

Chemical calculations with explanatory notes, problems and answers : specially adapted for use in colleges and science schools / R. Lloyd Whiteley ; with a preface by F. Clowes.

Contributors

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CHEMICAL

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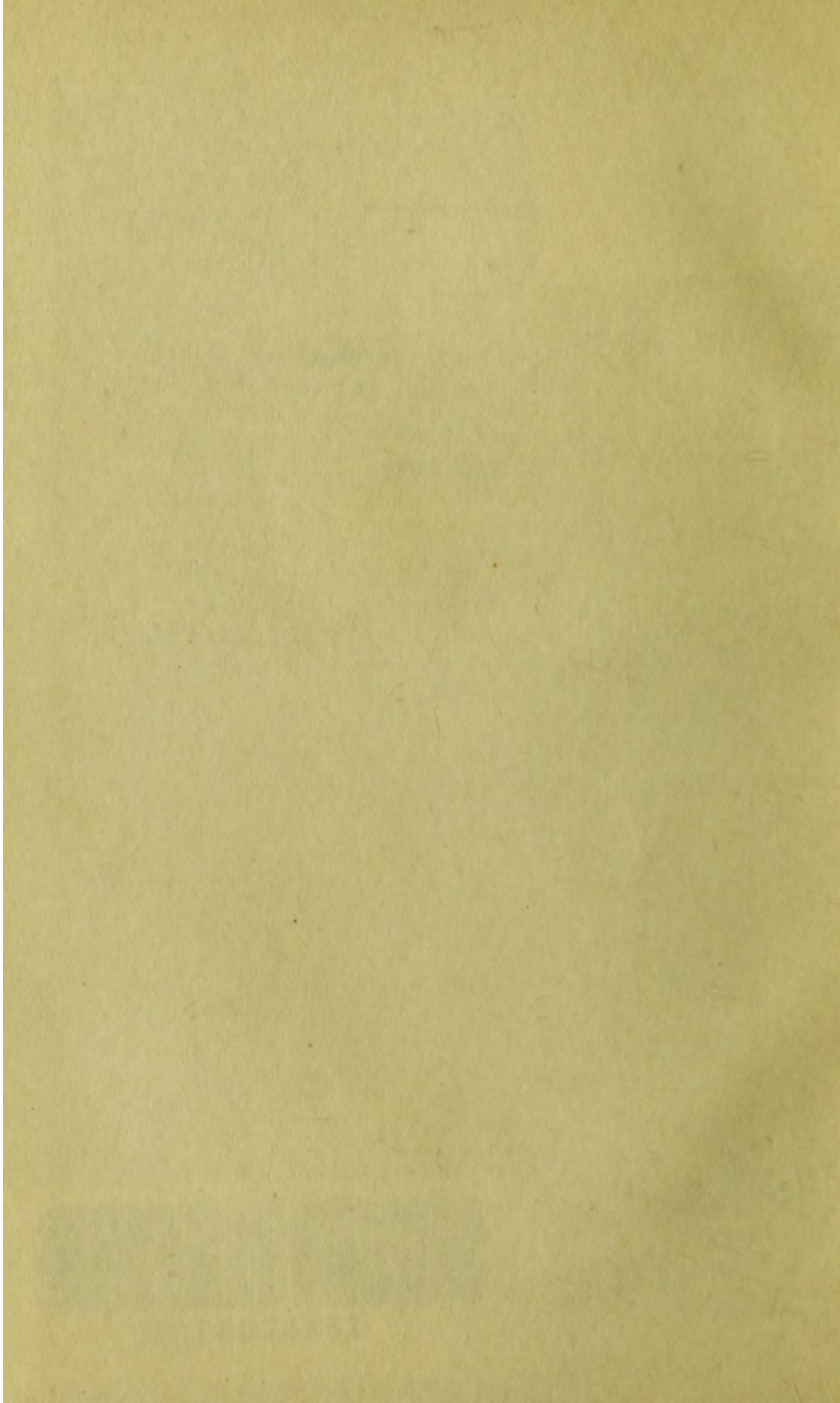
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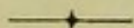
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P R E F A C E.

IN the division of chemical teaching into departments, which sooner or later becomes necessary in a growing College, the instruction of students in Chemical Calculations has for several years fallen to the lot of the author of this little treatise. Mr. WHITELEY has also, at the same time, been engaged in laboratory teaching, and in lecturing upon certain special branches of Chemistry. The text-book which he now issues accordingly bears manifest evidence, not only of his experience as a teacher, but also of his being well in touch with the calculations which are required by chemical students for various purposes, and with the chemical knowledge which elementary students may be assumed to possess. As a matter of fact, however, the author has wisely decided to give a short summary of chemical facts or processes before proceeding to explain the methods of calculation which are applied to them. Laboratory students will find a most useful and convenient explanation of the methods of calculating the results of specific gravity determinations, of analyses whether gravimetric, volumetric or gasometric, and of atomic and molecular weight determinations; they will find these also brought up to date as regards the methods to which they refer.

The book is not written for the use of candidates preparing for any special examinations. It is intended to form a part of the course of teaching or study suitable to the chemical student who wishes to equip himself for the various duties which any well-trained chemist may be called upon to perform. But it is safe to predict that it will be found to meet the requirements of candidates for the various University, Professional, and Government examinations which now serve as tests of chemical knowledge.

In wishing the little book the useful and extended career which it appears to me to merit, I am only giving expression to the hopes of many of the author's chemical friends and colleagues.

FRANK CLOWES.

AUTHOR'S PREFACE.

THIS little book has been written to supply the need of a work on Chemical Calculations that not only gives a fair selection of problems, but also a concise and yet explicit account of the methods of solving them.

The problems given are taken (i.) from those set by various examining bodies, including the Science and Art Department (S. & A. D.), and if their sources are not otherwise indicated they are denoted by an asterisk ; (ii.) from original memoirs and private sources.

In preparing this book special use has been made, amongst other chemical works, of Muir's 'Principles of Chemistry,' Ostwald's 'Outlines of General Chemistry,' Bunsen's 'Gasometry,' and the 'Journal of the Chemical Society.'

My heartiest thanks are here tendered to Mr. J. BERNARD COLEMAN for many valuable suggestions, and also, along with him, to Mr. A. E. BRISCOE and Mr. S. S. WHITELEY for assistance in reading the proofs and checking the answers to the problems given.

R. L. W.

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ATOMIC WEIGHTS.

THE atomic weights given in the first column are, with a few exceptions which are indicated by references, those given by Ostwald in his 'Outlines of General Chemistry.' The second column gives approximate numbers which for the purpose of simplicity have been used for the questions in this book, except where different numbers are given in the text.

Name	Symbol	Atomic Weight	Approximate Atomic Weight
Aluminium	Al	27.08	27
Antimony	Sb	120.3	120
Arsenic	As	75	75
Barium	Ba	137	137
Beryllium	Be	9.05 ¹	9
Bismuth	Bi	208.92 ²	209
Boron	B	11.01	11
Bromine	Br	79.96	80
Cadmium	Cd	111.8 ³	112
Cæsium	Cs	132.9	133
Calcium	Ca	40	40
Carbon	C	12	12
Cerium	Ce	140.2	140
Chlorine	Cl	35.45	35.5
Chromium	Cr	52.2	52
Cobalt	Co	59 [?]	59
Copper	Cu	63.3	63
Didymium	Di	142.5	142
Erbium	Er	166	166
Fluorine	F	19	19
Gallium	Ga	69.9	70
Germanium	Ge	72.3	72
Gold	Au	197.2	197
Hydrogen	H	1.003	1
Indium	In	113.7	114
Iodine	I	126.86	127
Iridium	Ir	193.2	193
Iron	Fe	56	56
Lanthanum	La	138.22 ⁴	138
Lead	Pb	206.91	207
Lithium	Li	7.03	7

¹ Krüss and Moraht.
² Partridge.

³ Classen.
⁴ Cleve.

Name	Symbol	Atomic Weight	Approximate Atomic Weight
Magnesium	Mg	24.33 ⁵	24
Manganese	Mn	55.05 ⁶	55
Mercury	Hg	200.4	200
Molybdenum	Mo	95.9	96
Nickel	Ni	59 ⁷	59
Niobium	Nb	94.2	94
Nitrogen	N	14.04	14
Osmium	Os	190.77 ⁷	191
Oxygen	O	16	16
Palladium	Pd	106.61 ⁸	107
Phosphorus	P	31.03	31
Platinum	Pt	195.5 ⁹	195
Potassium	K	39.14	39
Rhodium	Rh	103	103
Rubidium	Rb	85.4	85
Ruthenium	Ru	101.7	102
Samarium	Sm	150	150
Scandium	Sc	44.1	44
Selenium	Se	79.1	79
Silicon	Si	28.04	28
Silver	Ag	107.938	108
Sodium	Na	23.06	23
Strontium	Sr	87.5	87
Sulphur	S	32.06	32
Tantalum	Ta	183	183
Tellurion	Te	125	125
Terbium	Tr	159.48 ¹⁰	159
Thallium	Tl	204.1	204
Thorium	Th	232.4	232
Tin	Sn	119.1 ¹¹	119
Titanium	Ti	48.1	48
Tungsten	W	184	184
Uranium	U	239.4	240
Vanadium	V	51.2	51
Ytterbium	Yb	173.2	173
Yttrium	Y	89.02 ¹²	89
Zinc	Zn	65.5	65
Zirconium	Zr	90.7	91

⁵ Marignac, and Burton and Vorce (mean number).

⁶ Marignac, and Dewar and Scott (mean number).

⁷ Seubert.

⁸ Keiser.

⁹ Dittmar and Macarthur.

¹⁰ Boisbaudran.

¹¹ Bongartz and Classen.

¹² Cleve.

MISCELLANEOUS DATA.

1 millimetre	=	0.03937 inch
1 metre	=	39.3708 inches
1 „	=	3.2809 feet
1 „	=	1.0936 yards
1 kilom.	=	0.6214 mile
1 inch	=	2.5399 cm.
1 foot	=	3.0479 decm.
1 yard	=	0.9144 m.
1 mile	=	1.6093 kilom.

1 sq. centimetre	=	0.1551 sq. ft.
1 „ metre	=	10.7643 sq. ft.
1 „ „	=	1.196 sq. yds.
1 „ kilom.	=	0.3861 sq. mile
1 „ inch	=	6.4514 sq. cm.
1 „ foot	=	929 sq. cm.
1 „ yard	=	0.8361 sq. m.
1 „ mile	=	2.59 sq. kilom.

1 cub. centimetre	=	0.061027 cub. in.
1 „ decimetre	} =	61.027 cub. in
or 1 litre (l.)		
1 „ „	=	0.03532 cub. ft.
1 „ „	=	1.7608 pints
1 „ „	=	0.2201 gal.
1 „ metre	=	1.308 cub. yds.
1 „ inch	=	16.3862 c.c.
1 „ foot	=	28.315 ls.
1 „ „	=	6.314 gals. (6 $\frac{1}{4}$).
1 „ yard	=	0.7645 cb. m.
1 pint	=	567.93 c.c.
1 gallon	=	4.54346 ls.
1 „	=	277.274 cub. in.
1 „	=	0.16046 cub. ft.

gram	=	15.4323 grains
1 kilo.	=	2.2046 lbs.
1000 „ (1 tonne)	=	0.9842 ton
1 grain	=	0.0648 gm.
1 ounce (avoir.)	=	28.35 gms.
1 „ (troy)	=	31.1035 gms.
1 pound	=	453.593 gms
1 hundredweight (cwt.)	=	50.8024 kilos.
1 ton	=	1016.048 kilos.

1 cub. ft. of water at 39° F. weighs 62.425 lbs. = 998.8 ozs. (1,000)
 1 gallon „ „ 62° F. „ 10 lbs. = 70,000 grains.

d = diameter. r = radius.

Circumference of a circle ($d = 1$) = $\pi = 3.1416 = \frac{22}{7}$.

Area of a circle = $\pi r^2 = \frac{\pi}{4} d^2 = 0.7854 d^2$.

Area of a sphere = $4\pi r^2 = \pi d^2$.

Capacity of a sphere = $\frac{4}{3} \pi r^3 = 4.1888 r^3 = \frac{\pi}{6} d^3 = 0.5236 d^3$.

Capacity of a cylinder = area of base \times height.

To convert Twaddell hydrometer readings (R) into specific gravity (S)—

$$S = \frac{\frac{R}{2} + 100}{100}$$

To convert sp. gr. into Twaddell readings—

$$R = 200(S - 1).$$

Normal temperature and pressure = 0° C. and 760 mm.

1000 c.c. normal hydrogen weighs 0.0896 gm. (Crith.)

1000 c.c. „ air „ 1.293 gms.

1 c.c. mercury „ 13.596 gms.

1 gm. normal hydrogen occupies 11.16 ls.

1 gm. „ air „ 773 c.c.

Specific gravity of air (H = 1) = 14.44

Specific gravity of hydrogen
(air = 1) = 0.06926

Percentage composition of dry air (CO₂ free).

—	By Weight	By Volume	
		Approximate	Real
Nitrogen . . .	77	79	79.04
Oxygen . . .	23	21	20.96
	100	100	100.00

CHEMICAL CALCULATIONS.



CHAPTER I.

METRIC SYSTEM.

BEFORE the various calculations required in Chemistry can be profitably studied, a knowledge of the metric or decimal system of weights and measures, as given below, must be acquired.

STANDARDS OF LENGTH, VOLUME, AND MASS.

The metre is the standard of length in this system, and is the length, at 0° C., of a platinum bar which is deposited in Paris: the longer and shorter measures are multiples and sub-multiples of it by 10. The larger measures are denoted by Greek and the smaller by Latin prefixes, thus:—

1,000 metres	=	1 kilometre
100 „	=	1 hectometre
10 „	=	1 decametre
1 metre		
1 „	=	10 decimetres
1 „	=	100 centimetres
1 „	=	1,000 millimetres.

