **52,** 5165 (1930)) and Schumb and Brickford (*J. Am. Chem. Soc.*, **58,** 1038 (1936)). Silent discharge: Gunther and Cohn (*Z. physik. Chem.*, **B, 26,** 8 (1937)). Arc discharge: F. Haber and O. Oppenheimer (*Z. physik. Chem.*, **B, 16,** 443 (1932)). Many

references on the chemical effects of discharges are to be found in the following articles : E. J. B. Willey (*Trans. Faraday Soc.*, **30**, 230 (1934)) and K. R. Dixit (*Current Science*, **6**, 163 (1937)).

EXPLOSIVE REACTIONS

The velocity of explosive reactions changes abruptly from very small values to abnormally high values if the experimental conditions (temperature, pressure, etc.) are slightly varied. The usual methods of investigating chemical reactions are not applicable to explosive reactions, since their speed is far too great to be measured. Consequently measurements are restricted to finding out under what conditions these types of reactions occur and what their products are. Such investigations are occasionally supplemented by observations of the light emitted, by electric measurements and by determination of the velocity of the flame.

1. Determination of the Pressure and Temperature Limits of Explosive Reactions

(*a*) *Theoretical.* The experimental technique used for determining the pressure limits of explosive reactions is best understood from Figs. 257 and 258. In Fig. 257 the explosion limits are represented schematically as a function of the partial pressures of the components of the explosive mixture at a given temperature. In Fig. 258 the limits are shown for a mixture of given composition and pressures as a function of temperature. Explosion only occurs in the shaded portion. It will be recognised that mixtures with a given partial pressure of one component and with variable partial pressures of the other correspond to lines parallel to one of the axes (Fig. 257 (*b*)), that mixtures with constant ratio of the components but of variable total pressures correspond to lines passing through the origin (Fig. 257 (*a*)), and that mixtures of a given total pressure but variable ratio of the two components cut both axes at an angle of 45° (dotted line in Fig. 257 (*a*)). Thus the following general characteristics of the explosion limits can be read from Fig. 257 and Fig. 258 : (1) If the partial pressure of one component is kept constant, the explosion only occurs between certain values of the partial pressure of the other. (2) If the ratio of the two components is kept constant, the explosion only occurs between a lower and an upper value of the total pressure. Occasionally a second upper limit of pressure is found, above which the mixture is again liable to explode. (3) These pressure limits depend on temperature, and there is always a temperature below which no explosion occurs. (4) For a given total pressure the mixture only explodes if the ratio of the components is within certain limits. From these considerations it is evident

that when referring to upper and lower pressure limits it is essential to specify which limits are actually meant if ambiguity is to be avoided.

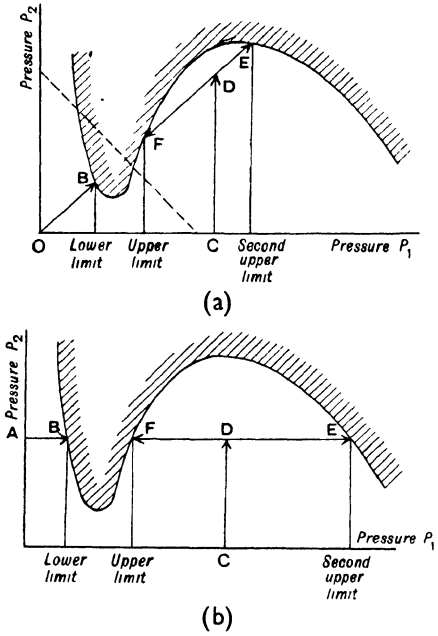


FIG. 257. Explosion limits at constant temperature.

The lower limit for mixtures with a component of constant partial pressure is found by filling one component of a desired pressure in the reaction vessel and then increasing the pressure of the other component until explosion occurs. (Step $A \rightarrow B$ on Fig. 257 (b)). The second upper limit can be found according to the same principle in this way : first a sufficient pressure of component (1) is introduced in the reaction vessel in order to reach C, then component (2) is added to point D, and finally the pressure of component (1) is further increased until explosion occurs (E). This roundabout path is necessary in order to avoid the explosion region. The pressure of component (1) cannot be increased above point B, since at point B explosion occurs.

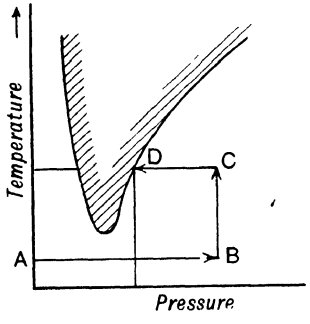


FIG. 258. Explosion limits at variable temperature.

If component (2) is condensable and the pressure fixed by that of the liquid, the first upper limit can be determined by reducing the pressure

from point D through pumping up to point F (Fig. 257 (b) since even then the partial pressure of (2) remains constant.

The lower limit for mixtures of constant composition is found by admitting the mixture of the two components along OB (Fig. 257 (a)). The upper limit can be determined by reducing the pressure from point D, which is reached via C as described above. The second upper limit can be reached by admitting further amounts of the mixture to that corresponding to point D or compressing the mixture.

An alternative method for the determination of the upper explosion limits may involve the change of the temperature of the reaction vessel (Fig. 258). In this method the gas mixture is filled in at a low temperature to a pressure higher than the upper explosion limit ($A \rightarrow B$), the temperature raised ($B \rightarrow C$), and the pressure reduced until explosion occurs ($C \rightarrow D$).

It will be evident that these considerations are only described to indicate the principles by means of which explosion limits may be determined. Thus it is not possible, for example, to foretell where a point D (Fig. 257), suitable for measuring the upper pressure limit, may be found if a new kind of explosive mixture is to be investigated. The above paragraphs are merely intended to show how such a point may be found.

If the pressure is kept constant and the temperature varied, the ignition temperature, i.e. the temperature above which the spontaneous ignition occurs, may be determined. Occasionally it is found that there is an upper ignition temperature above which no ignition occurs (D. T. A. Townend and M. R. Mandlekar, *Proc. Roy. Soc.*, **A**, **141**, 484 (1933); and **143**, 168 (1934)).

(b) *Experimental methods.* The experimental methods employed for the determination of pressure limits and ignition temperatures are simple. The occurrence of explosion or ignition can be observed by appearance of a flame, sudden change of pressure or a characteristic click. At low pressures the flame is very weak, and the flash accompanying the explosion may only be noticeable in a dark room. Some typical methods are represented in Figs. 259 to 264.

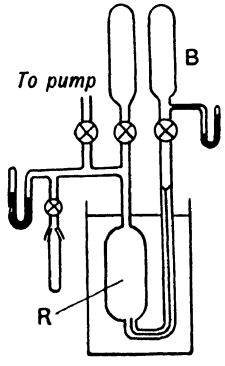


FIG. 259. The capillary method.

(α) *The capillary method* (Fig. 259) (N. Semenoff, *Z. Physik*, **46**, 109 (1927); A. Kowalsky, *Z. physik. Chem.*, **B**, **4**, 288 (1929); and H. W. Melville and E. B. Ludlam, *Proc. Roy. Soc.*, **A**, **132**, 108 (1931)) is a very convenient method for measuring the lower limit at constant partial pressure of one component. First the pressure of this component is adjusted, and then the second admitted slowly through the capillary. Below the explosion limit the pressure

increases in the reaction vessel R with time (provided the pressure is high enough in bulb B). As soon as the pressure in R has reached the lower limit, explosion sets in and there is a discontinuity in the time-pressure readings. The tedious reading of the manometer can be dispensed with if the experiments are made at low pressures, and the apparatus has once been calibrated by measuring the volume of R and the amount of gas streaming through capillary C in the unit of time at given pressure in B. This is done most conveniently in the absence of the first component. Then it is sufficient to measure the time which elapses from the opening of tap to B until the explosion occurs. This method has been used for experiments with mixtures of oxygen and phosphorous.

(β) *The withdrawal method* is the inverse process to the capillary method so it needs no further explanation. Examples of its use are given by A. Kowalsky (*Z. physik. Chem.*, **B**, **4**, 288 (1929)); H. W. Thompson and

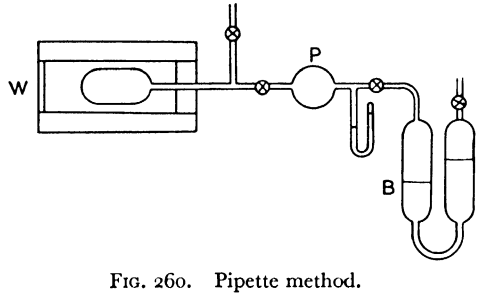


FIG. 260. Pipette method.

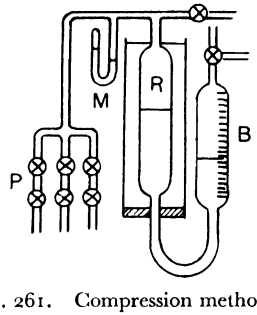


FIG. 261. Compression method.

C. N. Hinshelwood (*Proc. Roy. Soc.*, **A**, **122**, 610 (1929)); and G. Hadman and C. N. Hinshelwood (*Proc. Roy. Soc.*, **A**, **138**, 297 (1932)).

(γ) In *the pipette method* (Fig. 260) (C. N. Hinshelwood and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, **A**, **138**, 311 (1932)) a certain amount of explosive mixture is filled from the burette B into pipette P, and admitted into the evacuated reaction vessel, which is kept at the desired temperature. If no explosion occurs (observation through the window W), the pressure in the pipette is increased until the explosion limit is reached (cf. also A. V. Sagulin, *Z. physik. Chem.*, **B**, **1**, 275 (1928)).

(δ) *The compression method* (Fig. 261) is suitable for measuring the lower limit for mixtures of given composition (cf. R. H. Dalton and C. N. Hinshelwood, *Proc. Roy. Soc.*, **A**, **125**, 294 (1929); and R. H. Dalton, *Proc. Roy. Soc.*, **A**, **128**, 263 (1929)). The gases are admitted by means of the pipettes P of known volume. Since the volume of the reaction vessel R is also known, the initial pressure can be calculated. The gas mixture is compressed by mercury which is slowly transferred from the graduated

burette *B* into the reaction vessel. The pressure in *R* can be read on the manometer *M*, or more conveniently calculated from the amount of mercury transferred from burette *B*. Compression is continued until explosion occurs.

(ϵ) *The streaming method* (Fig. 262) (A. V. Sagulin, A. Kowalsky, D. Kopp and N. Semenoff, *Z. physik. Chem.*, **B, 6**, 307 (1930)) is used to determine the ignition temperature at different pressures and velocities of flow. The gaseous mixture is kept in the graduated vessel *G*, and passes through taps V_1 and V_2 and the reaction vessel R_1 heated in the electric furnace. By means of V_1 and V_2 both the pressure in the reaction vessel and the velocity of flow can be varied (see p. 299). The pressure is measured on manometer *M*, and the velocity of flow calculated from

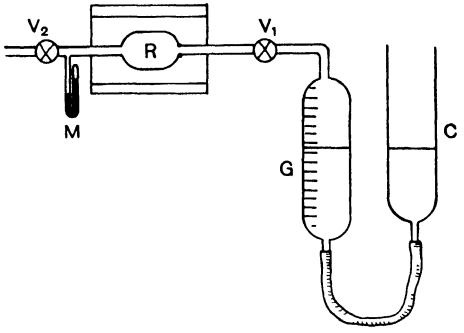


FIG. 262. Streaming method.

the amount of gas leaving the vessel *G*. The levelling vessel *C* is lifted automatically until the water levels in *C* and *G* are equal. When the required rate of flow and pressure are attained, the temperatures of the furnace is slowly increased until explosion occurs.

The occurrence of explosion does not only depend on gas composition, pressure and temperature, but also on the nature and amount of foreign gas added (N. Semenoff, *Z. Physik*, **46**, 109 (1927); H. W. Melville and E. B. Ludlam, *Proc. Roy. Soc.*, **A, 132**, 108 (1931)), dimensions of the reaction vessel (N. Semenoff, *loc. cit.*), its material (C. N. Hinshelwood and G. H. Grant, *Proc. Roy. Soc.*, **A, 141**, 29 (1933); Hinshelwood, E. A. Moelwyn-Hughes and A. C. Rolfe, *Proc. Roy. Soc.*, **A, 139**, 521 (1933)) and pretreatment, e.g. baking out (V. E. Cosslet and W. E. Garner, *Trans. Faraday Soc.*, **26**, 190 (1930)) and coating with KCl (A. A. Frost and H. N. Alyea, *J. Am. Chem. Soc.*, **55**, 3227 (1933)). Often different values of pressure limits or ignition temperatures are found, depending on whether the measurement is performed immediately after an experiment during which an explosion had occurred, or some time later (F. Haber, P. Harteck and L. Farkas, *Z. Elektrochem.*, **36**, 711 (1931)). For

the effect of sparking on the ignition temperature, see B. Lewis and C. D. Kreutz (*J. Chem. Phys.*, **1**, 89 (1933)).

2. Artificial Ignition

Explosion mixtures can be ignited artificially by means of a spark or a small flame. Ignition occurs only in certain pressure and temperature regions, which depend, however, on experimental conditions and on the igniting spark or flame.

The determination of the explosion limits of mixtures of inflammable gas with oxygen or air at room temperature and atmospheric pressure

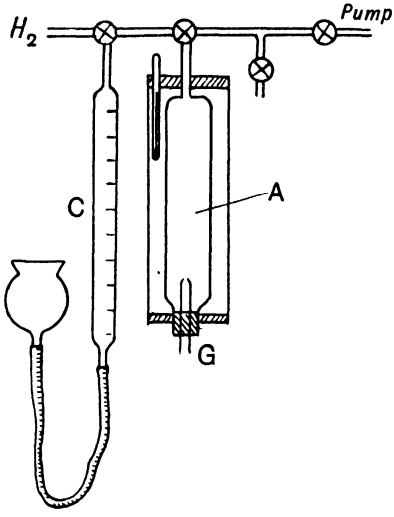


FIG. 263. Ignition by spark or flame.

by the flame method is very simple. A tube is filled with gas mixtures of different concentration, the stopper is then removed from one end of the tube and a small (coal gas) flame introduced. The explosion limits thus observed are different, depending whether horizontal or vertical tubes are used, and whether explosive mixtures are ignited at the upper or lower end of the vertical tube.

A simple arrangement for determination of the explosion limits of hydrogen-air mixtures is shown in Fig. 263 (H. W. Thompson, *Z. physik. Chem.*, **B**, **18**, 219 (1932)). The explosion tube *A* (60 mm. in diameter and 120 cm. long) is first filled with air ; then a given amount of hydrogen, measured in burette *C*, is added, stopper *G* being removed during the addition. The gases are allowed to mix in the tube, and are ignited by a spark or by a flame after removing the stopper (cf. also W. A. Bone, R. P. Fraser and F. Lake, *Proc. Roy. Soc.*, **A**, **131**, 1 (1930)).

If the explosive mixture is ignited by means of an electric spark, the pressure limits and the temperature of ignition depend on the intensity of spark. The experimental arrangement of G. Gorchakow and F. A. Lavrov (*Acta Physicochemica*, **1**, 139 (1934)) used in such an investigation is shown in Fig. 264. The explosive mixture (H_2+O_2) streams continuously through the reaction vessel under reduced pressure, in order to remove the products of slow combustion which are formed if such a gas mixture is admitted into an evacuated vessel. After some time the taps *B* and *C* are closed, and a spark is produced by closing the electric circuit through telegraph key *K*. The energy of the electric spark is controlled by resistance *R*. At given temperature and spark energy the pressure in the reaction vessel is changed until explosion occurs.

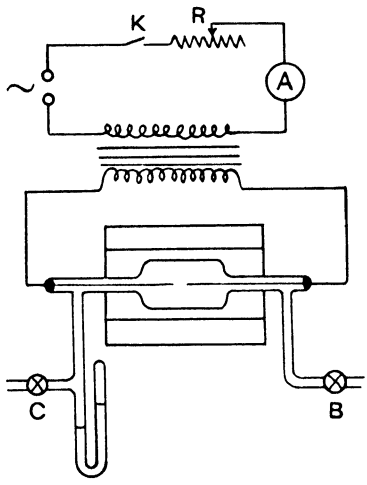
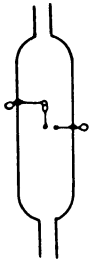


FIG. 264. Ignition by spark.

Another arrangement is described by F. A. Lavrov and A. L. Beshchastny (*Acta Physicochemica*, **1**, 975 (1935)). A. Kowalsky (*Z. physik. Chem.*, **B, 11**, 56 (1931)) used a spark gap consisting of two silver spheres of 5 mm. diameter at a distance of 0·2 mm. The spheres are soldered to platinum wires which are sealed into the reaction vessel. The spark is produced by connecting the spark gap to a condenser battery charged to a definite potential. The intensity of the spark may be controlled by varying the capacity of the condenser from 0·04 to 2μF.


FIG. 265. Sparking electrodes according to Bone.

By arranging the sparking electrodes as shown in Fig. 265 (W. A. Bone, F. R. Weston and D. A. Winter, *Proc. Roy. Soc.*, **A**, **123**, 286 (1929)) it is possible to heat *in vacuo*, and thus to free the metal from any occluded gas. A slight tilting of the vessel brings the electrodes into contact, and the heating current can then be passed through the electrodes.

3. Wall-less Inflammation

The effect of walls on explosive reactions can be entirely elminated by working with gas streams, according to F. Goldmann (*Z. physik. Chem.*, **B, 5**, 316 (1929)) and H. N. Alyea and F. Haber (*Z. physik. Chem.*, **B, 10**,

193 (1930)). These experiments were carried out in a metal chamber filled with nitrogen, into which hydrogen and oxygen were streamed through two thin porcelain tubes set at right angles. Both tubes were provided with independent heaters, and one was movable in order to allow the fine adjustment of the crossing point of the two gas streams. A movable thermocouple served to determine the temperature of each stream. By this method it was possible to show that inflammation occurred if a hydrogen stream of 20° C. intersected an oxygen stream at 580-590° C. This latter temperature could be reduced by 40° if a quartz rod of 520° C. was pushed in the point of intersection of the gas streams. An aluminium rod was without effect. These experiments indicate clearly the part played by the walls in explosive reactions.

4. Rapid Reaction and Induction Period

Near the explosion limits the velocity of the reaction is occasionally just within reach of experimental measurement. According to A. Kowalsky (*Phys. Z. Soviet.*, **1**, 595 (1932) ; **4**, 723 (1933)) pressure changes associated with such rapid reactions may be measured by means of a membrane gauge (p. 86). The movements of the membrane are registered by an optical beam on a rapidly moving photographic film. If the light beam is reflected from a mirror fastened on a tuning fork, before reaching the membrane the vibrations of the tuning fork are superposed on movements of the membrane and may serve as time marks. By this method reactions can be investigated which occur within a tenth of a second.

A very important feature of some explosive reactions is the so-called induction period which elapses before the reaction sets in. It may range from a fraction of a second to several minutes or more. It has been suggested that the induction period is due to some impurities which have to be destroyed before the reaction can start, but induction periods are also observable in absolutely pure mixtures. During the induction period the pressure remains constant, and according to the very careful chemical analysis of Bone and his collaborators (W. A. Bone and S. G. Hill, *Proc. Roy. Soc.*, **A, 126, 134** (1930) ; W. A. Bone, A. E. Haffner and H. F. Rance, *Proc. Roy. Soc.*, **A, 143**, 16 (1933)), there is probably no chemical reaction whatsoever.