The measures of area and volume are derived from these by squaring and cubing them respectively; and it

should be noticed and carefully remembered that, while the measures of length increase or decrease by powers of ten, those of area and volume vary by powers of a hundred and

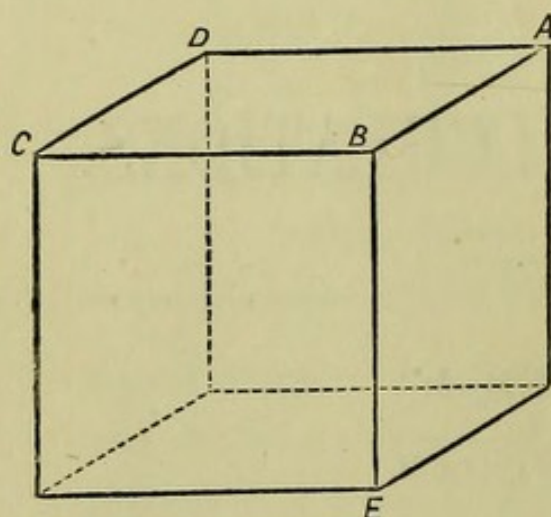


FIG. 1.

a thousand respectively. The reason of this will be readily understood by reference to the accompanying figure.

Suppose each edge of the cube to be 1 metre = 10 decimetres = 100 centimetres in length.

Then the area ABCD = $AB \times BC$, or = $10 \times 10 = 100$ square decimetres, or $100 \times 100 = 10,000$ square centimetres.

The volume of the cube = $AB \times BC \times BE$, or = $10 \times 10 \times 10 = 1,000$ cubic decimetres, or $100 \times 100 \times 100 = 1,000,000$ cubic centimetres.

Thus :—

1 metre	=	10 decimetres	=	100 centimetres	=	1,000 millimetres.
1 sq. "	=	100 sq. "	=	10,000 sq. "	=	1,000,000 sq. "
1 cub. "	=	1,000 cub. "	=	1,000,000 cub. "	=	1,000,000,000 cub. "

The standard of volume is the cubic decimetre or litre.

The standard of mass is the kilogram, which is the mass of a block of platinum deposited in Paris. This was originally designed to be the same mass as a cubic decimetre of water at 4° C., but is slightly less; 1 cubic decimetre of water at 4° C. actually = 1.000013 kilos.

For most scientific purposes it is usual to use the cubic centimetre as the unit of volume, and the gram as the unit of mass; and, except for very exact calculations, the mass of 1 cubic centimetre of water at 4° C. can be taken as 1 gram.

MEASURES OF LENGTH.

1 metre (m.)	=	10 decimetres (dcm.)
1 „	=	100 centimetres (cm.)
1 „	=	1,000 millimetres (mm.)
10 metres	=	1 decametre
100 „	=	1 hectometre
1,000 „	=	1 kilometre (km.)

MEASURES OF AREA.

1 square metre (sq. m.), or centiare	}	=	100 square decimetres (sq. dcm.)
„ „ „			= 10,000 „ centimetres (sq. cm.)
„ „ „		=	1,000,000 „ millimetres (sq. mm.)
100 square metres		=	1 are
10,000 „ „		=	1 hectare.

MEASURES OF VOLUME.

1 cubic metre (cb. m.), or stere	=	1,000 cubic decimetres (cb. dcm.)
1 „ „ „	=	1,000,000 „ centimetres (c.c.)
1 „ „ „	=	1,000,000,000 „ millimetres (cb. mm.)
1 cb. dcm. = 1,000 c.c. = 1 litre (l.)		

MEASURES OF MASS.

1 gram (gm.)	=	10 decigrams (dgm.)
1 „	=	100 centigrams (cgm.)
1 „	=	1,000 milligrams (mgm.)
1,000 grams	=	1 kilogram (kilo.)
1,000 kilograms	=	1 tonne.

Example 1.—How many kilometres, decimetres, and millimetres are there in 1,150 metres?

Referring to the table above, we find 1,000 metres = 1 kilometre \therefore 1,150 metres = 1.150 kilometres.

Again there are 10 decimetres in 1 metre \therefore $1,150 \times 10 = 11,500$ decimetres.

Also there are 1,000 millimetres in 1 metre \therefore $1,150 \times 1,000 = 1,150,000$ millimetres.

Example 2.—A cylinder 4 centimetres in diameter and 10 centimetres high is filled with distilled water. What is (i.) the capacity of the cylinder; (ii.) the weight in grams of the water contained in it? ¹

(i.) The capacity of a cylinder = area of base \times height.

Area of base = $\pi r^2 = 3.14 \times 2 \times 2 = 12.56$ square centimetres.

$12.56 \times \text{height} = 12.56 \times 10 = 125.6$ cubic centimetres.

(ii.) The weight of 1 cubic centimetre of water is approximately 1 gram, and therefore the weight of the water contained = $125.6 \times 1 = 125.6$ grams.

Example 3.—What is the weight in grains of 100 grams?

This weight may be found either (i.) by multiplying 100 by 15.4323, or (ii.) by dividing 100 by 0.0648, and equals 1543.23 grains.

QUESTIONS.

1. How many millimetres are there in 1.575 metres? How many in 0.5 metre? How many in 0.005 metre?

2. How many metres are there in 100,056 decimetres? How many metres in 1.5 decimetres? How many in 50 decimetres?

3. What is the area in square centimetres of a board 1.5 metres long by 0.25 metre wide?

4. A box is 0.5 metre high, 25 decimetres long, and 1.2 metres broad. What is its volume in cubic centimetres?

5. How many square centimetres are there in 105 square metres and 95 square decimetres respectively?

6. How many square metres in 105 square decimetres, in 196,578 square centimetres, and 2,753,002 square millimetres respectively?

7. How many square millimetres are there in 0.75 square metre, 0.06 square decimetre, and 1,005 square centimetres?

8. Express 6 inches, 1.25 feet, and 2.6 yards, both in metres and in millimetres.

¹ For data not given in this chapter see the list at the commencement of the book.

9. The top of a bench is 5 feet long and 1.75 feet wide. How many square decimetres is it in area?
 10. How many grams are there respectively in 2,000 decigrams and in 1,800 centigrams?
 11. How many centigrams are there in 21 grams, 1,900 milligrams, and 1,565 decigrams respectively?
 12. How many cubic centimetres are there in 100 litres, 0.5 litre, 15 cubic decimetres, and 0.5 cubic metre respectively?
 13. What are the respective areas of filter papers whose diameters are 5, 7.5, and 21 centimetres?
 14. How many grams of water will a cylinder 9 decimetres high and 5 centimetres in diameter hold?
 15. How many pints are there in 2.5 litres?
 16. How many litres are there in 2 gallons?
 17. Express 10 grams per litre in ounces per gallon.
 18. What is the strength, in grams per litre, of a solution of tannic acid 2 ounces per gallon?
 19. How many grams are there in 150 grains?
 20. In 10 pounds avoirdupois how many grams and kilograms are there respectively?
 21. How many ounces are there in 3.5 kilograms?
 22. How many gallons of water will be contained by a rectangular tank 5 feet long, 4 feet wide, and 2 feet deep?
 23. A rectangular tank with a semi-cylindrical bottom is 8 feet long, 4 feet wide, and 4 feet deep at the deepest point. What is the volume of the tank (i.) in gallons and (ii.) in litres?
 24. What is the weight in kilograms of 1.8 cubic feet of water?
 25. What is the volume in gallons of a cubic metre?
 26. If a cylinder holds 141.3 grams of water, and its height is 20 centimetres, what is its diameter?
-

CHAPTER II.

CONVERSION OF THERMOMETRIC SCALES.

THERE are three thermometers in more or less common use, viz. :—

The Celsius or Centigrade (C.), the Réaumur (R.), and the Fahrenheit (F.): of these the first is universally used for scientific purposes.

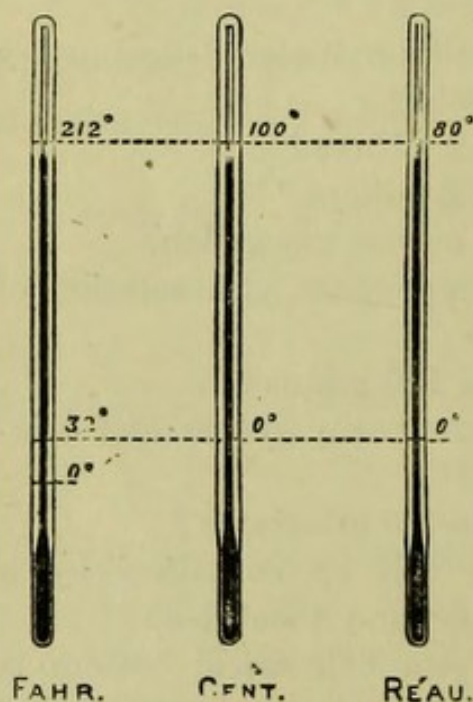


FIG. 2.

They possess two fixed points, viz. (i.) that which represents the temperature of melting ice, and (ii.) that which indicates the temperature of boiling water at 760 mm. pressure. On the Centigrade and Réaumur thermometers the zero is identical with the temperature of melting ice, but on the Fahrenheit scale it is 32° F.

below that temperature. The boiling-point of water is denoted on the Centigrade thermometer by 100° C., on the Réaumur by 80° R., and on the Fahrenheit by 212° F. Consequently

$$100^{\circ} \text{ C.} = 80^{\circ} \text{ R.} = 180^{\circ} \text{ F.}; \text{ also } \frac{\text{C.}}{100} = \frac{\text{R.}}{80} = \frac{\text{F.} - 32}{212 - 32}$$

From these facts are deduced the following rules for the conversion of the degrees of one scale into those of either of the others.

To convert—

Centigrade into Réaumur $\text{R.}^{\circ} = \frac{4}{5} \text{ C.}^{\circ}$

Centigrade into Fahrenheit $\text{F.}^{\circ} = \frac{9}{5} \text{ C.}^{\circ} + 32.$

Réaumur into Centigrade	$C.^{\circ} = \frac{5}{4} R.^{\circ}$
Réaumur into Fahrenheit	$F.^{\circ} = \frac{9}{4} R.^{\circ} + 32.$
Fahrenheit into Centigrade	$C.^{\circ} = \frac{5}{9} (F.^{\circ} - 32).$
Fahrenheit into Réaumur	$R.^{\circ} = \frac{4}{9} (F.^{\circ} - 32).$

Example 1.—Express $25^{\circ} C.$ in degrees Réaumur.

By the rule given, $\frac{4}{5}$ of $25 = 20^{\circ} R.$

Example 2.—Express $-12^{\circ} R.$ in degrees Fahrenheit.

By the rule given, $\frac{9}{4} \times -12 + 32 = \frac{-108}{4} + 32$
 $= -27 + 32 = 5^{\circ} F.$

Example 3.—Express $55^{\circ} F.$ in degrees Centigrade.

By the rule given, $\frac{5}{9} (55 - 32) = \frac{5}{9} \times 23 = \frac{115}{9} = 12.77^{\circ} C.$

Example 4.—Express $9^{\circ} F.$ in degrees Centigrade.

By the rule given, $\frac{5}{9} (9 - 32) = \frac{5}{9} \times -23 = \frac{-115}{9}$
 $= -12.77^{\circ} C.$

QUESTIONS.

1. Express the following temperatures in degrees Réaumur:—

$270^{\circ} C.$ $-5^{\circ} C.$ $19.5^{\circ} C.$ $200^{\circ} F.$
 $19^{\circ} F.$ $0^{\circ} F.$ $-19^{\circ} F.$

2. Express the following temperatures in degrees Fahrenheit:—

$15^{\circ} C.$ $-10^{\circ} C.$ $-45^{\circ} C.$
 $220^{\circ} R.$ $-20^{\circ} R.$ $-5.6^{\circ} R.$

3. Express the following temperatures in degrees Centigrade:—

$-4^{\circ} F.$ $31^{\circ} F.$ $0^{\circ} F.$ $291^{\circ} F.$
 $-20^{\circ} R.$ $7.6^{\circ} R.$ $192^{\circ} R.$

CHAPTER III.

DENSITY AND SPECIFIC GRAVITY.

It is necessary to discriminate carefully between the terms 'mass' and 'weight.' The mass of a body is the amount of matter in it, and is an invariable quantity; but the force with which it is attracted by the earth—i.e. its weight—is variable, and differs according to the place where it is estimated.

Bearing in mind the above-mentioned facts, the **absolute density** of a substance may be defined as the number of units of mass contained in unit volume.

The mass of a body is directly proportional to both its density and volume, or $M = DV$, where $M =$ mass, $D =$ density, and $V =$ the volume.

In the metric system the **unit volume** for solids and liquids is the cubic centimetre, and the **unit of mass** is the gram.

Relative density, or specific gravity (sp. gr.), is the ratio between the masses of equal volumes of two substances, one of which is the standard. Since we compare masses by weighing them, it practically comes to the same thing if we describe it as the ratio between the weights of the two substances.

For solids and liquids pure distilled water at the temperature of 4° C. is taken as standard; but this temperature is not always adhered to, because it is often convenient to use one more easily obtainable, namely, 15.5° C.

In consequence of the units used in the metric system, the same number represents both the density and the specific gravity of a substance; if, however, the English units for volume and mass, the cubic foot and pound, are used, the

numbers representing the density and specific gravity are different. Thus the density of water is, approximately, 62.5, if the English units are used, because 1 cubic foot of water contains that number of pounds. The specific gravity of water is, however, 1, as in the metric system.

There are several methods of determining the specific gravity of a substance, the processes varying according to the physical and chemical properties of the material in question. For exact details of the methods employed, works on physics must be consulted ; but the principles of them will now be indicated.

SPECIFIC GRAVITY OF SOLIDS.

1. If a solid is insoluble in water two data are necessary : (i.) the weight of the solid in air ; (ii.) the loss of weight occasioned by weighing it in water, which is equal to the weight of the water displaced. Then, if W is the weight of the solid in air, and W' the weight in water, the specific gravity $S = \frac{W}{W - W'}$.

2. If soluble in water the solid may be weighed in some liquid of known specific gravity, s , in which it is insoluble ; and if W is the weight of the solid in air, W'' the weight in the liquid used, then $S = \frac{W}{W - W''} \times s$.