The induction period is either connected with the slow formation of certain adsorption layers on the walls of the reaction vessel, or with slowly developing non-stationary chains, according to N. Semenoff (*Phys. Z. Soviet.*, **1**, 546 (1932)). It is dependent on the pressure, gas composition and surface of the vessel, and decreases with increasing temperature. L. Farkas (*Z. Elektrochem.*, **37**, 670 (1931)) measured the induction period

in a mixture of hydrogen sulphide and oxygen by an oscillograph. A fine Wollaston wire was stretched in the reaction vessel, balanced in a Wheatstone bridge at the initial temperature (250° C.) and pressure (300 mm.). The galvanometer of the bridge was replaced by an oscillograph of high sensitivity. Since the heat capacity of the wire was very small, the temperature of the wire could follow the temperature of the gases in the reaction vessel without appreciable lag. A deflection of the oscillograph beam corresponded to a change of temperature in the reaction vessel. The oscillograph revealed the following facts. The induction period of 14·3 seconds consisted of two parts (cf. also H. W. Thompson and N. S. Kelland, *J. Chem. Soc.*, 1809 (1931)) : during the first 12·5 seconds the temperature did not change at all ; in the following 1·8 seconds the temperature rose to 342° C., when the explosion occurred.

Two other interesting observations deserve mention. According to H. W. Thompson (*Nature*, **127**, 629 (1931)), in mixtures of hydrogen sulphide and oxygen, a series of explosions (up to five) can occasionally be observed, separated from each other by a few seconds. L. Farkas, F. Haber and P. Harteck (*Naturwiss.*, **18**, 267 (1930)) illuminated a mixture of oxygen and hydrogen or oxygen and carbon monoxide containing 0·5-1 per cent. ammonia at 420° C. for a short time by a zinc spark. The mixture exploded after induction periods ranging from 1 second to 12 minutes, depending on the composition of the gas and on the intensity and duration of the illumination.

5. Explosions at very High Pressures

Explosion vessels withstanding pressures up to 10,000 atmospheres are described by W. A. Bone, D. M. Newitt and D. T. A. Townend (*Proc. Roy. Soc.*, **A**, **139**, 57 (1933)). In order to remove the gaseous products of an explosion suddenly from the zone of high temperature an explosion vessel with a cooling chamber has been designed by D. T. A. Townend and L. E. Outridge (*Proc. Roy. Soc.*, **A**, **139**, 74 (1933)). The ignition of the explosive mixture by spark is performed in the explosion chamber, which is separated from a much larger expansion chamber by a metal disc. The dimensions of this disc are such as to ensure its bursting at the explosion pressure. Thus the products of explosions are immediately released into the expansion chamber.

6. Optical Observations

The object of optical observations on flames is to determine the intensity and spectrum of the radiation emitted, and to decide whether this radiation is due to chemical or thermal excitation. The investigation of flame spectra is done in the visible or ultra-violet region photographically

(cf. K. F. Bonhoeffer and F. Haber, *Z. physik. Chem.*, **137**, 263 (1928)), and in infra-red region by the usual methods of infra-red spectroscopy (W. E. Garner, D. A. Hall and F. E. Harvey, *J. Chem. Soc.*, 641 (1931) ; W. E. Garner and D. A. Hall, *J. Chem. Soc.*, 2037 (1930)).

The second question can be examined by different methods. One method involves the measurement of the coefficients of emission and absorption of the flame and its temperature by means of a thermocouple or similar device. If the temperature calculated from the ratio of the

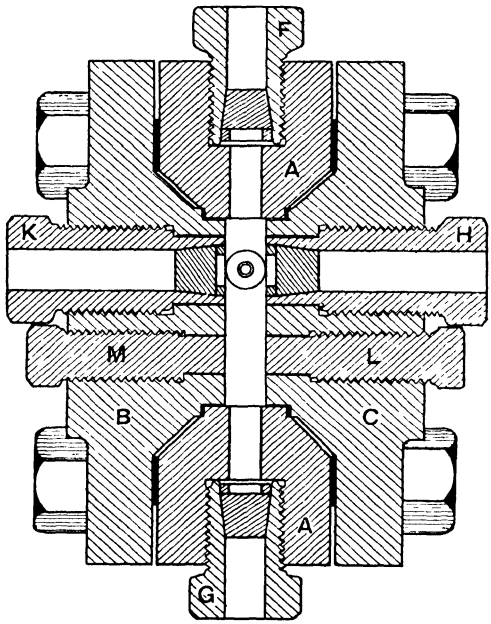


FIG. 266. Combustion chamber for high pressure flames.

emission and absorption coefficients for any wavelength according to the laws of black body radiation corresponds to the temperature determined experimentally, the radiation is due to thermal excitation (H. E. Hershey, *Ind. Eng. Chem.*, **24**, 867 (1922)). According to another method developed by Kurlbaum and Féry the temperature of the flame measured thermometrically is compared with the temperature of a black body behind the flame at which the radiation of the flame and of the black body appears to be of the same intensity at the same wavelength (cf. E. Griffiths and J. H. Awbery, *Proc. Roy. Soc.*, **A, 123**, 401 (1929) ; G. W. Jones, B. Lewis and H. Seaman, *J. Am. Chem. Soc.*, **54**, 2166 (1932)).

As far as these measurements concern free-burning flames, e.g. Bunsen flames, the experimental technique needs no further explanation. Flames

in closed systems are observed through suitable windows. The cross-section of combustion chambers for high pressure flames as described by W. A. Bone and F. G. Lamont (*Proc. Roy. Soc.*, **A, 144**, 250 (1924)) ; (cf. also D. M. Newitt and F. G. Lamont, *Proc. Roy. Soc.*, **A, 139**, 83 (1923)) is shown in Fig. 266. *A* is a massive ring, 12 inches in diameter, closed by two end plates *B* and *C* by six bolts. The high pressure gases enter the combustion chamber from opposite directions through tubes which are perpendicular to the plane of the figure. Observations are made through quartz windows fitted in the plugs *F*, *G*, *H* and *K*. The windows are carefully ground into the plugs and fastened by ring-screws (see p. 323). The whole apparatus is made of stainless steel in order to withstand the corrosive action of the hot flame. The gases from the flame leave the combustion chamber by special tubes. The flame is started at low pressure by lighting it through plug *L* or *M* by a taper. Then the plug is replaced and the pressure gradually increased until the required pressure is reached.

7. Various Methods for investigating Explosive Reactions

There are a great many methods for the investigation of flames and explosions which cannot be dealt with here in detail. The following examples suffice to show their applications : Determination of flame and detonation velocity by photographic and electric methods : W. A. Bone and R. P. Fraser (*Proc. Roy. Soc.*, **A, 130**, 542 (1931)). Photography of shock and detonation waves in explosions : W. Payman and H. Titman (*Proc. Roy. Soc.*, **A, 152**, 418 (1935)) ; W. Payman, H. Titman and D. W. Woodhead (*Proc. Roy. Soc.*, **A, 148**, 604 (1935)). Measurements of temperature and electrical conditions in flames : E. Griffiths and J. H. Awbery (*Proc. Roy. Soc.*, **A, 123**, 401 (1929)) ; W. A. Bone, R. P. Fraser and W. H. Wheeler (*Proc. Roy. Soc.*, **A, 132**, 1 (1931)). Determination of ignition temperatures : H. F. Coward (*J. Chem. Soc.*, 1387 (1934)) ; Prettre (*L'inflammation et la combustion explosive au milieu gareux*, Paris (1933)). Investigations of combustions in combustion engines : A. R. Ubbelohde, J. W. Drinkwater and A. C. Egerton (*Proc. Roy. Soc.*, **A, 153**, 103 (1936)) ; A. v. Philippovich (*Z. Elektrochem.*, **42**, 472 (1926)) ; A. E. Hershey (*Ind. Eng. Chem.*, **24**, 867 (1932)) ; L. Withrow and G. M. Rassweiler (*Ind. Eng. Chem.*, **18**, 528 (1926)) ; **24**, 528 (1932) ; **25**, 923, 1359 (1933)).

8. Precautions

When working with explosive reactions utmost care must be exercised. Since explosions at low pressure are usually harmless and explosion experiments above atmospheric pressures are done in pressure-proof

metal equipment, the most dangerous pressure range is that around atmospheric pressure when glass or silica are used for reaction vessels.

The reaction vessel has to be shielded by a metal screen (often the furnace surrounding the vessel will serve this purpose) or by strong plate glass. If visual observations have to be made, a mirror should be used to prevent exposure to broken glass should the apparatus be shattered by the explosion. Special care should be taken to avoid any possibility of the explosion spreading from the reaction vessel into the storage vessel. This might happen, e.g. in determining the lower explosion limit according to the capillary method, which should therefore be used rather cautiously at medium pressures. Capillary tubing, metal gauze and layers of sand may be used to prevent backfire. A safety valve can be constructed by cementing with wax a piece of plate glass on a flange made at the end of a tube. The flat window will be pushed off at a sudden pressure shock. Larger amounts of explosive gas mixture should not be kept in connection with the reaction vessel. It is safer to prepare only a limited quantity each time, and to surround the storage vessels with strong wire gauze to keep the broken parts from flying in every direction.

APPENDIX

A. SOME IMPORTANT PHYSICAL CONSTANTS

Table 45 contains some physical constants according to Birge (*Review of Modern Physics*, **1**, 1 (1929)).