3. If the solid will not sink in the liquid employed it is customary to attach to it a sinker—i.e. a piece of some heavy material which is sufficient to sink it beneath the surface of the liquid. Let W = the weight of the solid in air, w = the weight of the sinker in the liquid, w' = the weight of the sinker + the solid in the liquid ; then, if water is the liquid employed,

$$S = \frac{W}{W + w - w'}$$

if any other liquid is used, of specific gravity, s ,

$$S = \frac{W}{W + w - w'} \times s.$$

SPECIFIC GRAVITY OF LIQUIDS.

4. The specific gravity of a liquid is usually obtained either by means of a specific-gravity bottle, or, what comes to the same thing, by using a Sprengel-tube. In either case there are three weights required : (i.) the weight of the vessel used = w ; (ii.) the weight of the vessel full of water at 15.5° C. = W' ; and (iii.) the weight of the vessel full of the liquid in question = W also at 15.5° C. Then

$$S = \frac{W - w}{W' - w}.$$

5. The specific gravity of a liquid may also be taken by weighing a suitable plummet both in the liquid and in water ; and if the weight of the plummet in air = w , in water = w_1 , and in the liquid = w_2 , then

$$S = \frac{w - w_2}{w - w_1}.$$

6. The specific gravity of a mixture of two liquids whose volumes and specific gravities are known, may be calculated, provided no alteration of volume occurs, from the following formula :—

$$S = \frac{r_1 d_1 + r_2 d_2}{r_1 + r_2},$$

where r_1 and r_2 are the volumes of the two liquids, and d_1 and d_2 are their specific gravities.

From the formula just given may also be deduced the following one :—

$$r_2 = r_1 \left(\frac{d_1 - s}{s - d_2} \right).$$

By means of this formula the amount, r_2 , of a diluent of specific gravity d_2 , necessary to dilute a known quantity, r_1 , of another liquid of specific gravity d_1 , so as to produce a liquid of specific gravity s , can be calculated.

Example 1.—A block of graphite, density 2.2, is 5 cm. high, 8 cm. long, and 2 cm. broad. Find its mass.

By definition mass is proportional to both density and volume, $M = DV$.

$\therefore M = 2.2 \times (5 \times 8 \times 2) \text{ c.c.} = 2.2 \times 80 = 176$, or the mass of the graphite is 176 grams.

Example 2.—A specific-gravity bottle contained, when full, 30.6372 grams of dilute sulphuric acid, and when full of distilled water 22.9774 grams. Calculate the specific gravity of the acid.

Since specific gravity is the ratio between the weights of the sulphuric acid (W) and the water (W') we have, according to definition—

$$S = \frac{W}{W'} = \frac{30.6372}{22.9774} = 1.333.$$

DENSITY AND SPECIFIC GRAVITY OF GASES.

The terms **density** and **specific gravity** are so often incorrectly used as synonymous that it is difficult, when speaking about the absolute density and specific gravity of gases, to give accurate definitions and yet avoid being misunderstood. It must therefore be remembered that the definitions of density and specific gravity already given (page 8) are general in their application, and thus apply to gases as well as solids and liquids: but, while the gram is retained as unit of mass, for purposes of calculation 11.16 ls. is used as unit of volume for gases. The following facts account for this change of unit: (i.) The cubic centimetre is much too small to serve as unit volume for gases. (ii.) By the use of either the cubic centimetre, or

the litre, which is sufficiently large for use, the density would be expressed in fractional parts of a gram.

Such fractions would be inconvenient, and Hofmann therefore proposed to make the weight of 1 litre of hydrogen, measured at 0° C. and 760 mm. pressure, the unit of mass under the name of the **crith** (0.0896 gm.), and so express the density of gases in criths ; but the fact that the term belongs to no recognised system of measures was sufficient to prevent its adoption. On the other hand, although the volume adopted, 11.16 ls., is fractional, it is constant ; and the densities obtained by its use are practically whole numbers. The **absolute density of a gas** may therefore be defined as the mass of 11.16 litres of it at 0° C. and 760 mm. pressure. For the sake of clearness of expression, the term **specific gravity of a gas** will be used in this work when the specific gravity is referred to air ; and the term **vapour density** will denote its specific gravity referred to hydrogen.

In 1811 Avogadro enunciated the hypothesis that 'equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules.'

This hypothesis has since received ample support from dynamical reasoning, and Clerk Maxwell says :—' If equal volumes of two gases are at equal temperatures and pressures, the number of molecules in each is the same, and therefore the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong.'

Now, 22.32 litres of hydrogen, measured at 0° C. and 760 mm. pressure, weigh 2 grams ; but 2 grams is the molecular weight of hydrogen expressed in terms of the gram ; so this number is termed the gram-molecule of hydrogen. Bearing in mind Avogadro's law, it is therefore evident that, if we ascertain the weight of 22.32 litres of

any other gas, under the same conditions of temperature and pressure, we actually obtain the gram-molecule of the gas.

Thus :—

22.32	litres of hydrogen	. weigh	2	grams
22.32	„ „ oxygen	„	32	„
22.32	„ „ nitrogen	„	28	„
22.32	„ „ marsh gas	„	16	„
22.32	„ „ carbon dioxide	„	44	„

when these gases are measured at normal temperature and pressure.

Taking hydrogen as unity—

The vapour density of oxygen . becomes $\frac{32}{2} = 16$.

„ „ „ „ marsh gas „ $\frac{16}{2} = 8$.

„ „ „ „ carbon dioxide „ $\frac{44}{2} = 22$.

The vapour density of a substance is therefore half its molecular weight, and consequently if the vapour density is known the molecular weight is also known.

Of course, it is not necessary actually to use 22.32 litres for the determination of the vapour density of a gas, since, because that is the ratio between the weights of equal volumes, any volume can be used in the experiment. The gas may also be weighed at any temperature and pressure, because corrections for temperature and pressure can easily be applied (see Chapter VI.).

The molecular weight of a gas can also be obtained from its specific gravity by the equation $M = \frac{2d}{0.06926}$
 $= d \times 28.88$; where M = the molecular weight, d = the specific gravity referred to air, and 0.06926 = the specific gravity of hydrogen referred to air. The actual methods for determining vapour density and specific gravity are given in the chapter on the Determination of Molecular Weights.

QUESTIONS.

1. What is the mass in grams of a copper cylinder 2 centimetres in diameter and 10 centimetres in height if the density of copper = 8.9 ?

2. Find the mass of 50 cubic centimetres of benzene if its density = 0.85.

3. A cube of silver 5 centimetres along each edge weighs 1312.5 grams. What is its specific gravity ?

4. What is the specific gravity of a liquid of which a cylinder of 141.3 cubic centimetres capacity holds 211.95 grams ?

5. Find the specific gravity of alcohol from the following data :—

Weight of specific-gravity bottle empty	. . .	20.3920 grams.
„ „ „ filled with water	. . .	70.3412 „
„ „ „ „ alcohol	. . .	61.6515 „

6. Calculate the specific gravity of petroleum ether, given :—

Weight of empty specific-gravity bottle	. . .	26.8950 grams.
„ water and „ „ together	. . .	64.7984 „
„ petroleum ether and specific-gravity bottle together	. . .	51.8154 „

7. A Sprengel-tube filled with distilled water at 15.5° C. weighed 16.659 grams; the same tube filled with petroleum ether at 15.5° C. weighed 14.471 grams; the weight of the empty tube was 10.500 grams. Determine the specific gravity of the ether.

8. Determine the specific gravity of loaf sugar from the following data :—

Weight of sugar in air	. . .	5.8780 grams
„ „ „ petroleum ether	. . .	3.3595 „
Specific gravity of the petroleum ether	=	0.645.

9. Calculate the specific gravity of alcohol from the following numbers :—

Sprengel-tube empty weighed	. . .	8.9345 grams.
„ filled with water weighed	13.4527	„
„ „ alcohol	12.6660	„

10. A Sprengel-tube held 3.598 grams of glycerin and

3.041 grams of water. What is the specific gravity of the glycerin?

11. Find the specific gravity of the Kissingen mineral water at Harrogate from the following data:—

Weight of specific-gravity bottle	19.3567 grams.
" " " " + distilled water		
	at 15.5° C.	84.1839 "
" " " " + mineral water		
	at 15.5° C.	84.4602 "

12. A piece of Iceland spar, which weighed 2.974 grams in air, weighed 1.8755 grams in water. Determine its specific gravity.

13. A piece of an alloy, which weighed 70.7834 grams in air, weighed 8.2974 grams less in water. What was the specific gravity of the alloy?

14. A piece of lead weighed 39.9 grams in air and 36.368 grams in water. Determine the specific gravity of the lead.

15. A sinker, which weighed 7.58 grams in air, weighed 5.05 grams in alcohol and 4.538 grams in water. Calculate the specific gravity of the alcohol.

16. A piece of paraffin wax weighed 1.0065 grams in air; it was attached to a sinker which weighed 1.8755 grams in water, and the wax and sinker together weighed 1.749 grams in water. Calculate the specific gravity of the wax.

17. Calculate the specific gravity of sand from the following data:—

Weight of bottle	26.8950 grams.
" " sand	3.1125 "
" " bottle with sand, and filled with water		66.7210 "
" " " filled with water only	64.7985 "

*18. A piece of lead weighs 50 grams in air, and when suspended in a liquid whose specific gravity is 1.2 it weighs 44.6 grams. Determine the specific gravity of the lead.

CHAPTER IV.

CALCULATION OF THE PERCENTAGE COMPOSITION OF A COMPOUND.

To ascertain the percentage composition of a compound first calculate its molecular weight. Since the molecular weight of a compound is the sum of the weights of the atoms which compose it, it is obtained by multiplying the atomic weight of each element in the compound by the number of atoms of that element present, and adding these quantities together. The following proportion will then serve to calculate the percentage composition :—

$$\left. \begin{array}{l} \text{The molecular} \\ \text{weight of a} \\ \text{compound} \end{array} \right\} : 100 :: \left\{ \begin{array}{l} \text{the weight of an} \\ \text{element present} \\ \text{in the molecule} \end{array} \right\} : \left\{ \begin{array}{l} \text{the percentage} \\ \text{amount of} \\ \text{that element} \end{array} \right.$$

Example.—Find the percentage composition of sodium sulphate ($\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$).

In the molecule of this compound there are 2 atoms of sodium, 1 atom of sulphur, 14 atoms of oxygen, and 20 atoms of hydrogen ; and, therefore—

$$\begin{array}{rcl} \text{Sodium (Na)} & = & 23 \times 2 = 46 \\ \text{Sulphur (S)} & = & 32 \times 1 = 32 \\ \text{Oxygen (O)} & = & 16 \times 14 = 224 \\ \text{Hydrogen (H)} & = & 1 \times 20 = 20 \end{array}$$

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The percentage composition is then obtained according to the rule given, as the result of the following calculations :—

$$\begin{array}{rcl} 322 : 100 :: 46 : & \text{percentage amount of sodium} & = 14.286 \\ 322 : 100 :: 32 : & \text{'' '' '' sulphur} & = 9.938 \\ 322 : 100 :: 224 : & \text{'' '' '' oxygen} & = 69.565 \\ 322 : 100 :: 20 : & \text{'' '' '' hydrogen} & = 6.211 \end{array}$$

100.000

It will be noticed that, in these calculations, one of the percentage amounts can be found by difference ; but it is well to remind the student, that a number so obtained is dependent for its accuracy upon the correctness of the preceding calculations, and if one of them is wrong, that number will also be wrong.

QUESTIONS.

Find the percentage composition of—

1. KHSO_4 .
2. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.
3. $\text{Ca}_3(\text{PO}_4)_2, \text{Ca}_2(\text{PO}_4)\text{F}$. (Apatite.)
4. N_2O_5 .
5. $4\text{CaSiO}_3, \text{H}_2\text{O}$. (Xonaltite.)
6. $4\text{H}_2\text{CaSi}_2\text{O}_6, \text{KF}, 4\text{H}_2\text{O}$. (Apophyllite.)
7. $\text{Cu}_3(\text{PO}_4)_2, 3\text{H}_2\text{O}$.
8. $\text{Cr}_2\text{O}(\text{OH})_4$. (Guignet's green.)
9. $\text{Al}_2\text{K}_2(\text{SO}_4)_4, 24\text{H}_2\text{O}$.
10. $\text{CrO}_2, \text{Pb}_2\text{O}_3$. (Basic Lead Chromate.)
11. $\text{C}_6\text{H}_5\text{NH}_2$.
12. $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$.
13. $3\text{Ca}_3(\text{PO}_4)_2, \text{CaCO}_3$.

CHAPTER V.

*CALCULATION OF EMPIRICAL FORMULÆ FROM
PERCENTAGE COMPOSITION.*

By an empirical formula is meant the simplest formula deducible from the percentage composition of a compound. Whether the empirical is also the molecular formula must be determined by considerations which are discussed in Chapter XIII.

In order to obtain the empirical formula of a compound, the percentage amount of each element in it is divided by the atomic weight of that element, and the results so

obtained are arranged in the order of their numerical greatness.

The smallest of these numbers is taken as unity and the remaining numbers are divided by it; the quotients then represent the ratios of the number of atoms of each element present to each other.

Thus the percentage composition of anhydrous sodium carbonate (Na_2CO_3) is—

$$\text{Na} = 43.40, \text{C} = 11.32, \text{O} = 45.28, = 100.$$

These numbers when divided by their atomic weights yield the following result:—

$$\text{Na} = 43.40 \div 23 = 1.886$$

$$\text{C} = 11.32 \div 12 = 0.943$$

$$\text{O} = 45.28 \div 16 = 2.830.$$

The numbers 1.886 and 2.830 are then divided by 0.943, and the relation of the number of atoms $\text{C} = 1 : \text{Na} = 2 : \text{O} = 3$ is obtained, i.e. the simplest or empirical formula of sodium carbonate is Na_2CO_3 .

If, as in the case of calcium phosphate ($\text{Ca}_3\text{P}_2\text{O}_8$), in which the simplest ratios are $\text{P} = 1 : \text{Ca} = 1.5 : \text{O} = 4$, fractional numbers are obtained, since fractional parts of atoms are not conceivable, they must be multiplied by some factor so as to bring them to whole numbers. Thus in the case mentioned, if the series is multiplied by 2 the ratios $\text{P} = 2 : \text{Ca} = 3 : \text{O} = 8$ are obtained, or an empirical formula $\text{Ca}_3\text{P}_2\text{O}_8$.