TABLE 45

Velocity of light	$c = 2{\cdot}99796 \times 10^{10}$ cm. sec.$^{-1}$.
Litre	1000·027 cm.^{3}.
Volume of ideal gas	$22{\cdot}4141 \times 10^3$ cm.^{3} . mol^{-1}.
Normal atmosphere	$1{\cdot}013249 \times 10^6$ dyne . cm.$^{-2}$.
Mechanical equivalent of heat	$J = 4{\cdot}1852$ abs.-joule . cal^{-1}.
Faraday constant	$F = 96494$ int.-coul. g.-equiv.$^{-1}$.
Electronic charge	$e = 4{\cdot}770 \times 10^{-10}$ abs.-es-units.
Planck's constant	$h = 6{\cdot}547 \times 10^{-27}$ erg sec.
Maximum density of water	0 999973 g. cm.$^{-3}$.
Normal acceleration of gravity	$g = 980{\cdot}665$ cm. sec.$^{-2}$.
Density of Hg at 0° C.	13·59509 g. cm.$^{-3}$.
Avogadro's number	$N = 6{\cdot}064 \times 10^{23}$ mol^{-1}.
Gas constant per mole	$R = 8{\cdot}3136 \times 10^7$ erg . deg.$^{-1}$. mol^{-1}.
,, ,,	$R = 1{\cdot}9864$ cal. . deg.$^{-1}$. mol^{-1}.
,, ,,	$R = 8{\cdot}2046 \times 10^{-2}$ litre . atmos. . deg.$^{-1}$. mol^{-1}
,, ,,	$R = 82{\cdot}048$ cm.^{3} . atmos. . deg.$^{-1}$. mol^{-1}.
Boltzmann constant	$k = 1{\cdot}3708 \times 10^{-16}$ erg . deg.$^{-1}$.

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AUTHOR INDEX

Ablesowa, K. S., 348, 351
Abraham, H., 143
Adams, R., 340
Adkins, H., 341, 343
Adwentowski, K., 163
Ahlberg, J. E., 113
Allolio, R., 348
Allsopp, C. B., 373
Alyea, H. N., 363, 365
Ambler, H. R., 174
Anderson, J. O., 202, 203, 210
Anderson, L. C., 160
Anderson, R. P., 174
Andrews, 236
Andrews, M. R., 150
Angerer, E. v., 371
Archer, C. T., 14
Aston, F. W., 200
Awbery, J. H., 368, 369

Bach, F., 293
Bacon, J. S., 150
Badger, R. M., 209
Baeyer, A., 168
Bakshi, J. B., 28
Balandin, A. A., 301, 353
Ballard, S. S., 26
Baly, E. C. C., 206, 373
Bardwell, D. C., 53
Barker, E. F., 165
Barkhausen, H., 89
Barnes, B. T., 222, 226, 228
Barnes, R. B., 291
Barratt, S., 210
Barrer, R. M., 137, 179, 268
Bartlett, E. P., 190
Basch, R., 11, 12
Bates, F., 227
Bates, J. R., 160, 202, 203, 210, 225, 227, 243, 304
Baturcas, T., 173
Baumann, P. B., 11
Bay, Z., 231, 390
Bayliss, N. S., 209
Beckmann, A. O., 212
Beebe, R. A., 100
Belchetz, L., 304
Bellenot, H., 239
Bender, P., 331
Benedict, W. S., 290, 291, 331
Benford, F., 250
Benton, A. F., 296, 338
Beretta, U., 330
Bergmann, P., 331
Berl, E., 341
Berliner, A., 348
Bernreuther, F., 330
Berthoud, A., 239, 373
Beshchastny, A. L., 365
Beutler, H., 26, 27, 308, 331
Bevan, R. C., 337
Bhatt, L. A., 321
Bidwell, C. C., 129
Birge, R. T., 371
Bitner, R. E., 238
Bjerrum, N., 29
Blacet, F. E., 180
Blodgett, K., 123
Bodenstein, M., 28, 29, 62, 63, 86, 158, 160, 174, 239, 267, 280, 296, 297, 326, 330
Boehm, E., 307, 356
Bogdan, M., 134
Bogdandy, S V., 310
Bol, C., 225
Bolland, J. L., 169, 194, 197, 217, 282
Bone, W. A., 270, 281, 320, 323, 364, 365, 367, 369, 372
Bonhoeffer, K. F., 92, 154, 190, 214, 277, 284, 293, 307, 349, 356, 368, 372, 373
Booth, H. S., 173
Borisoff, P. P., 342
Bork, A., 353
Bose, I. C., 23
Boughton, W. A., 68
Boulin, C., 173
Bovie, W. T., 228
Bowen, E. J., 232, 263
Bowman, F., 290
Brackett, F. P., 228
Brattain, R. R., 291
Bratzler, K., 287
Brauer, G., 268, 296
Braune, H., 11, 12, 29

Bredig, G., 348
Brenschede, W., 54, 330
Brett, G. F., 354
Brickford, F. A., 358
Brickwedde, F. G., 139
Bridgman, P. W., 273, 321
Briers, F., 239
Bright, A. C., 87
Briske, H., 133
Brown, C. L., 170
Brown, G. W., 27
Bruns, B., 342, 343, 351
Buckley, E. O., 87
Budde, E., 334
Burch, C. R., 52, 67, 82
Burger, H. J., 252
Burk, R. E., 352
Burkhardt, H., 341
Burrell, G. A., 173, 204
Burrow, J. H., 69
Burt, R. C., 150
Burwell, R. L., 290, 340
Busch, H., 345
Buttenbender, G., 26
Byk, H. T., 52, 54
Byrne, B. J., 322

Cady, F. E., 111
Cahn, L., 341
Calingaert, C., 173
Callendar, H. L., 121, 122
Calvert, H. R., 329, 331
Calvin, M., 296
Campbell, N. R., 77, 187, 188, 261, 374
Caress, A., 354
Cario, G., 313
Caruthers, J. E., 66
Carver, E. K., 83, 84
Cath, P. G., 203
Chadwell, H. M., 95
Chakravarty, K. M., 28
Chamberlain, D. S., 174
Chapman, D. L., 239, 268, 280, 335, 336, 337, 345, 347, 349, 352
Cheeseman, G. H., 170, 213
Chesebro, P. R., 28
Christiansen, C., 234
Christiansen, J. A., 131, 180
Clark, R. J., 75
Coblentz, W., 111
Coehn, A., 373
Cohn, G., 358
Conn, G. K. T., 253
Connor, R., 341
Constable, F. H., 352
Cook, W. R., 11
Cooke, E. M., 132
Coolidge, A. S., 91
Coons, C. E., 93
Cooper, D., 343
Cooper, R., 343
Copeland, L. C., 157
Corson, B. B., 306
Cosslet, V. E., 363
Coward, H. F., 369
Cox, R. T., 74
Cramer, H. I., 343
Crist, R. H., 223, 224
Curtis, W. E., 210

Dalton, R. H., 177, 362
Damkohler, G., 317
Daniels, F., 87, 212, 223, 224, 249, 254, 324
Darbyshire, O., 210
Datta, A. K., 27
Day, A. L., 111
Daynes, H. A., 179, 287, 374
Deitz, V., 93
Delfosse, J. M., 169
Dennis, L. M., 173
Désirant, M., 26
Dieke, G. H., 214
Diels, O., 343
Dilley, J. R., 326
Dirac, P. M., 23
Dixit, K. R., 359
Doctor, E., 174
Dodge, B. F., 29
Dohse, H., 351
Doht, W., 170
Donath, E., 314
Draper, 334, 335
Drinkwater, J. W., 369
Duchesne, J., 26
Dunbar, R. E., 343
Dunoyer, L., 46, 93, 97, 372
Dushman, S., 60, 87, 88, 89, 97, 372
Dux, W., 62, 63, 86, 280, 330

Easley, M.A., 228
Edlefson, N. E., 231
Edwards, R. S., 11, 12, 179
Egerton, A. C., 139, 204, 369
Egloff, G., 303
Einstein, A., 15, 23
Eisenschimmel, W., 331
Elenbaas, W., 225
Eley, D. D., 193, 350
Elliott, A., 27
Ellis, D., 227
Ellis, E. W., 181, 183

Ellis, O. C. de C., 372
Emeléus, H. J., 170, 213
Emeléus, K. G., 358
Emmett, P. H., 338
Engels, J., 29
Espe, W., 68, 372
Estermann, I., 52, 54
Eucken, A., 12, 14, 314, 328
Evering, B. L., 166

Fairbrother, F., 229
Fajans, E., 335, 350
Fajans, K., 256
Falckenstein, K. W. v., 29
Farkas, A., 24, 29, 155, 191, 192, 193, 217, 243, 280, 315, 317, 332, 336, 337, 338, 346, 349, 352
Farkas, L., 29, 92, 154, 193, 243, 280, 315, 326, 331, 337, 349, 352, 363
Fehr, R. B., 238
Feitknecht, W., 38, 63
Fenning, R. W., 29
Ferguson, J. B., 29
Fermi, E., 23
Féry, 368
Finch, G. I., 348, 349
Fink, C. G., 29
Fischer, Fr., 28
Foerst, J. P., 228
Folkers, K., 341
Foord, S. G., 86, 100, 293, 316
Forbes, G. S., 223, 228, 249, 254, 257
Förster, T., 296
Forsythe, W. E., 111, 222, 226, 228
Found, C. G., 87, 88, 89, 97
Francis, M., 76
Franck, J., 27, 31
Frankenburger, W., 304, 331, 348
Fraser, R. P., 364, 369
Frazer, R. G. P., 77, 78
Frey, F. E., 28
Friederici, K., 172, 206
Frisch, P., 268
Frost, A. A., 363
Frost, A. V., 28
Frost, A. W., 28
Frumkin, A., 342, 343
Fuchs, E., 131

Gádke, W., 343
Gaede, W., 43, 45, 46, 47, 48, 50, 76, 93, 94
Gajendragad, N. G., 28
Gans, D. M., 358
Gardner, J. B., 304
Garner, W. E., 87, 341, 363, 368
Garstang, W., 276
Gauger, A. W., 348
Gehrcke, E., 231
Geib, K. H., 277, 288, 296, 356, 372
Gerbes, O., 181, 183
Gerdien, H., 129, 270
Germann, A. F. O., 71, 72, 173
Germann, F. E. E., 176
Gero, L., 27
Ghosh, J. C., 28
Giauque, W. F., 164, 197, 203
Gibson, G. E., 209
Ginsburg, N., 165
Goetz, A., 372
Goldmann, F., 365
Goldwasser, S., 100
Goodeve, C. F., 212
Gordon, N. E., 256
Gorschkow, G., 365
Gouy, M., 143
Grant, G. H., 363
Gray, L. T. M., 210
Gray, R. W., 200
Gray, S. C., 125
Gregora, G., 335
Gregory, H. S., 14
Grew, K. E., 316
Griffin, C. W., 343
Griffith, R. A., 373
Griffith, R. O., 373
Griffiths, E., 368
Grignard, V., 173
Groot, de W., 225
Groth, W., 329, 331, 333
Gunther, P., 358
Gutmann, O., 170
Guye, P. A., 176

Haase, Th., 268
Haber, F., 29, 90, 272, 274, 289, 358, 363, 365, 368
Hadman, G., 362
Haffner, A. E., 281, 321
Hahn, D. A., 373
Halban, H., 209
Hale, C. F., 77
Halford, J. O., 160
Halford, L. C., 202, 203, 210
Hall, D. A., 368
Hall, W. K., 345, 349
Ham, W. R., 238
Hantzsch, A., 257
Harkins, W. D., 358
Harle, H., 12
Harries, C., 156
Harrington, E. L., 46

Harris, L., 257
Harrison, G. R., 228, 238
Harteck, P., 16, 95, 96, 157, 190, 214, 284, 288, 307, 329, 333, 356, 358, 363, 373
Hartel, H. v., 311, 312
Harvey, F. E., 368
Hassé, H. R., 11
Hedley, T. J., 179
Heidemann, E., 267
Heidt, L. J., 223, 249, 254, 257
Heitler, W., 27
Hemptinne, M. de, 169
Henglein, F. A., 202
Henning, F., 104, 106, 111, 204
Henri, V., 213
Hercus, E. O., 14
Hering, E., 84
Hershey, H. E., 368, 369
Hertel, E., 330
Hertz, G., 308
Herzeberg, G., 26, 27, 209, 211
Herzfeld, K. F., 2, 9, 26, 27, 371
Hesthal, C. E., 228, 238
Heuse, W., 84
Hickman, K. C. D., 52, 53
Hickson, K., 82
Hilferding, K., 244
Hill, A. V., 252
Hinshelwood, C. N., 6, 38, 276, 315, 319, 335, 352, 362, 372
Hirst, A. A., 179
Hitchcock, L. B., 173
Ho, H. L., 52
Hofeditz, W., 166
Hofer, A., 274
Hoffman, R. M., 224
Hollaender, A., 228
Holmes, H. H., 212
Holweck, M., 46
Hoover, G. I., 353
Hopfield, J. J., 64
Howard, H. C., 188
Hückel, E., 339
Huffman, H. M., 372
Huffman, J. R., 180
Hughes, A. L., 349
Hughes, D. R., 337
Hunter, E., 325
Hurd, C. H., 173
Hurst, W. W., 179
Huppke, W. F., 28
Hyde, E. P., 111

Ibbs, T. L., 179, 316
Ingold, C. K., 244
Ipatieff, V. N., 272, 306, 373
Ireton, H. J. C., 354
Iwanikow, P. J., 28

Jacquerod, A., 72
Jaeger, R., 259
Jatkar, S., 28
Jaycox, E. K., 89
Joffé, C. L., 257
Johnson, C. R., 173
Johnson, F. M. G., 202
Johnson, H. L., 197
Johnson, M. G., 85
Johnston, E. H., 324
Johnston, H. L., 164
Johnston, W. R., 166
Jones, E. J., 354
Jones, G. W., 368
Jones, R. V., 252
Jost, W., 210, 372
Jungers, J. C., 167, 203, 212, 290

Kab, G., 348
Kadow, W.,
Kalberer, W., 341, 351
Kaminsky, J., 257
Kassel, L. S., 31, 372
Katayama, M., 29
Kaye, G. W. C., 42, 49, 51, 56, 59, 88, 372
Kellermann, K., 238, 239, 335
Kerschbaum, F., 90
King, A. S., 127
King, E. B., 91
Kingman, F. E. T., 87, 340, 341
Kirkbride, F. W., 214
Kirkby, W. A., 372
Kirkpatrick, D. E., 27
Kistiakowsky, G. B., 173, 174, 211, 214, 236, 257, 269, 301, 304, 315, 327, 374
Klar, R., 339
Klemenc, A., 11, 12, 374
Klingelhoeffer, W. C., 158, 358
Klinkhardt, H., 304, 331
Kluge, I., 259
Klumb, H., 268
Knauer, F., 77
Knauss, H. P., 26
Knoke, S., 29
Knoll, M., 372
Knowles, H. B., 254
Knudsen, M., 20, 84, 89, 93, 96, 97, 98, 99, 349, 371
Kohler, L. R., 246
Kohlrausch, F., 371
Kokotschaschwili, V., 335
Kolthoff, I. M., 256

Kopp, D., 300, 363
Kopsch, U., 157, 307, 356
Kornfeld, G., 217
Korvezee, A. E., 29
Kowalsky, A., 300, 361, 362, 363, 365, 366
Kratz, H., 341
Kraus, C. A., 170
Krauss, A., 290
Kreutz, C. D., 364
Kroczek, I., 68
Kuenecke, E., 343
Kuhn, H., 27
Kulkarni, G., 28
Kummerow, H., 134
Kundt, A., 89
Kunsman, C. H., 355
Kurlbaum, 368
Kurt, O. E., 157
Kuss, E., 106, 162, 172, 201, 204

Laby, T. H., 14
Ladenburg, E., 85
Lake, F., 364
Landsberg, G., 211, 237
Langmuir, I., 47, 48, 89, 90, 123, 175, 336, 352
Laszlo, H. de, 69
Lau, E., 231
Lauer, W. M., 256
Lautsch, W., 166
Lavrov, F. A., 365
Lawrence, E. O., 231
Lazier, W. A., 340
Leatherman, M., 190
Lehmann, E., 85
Lehmann, H. L., 293
Lehrer, E., 201
Leifson, S., 209, 210, 211, 212
Leighton, P.A., 180, 249, 254, 223
Leipunsky, A. I., 354
Leiss, C., 228
Lenher, S., 304
Leob, L. B., 371
Le Rossignol, R., 272, 273, 274
Lewis, B., 38, 63, 364, 368
Lewis, G. N., 202, 205, 372
Libeau, P., 173
Lifshitz, F., 257, 373
Lind, S. C., 53, 86, 167, 211, 355
Linke, R., 12
Lipp, P., 211
Livingston, R., 86, 211, 355
Lochte-Holtgreven, W., 313
Locker, G. L., 258, 259, 260
London, F., 30
Long, E. A., 197
Loomis, F. W., 26
Loschmidt, J., 4, 16
Lowe, F., 289
Lucas, R., 29
Ludewigs, W., 11
Ludlam, E. B., 211, 334, 361, 363
Lunberg, W. O., 113
Lundell, G. E. F., 254
Lunt, R. W., 358
Luther, R., 371
Lyman, T., 373

Maass, O., 14, 173, 204
MacDonald, G. D., 180
MacDonald, R. T., 202
Machin, W., 263
Mackenzie, J. E., 16
Maddock, A. J., 218, 220, 234
Magnus, A., 339, 341
Mandelkar, M. R., 361
Marek, L. F., 373
Martin, E. v., 27
Martin, G., 173
Martin, H., 328
Marshall, A. L., 331
Marshall, S., 14
Masamichi, So, 87
Massenez, C., 172
Maxted, E. B., 271, 343, 350, 373
Maxwell, J. C., 5, 7, 20, 30
Mayrhofer, K., 348
McBain, J. W., 373
McIntosh, D., 85, 202, 204
McKeown, A., 373
McLane, S., 123
McLennan, J. C., 354
McMorris, J., 28
Mecke, R., 209
Meek, C. A., 358
Meer, N., 312, 313
Meinert, R. N., 173
Melville, H. W., 16, 48, 81, 84, 125, 169, 194, 197, 213, 215, 217, 237, 241, 243, 244, 280, 282, 332, 338, 361, 363
Melvin, E. H., 329
Meyer, H., 68
Mitchell, A. C. G., 2
Mitchell, J. S., 250
Mittasch, A., 343
Moelwyn-Hughes, E. A., 293, 362, 363, 372
Moles, E., 173
Moll, W. J. H., 250, 252
Molthan, W., 48
Mond, L., 348
Moon, C. H., 350
Mooney, R. B., 211

Morgan, G. T., 179
Morikawa, K., 291, 331
Morley, E. W., 149
Morozov, N. M., 339
Morris, S. D. D., 69
Morris, V. N., 343
Moser, E., 14
Moser, H., 147, 149, 161
Moser, L., 174, 374
Moss, E. B., 253
Motschan, I., 354
Muchlinski, H., 202
Müller-Skjold, F., 217
Mulliken, R. S., 27
Mündel, C. F., 84
Murison, C. A., 348

Nagasako, N., 269, 324
Narayana, T. S., 334
Nasini, A. G., 12
Nernst, W., 29
Neujmin, H., 328
Neumann, B., 28
Newbury, K., 84
Newitt, D. M., 174, 304, 320, 321, 322, 323, 367, 369, 372
Newman, F. H., 227
Newton, R. H., 29
Norris, J. F., 173
Norrish, R. G. W., 66, 129, 158, 292, 316
Noyes, W. A., 164, 214, 303, 329, 332, 334
Nusbaum, R. E., 26

Obermeyer, J. v., 16
Ootuka, H., 310
Oppenheimer, F., 329
Oppenheimer, O., 358
Orr, W. J. C., 138
Osswald, G., 257
Ostwald, W., 371
Outridge, L. E., 270, 367