The reason for the method of calculation given above may be shown thus. By the terms of the atomic theory each atom possesses a definite weight and always combines with other atoms in some multiple of that weight. In the molecular weight of a compound the amounts of each element are in the same proportion to each other as they are in the percentage composition; so that, taking

the atomic weights of sodium, carbon, and oxygen as 23, 12, and 16 respectively, in the **molecular composition** of anhydrous sodium carbonate (Na_2CO_3) there are 2 atoms of sodium=46 parts, 1 atom of carbon=12 parts, and 3 atoms of oxygen=48 parts; a total of 106 parts by weight; while in the **percentage composition** of the same body there are 43.40 parts of sodium, 11.32 parts of carbon, and 45.28 parts of oxygen; a total of 100 parts.

Now just as on dividing the quantity of each element in the molecular composition, by its atomic weight, a relation of the number of atoms composing the molecule is obtained of $\text{Na} : \text{C} : \text{O} :: 2 : 1 : 3$; so, since in the percentage composition of the same substance the quantities are **similarly proportional** to each other, on dividing the percentage amounts by the atomic weights, numbers are obtained which, **though not the same numbers, yet bear exactly the same ratio to each other**. From these numbers there can easily be calculated, by the method given, the smallest number of atoms of each element which can form the compound, and this will be the empirical formula.

It should be noted here that in the example which has been considered the percentage amounts have been accurately calculated, but an ordinary analysis yields numbers which usually deviate slightly from the calculated quantities; nevertheless the same rule is followed, as the numbers obtained on dividing these quantities by the atomic weights will still bear a simple relation to each other.

EMPIRICAL FORMULÆ OF MINERALS.

The methods employed in the calculation of the formulæ of minerals are very similar to the one given in the former part of the chapter. The principal difference arises from the fact that in the percentage compositions started from, the quantities composing the compound are not denoted in atomic, but in molecular proportions, and con-

sequently the amount of each constituent must be divided by its molecular weight.

Example.—The analysis of a specimen of sapphirine gave the following percentage composition :—

Silica	12·83
Alumina	65·29
Ferric Oxide	0·93
Ferrous Oxide	0·65
Magnesia	19·78
Loss on Ignition	0·31
	99·79

Find its empirical formula.

Proceeding in a similar way to that indicated in the earlier portion of the chapter, but dividing by molecular weights, the following result is obtained :—

$$\begin{aligned} \text{Silica (SiO}_2\text{)} &= \frac{12\cdot83}{60} = 0\cdot2138 \\ \text{Alumina (Al}_2\text{O}_3\text{)} &= \frac{65\cdot29}{102} = 0\cdot6400 \\ \text{Ferric Oxide (Fe}_2\text{O}_3\text{)} &= \frac{0\cdot93}{160} = 0\cdot0058 \\ \text{Ferrous Oxide (FeO)} &= \frac{0\cdot65}{72} = 0\cdot0090 \\ \text{Magnesia (MgO)} &= \frac{19\cdot78}{40} = 0\cdot4945. \end{aligned}$$

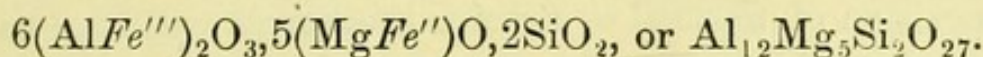
These numbers show no clear relation to each other except that

the alumina : silica :: 3 : 1 ;

and the magnesia : silica very nearly as $2\frac{1}{2}$: 1.

Now ferric oxide and alumina are isomorphous oxides, i.e. they can replace each other in their compounds.

Magnesia and ferrous oxide are also isomorphous, and, consequently, sapphirine may be looked upon as a silicate of alumina and magnesia (since these are present in the greatest quantity) in which these bases have been partly replaced by ferric and ferrous oxides respectively. The amounts of the ferric and ferrous oxides, which are now in molecularly equivalent quantities, must therefore be added to those of the alumina and magnesia, and the ratios will thus become $\text{SiO}_2 = 0.2138 : (\text{AlFe}''')_2\text{O}_3 = 0.6400 + 0.0058 = 0.6458$: and $(\text{MgFe}'')\text{O} = 0.4945 + 0.0090 = 0.5035$. These figures will then give a formula closely approximating to



The above problem might be solved in a different manner. Calculate first the amounts of alumina and magnesia respectively equivalent to the ferric and ferrous oxides, in the percentage composition; add these amounts to those of the alumina and magnesia actually present, and divide the new totals by the molecular weight.

The method of performing this is as follows:—

$$\text{wgt. Fe}_2\text{O}_3 \text{ found} \times \frac{\text{mol. wgt. Al}_2\text{O}_3}{\text{mol. wgt. Fe}_2\text{O}_3} = \text{equi. wgt. Al}_2\text{O}_3$$

$$\text{wgt. FeO found} \times \frac{\text{mol. wgt. MgO}}{\text{mol. wgt. FeO}} = \text{equi. wgt. MgO.}$$

Thus:—

$$0.93 \text{ per cent. Fe}_2\text{O}_3 \times \frac{102}{160} = 0.59 \text{ per cent. Al}_2\text{O}_3$$

$$0.65 \quad \text{,,} \quad \text{FeO} \times \frac{40}{72} = 0.36 \quad \text{,,} \quad \text{MgO};$$

so the calculated total of $\text{Al}_2\text{O}_3 = 65.29 + 0.59 = 65.88$, and the calculated total of $\text{MgO} = 19.78 + 0.36 = 20.14$.

These new amounts divided by the molecular weights give the following ratios :—

$$\text{SiO}_2 = \frac{12.83}{60} = 0.2138$$

$$\text{Al}_2\text{O}_3 = \frac{65.88}{102} = 0.6458$$

$$\text{MgO} = \frac{20.14}{40} = 0.5035 ;$$

but these are the same as those obtained by the first method, and therefore lead to the same formula, $\text{Al}_{12}\text{Mg}_5\text{Si}_2\text{O}_{27}$.

Either of the above methods if applied to the percentage composition of natural or artificial minerals will lead to an approximate formula, and perhaps that given first, as being simpler, is the better one to use.

QUESTIONS.

Calculate the Empirical Formulæ of the substances which possess the following percentage composition :—

<table style="width: 100%; border-collapse: collapse;"> <tr><td style="width: 10%;">1.</td><td style="width: 70%;">Oxygen</td><td style="width: 20%; text-align: right;">38.10</td></tr> <tr><td></td><td>Hydrogen</td><td style="text-align: right;">0.80</td></tr> <tr><td></td><td>Phosphorus</td><td style="text-align: right;">24.60</td></tr> <tr><td></td><td>Sodium</td><td style="text-align: right;">36.50</td></tr> <tr><td></td><td></td><td style="text-align: right; border-top: 1px solid black;">100.00</td></tr> <tr><td></td><td></td><td style="text-align: right; border-top: 3px double black;">100.00</td></tr> </table>	1.	Oxygen	38.10		Hydrogen	0.80		Phosphorus	24.60		Sodium	36.50			100.00			100.00	<table style="width: 100%; border-collapse: collapse;"> <tr><td style="width: 10%;">4.</td><td style="width: 70%;">Nitrogen</td><td style="width: 20%; text-align: right;">9.09</td></tr> <tr><td></td><td>Oxygen</td><td style="text-align: right;">20.77</td></tr> <tr><td></td><td>Silver</td><td style="text-align: right;">70.13</td></tr> <tr><td></td><td></td><td style="text-align: right; border-top: 1px solid black;">99.99</td></tr> <tr><td></td><td></td><td style="text-align: right; border-top: 3px double black;">99.99</td></tr> </table>	4.	Nitrogen	9.09		Oxygen	20.77		Silver	70.13			99.99			99.99
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7. Carbon	49.05
Hydrogen	5.14
Oxygen	17.20
Nitrogen	28.61

100.00

8. Lithium	4.93
Potassium	27.51
Sulphur	22.52
Oxygen	45.04

100.00

9. Copper	33.69
Hydrogen	0.53
Arsenic	40.11
Oxygen	25.67

100.00

10. Sodium	11.85
Mercury	51.55
Chlorine	36.60

100.00

11. Lead	66.56
Boron	7.07
Oxygen	20.58
Water	5.79

100.00

12. Calcium	38.71
Phosphorus	20.00
Oxygen	41.29

100.00

13. Sodium	14.41
Antimony	25.05
Sulphur	26.72
Water	33.82

100.00

Calculate the formulæ of the following minerals from their percentage composition.

Kobell found in a mineral.

14. SiO ₂	55.62
CaO	26.59
Al ₂ O ₃	0.53
Water	17.00

99.74

D.Sc.Lond.

Paragonite from the Zillerthal.

15. SiO ₂	62.24
MgO	30.22
FeO	2.66
H ₂ O	4.97

100.09

	Dolomite.			Petalite.	
16.	CO ₂	44.00	19.	SiO ₂	68.68
	SiO ₂	2.20		CaO	0.79
	Fe ₂ O ₃	2.00		MgO	0.34
	CaO	37.30		Li ₂ O	1.88
	MgO	13.99		K ₂ O	2.30
		99.49		Na ₂ O	1.91
		99.49		Fe ₂ O ₃	0.96
	Garnet.			Al ₂ O ₃	23.27
17.	SiO ₂	41.34			100.13
	CaO	32.28			100.13
	Al ₂ O ₃	18.86		Eudidymite.	
	Fe ₂ O ₃	6.18	20.	SiO ₂	73.11
	Cu ₂ O	0.32		BeO	10.62
	MgO	0.12		Na ₂ O	12.24
	K ₂ O	0.91		H ₂ O	3.79
	Na ₂ O	0.72			99.76
		100.73			99.76
		100.73		Albite.	
	Hornblende from Socotra.		21.	SiO ₂	69.00
18.	SiO ₂	50.01		Al ₂ O ₃	19.43
	Fe ₂ O ₃	28.30		CaO	0.20
	FeO	9.87		Na ₂ O	11.47
	MgO	0.34			100.10
	MnO	0.63			100.10
	CaO	1.32			
	Na ₂ O	8.79			
	K ₂ O	0.72			
		99.98			
		99.98			

CHAPTER VI.

*INFLUENCE OF TEMPERATURE AND PRESSURE
UPON THE VOLUME OF GASES.*

TEMPERATURE. LAW OF CHARLES.

It is well known that gases expand on being heated, and contract on being cooled. The law which governs this alteration in volume is attributed to both Charles and Gay Lussac, and may be stated as follows :—

For every increase or decrease in temperature of 1° C. the volume of the same mass of a gas expands or contracts $\frac{1}{273}$ of its volume at 0° C., provided the pressure remains constant. The fraction $\frac{1}{273}$, which is also expressed decimally as 0.003665, is known as the **coefficient of the expansion of gases**.

This law is not absolutely accurate, but is quite sufficiently so for all ordinary requirements. It will be readily understood from the above law that

273	volumes of gas at 0° C. will become
273 + 1	„ „ 1° C.
273 + 2	„ „ 2° C.
273 + t	„ „ t° C.

On the other hand, the volume decreases in the same manner for every decrease of 1° C., thus :—

273	. volumes at 0° C. become
273 - 1	„ „ -1° C.
273 - 2	„ „ -2° C.
273 - t	„ „ $-t^{\circ}$ C.

Here $T=273+27=300$. $T'=273-5=268$. $V=500$.

$\therefore 300 : 268 :: 500 : V'$, and

$$V' = \frac{268 \times 500}{300} = 446.6 \text{ c.c.}$$

It should also be remembered that the density of a gas is inversely as the absolute temperature; so that if T and T' are the original and new **absolute** temperatures, and D and D' the corresponding densities, then

$$D : D' :: T' : T.$$

Example 3.—The density of oxygen is 16, that of nitrogen is 14, at 0°C . and 760 mm. At what temperature will oxygen have the same density as nitrogen at 0°C ., providing that the pressure remains constant?

Here $D=16$. $D'=14$. $T=273$. $T'=273+t$, where t =the degrees on the Centigrade scale, through which the gas must be heated.

Proceeding according to the proportion just given—

$$\begin{aligned} 16 : 14 :: 273+t : 273 ; \\ \therefore 14(273+t) &= 16 \times 273 ; \\ \therefore t &= \frac{4368-3822}{14} = 39^\circ \text{C.} \end{aligned}$$

PRESSURE. LAW OF BOYLE.

This law states that—

The volume of the same mass of any gas varies inversely with the pressure to which it is subjected, provided that the temperature remains constant. Therefore if P , P' and V , V' represent the original and new pressures and volumes respectively, then

$$P' : P :: V : V'.$$

The law is also sometimes stated, 'The product of the pressure and volume is a constant quantity,' or $PV=P'V'$.

While the **volume** of a gas varies inversely as the pres-

sure, it should be noted that the density varies directly as the pressure; so that if D and D' are the densities then

$$P : P' :: D : D'.$$

Example 4.—Five hundred litres of oxygen are measured at 760 mm. and 0° C. What volume will they occupy at 1,000 mm. and 0° C. ?

According to the proportion given above—

$$\begin{aligned} P' : P &:: V : V' ; \\ 1000 : 760 &:: 500 : V' ; \\ \therefore V' &= \frac{760 \times 500}{1000} = 380 \text{ ls.} \end{aligned}$$

Example 5.—The density of hydrogen at 0° and 760 mm. is 1. At what pressure will it become 2 ?

$$\begin{aligned} \text{Here, since } P : P' &:: D : D' \\ 760 : P' &:: 1 : 2 ; \\ \therefore P' &= \frac{760 \times 2}{1} = 1520 \text{ mm.} \end{aligned}$$

When a gas is subjected to change of temperature and pressure simultaneously, Boyle's and Charles' laws have both to be taken into account, and the new volume may then be looked upon as the resultant product of two forces. In this case the equation $\frac{PV}{T} = \frac{P'V'}{T'}$ holds good.

Example 6.—Five hundred cubic centimetres of chlorine are measured at 27° C. and 750 mm. pressure. The temperature is increased to 77° C., and the pressure to 1,000 mm. Find the new volume.