Paal, C., 339
Palmer, F., 70
Palmer, W. G., 352
Paneth, F., 79, 166
Parker, A. E., 212
Parks, G. S., 372
Pastorff, H., 27
Patat, F., 328
Patkowski, J., 210
Payman, W., 369
Pearson, T. G., 84, 304
Pease, R. N., 28, 338, 339, 342
Pellaton, M., 202
Perrin, M. W., 354
Peters, K., 79, 358
Pfund, A. H., 74
Philippovich, A. v., 369
Phipps, T. E., 157
Pichler, H., 28
Picon, M., 173
Pike, E. W., 150
Pinkus, A., 68
Pirani, M. V., 18, 77
Pitzer, E. C., 256
Plaut, H., 28
Plotnikow, V. A., 39, 326, 373
Pohl, W., 29
Poindexter, F. E., 349
Polanyi, M., 308, 310, 312, 313, 350
Popov, B., 328
Porter, F., 53, 59
Predwoditeleff, A., 211
Prescott, C. H., 177
Preuner, G., 29
Prichard, C. R., 352
Purdum, R. B., 338

Rabinowitch, E., 209, 293, 294
Rae, W. N., 371
Rajewski, B., 259
Ramsay, W., 200, 348
Ramsperger, H. C., 62, 209
Rance, H. F., 281
Randall, M., 372
Rankine, A. O., 12
Rassweiler, G. M., 369
Rawlins, F. I. G., 373
Rayleigh, Lord, 83, 84, 100, 268, 289
Reave, L., 180
Reichel, S. v., 65
Reiff, H. J., 74
Reilly, J., 371
Reitz, O., 293
Remi, W., 11, 12
Reyerson, L. H., 343
Reynolds, N. B., 89
Reynolds, P. W., 268, 336, 347, 352
Ribaud, G., 209
Rice, F. O., 166, 372
Rice, O. K., 166, 372
Richardson, C. W., 343
Richter, H., 341
Rideal, E. K., 179, 250, 304, 336, 337, 338, 343, 348, 351, 352, 353, 354, 373
Riechemeier, O., 27, 285
Ritchie, D., 261, 374
Ritchie, M., 158, 168, 242, 292, 334
Ritter, G., 200
Roberts, B. J. P., 82
Roberts, J. K., 80, 99, 123

Robertson, I. K., 238
Robertson, I. W., 204
Rodebush, W. H., 93, 158, 358
Roeder, E., 307, 358
Roginsky, S., 348, 354
Rolfe, A. C., 363
Rollefson, G. K., 80
Rosen, B., 26
Rosenberg, G. v., 202
Rossi, C., 12
Rowley, H., 346
Roxburgh, H. L., 81, 125, 227
Rubens, W., 236
Rudberg, E., 256
Rudkowski, D. M., 28
Ruff, O., 173
Ruhoff, J. R., 173
Rummel, K. W., 352
Ryder, H. M., 83, 175, 176

Sabatier, P , 338, 373
Sachsse, H., 154, 287, 326, 331
Saggers, L., 64
Sagulin, A. V., 300, 362, 363
Salant, E. O , 27
Salley, D. J., 304, 331
Sand, H. J. S., 68
Sanford, C. R., 52, 53
Sarkey, M. D., 89
Sasse, E., 28
Sauter, E., 341
Schay, G., 310
Schechter, A., 354
Scheel, K., 84
Scheffer, F. E. C., 204
Schenk, P. W., 326, 330
Schiflett, C. H., 167
Schleiermacher, A., 14
Schmid, R., 27
Schmidt, H., 347
Schmidt, H. W., 16
Schmidt, J., 28
Schneider, E. G., 329
Schultz, P. W., 202, 205
Schultze, G. R., 277
Schumacher, H. J., 63, 173, 174, 267, 268, 326, 330, 331
Schumb, W. C., 358
Schupp, W., 29
Schuster, C., 351
Schwab, G. M., 36, 54, 347, 373
Schwamburger, E., 348
Schwarz, R., 341
Schwarz, H., 180
Scott, A. F., 173
Seaman, H., 368
Sebastian, J. J., 188
Seitz, F., 291
Semenoff, N., 41, 300, 361, 363
Semerano, G., 323
Senderens, J. B., 338
Senftleben, H., 27, 285
Senter, G., 72
Sharkowa, W. R., 28
Shepherd, M., 59
Sherman, A., 155, 342
Shields, J., 348
Shrader, J. E., 83
Shriner, R. L., 340
Sickman, D. V., 131, 340
Siebert, F. M., 173
Siedentopf, K., 209
Siegel, W., 29
Siemens, H. v., 203
Simard, R. G., 257
Simon, H., 89
Simon, L. J., 173
Skinner, H. W. B., 69
Skita, A., 339
Slack, C. M., 268
Smith, C. J., 12
Smith, G. F., 149
Smith, H. A., 173, 304, 327
Smith, W., 334
Soddy, F., 60, 190
Soller, T., 100
Somieski, C., 170, 205
Sonkin, S., 223, 238
Sosman, R. B., 111
Spence, L. U., 173
Sponer, H., 2, 3, 26, 27
Sprengel, 57
Sprenger, G., 173
Stande, H., 234, 235
Stanley, L. F., 77
Stark, J., 211
Starkweather, H. W., 339
Stauf, F. W., 12
Steacie, E. W. R., 277
Steele, B. D., 59
Steiger, G., 63, 174, 267, 326, 330
Stein, O., 210
Steiner, W., 9, 231, 244, 290, 306, 307, 308
Stern, O., 77
Stewart, J., 213
Stewart, L., 342
Stock, A., 59, 63, 104, 106, 162, 170, 172, 173, 200, 201, 204, 205, 206, 351
Stolzenberg, H., 173
Strassen, H. zur, 335
Strong, H. W., 322
Strother, C. O., 99, 341

Stuart, N., 348
Style, D. W. G., 210
Suhrmann, R., 12
Summerhays, W. P., 179
Sunde, C. J., 256
Sutherland, G. B. B. M., 373
Sutherlane, W., 10, 89
Sutton, T. C., 184
Swallow, J. C., 132
Swearingen, J. S., 181, 183
Swinehart, C. F., 173

Tammann, G., 350
Taylor, A. M., 373
Taylor, G. B., 339
Taylor, H. B., 173
Taylor, H. S., 99, 131, 155, 203, 212, 225, 227, 243, 277, 290, 291, 304, 331, 339, 340, 341, 342, 343, 348, 373
Taylor, J., 26
Taylor, J. B., 123, 158
Taylor, R., 179
Taylor, T. S., 200
Teller, E., 27
Terenin, A., 236
Terres, E., 28
Theodoroff, P., 354
Thiesen, M., 84
Thompson, H. W., 362, 364
Thomson, G. P., 348
Titani, T., 11, 12, 95
Titman, H., 369
Tizard, H. T., 29
Todd, G. W., 14
Tolman, R. C., 9
Töpler, 42, 46, 57, 59
Townend, D. T. A., 320, 321, 361, 367, 372
Trautz, M., 29
Travers, M. W., 72, 163, 206, 381
Trenner, N. R., 284
Treub, J. P., 204
Trifel, A. G., 28
Tropsch, H., 303
Tuck, J. L., 193, 229
Twyman, F., 373

Ubbelohde, A. R., 139, 369
Unger, W., 330
Urbain, E., 173
Urry, W. D., 268
Utterback, C. L., 84

Van Cleave, A. B., 14
Van Dusen, M. S., 122
Vaughan, W. E., 173, 303, 329, 332, 334
Vaughen, J. V., 340
Volmer, M., 133, 134, 269, 324
Voorhees, V., 340

Wachenheim, L., 29
Wagner, O. H., 358
Wallace, J., 129
Walls, H. J., 237
Walters, E., 239
Wansbrough-Jones, O. H., 65, 354
Waran, H. P., 48
Warburg, E., 89, 227
Wartenberg, H. v., 26, 277
Watson, S., 28
Watson, W. M., 212
Weaver, E. R., 59
Weber, S., 14
Weigert, F., 227, 234, 235, 238, 239, 335, 373
Weinhardt, H. W., 89
Welbergen, H. J., 274, 326
Wells, 227
Wenner, R. R., 212
Wenther, 238
Wentzel, W., 11, 12
Weston, F. R., 365
Wheeler, W. H., 369
Wicke, F. W., 306
Wiebe, R., 202
Wieland, K., 212
Wien, W., 238
Wiig, E. O., 236, 315, 327
Willard, J., 65
Willey, E. J. B., 293, 358, 359
Williamson, A. T., 59, 340, 341
Willstatter, R., 272, 338
Wilson, C. L., 244
Wilson, D. A., 256
Winch, G. T., 263
Winkelmann, A. A., 16
Winkler, L. W., 164
Winter, D. A., 365
Winter, E., 342
Wintergerst, E., 16
Wirtz, K., 193, 352
Withrow, L., 369
Wohl, K., 29
Wolf, L., 65
Wolgast, K., 297
Wood, R. W., 153, 215, 236, 276, 277, 349, 356, 357
Wood, W. C., 209, 294
Woodhead, D. W., 369
Worswick, B., 11
Worthing, A. G., 111

Wrede, E., 95, 154, 358
Wright, C. H., 173
Wwedenski, A. A., 28

Yost, D. M., 28

Zabel, R. M., 68
Zahn, C. T., 101
Zehden, W., 313
Zeigler, W., 328
Zeigler-Wellmann, M., 328
Zeise, H., 372
Zelinsky, N. D., 342
Zemansky, M., 2, 263

SUBJECT INDEX

Absorption spectra of gases, 209 ff.
Accommodation coefficient, thermal, 18
Acetylene, dideutero-, preparation of, 167
Acetylene, extinction coefficient of, 211
Acetylene, preparation of, 167
Actinometers, chemical, 254
Activation energy, 37
Activation energy, apparent, 37, 38
Activation, energy true, 37
Adsorption, heat of, 38
After-effect, photochemical, 238
Aldehydes, extinction coefficient of, 213
Alpha-rays, 355
Ammonia, extinction coefficient of, 211
Ammonia, preparation of, 162
Ammonia, trideutero-, absorption spectrum of, 212
Ammonia, trideutero-, preparation of, 162
Ammonia, vapour pressure of, 107, 108
Antimony trihydride, preparation of, 170
Apparatus, cleaning of, 142
Apparatus, set-up of, 141
Arrhenius' equation, 37
Arrhenius' equation, modified, 38
Arsenic trihydride, preparation of, 169
Arsine, absorption spectrum of, 213
Association, 29, 30, 31
Atoms, concentration measurement of, 290
Atoms, reactions of, 307
Avogadro's number, 4