The following proportion indicates the change of volume due to change of pressure :—

$$\begin{aligned} 1000 : 750 &:: 500 : V' ; \\ \therefore V' &= \frac{750 \times 500}{1000} = 375 \text{ c.c.} \end{aligned}$$

But while the pressure tends to diminish the volume, increase of temperature acts in the other direction according to the following proportion :—

$$273 + 27 : 273 + 77 :: 375 : V' ;$$

$$V' = \frac{350 \times 375}{300} = 437.5 \text{ c.c.}$$

This result may also be obtained by means of the double proportion :—

$$1000 : 750 :: 500 : V' ;$$

$$300 : 350 ::$$

$$\therefore V' = \frac{750 \times 350 \times 500}{1000 \times 300} = 437.5 \text{ c.c.}$$

Or, using the last equation, given on page 28.

$$\frac{500 \times 750}{273 + 27} = \frac{1000 \times V'}{273 + 77} ;$$

$$\therefore V' = (\text{as above}) \frac{500 \times 750 \times 350}{300 \times 1000} = 437.5 \text{ c.c.}$$

QUESTIONS.

1. A certain mass of gas occupying 120 cubic centimetres at 15° C. is measured at 30° C., 0° C., and - 10° C. respectively. What will be the volume of the gas at those temperatures ?

2. 300 volumes of hydrogen measured at - 10° C. become heated to 10° C. What is the new volume ?

3. 117 grams of common salt yield 22.32 litres of chlorine at 0° C. and 760 mm. pressure. When the temperature rises to 17° C., and the pressure decreases to 730 mm., what is the new volume ?

4. 250 litres of hydrogen measured at 745 mm. and - 15° C. become heated to 20° C., while the pressure changes also to 765 mm. What is the new volume ?

5. 25 volumes of ammonia measured at - 10° C. are heated until they occupy 30 volumes. To what temperature must they have been raised to accomplish this change ?

6. 216 grams of mercuric oxide yield 11.16 litres of oxygen

at 0° C. and 760 mm. What will be the volume occupied if the barometer stands at 745 mm. ?

7. 273 litres of hydrogen are measured at 755 mm. pressure. What will be the new volume if the pressure is altered to 900 mm., the temperature remaining constant ?

8. A freely expansible balloon filled with 1,000 litres of hydrogen at 750 mm. pressure, is subjected alternately to pressures of 800 mm. and 700 mm. By what fraction will its original volume be decreased and increased respectively ?

9. 220 volumes of nitrogen have a density of 14. The pressure is altered so that the density becomes 12. What is the new volume ?

10. At 760 mm. pressure the density of air is 14.44. At what pressure will it be the same as that of normal hydrogen ?

11. At what temperature will air have the same density as oxygen at 0° C. if the density of air is 14.44 ?

12. Oxygen at 0° C. and 760 mm. has a density of 16. When the pressure is 700 mm., and the density 20, what is the temperature ?

13. 250 cubic centimetres of hydrogen at 0° C. and 760 mm. pressure are heated to 177° C. Supposing that the gas is in a closed vessel without room for further expansion, what will be the new pressure ?

14. A hermetically sealed flask can only stand an internal pressure of three atmospheres. Supposing the gas with which it is filled to have been measured at 15° C. and 760 mm., at what temperature will the pressure of the gas break the flask ?

15. A certain mass of gas measures 200 c.c. at 15° C. and 760 mm. pressure. At what temperature will it measure 650 c.c. if the pressure is 750 mm. ?

CHAPTER VII.

CALCULATIONS DEPENDING ON CHEMICAL EQUATIONS.

THREE facts must be borne in mind :—

(i.) That the atomic weight of an element is a constant quantity.

(ii.) That the same chemical substance is always made up of the same elements in the same proportions.

(iii.) That a chemical equation represents the results of chemical action. In such an equation there must always be the same number of atoms, of each element entering into the reaction, on both sides of the equation ; and consequently there will also be represented the same weight of matter on each side of it.

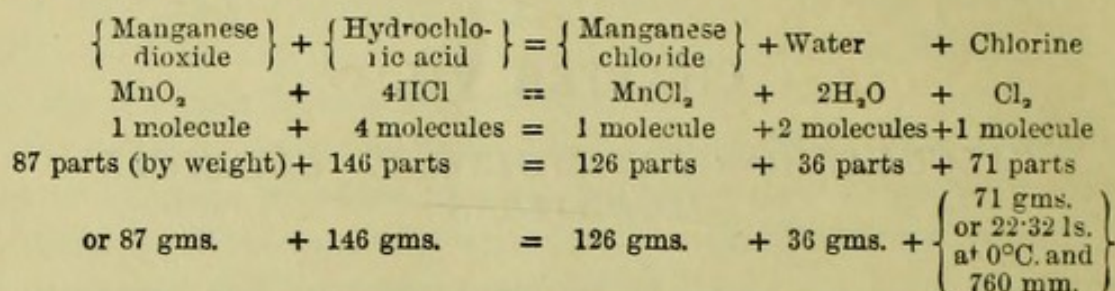
The sign = in these equations denotes 'yields.'

If these statements are remembered, it will be easily understood that the proportions represented by an equation hold good for any weight whatever. Also, if the equation representing a reaction is known, and the weight of one of the substances used in the reaction is known too, then the amounts of any other substance required to complete the reaction, or of any of the substances produced in it, can be immediately calculated. In such a case any excess over the required quantities remains absolutely unused.

Such facts are of the greatest possible importance, not only for purely scientific, but also for technical purposes, since a knowledge of them enables chemical manufacturing processes to be controlled.

The equation which represents the action of hydrochloric acid on black oxide of manganese will serve, in conjunction with the following examples, to illustrate the above state-

ments. Below the equation are given some of the facts it represents :—



If this equation is examined it will be seen that it fully complies with the requirements enunciated above.

It must be carefully remembered that the first thing to do when calculating the results of a chemical reaction is to write down the equation representing it.

Example 1.—50 grams of manganese dioxide are heated with excess of hydrochloric acid. What weight of chlorine is produced?

According to the preceding equation, 87 parts of manganese dioxide yield 71 parts of chlorine ; therefore 50 parts will yield less in the following proportion :—

$$\begin{array}{l}
 87 : 50 :: 71 : x ; \\
 \therefore x = \frac{50 \times 71}{87} = 40.8 \text{ gms. of chlorine.}
 \end{array}$$

Example 2.—I need 50 grams of chlorine. How much hydrochloric acid containing 20 per cent. of real acid is necessary to produce it?

By the equation given, 71 grams of chlorine require 146 grams of real acid ; consequently 50 grams will require proportionately less ; and the amount so obtained must be corrected for the dilution of the acid in the proportion of 20 : 100. The following proportion will consequently give the desired amount :—

$$\begin{array}{l}
 71 : 50 :: 146 : x ; \\
 20 : 100 :: \\
 \therefore x = \frac{50 \times 100 \times 146}{71 \times 20} = 514 \text{ gms. hydrochloric acid.}
 \end{array}$$

One other fact must be noted, viz. that where any of the substances concerned in an equation are gases, if the molecular weights are taken in grams the volume in litres of the gas, or gases, is known. This follows because the gram-molecule (page 12) of a gas at 0° C. and 760 mm. measures 22·32 litres. The volumes of gas produced by the use of different amounts of material can thus be directly calculated ; or conversely the quantities required to give different volumes may be ascertained.

Example 3.—73 grams of hydrochloric acid are heated with excess of manganese dioxide. Calculate the volume of chlorine produced.

By the equation 22·32 litres of chlorine are produced from 146 grams of hydrochloric acid ; therefore 73 grams of acid will produce proportionately less :—

$$146 : 73 :: 22\cdot32 : x ;$$

$$\therefore x = \frac{73 \times 22\cdot32}{146} = 11\cdot16 \text{ ls. chlorine.}$$

QUESTIONS.

1. 10 grams of pure marble are dissolved in hydrochloric acid. Calculate what bulk of gas at 0° C. and 760 mm. would be given off. S. & A. D.

2. What volume of gas measured at 0° C. and 760 mm. would you obtain by heating 10 grams of oxalic acid with sulphuric acid ? S. & A. D.

3. A solution of nitric acid of specific gravity 1·46 contains 80 per cent. of HNO₃. What weight of this solution is theoretically required to dissolve 10 grams of copper oxide ?

S. & A. D.

4. How many cubic centimetres of oxygen and of hydrogen are obtainable from 10 grams of water ? S. & A. D.

5. What weight of sulphur is contained in 100 grams of sulphuretted hydrogen ? S. & A. D.

6. What weight of hydrogen is contained in 250 grams of water ? S. & A. D.

7. If 10 grams of pure alcohol were completely burned, what would be the weight of each product formed?

S. & A. D.

8. How many litres of oxygen are required to burn completely (i.) 120 grams of sulphur and (ii.) 155 grams of phosphorus?

S. & A. D.

9. What volume of aqueous hydrochloric acid, containing 36.5 grams HCl per litre, will be required to neutralise 224.5 grams of $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$?

S. & A. D.

10. How would you obtain ethane (ethyl hydride) from ethyl iodide? What bulk of this gas measured at 0°C . and 760 mm. could be obtained from 10 grams of ethyl iodide?

S. & A. D.

11. How many litres of oxygen gas measured at 10°C . and 755 mm. can be obtained from 1 kilo. of potassium chlorate?

1 litre of oxygen at 0°C . and 760 mm. = 1.43 grams.

S. & A. D.

12. How many milligrams of hydrogen will be formed (i.) when 230 milligrams of sodium are thrown on water, (ii.) when 649 milligrams of zinc are dissolved in sulphuric acid?

$\text{Zn} = 64.9$.

S. & A. D.

13. How many tons of sulphuric acid can theoretically be manufactured from 500 tons of pyrites containing 48 per cent. of sulphur?

S. & A. D.

14. Describe how ethyl alcohol can be obtained from cane sugar. Calculate the weight of alcohol obtainable from 1,000 grams of cane sugar.

S. & A. D.

15. How many tons of oil of vitriol containing 70 per cent. H_2SO_4 are needed to convert 100 tons of salt into salt cake?

S. & A. D.

16. If 22.4 litres of hydrogen at 0°C . and 760 mm. pressure weigh 2 grams, what will be the weight of an equal bulk of ammonia at 100°C . and 380 mm. pressure?

S. & A. D.

17. How many grams of oxygen will be needed to burn completely 500 c.c. of ethane, measured at 10°C . and 750 mm. pressure, and what diminution of volume will occur when the residue is treated with potash?

S. & A. D.

18. What weight of pure nitric acid would contain 100 grams of oxygen; and what weight of pure hydrochloric acid would contain 100 litres of chlorine at the standard temperature and pressure?

S. & A. D.

19. If 12 grams of pure carbon be completely burnt in the oxygen which is obtained by decomposing 122.5 grams of potassic chlorate, what is the weight of the product of the combustion formed, and what is the weight, if any, of oxygen remaining?
S. & A. D.

20. What weight in kilos. of zinc and sulphuric acid will yield hydrogen enough to fill a balloon of 350 c.c. capacity at 15° C. and 735 mm. pressure; and what fraction of the gas will escape when the balloon has reached an elevation where the barometer stands at 355 mm., supposing the temperature constant?
S. & A. D.

* 21. A quantity of carbon monoxide is passed through a red-hot tube containing ferric oxide. The resulting gas is absorbed by caustic potash. The gain in weight of the caustic potash was 0.86 gram. What was the volume of the carbon monoxide at standard temperature and pressure?

* 22. What weight of air is required for the complete combustion of 1 litre of marsh gas measured at 10° C. and 752 mm. pressure? What are the volumes of the products, measured at 300° C. and the same pressure?

* 23. What weight of air is needed for the complete combustion of 4 grams of olefiant gas? What volume would the resulting mixture occupy at 200° C. and 760 mm. pressure?

24. If air contains 21 per cent. by volume of oxygen, how many litres of it at standard temperature and pressure are required to burn completely 18 grams of carbon, and what would be the volume of the product formed?

Weight of 11.2 litres of O = 16 grams. S. & A. D.

25. All the gas obtained by treating 3 grams of calc-spar with acid is heated to 210° C. and then cooled to 15° C. State what volume in cubic centimetres it will occupy in each case, the barometer remaining at 760 mm.
S. & A. D.

26. What increase in weight will occur on burning 10 grams of phosphorus in a tube through which oxygen is passed, supposing that none of the product is lost? How would you regain the phosphorus from the substance thus formed?

S. & A. D.

* 27. By boiling 20 grams of a 10 per-cent. solution of hydrogen dioxide, what volume of oxygen at 12° C. and 750 mm. pressure can be collected?

28. What volume of atmospheric air, measured at 15° C.

and 750 mm., is required for the complete combustion of 1 gram of sulphur ? Matric. Lond.

* 29. 30 grams of oxygen are passed over red-hot carbon. What weight of carbon monoxide is produced, and what is its volume at 750 mm. and 18° C ?

* 30. What volume of chlorine would be obtained at 15° C. and 740 mm. by heating 10 grams of pure manganese dioxide with excess of hydrochloric acid ?

31. If 100 parts by weight of air contain 23 of oxygen and 77 of nitrogen, how many tons of air would be needed to burn one ton of coal, consisting of carbon 90.55, hydrogen 4.14, nitrogen 1.26, oxygen 2.35, ash 1.70 parts per cent. ? Assume that, on burning, the carbon is converted into carbon dioxide and the hydrogen into water ; that the nitrogen is evolved as such ; and that the ash is already fully oxidised.

Matric. Lond.

32. The formation of nitrous oxide is represented by the equation $\text{NH}_4\text{NO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}$. How many grams of ammonic nitrate are required to form 2,000 c.c. of N_2O ?

Int. Sc. Lond.

65 33. How many grams of ammonium sulphate are necessary for the preparation of 15 litres of ammonia measured at 19° C. and 800 mm. ?

0750
719.25 34. What weight of oxygen gas could be obtained from 100 grams of pure potassium chlorate ? If the chlorate used contained 10 per cent. of its weight of potassium chloride, what would be the difference in the amount of oxygen obtained ?

S. & A. D.

CHAPTER VIII.

COMBINATION OF GASES BY VOLUME.

THERE is little difficulty attending the solution of problems on the combination of gases by volume, provided that the relations existing between the molecular weights of gases and their volumes are carefully remembered.