Barlow formula, 270
Barretter resistance, 130
Bodenstein's greaseless glass valve, 62
Boron hydrides, preparation of, 170
Boron trifluoride, preparation of, 173
Bromine, extinction coefficient of, 209, 210
Budde effect, 334
n-Butane, preparation of, 173
Butene-1, preparation of, 173
Butene-2, preparation of, 173

Cadmium arc, 227
Capillary burettes, 180 ff.
Carbon dioxide, preparation of, 161
Carbon dioxide snow, 135
Carbon dioxide, vapour pressure of, 108, 109
Carbon disulphide, vapour pressure of, 106, 107
Carbon monoxide, preparation of, 161
Carbon suboxide, preparation of, 173
Carbonyl chloride, preparation of, 173
Catalysts, 335 ff.
Catalysts, composite, 343
Catalysts, metallic, 335
Catalysts, poisoning of, 348
Catalysts, sintering of, 349
Catalysts, supported, 342
Catalysts, testing of, 305
Chain reaction, 41
Chain reaction, length of, 41
Charcoal, 341
Chemical reaction, inertia of, 30
Chemical reaction, rate of, 29
Chemical reaction, velocity of, 29
Chemical reactions, types of, 29
Chlorine, atomic, preparation of, 158
Chlorine dioxide, preparation of, 174
Chlorine, extinction coefficient of, 209, 210
Chlorine monoxide, preparation of, 174
Chlorine, preparation of, 158
Chromium oxide catalyst, 340
Coefficient of diffusion, 14
Coefficient of extinction, 207
Coefficient of heat conductivity, 12
Coefficient of viscosity, 10
Collisions, 6
Collisions between molecules, 6
Collisions of the second kind, 31
Collisions, triple, 9
Collisions with surface, 8
Combustion, 368, 369
Copper catalyst, 338
Copper chromite catalyst, 341
Cut-off, all-glass, 65
Cut-off for high temperatures, 65
Cut-off, mercury, 62
Cyanogen, preparation of, 167

Density balance, *see* gas density balance
Detonation, 369

Deuterium bromide, extinction coefficient of, 210, 211
Deuterium bromide, preparation of, 160
Deuterium, estimation of, 193
Deuterium iodide, extinction coefficient of, 210, 211
Deuterium iodide, preparation of, 160
Deuterium, ortho-, estimation of, 190
Deuterium, ortho-, preparation of, 155
Deuterium, preparation of, 152
Diffusion, 14, 15, 16
Diffusion, coefficient of, 14
Diffusion of gases through glass, 268
Dilute flames, 308 ff.
Discharge, electric, 356 ff.
Distance, internuclear, 2, 3
Distribution of energy in polyatomic molecules, 38
Dissociation, 29
Draper effect, 334
Drying materials, 149

Effusion of gas through holes, 18
Einstein's displacement law, 15
Electrocell, 262
Electrons of controlled speed, 354
Energy, distribution of, 20 ff.
Energy of activation, 30, 37
Energy of dissociation, 26
Energy of vibrating rotator, 23
Energy, rotational, 22, 23, 25
Energy, vibrational, 22, 25
Equilibrium, chemical, 25 ff.
Equilibrium, chemical, constant of, 25, 27, 28
Ethane, preparation of, 165
Ethyl radicals, preparation of, 166
Ethylene, extinction coefficient of, 211
Ethylene, preparation of, 166
Ethylene, vapour pressure of, 108, 109
Exchange, atomic, 29
Exchange, molecular, 29
Experimental arrangement for catalytic reactions, 352, 353
Experimental arrangement for gas reactions, 141, 142
Experimental arrangement for photochemical reactions, 241 ff., 327 ff.
Experimental arrangement for reactions at high pressures, 320 ff.
Explosions at high pressures, 367
Explosion limits, 359
Explosion limits, determination of, 361 ff.
Explosive reactions, 40, 359
Explosive reactions, precautions for, 369
Extinction coefficient, 207
Extinction coefficients of glasses, 246

Filaments, arrangement of, 343, 344
Filaments, temperature control of, 346
Filaments, temperature distribution of, 123, 344 ff.
Filaments, temperature of, 125
Films of metals, 336, 348
Filters, 232 ff.
Filters, Christiansen, 234
Filters, Wratten, 234
Fittings for high pressure vessels, 272 ff.
Flames, 367, 369
Flames, dilute, 308 ff.
Flow meters, 102
Flow methods, 302 ff.
Flow methods, theoretical, 296
Flow, production of, 299
Formaldehyde, absorption spectrum of, 214
Furnace, carbon tube, 127
Furnace, molybdenum, 129
Furnace, resistance, 127, 128, 129, 178

Galvanometers, 251
Gas analysis, low pressure, 175 ff.
Gas analysis, micro-, 174
Gas analysis, micro-, by low temperature distillation, 187 ff.
Gas analysis with capillary burettes, 180 ff.
Gas density, 296
Gas density balance, 199
Gas holders, 146
Gas, inert, estimation of, 190
Gas mixtures, ternary, analysis of, 196 ff.
Gas reactions, heterogeneous, 33, 275
Gas reactions, homogeneous, 33, 275
Gases, measuring volume of, 148
Gases, mixing of, 316
Gases, preparation of, 145
Gases, storage of, 146, 148
Gauge, *see* manometer
Gauze screens, 237
Getters, 60
Glass, resistance to pressure of, 269
Glass windows, thin, 268, 269
Glasses, extinction coefficients of, 246
Glasses, properties of, 266 ff.
Glow discharge, 356, 357, 358
Greaseless glass valve, 62
Greases, low vapour pressure, 67
Greases, vapour pressure of, 67, 68

Heat conductivity, *see* thermal conductivity
Heat of adsorption, 38
High pressure explosions, 367
High pressure, production of, 320
Hydrazine, absorption spectrum of, 212

Hydrocyanic acid, preparation of, 168
Hydrogen, atomic, preparation of, 153
Hydrogen, atomic, reactions of, 307
Hydrogen bromide, extinction coefficient of, 210, 211
Hydrogen bromide, preparation of, 159
Hydrogen chloride, preparation of, 159
Hydrogen chloride, vapour pressure of, 108, 109
Hydrogen deuteride, estimation of, 193
Hydrogen iodide, extinction coefficient of, 210, 211
Hydrogen iodide, preparation of, 160
Hydrogen lamp, 230, 231, 232, 329
Hydrogen, liquid, handling of, 136
Hydrogen modifications, estimation of, 190 ff.
Hydrogen, para-, estimation of, 190
Hydrogen, para-, preparation of, 154
Hydrogen, preparation of, 151
Hydrogen selenide, preparation of, 174
Hydrogen sulphide, extinction coefficient of, 212
Hydrogen sulphide, preparation of, 168
Hydrogen telluride, preparation of, 174

Ignition, 364
Impulse discharge, 358
Induction period, 366
Inflammation, wall-less, 365
Intensity filters, 236
Interferometer, 289
Internuclear distance, 2, 3
Iodine, extinction coefficient of, 209, 210
Ions of controlled speed, 354
Iron catalyst, 339
Isobutane, preparation of, 173

Joints, copper-glass, 69
Joints, fluorite-glass, 70
Joints, invar-glass, 69
Joints, metal-glass, 324
Joints, metal-silica, 68, 69, 70
Joints, soda glass-Pyrex glass (Jena glass), 267

Katharometer, 178
Kinetics, chemical, 29
Knudsen effect, 20
Kromayer lamp, 227

Lamps, hydrogen, 230, 231, 232, 329
Lamps, mercury, 214 ff.
Lamps, mercury, capillary, 220, 223
Lamps, mercury, high pressure, 218
Lamps, mercury, high voltage, 215, 216
Lamps, mercury, hot cathode, 217, 221, 222, 223
Lamps, mercury, low pressure, 215
Lamps, sodium vapour, 229
Lamps, tungsten arc, 228
Lamps, tungsten filament, 228
Lamps, xenon, 329
Leak tester, 142
Liquid air, boiling point of, 206
Liquid air, constant level device for, 140
Liquid air traps, pumped out, 150
Loschmidt's number, 4
Lubricants, inorganic, 68

Magnesium flashlight, 335
Malachite green actinometer, 257
Manganous chromite catalyst, 341
Manganous oxide catalyst, 340
Manometer, absolute, for low pressures, 92
Manometer and source for hot vapours, 101, 102
Manometer, Bourdon, 85
Manometer, clicker, 87
Manometer, Foord, 86
Manometer, inverted cup, 84
Manometer, ionisation, 87 ff.
Manometer, McLeod, 73 ff.
Manometer, McLeod, calibration of, 74
Manometer, McLeod, reading of, 75
Manometer, mercury U-tube, for low pressures, 82 ff.
Manometer, mercury U-tube, for low pressures according to Pearson, 84
Manometer, ' neutral disc ' for high pressures, 322
Manometer, Pirani, 76 ff.
Manometer, Pirani, method of operation of, 79
Manometer, Pirani, micro-, 81
Manometer, quartz fibre, 89 ff.
Manometer, quartz spiral, 86
Manometer, Rayleigh, 83
Manometer, Rohn, 87
Manometer, sensitive, calibration of, 96, 97, 98
Manometer, slit, according to Wrede-Harteck, 95, 96
Manometer, U-tube mercury, 71, 72, 73, 81
Manometer, U-tube oil, 82
Manometer, viscosity, 89
Manometric methods, 279
Manostat, 99, 100, 101
Maxwell's law, 5
Mean free path, 6, 7
Melting points, 126