Irrespective of weight, it is customary to speak of the molecule of a gas as occupying, under normal conditions,

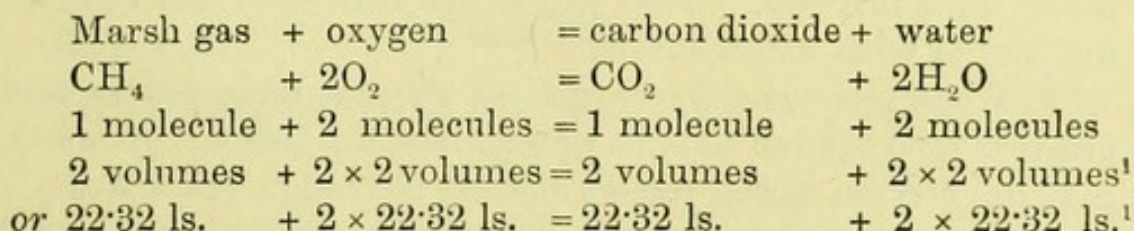
the same volume as 2 atoms of hydrogen. Thus the molecules of hydrogen, oxygen, marsh gas, and carbon dioxide are said to occupy 2 volumes.

But although it is conceivable that the molecules of elementary gases, such as hydrogen and oxygen, can be divided into half-molecules, which then occupy 1 volume, it is not conceivable that the molecules of compound gases, such as marsh gas or carbon dioxide, can be so divided, because that would require the carbon atom itself to be divisible.

When the question of weight, as well as volume, is considered, then the gram-molecule (page 12), which occupies 22.32 litres, is used.

In working out problems in this subject, therefore, it is only necessary to remember that, at 0° C. and 760 mm. pressure, the molecule of a gas occupies 2 volumes, and that the gram-molecule occupies 22.32 litres.

Take, for example, the equation representing the combination of marsh gas with oxygen.



Thus it is evident that marsh gas requires twice its own volume of oxygen to burn it, and yields its own volume of carbon dioxide and twice its volume of steam (if the temperature is above 100° C.). At temperatures below 100° C. the steam will of course be condensed.

Example.—15 litres of marsh gas are mixed with 40 litres of oxygen and exploded. What volume of carbon dioxide is produced, and what volume of oxygen remains?

By the equation given, 22.32 litres of marsh gas produce

¹ At temperatures over 100° C.

22.32 litres of carbon dioxide ; therefore, keeping the same proportion, 15 litres of marsh gas will produce 15 litres of carbon dioxide.

Also, by the equation given, 22.32 litres of marsh gas require 44.64 litres of oxygen, and therefore 15 litres will require 30 litres of oxygen.

But 40 litres of oxygen were added ;

∴ there are $40 - 30 = 10$ litres of oxygen remaining.

QUESTIONS.

In all these calculations consider the carbon as burning to carbon dioxide, hydrogen to water, and nitrogen as remaining unchanged.

1. What volume of carbon dioxide must be passed over red-hot charcoal to yield 159 litres of carbon monoxide ?

S. & A. D.

2. 100 volumes of air, containing 21 volumes of oxygen, are mixed with 70 volumes of hydrogen and an electric spark passed through the mixture. What will be the volume of gas remaining, and of what will it consist ?

S. & A. D.

3. How many c.c. of oxygen at normal temperature and pressure are required to burn completely (i.) 500 c.c. of marsh gas ; (ii.) 500 c.c. of the vapour of ethyl alcohol ?

S. & A. D.

4. In order to burn completely 2 litres of the following gases, what volume of oxygen will be needed, and what volume of CO_2 will be formed—methane, olefiant gas, ethyl hydride ?

S. & A. D.

5. 50 volumes of a gas, mixed with 70 volumes of oxygen, give after explosion 50 volumes of carbon dioxide, and after its absorption by potash 45 volumes of oxygen. What was the gas ?

S. & A. D.

6. 11.2 litres of cyanogen at 0°C . and 760 mm. are burnt. What will be the products of the combustion, and what bulk will they occupy, measured at 0°C . and 760 mm. ?

S. & A. D.

7. 50 c.c. of oxygen are mixed with 500 c.c. of hydrogen, both measured at the normal temperature and pressure. An electric

spark is passed through the mixture. What volume, if any, of gas will remain, and how would you ascertain which it is?

S. & A. D.

8. How many volumes of oxygen are required for the complete combustion of 500 volumes of each of the following gases, and how many volumes of CO_2 will in each case be formed—olefiant gas, acetylene, cyanogen, marsh gas? S. & A. D.

9. What volume of air containing 21 per cent. of oxygen is required to burn a litre of marsh gas? S. & A. D.

10. What volume of chlorine at normal temperature and pressure would be required to combine with (i.) 10 litres of olefiant gas (C_2H_4); (ii.) to decompose 10 litres H_2S ; (iii.) to decompose 10 grams KI? Matric. Lond.

* 11. 250 cubic centimetres of chlorine gas, measured at 10°C . and 750 mm. pressure, are shaken with ammonia. What volume of nitrogen is liberated, measured at the same temperature and pressure?

12. What volume of air would be required for the complete combustion of 100 litres of gas, containing hydrogen 46, marsh gas 40, olefiant gas 14 per cent. by volume? Int. Sc. Lond.

CHAPTER IX.

CALCULATION OF THE RESULTS OF QUANTITATIVE ANALYSIS.

METHODS OF QUANTITATIVE CHEMICAL ANALYSIS

QUANTITATIVE chemical analysis may be divided into two branches—viz. gravimetric and volumetric. It is not possible here to do more than briefly indicate the typical methods of these two sections.

In gravimetric analysis the amount of an element, or group of elements, present in a compound may be estimated in four different ways:—

(i.) It may be estimated directly, as when the moisture is driven off by heat from a weighed quantity of substance, which is then reweighed. The loss in weight is due to

the moisture which was present in the portion taken, and from its amount the percentage can be calculated.

(ii.) A weighed portion of the substance may be changed by suitable treatment into a new compound and reweighed : then from the difference in weight, and the known composition of the new compound, either the percentage amount of pure substance in the original material, or that of one of the elements in it may be estimated. Thus sodium chloride may be changed into sodium sulphate, and, from the percentage of sodium known to be present in the sulphate, the amount of sodium which was present in the chloride may be calculated, and its purity consequently ascertained.

(iii.) A weighed portion of the material to be analysed is dissolved in a convenient solvent, and the element, or group of elements, is precipitated from its solution, by the use of a suitable reagent, in an insoluble form, as hydrate, sulphate, &c. These insoluble precipitates are washed, dried, and weighed, and from their known composition the percentage amount of the elements in question in the original substance may be calculated. For example, the copper in copper sulphate can be precipitated as copper oxide, and, from the known composition of that body, when anhydrous, the amount of copper present in the sample of copper sulphate can be found ; or, the acid radicle (SO_4) in it can be precipitated, by means of barium chloride, in the form of barium sulphate, and from the weight of this precipitate the amount of the acid radicle (SO_4) ascertained.

(iv.) The preceding method may be made use of in indirect determinations ; as, for example, the amount of potassium present in potassium chloride can be estimated by precipitating the chlorine in the compound as silver chloride, and from the weight of that precipitate the amount of potassium may be calculated.

Volumetric analysis is of most use when either the amount of acidity or alkalinity of a substance has to be

ascertained ; where the reducing or oxidising value of materials has to be determined ; or, occasionally, it is made use of in precipitating compounds from solutions.

For the various purposes mentioned standard solutions are required, which may be normal (N), semi-normal ($\frac{N}{2}$), deci-normal ($\frac{N}{10}$), or centi-normal ($\frac{N}{100}$).

A normal solution is one which contains the equivalent in grams of an element, acid, alkali, or salt, per litre of solution.

By equivalent is meant in this case the amount of a body which is equal in effect to 1 atom of sodium, or 1 molecule of sodium hydrate, or 1 molecule of a mono-basic acid, such as HCl.

Thus the molecular weight, 36.5 grams, of real hydrochloric acid in 1 litre gives a normal solution of hydrochloric acid.

The molecular weight, 63 grams, of pure nitric acid

Half molecular weight, 49 " " sulphuric acid

The molecular weight, 40 " " sodium hydrate

Half molecular weight, 53 " " " carbonate

all give normal solutions of the respective compounds, and each of these solutions is exactly equivalent to the other, volume for volume. Thus :—

1 c.c. of normal HCl	will exactly neutralise	1 c.c. of normal NaOH
1 " " HCl	" " "	1 " " Na_2CO_3
1 " " H_2SO_4	" " "	1 " " Na_2CO_3
1 " " H_2SO_4	" " "	1 " " NaOH
1 " " HNO_3	" " "	1 " " KOH.

Of course, 1 c.c. of a normal solution is equivalent to 2 c.c. of a semi-normal, 10 c.c. of a deci-normal, or 100 c.c. of a centi-normal solution.

Occasionally, in practice, solutions are not made up accurately to normal strength. In such cases it is customary to standardise them by comparison with some solu-

tion of known strength and to express the divergence from normal value by means of a factor.

Thus if a solution of sulphuric acid is found to contain 52 grams per litre, instead of 49, it may be labelled sulphuric acid $N \times 1.0612$, or 1 c.c. = 0.052 gram H_2SO_4 .

If a solution is too weak, it must be labelled in a corresponding manner with a number less than unity.

Examples in Gravimetric Analysis.—*Example 1.*—4.018 grams of pearl ash lost, by drying at $100^\circ C.$, 0.488 gram. Find the percentage amount of moisture present.

Here,

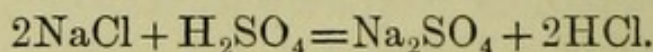
$$\left\{ \begin{array}{l} \text{The amount of} \\ \text{pearl ash taken} \end{array} \right\} : 100 :: \left\{ \begin{array}{l} \text{the loss of} \\ \text{weight} \end{array} \right\} : \left\{ \begin{array}{l} x, \text{ the percentage} \\ \text{amount of moisture} \end{array} \right\}$$

$$4.018 : 100 :: 0.488 : x;$$

$$\therefore x = \frac{100 \times 0.488}{4.018} = 12.14 \text{ per cent. moisture.}$$

Example 2.—1.1285 grams of pure sodium chloride were treated with sulphuric acid, and afterwards the excess of acid was driven off by heat. The resulting sodium sulphate was then weighed, and = 1.3624 grams. Determine the percentage amount of sodium in the sodium chloride.

The equation representing the action of sulphuric acid on salt is



Here $2NaCl$ produce Na_2SO_4 , i.e. there is the same amount of sodium in $2NaCl$ as in Na_2SO_4 .

The molecular weight of Na_2SO_4 is 142, and it contains 46 parts Na. Consequently

$$\left\{ \begin{array}{l} \text{The molecular} \\ \text{weight of the} \\ \text{sodium sul-} \\ \text{phate} \end{array} \right\} : \left\{ \begin{array}{l} \text{sodium sulphate} \\ \text{found} \end{array} \right\} :: \left\{ \begin{array}{l} \text{the sodium in} \\ \text{the molecular} \\ \text{weight of the} \\ \text{sulphate} \end{array} \right\} : \left\{ \begin{array}{l} x, \text{ the sodium} \\ \text{in the su-} \\ \text{phate found} \end{array} \right\}$$

$$\therefore 142 : 1.3624 :: 46 : x$$

$$\therefore x = \frac{1.3624 \times 46}{142} = 0.4413 \text{ gm. sodium.}$$

But this is the amount of sodium which was present in the original NaCl; therefore to obtain the percentage present in that, the further proportion must be stated:—

Salt taken : 100 :: sodium found : $\left\{ \begin{array}{l} x, \text{ the percentage of} \\ \text{sodium in NaCl} \end{array} \right\}$

$$\therefore 1.1285 : 100 :: 0.4413 : x ;$$

$$\therefore x = \frac{100 \times 0.4414}{1.1285} = 39.10 \text{ per cent. sodium ;}$$

or combining the two sums—

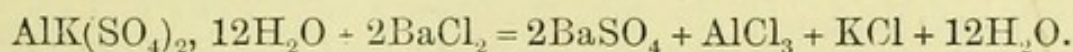
$$142 : 1.3624 :: 46 : x ;$$

$$1.1285 : 100$$

$$\therefore x = \frac{1.3624 \times 46 \times 100}{142 \times 1.1285} = 39.10 \text{ per cent. sodium.}$$

Example 3. — 1.0353 grams of potash alum yielded 1.0217 grams of barium sulphate. Determine the percentage amount of sulphuric acid (SO₄) present in the sample.

The equation which represents the reaction is—



The molecular weight of BaSO₄ is 233, and contains 96 parts of SO₄, and the weight of BaSO₄ found will contain a proportionate amount. This calculated quantity will be the same as that present in the weight of alum taken, so that this problem may be solved similarly to the last one.

$$233 : 1.0217 :: 96 : x, \text{ the percentage amount of SO}_4 ;$$

$$1.0353 : 100 ::$$

$$\therefore x = \frac{1.0217 \times 96 \times 100}{233 \times 1.0353} = 40.66 \text{ per cent. SO}_4.$$

As an example illustrating method iv. (p. 40), but still more indirect in calculation, may be given the following:—

Example 4.—1.449 grams of the mixed chlorides of potassium and sodium contained 0.7739 gram of chlorine. Calculate the percentage amount of each of the chlorides present.

If the whole of the chlorine found had been present as KCl there would be 1.6241 grams of chlorides ; for

$$\left\{ \begin{array}{l} \text{The atomic weight} \\ \text{of Cl} \end{array} \right\} : \left\{ \begin{array}{l} \text{the Cl} \\ \text{found} \end{array} \right\} :: \left\{ \begin{array}{l} \text{the molecular} \\ \text{weight of KCl} \end{array} \right\} : \left\{ \begin{array}{l} x, \text{ the KCl equiva-} \\ \text{lent to the Cl found} \end{array} \right\}$$

$$35.5 : 0.7739 :: 74.5 : x ;$$

$$\therefore x = \frac{0.7739 \times 74.5}{35.5} = 1.6241 \text{ grams KCl.}$$

The actual amount of the chlorides is, however, 1.449 grams, a deficiency of $1.6241 - 1.449 = 0.1751$ gram.

Now,

$$\left\{ \begin{array}{l} \text{The difference} \\ \text{between the} \\ \text{molecular} \\ \text{weights of KCl} \\ \text{and NaCl} \end{array} \right\} : \left\{ \begin{array}{l} \text{the deficiency} \\ \text{in weight} \\ \text{found} \end{array} \right\} :: \left\{ \begin{array}{l} \text{the molecular} \\ \text{weight of} \\ \text{NaCl} \end{array} \right\} : \left\{ \begin{array}{l} x, \text{ the NaCl present} \\ \text{in the mixed} \\ \text{chlorides} \end{array} \right\}$$

The molecular weight of KCl = 74.5, of NaCl = 58.5, and $\text{KCl} - \text{NaCl} = 74.5 - 58.5 = 16$;

$$\therefore 16 : 0.1751 :: 58.5 : x ; \text{ and}$$

$$x = \frac{0.1751 \times 58.5}{16} = 0.6402 \text{ gram NaCl in the mixed chlorides.}$$

Since there were 1.449 grams chlorides,

$$1.449 - 0.6402 = 0.8088 \text{ gram KCl.}$$

To find the percentage amount is then easy ; for

$$1.449 : 100 :: 0.6402 : x, \text{ percentage NaCl ;}$$

$$\therefore x = \frac{100 \times 0.6402}{1.449} = 44.18 \text{ per cent. NaCl,}$$

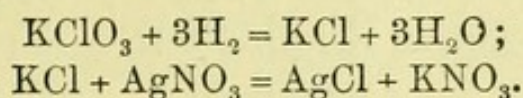
and $1.449 : 100 :: 0.8088 : x, \text{ percentage KCl ;}$

$$\therefore x = \frac{100 \times 0.8088}{1.449} = 55.81 \text{ per cent. KCl.}^1$$

Examples in Volumetric Analysis.—*Example 5.*—The potassium chloride produced by the reduction of 0.32 gram potassium

¹ See Appendix.

chlorate is titrated¹ with deci-normal silver nitrate, of which 26 c.c. are required. Calculate the percentage of chlorine in the specimen. The equations representing the reactions are—



Since the mol. wgt. of $\text{AgNO}_3 = 170$, a normal solution will contain 170 grams in 1 litre of solution; \therefore 1 c.c. will contain 0.170 gram AgNO_3 .

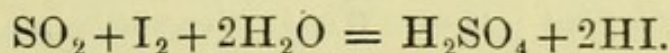
If the solution is deci-normal, since only $\frac{1}{10}$ of 170 grams is dissolved, 1 c.c. will equal 0.0170 gram AgNO_3 .

Now 170 grams AgNO_3 will precipitate 35.5 grams of chlorine as AgCl ; \therefore 1 c.c. of N AgNO_3 ($= 0.17$ gram) will precipitate (or is equivalent to) 0.0355 gram of chlorine; and \therefore 1 c.c. of $\frac{\text{N}}{10}$ AgNO_3 ($= 0.017$ gram) will precipitate (or is equivalent to) 0.00355 gram of chlorine.

In the example given, 26 c.c. of $\frac{\text{N}}{10}$ AgNO_3 were used; $\therefore 26 \times 0.00355 =$ the weight of Cl, to which they are equivalent; and, since that is obtained from 0.32 gram KClO_3 , the percentage amount is found by the following proportion:—

$$\begin{aligned} 0.32 : 100 :: 26 \times 0.00355 : x; \\ x = \frac{100 \times 26 \times 0.00355}{0.32} = 28.84 \text{ per cent. chlorine.} \end{aligned}$$

Example 6.—100 c.c. of a solution of sulphurous acid required 5.15 c.c. of $\frac{\text{N}}{10}$ iodine solution (1 c.c. = 0.0127 gm.) to completely oxidise it. Find the weight of SO_2 per litre of solution.



¹ To titrate a solution means to ascertain the *titre*, or strength, of it by volumetric methods

Since one molecule of iodine oxidises one molecule of sulphur dioxide ; therefore—

254 parts of iodine oxidise 64 parts of sulphur dioxide;
 now 100 c.c. of solution required 5.15×0.0127 gm. iodine ;
 \therefore 1000 c.c. „ „ require 51.5×0.0127 „ „
 and $\therefore 254 : 51.5 \times 0.0127 :: 64 : x$, the SO_2 in solution.

$$\therefore x = \frac{51.5 \times 0.0127 \times 64}{254} = 0.1648 \text{ gm. SO}_2 \text{ in 1 litre.}$$

QUESTIONS.

1. 1.2277 grams of crystallised copper sulphate lost, on drying at 200°C. , 0.4456 gram. Calculate the percentage of water of crystallisation present.

2. 0.3207 gram of common salt yielded 0.7842 gram of silver chloride. Determine the percentage of chlorine present in the salt.

3. 1.5228 grams of potash alum gave after precipitation with ammonia, and subsequent ignition of the precipitate, 0.1649 gram of alumina. What is the percentage of aluminium in the specimen of alum ?

4. 1.481 grams of potash alum were dried, first in a water-bath, and then carefully over a bunsen flame. From the loss of weight, 0.6735 gram, calculate the percentage amount of water present.

5. 1.3878 grams of dolomite yielded, on treatment with dilute hydrochloric acid, 0.5749 gram CO_2 . Find the percentage of CO_2 in the sample.

6. 1.3878 grams of dolomite gave 0.0129 gram Fe_2O_3 . What was the percentage of Fe_2O_3 present ?

7. 2.5978 grams of pearl ash were dissolved in water, and diluted to 250 c.c. 50 c.c. of this solution were withdrawn, acidified with HCl , and the potassium precipitated as 2KCl.PtCl_4 , yielding 1.5596 grams. Calculate the percentage of potassium present in the pearl ash.

8. 0.5533 gram of lead sulphate was obtained from 1.549 grams of flint glass. What percentage of lead oxide (PbO) was present in the glass ?

9. 1.4566 grams of flint glass yielded 0.3799 gram of the chlorides of potassium and sodium. The mixed chlorides gave

0.6459 gram of $2\text{KCl}, \text{PtCl}_4$. Find the percentage of soda (Na_2O) present in the glass.

*10. A mixture of BaO and CaO weighing 2.5 grams is transformed into the mixed sulphates, and then weighs 5 grams. Find the quantity of BaO and CaO respectively present in the mixture.

11. 0.2705 gram substance gave when burnt 0.9305 gram CO_2 and 0.1487 gram of H_2O . Calculate the percentage composition. S. & A. D.

12. Calculate the percentage composition of a hydrocarbon from the following data:—Weight of substance, 0.2500 gram; carbon dioxide, 0.8085 gram; water, 0.2655 gram.

S. & A. D.

13. 0.333 gram of a non-nitrogenous body gave when burnt 0.4885 gram of carbon dioxide, and 0.2099 gram of water. Calculate its empirical formula. S. & A. D.

14. How is phosphoryl chloride prepared? Calculate the percentage amount of chlorine contained in it from the following analytical results:—

Weight of phosphoryl chloride taken . 1.3156 grams.

Weight of silver chloride found . . 3.6907 „

$\text{Ag} = 107.63$; $\text{Cl} = 35.37$.

Int. Sc. Lond.

15. 1.33 grams of a mixture of the chlorides of potassium and sodium gave 2.87 grams of silver chloride. Calculate the percentage composition of the mixture.

16. 0.6195 gram of coal, after ignition with sodium carbonate, yielded by suitable treatment 0.1682 gram of barium sulphate. Calculate the amount of sulphur present in the coal.

17. 0.4182 gram of a mixture of silver chloride and bromide was heated in a stream of chlorine gas. On reweighing its weight was 0.342 gram. Find the percentage of silver bromide present.

18. 6.2729 grams of brass yielded 0.4779 gram of lead sulphate. Calculate the percentage amount of lead in the brass.

19. 1.4789 grams of a red brick yielded 0.4069 gram of a mixture of Fe_2O_3 and Al_2O_3 . 0.3779 gram of the finely powdered mixed oxides was ignited in a current of dry hydrogen, and lost 0.0188 gram. Determine the percentage amounts of Al_2O_3 and Fe_2O_3 in the brick.

* 20. A litre, measured at 0° C. and 760 mm., of a mixture of air and carbonic anhydride was shaken with baryta water. The resulting precipitate weighed 0.32 gram. What is the percentage by volume of the carbon dioxide in the mixture?

21. Calculate the percentage of NO_3 in potassium nitrate from the following data:—

Weight of platinum crucible + SiO_2 = 19.0697 grams.

“ “ + SiO_2 + KNO_3 = 19.8787 “

“ “ + SiO_2 + K_2SiO_3 = 19.4458 “

22. 37.6 c.c. of deci-normal silver nitrate solution were required for the titration of 50 c.c. of ammonium chloride solution. What is the amount per litre of the latter salt?

23. 200 c.c. of a solution of sulphurous acid require 10.30 c.c. of deci-normal iodine solution. Find the weight of SO_2 in grams per litre. $\text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} = 2\text{HI} + \text{H}_2\text{SO}_4$.

24. 20 c.c. of a solution of caustic soda require 20.4 c.c. of normal sulphuric acid for complete neutralisation. What is the strength of the soda in grams per litre?

25. 10.862 grams of bleaching powder were made into a cream with distilled water, and diluted to 1 litre. The available chlorine in the mixture was estimated by titration with arsenious acid. 50 c.c. of the mixture required 48.9 c.c. arsenious acid, of which 1 c.c. = 0.003593 gram Cl. What was the percentage of available chlorine in the sample?

26. 16.0823 grams of soda ash were dissolved in 500 c.c. of water. 50 c.c. of this solution required 17.4 c.c. of sulphuric acid ($\text{N} \times 0.9794$) for neutralisation. Determine the percentage of soda (Na_2O) in the sample.

27. 2.9614 grams of tartar emetic were dissolved in 250 c.c. of water. 25 c.c. of this solution, after addition of sodium bicarbonate, were titrated with iodine solution and required 17.25 c.c. Taking $2\text{I}_2 = \text{Sb}_2$, and the strength of the iodine solution to be 1 c.c. = 0.01255 gram iodine, find the percentage of antimony in the tartar emetic.

28. 0.3485 gram of potassium dichromate was boiled with hydrochloric acid, and the chlorine evolved was passed into a solution of potassium iodide. The iodine thus liberated required 70.80 c.c. of sodium thiosulphate for its titration.

1 c.c. of $\text{Na}_2\text{S}_2\text{O}_3$ solution = 0.0127 gram iodine;

$\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = \text{Cr}_2\text{Cl}_6 + 2\text{KCl} + 14\text{H}_2\text{O} + 3\text{Cl}_2$.

Calculate the percentage of potassium dichromate in the sample.

29. 1.0005 grams of borax ($\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$) were transformed into sodium chloride. This when titrated with $\frac{\text{N}}{10}$ silver nitrate required 52.6 c.c. Find the percentage of boric anhydride (B_2O_3) in the borax.

30. 0.2151 gram of uric acid was heated with soda lime, and the evolved ammonia absorbed by hydrochloric acid. The ammonium chloride solution was evaporated to dryness and redissolved in water, and the chlorine precipitated as silver chloride, of which 0.739 gram was obtained. What percentage of nitrogen did the uric acid contain? S. & A. D.

CHAPTER X.

ATOMIC WEIGHT DETERMINATIONS.

AN atom may be defined as the smallest portion of an element which can enter into combination with other elements.

The atom of every element possesses its own definite weight. Hydrogen is the lightest body known, and the atomic weights are usually numbers which are multiples of the atomic weight of hydrogen taken as unit, although with some it is now customary to refer them to oxygen 16 ($\text{H} = 1.003$).

Though every atom possesses a definite weight, what that weight really is, is not known: **all atomic weights are therefore relative, not absolute, numbers.**

Very careful and accurate researches are requisite in order to ascertain the true atomic weight of any element. To obtain this weight the amount of the element which is equivalent to, or will combine with, one atom of hydrogen must be ascertained. The equivalent weight of an element, however, is not necessarily its atomic weight; because, if the element is di-, tri-, or poly-valent, the combining weight

will require multiplying by a suitable whole number in order to convert it into an atomic weight.

The determination of these whole numbers is often a work of considerable difficulty, and they can only be fixed by reference to Newlands' and Mendeléef's law of the periodicity of the elements; the specific heat of the element (Dulong and Petit's law); the vapour density, or isomorphism, of the element or its compounds.

A short explanation of the use of these different factors in establishing the atomic weight of an element is given below.

PERIODIC LAW.

This law was first formally stated by Newlands, in 1864, as the Law of Octaves, but its value was not generally recognised till Mendeléef, and Lothar Meyer, in 1869, independently enunciated it in a new form, and they show that the properties of the elements are periodic functions of their atomic weights. This statement will be best realised by examining the modified table of Mendeléef's arrangement given on page 51.

In this table the elements are arranged in groups of seven, in the order of their atomic weights, and a distinct periodicity in their properties, *e.g.* atomic volume, density, &c., may be observed. This phenomenon is often much more marked if alternate, instead of consecutive, groups of seven are compared, and is brought out more clearly if gaps are left in the groups for elements as yet undiscovered; thus the positions now occupied by the elements Ga, Ge, and Sm, were originally vacant.

Each of these **groups** of elements roughly corresponds to a natural family, and together they form **series**. Let any element Y be taken, which stands between X and Z, the elements next before and after it in a **series**, and between A and B, those before and after in the **groups** as given on p. 51; then it may be said that the atomic weight,

MENDELÉEFF'S TABLE (MODIFIED).