Mercury, cleaning of, 142
Mercury cut-offs, 62
Mercury lamps, *see* lamps, mercury
Mercury-sensitized reactions, 331
Metals, reflectivity of, 246
Methane, preparation of, 165
Methane, vapour pressure of, 109, 110
Methylacetylene, preparation of, 173
Methyl bromide, preparation of, 173
Methyl chloride, preparation of, 173
Methyl deuteride, preparation of, 165
Methyl fluoride, preparation of, 173
Methyl radicals, preparation of, 166
Molar volume, 4
Molecular radius, 2, 3
Molecular velocity, 4 ff.
Molecules, diameter of, 2, 3
Molecules, number of, 4
Molecules, shape of, 1, 3, 4
Moment of inertia, 22
Monochloracetic acid actinometer, 256
Monochromatic light by focal isolation, 236
Monochromatic light, filters for, 234
Monochromators, 249

Nickel catalyst, 338
Nitric oxide, absorption spectrum of, 212
Nitric oxide, preparation of, 163
Nitrogen dioxide, extinction coefficient of, 212
Nitrogen peroxide, preparation of, 164
Nitrogen, preparation of, 162
Nitrogen, vapour pressure of, 110, 111, 203
Nitrosyl chloride, preparation of, 173
Nitrous oxide, preparation of, 164
Nitryl chloride, preparation of, 173

Oils, low vapour pressure, 67
Order of reaction, 317
Oxygen, absorption spectrum of, 209
Oxygen, atomic, preparation of, 157
Oxygen, atomic, reactions of, 307
Oxygen, diffusion of, through silver, 158
Oxygen, preparation of, 156
Oxygen, vapour pressure of, 110, 111, 201
Ozone, extinction coefficient of, 209

Para-hydrogen, 154, 190, 317, 332
Palladium black, 338
Palladium, colloidal, 339
Partition function, 20 ff.
Partition function for a diatomic gas, 21, 22
Partition function for a monatomic gas, 21
Partition function for a polyatomic gas, 24
Perforated plates, 237
Phosphine, absorption spectrum of, 213
Phosphine, preparation of, 168
Phosphine, trideutero, preparation of, 169
Photochemical reactions, 39
Photochemical reactions, rate of, 39
Photo-electric cells, 260
Photo-electric photometer, 263
Photo-electric quantum counter, 258
Photo-electric relay, 251
Photo-element, 293, 294
Photometer, photo-electric, 263
Photometry, 292
Photronic cells, Weston, 261
Plane-parallel windows, 326
Platinizing solution, 324
Platinum black, 338
Platinum, colloidal, 339
Platinum oxide catalyst, 340
Poiseuille formula, 20
Poisoning of catalysts, 348
Polarimetry, 290
Pressure, adjustment of, 315
Pressure compensation, 325
Pressure, control of, 42, 99
Pressure gauges, *see* manometers
Pressure limits of explosion, 359
Pressure, measurement of, 71
Pressure reactions, 320 ff.
Pressure, units of, 71
Primary processes, photochemical, 33
Propane, preparation of, 173
Propylene, preparation of, 173
Pump, circulating, 46, 49, 53, 54, 56, 301
Pump, condensation, 47
Pump, diffusion, 47 ff.
Pump, diffusion, for oil and ester, 52, 53
Pump, diffusion, metal, 49 ff.
Pump, diffusion, orifice for, 47, 48
Pump, diffusion, speed of, 52
Pump, diffusion two-stage, 49
Pump, filter, 42
Pump, high vacuum, 46 ff.
Pump, molecular, 46
Pump, rotary mercury, 45
Pump, rotary oil, 43, 44, 45
Pump, water jet injector, 42
Pumps, rotary oil, precautions for, 45
Pumps, speed of, 42, 55, 56, 59
Pumps, vacuum, performance of, 54, 55
Prytz's cut-off, 63
Pyrometer, 104
Pyrometer, disappearing filament, 111
Pythagoras mass, 270

Quantum counter, photo-electric, 258
Quantum number, rotational, 22
Quantum number, vibrational, 22

Quantum yield, determination of, 257
Quartz fibre manometer, 89 ff.
Quartz, properties of, 267
Quartz spiral manometer, 86

Radiation, measurement of, 250
Radiation, sources of, 214
Rate of chemical reaction, *see* reaction, chemical, rate of
Reaction, chemical, dependence of, on concentration, 32
Reaction, chemical, dependence of, on temperature, 30
Reaction, chemical, half-life time of, 31
Reaction, chemical, initial rate of, 319
Reaction, chemical, order of, 32
Reaction, chemical, rate of, 31
Reaction, chemical, temperature coefficient of, 38
Reaction, gas, *see* gas reaction
Reaction of zero order, 37
Reaction order, 317 ff.
Reaction, progress of, with time, 278
Reaction, rapid, 366
Reaction rate, dependence of, on temperature, 37
Reaction rate, dependence on pressure of, 33 ff.
Reaction, sensitized by mercury, 331
Reaction, thermal, bimolecular, 34
Reaction, thermal, termolecular, 34
Reaction, thermal, unimolecular, 34
Reaction vessels, *see* vessels
Reactions at high pressures, 320 ff.
Reactions, bimolecular, 32
Reactions, catalytic, 31, 36
Reactions, explosive, 32, 40, 359
Reactions in adsorbed layer, 351
Reactions, monomolecular, 32, 34
Reactions, photochemical, 31
Reactions, sensitized, 31
Reactions, stationary, 32
Reactions, termolecular, 32
Reactions, thermal, 33
Reflections of light on reaction vessels, 247
Reflectivity of metals, 246
Refractory materials, 270
Resistance, electric, temperature coefficient of, 124
Resonance lines of mercury, cadmium and zinc, 225
Ring discharge, 358

Sectors, 238
Shaking devices, 350
Silane, absorption spectrum of, 213
Silica gel, 341
Silica, properties of, 266
Silicon hexafluoride, preparation of, 173
Silicon hydrides, preparation of, 170
Silicon tetrafluoride, preparation of, 173
Sinter-Korund, 270
Sintering of catalysts, 349
Slip, coefficient of, 17
Sodium arc lamp, 313
Sodium, electrolysis of—through glass, 149
Sodium vapour lamp, 229
Space-time-yield, 299
Sparks, condensed, 227, 228
Spectroscopy, infra-red, 291
Spectroscopy, ultra-violet, 290
Speed of chemical reaction, *see* reaction, chemical, rate of
Sprengel pump, 57
Square term, 38
Statistical weight, 21
Stibine, absorption spectrum of, 213
Stop watches, 313, 314
Streaming through tubes, 19
Sulphur dioxide, absorption spectrum of, 212
Sulphur dioxide, preparation of, 168
Sulphur dioxide, vapour pressure of, 106, 107
Summation of state, 21

Taps, *see* valves and cut-offs
Taps, glass, 61
Taps, sampling, 146, 316
Temperature, brightness, 112
Temperature distribution in a heated filament, 123, 344 ff.
Temperature limits of explosion, 359
Temperature of heated filaments, 125
Temperature, regulation of, 127
Temperature regulator, automatic, 132
Temperature, true, 112
Temperatures, high, liquid baths for, 133
Temperatures, low, production of, 135
Temperatures, standard, 115
Tensile strength, 271
Thermal conductivity, 12, 13, 14
Thermal conductivity at low pressures, 18
Thermal conductivity, coefficient of, 12
Thermal conductivity methods, 190 ff., 281 ff.
Thermal conductivity of metals, 124
Thermocouple, *see* thermometer, thermoelectric
Thermometer, gas, 103
Thermometer, pentane, 103
Thermometer, platinum resistance, 121

Thermometer, thermo-electric, 104, 113
Thermometer, thermo-electric, calibration of, 114
Thermometer, vapour pressure, 103, 104
Thermometer, vapour pressure, tables for, 106 ff.
Thermometers, thermo-electric, electromotoric force of, 115 ff.
Thermopiles, 251, 253, 292
Thermo-regulators, 130
Thermostats, 326
Thermostats for low temperature, 137, 138
Time, measurement of, 313
Time switches, 134
Tombac tubing, 62, 64, 66
Topler pump, 57, 58, 59
Traps for rotary oil pumps, 56, 57
Tungsten arc lamp, 228
Tungsten filament lamps, 228

Uranyl oxalate actinometer, 254

Vacuscope, 94
Valve, all-glass capillary, 64
Valve, glass, greaseless, of Bodenstein, 62
Valve, greaseless, of Ramsperger, 62, 63
Valve, micrometer needle, 63, 64
Valve, regulating, 64
Valve, silver, 63
Valves, controlling gas flow, 65
Vapour pressure of waxes, 68
Vapour pressure tables, 106 ff., 201 ff.
Velocity, molecular, 4, 5, 6
Velocity, molecular, average, 5
Velocity, molecular, mean square root, 5
Velocity, molecular, most probable, 5
Velocity of chemical reaction, *see* reaction, chemical, rate of
Vessel, 302
Vessel-light source combinations, 243, 305
Vessel-light source combination for short wave ultra-violet, 328
Vessel-McLeod gauge combination, 244
Vessels, cleaning of, 277
Vessels for high pressures, 270
Vessels for photochemical reactions, 241
Vessels, glass, 266
Vessels, metal, 270
Vessels, reflection of light on, 247
Vessels, silica, 266
Vibrations, 22, 24
Viscosity, 10, 11
Viscosity at low pressures, 16
Viscosity, coefficient of, 10

Wall reactions, 275
Wall-less inflammation, 365
Waxes, vapour pressure of, 68
Windows for ultra-violet light, 328
Windows, thin, of silica, 327
Wires for vacuum tubes, 70

Xenon lamp, 329

Zinc chromite catalyst, 341
Zinc oxide catalyst, 340
Zinc spark, 227

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