Series	1	2	4	6	8	10	12
R ₂ O	—	Li = 7	K = 39	Rb = 85	Cs = 133	—	—
RO	—	Be = 9	Ca = 40	Sr = 87	Ba = 137	—	—
R ₂ O ₃	—	B = 11	Sc = 44	Y = 89	La = 138	Yb = 173	—
RO ₂	H ₄ C	C = 12	Ti = 48	Zr = 91	Ce = 140	—	Th = 232
R ₂ O ₅	H ₃ N	N = 14	V = 51	Nb = 94	Di = 142	Ta = 183	—
RO ₃	H ₂ O	O = 16	Cr = 52	Mo = 96	Sm = 150?	W = 184	U = 240
R ₂ O ₇	HF	F = 19	Mn = 55	—	—	—	—
—	—	—	{ Fe = 56 Co = 59 Ni = 59 }	Ru = 102 Rh = 103 Pd = 107	—	Os = 191 Ir = 193 Pt = 195 }	—
R ₂ O	H = 1	Na = 23	Cu = 63	Ag = 108	—	Au = 197	—
RO	—	Mg = 24	Zn = 65	Cd = 112	—	Hg = 200	—
R ₂ O ₃	—	Al = 27	Ga = 70	In = 114	Tr = 159?	Tl = 204	—
RO ₂	H ₄ R	Si = 28	Ge = 72	Sn = 119	—	Pb = 207	—
R ₂ O ₅	H ₃ R	P = 31	As = 75	Sb = 120	Er = 166	Bi = 209	—
RO ₃	H ₂ R	S = 32	Se = 79	Te = 125	—	—	—
R ₂ O ₇	HR	Cl = 35.5	Br = 80	I = 127	—	—	—
Series	—	3	5	7	9	11	13

atomic volume, and density of Y will be the means of those of the same constants of X and Z, and A and B, respectively : *e.g.* the properties of Sr are midway between those of Rb and Y in series 6, and those of Ca and Ba in group II. The elements of each group show a gradation of properties from the lowest to the highest atomic weight. This statement may be verified by the consideration of the properties of the elements forming group IV. It will also be seen that the members of the even and odd series of this group respectively, are more alike when taken separately, than when all the series are taken together.

It may also be noted that, while the members of the groups show marked similarities, those of the series formed by these groups differ in properties.

The manner in which the atomic properties of an element, when considered in the light of the above arrangement, help to determine the true position of the element in the atomic series, and to control its atomic weight, will now readily be perceived.

DULONG AND PETIT'S LAW. ATOMIC HEAT.

This law was stated by its discoverers thus : 'The atoms of all elements have the same capacity for heat.' This may also be stated in another manner :—

The product of the specific heat¹ of an element and its atomic weight is a constant quantity. This number, which is called the **atomic heat** of the element, is **approximately 6.4**.

The law is not absolutely correct, but, according to Kopp, while the atomic heat of all elements whose atomic weights are over 30 is normal, if below 30, it is abnormal

¹ The unit of heat is the amount of heat required to raise 1 gram of water from 0° C. to 1° C., and is called the calorie. Different bodies have different specific heats. The specific heat of a substance may be defined as the amount of heat required to raise 1 gram of it through 1° C.

at ordinary temperatures ; though there is evidence to show that, if the specific heat be taken at a higher temperature, the atomic heat then approaches 6.4.

The determination of the specific heat of an element is thus of great importance, as it often enables us to decide which of different proposed numbers, all multiples of the equivalent or combining weight of the element, shall be taken as the atomic weight.

As an example, magnesium might be instanced. If the combining weight, 12, were taken as the atomic weight of this element, it would yield an oxide, Mg_2O ; a sulphate, Mg_2SO_4 ; a nitrate, $MgNO_3$; and a chloride, $MgCl$. The specific heat, however, is 0.25, and $0.25 \times 12 = 3.0$; an atomic heat which is only half the normal number ; so that the combining weight is doubled, and the atomic weight taken as 24, while the formulæ of its compounds become MgO , $MgSO_4$, $Mg(NO_3)_2$, and $MgCl_2$ respectively.

VAPOUR DENSITY.

It has been already shown that the vapour density of a body is half its molecular weight.

If, then, the vapour density of the element or some of its compounds, as well as its equivalent weight, is known, it is often possible to decide which number shall be taken as atomic weight.

Phosphorus will serve to illustrate this. Its specific heat is of doubtful value, but points to the number 31 as atomic weight ; the vapour density of phosphorus itself, however, would lead to 62 being accepted ; but since the hydride, PH_3 , has a vapour density of 17, the number 31, which corresponds to such a density, is received as correct.

ISOMORPHISM.

Mitscherlich, in 1819, showed that similar chemical substances, either elements or compounds, often crystallise

in identical crystalline forms. This phenomenon has received the name of **isomorphism**.

A good example of isomorphism is found in the crystalline forms of calc spar, dolomite, magnesite, spathic iron ore, calamine, and diallogite, which are the carbonates of calcium, calcium and magnesium, iron, zinc, and manganese. All these crystallise in similar rhombohedra. This similarity of crystalline structure has been useful in fixing the atomic weights of strontium and barium, which are isomorphous with calcium and lead, while that of scandium was established by its isomorphism with aluminium.

CALCULATION OF ATOMIC WEIGHTS.

Although it is thus evident that to ascertain the atomic weight of an element more than one class of quantitative determination is necessary, in this chapter we are concerned mainly with one of them, which is required in all cases—viz. the results obtained by the accurate analysis of pure compounds of the element. From these can be determined the amount of it which combines with other elements, and its equivalent weight thus ascertained. For this purpose it is customary to choose, as far as possible, compounds in which the atomic weights of the elements not under consideration have been most accurately determined—*e.g.* such elements as silver, chlorine, bromine, sulphur, or oxygen.

In some cases the element is estimated directly, either as metal, oxide, sulphide, sulphate, or some other compound; in others it is found indirectly, by ascertaining the amount of the element, or group of elements combined with it—*e.g.* the chlorine or bromine—and calculating from such data the required atomic weight.

It should therefore be thoroughly understood that, in calculating the atomic weight of an element, what has first

to be determined is the ratio of the weight with which the element in question combines with the atomic weights of monad elements.

This ratio is known when the weight, with which the element combines with an ascertained weight of either one element, or a group of elements of fixed atomic weight, is determined. The ratios so obtained are either referred to $H=1$, $O=15.96$; or Meyer and Seubert's ratios, viz. $O=1$, $H=0.06265$, $Ag=6.7456$, $Cl=2.21586$, are used.

Two examples will, perhaps, make these statements clear.

It is required to find the atomic weight of titanium: this may be found, amongst other methods, by the analysis of the chloride, $TiCl_4$.

From a known weight of this chloride the atomic weight may be calculated (i.) directly by obtaining the corresponding weight of the oxide TiO_2 , i.e. the ratio of $TiCl_4 : TiO_2$, and (ii.) indirectly by estimating the amount of silver chloride produced by precipitating the chlorine with silver nitrate, i.e. the ratio $TiCl_4 : 4AgCl$.

Of course, in these calculations the tetravalency of titanium is assumed.

In case (i.) the TiO_2 is proportional to the $TiCl_4$, and therefore to the Ti contained in it; in case (ii.) $4AgCl$ is also proportional to the $TiCl_4$, and therefore to the Ti.

Example 1.—6.569 grams of $TiCl_4$ yielded 2.770 grams of TiO_2 . Taking $O=16$, $Cl=35.5$, find the atomic weight of titanium.

According to case (i.) we have the following proportion:—

$$\begin{aligned} TiCl_4 \text{ taken} : TiO_2 \text{ produced} &:: \text{mol. wgt. } TiCl_4 : \text{mol. wgt. } TiO_2 \\ 6.569 &: 2.770 &:: Ti + 142 &: Ti + 32 \\ & & (Ti + 32) 6.569 &= (Ti + 142) 2.770 \\ Ti (6.569 - 2.770) &= 393.34 - 210.208 \\ 3.799 Ti &= 183.132 \\ \therefore Ti &= \frac{183.132}{3.799} = 48.2; \end{aligned}$$

i.e. 48.2 is the ratio in which 1 atom Ti combines with 4 atoms Cl, or 2 atoms O, and is thus the amount of Ti which is equivalent to 4 atoms of hydrogen. Since titanium is tetravalent, that number is therefore its atomic weight.

In order to avoid the use of an algebraic equation, the problem may be worked more simply thus:—

$$\left. \begin{array}{l} \text{Loss of wgt. in changing} \\ \text{TiCl}_4 \text{ taken into TiO}_2 \end{array} \right\} : \left\{ \begin{array}{l} \text{the difference} \\ \text{between mol. wghts.} \\ \text{of TiCl}_4 \text{ and TiO}_2 \end{array} \right\} :: \text{TiCl}_4 \text{ taken} : \left\{ \begin{array}{l} x, \text{ the mol.} \\ \text{wght. of} \\ \text{TiCl}_4. \end{array} \right.$$

$$6.569 - 2.770 : (\text{Ti} + 142) - (\text{Ti} + 32) :: 6.569 : x$$

$$\therefore x = \frac{110 \times 6.569}{3.799} = 190.2.$$

Mol. wgt. of $\text{TiCl}_4 - \text{Cl}_4 = 190.2 - 142 = 48.2 =$ the atomic weight of titanium.

Example 2.—3.312 grams of TiCl_4 yielded 10.002 grams of AgCl . Find the atomic weight of titanium. $\text{Ag} = 108$, $\text{Cl} = 35.5$.

Since titanium is tetravalent, TiCl_4 will yield 4AgCl , and the following proportion is obtained:—

$$\text{TiCl}_4 \text{ taken} : \text{AgCl found} :: \text{mol. wgt. TiCl}_4 : 4\text{AgCl}$$

$$3.312 : 10.002 :: \text{Ti} + 142 : 574$$

$$(\text{Ti} + 142) 10.002 = 574 \times 3.312$$

$$10.002 \text{ Ti} = 1901.088 - 1420.284$$

$$\therefore \text{Ti} = \frac{480.804}{10.002} = 48.07.$$

This may also be worked more quickly and simply thus:—

$$\text{AgCl found} : 4\text{AgCl} :: \text{TiCl}_4 \text{ taken} : x, \text{ mol. wgt. TiCl}_4$$

$$10.002 : 574 :: 3.312 : x$$

$$\therefore x = \frac{574 \times 3.312}{10.002} = 190.07.$$

Mol. wgt. $\text{TiCl}_4 - \text{Cl}_4 = 190.07 - 142 = 48.07$, which is the atomic weight of titanium.

QUESTIONS.

1. Calculate the atomic heat of phosphorus (cryst.) from Regnault's determinations of its specific heat: (i.) 0.174, (ii.) 0.189; also of red phosphorus (iii.) 0.170.

2. Dewar found the specific heat of the diamond at temperatures between 20° – 1040° C. to be 0.366. Weber found the specific heat to be 0.4589 at 985° C. Calculate the atomic heats at these temperatures from these data. What atomic weight for carbon would the former result, if correct, lead to?

3. The specific heat (i.) of iron is 0.1140; (ii.) of lead, 0.0315; (iii.) of potassium, 0.1660. Explain the meaning of these numbers and calculate the atomic heats of these metals.

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4. The specific heat (i.) of zinc is 0.0955; (ii.) of arsenic, 0.083; (iii.) of tin, 0.0562; (iv.) of iodine, 0.0541; (v.) of platinum, 0.0325; (vi.) of beryllium, 0.408. Calculate the atomic weights of these elements from these data.

5. The atomic heat (i.) of lithium is 6.6; (ii.) of calcium, 6.8; (iii.) of cobalt, 6.3; (iv.) of gallium, 5.45; and (v.) of bromine, 6.7. Find the specific heats of these elements from these numbers.

6. S. G. Rawson found that 1.14319 grams of ammonium dichromate gave 0.68987 gram of chromic oxide. Find the atomic weight of chromium. $O = 15.96$; $N = 14.02$.

7. 100 parts of pure silver, dissolved in nitric acid, require for exact precipitation 69.1 parts of potassium chloride. Assuming the atomic weights $K = 39.1$, $Cl = 35.5$, and the specific heat of silver, 0.057, calculate the atomic weight of silver.

*8. 1.6517 grams of calcite, containing as impurity 0.003 gram of silica, after ignition, weighed 0.9274 gram. Calculate the atomic weight of calcium. $O = 15.96$; $C = 11.97$; $H = 1$.

*9. A metal yields a chloride containing 66.14 per cent. of chlorine, and having the specific gravity 7.44. What is its atomic weight?

*10. The chloride of an element contains 60.4 per cent. of chlorine; the specific heat of the element is 0.09. What is the atomic weight of the element?

11. Liebig and Redtenbacher found that 28.803 grams of silver acetate yielded 18.612 grams of metallic silver. Assuming the formula $C_2H_4O_2$ for acetic acid, calculate from the above numbers the atomic weight of carbon.

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12. Calculate the atomic weight of titanium correctly to two places of decimals from each of the following statements:—

- (i.) 2.43275 grams of TiCl_4 required 5.52797 grams Ag.
 (ii.) 3.31222 grams TiCl_4 yielded 10.00235 grams AgCl.
 (iii.) 6.23398 grams TiCl_4 gave 2.62825 grams TiO_2 .

$$\text{Ag} = 6.7456; \text{Cl} = 2.21586; \text{O} = 1; \text{H} = 0.06265.$$

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13. Mallet determined the atomic weight of aluminium (i.) by estimating the hydrogen evolved by the action of caustic soda on the metal, when 5.2632 grams of aluminium gave 5.2562 grams of water; (ii.) by analysis of the bromide, when 8.6492 grams of the bromide required 10.4897 grams of metallic silver for precipitation. Required the atomic weight of aluminium from (i.) and (ii.). $\text{Ag} = 107.66; \text{Br} = 79.75; \text{O} = 15.96$.

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14. 2.0876 grams of hydrogen, when passed over heated oxide of copper, yielded 18.7406 grams of water. Calculate the atomic weight of oxygen.

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15. Thorpe and Young obtained 1.6707 grams of silica from 9.63007 grams of silicon tetrabromide. Calculate the atomic weight of silicon from the ratios $\text{Br} = 4.99721; \text{O} = 1; \text{H} = 0.06265$.

16. From the following data given by Brauner determine the atomic weight of cerium. 53.77424 grams of cerium sulphate, $\text{Ce}_2(\text{SO}_4)_3$, yielded 32.57367 grams of ceric oxide (CeO_2). $\text{O} = 16; \text{S} = 32.06$.

17. In one of Cleve's experiments 0.7447 gram of samarium oxide (Sm_2O_3) yielded 1.2583 grams of samarium sulphate, $\text{Sm}_2(\text{SO}_4)_3$. Find the atomic weight of samarium if $\text{SO}_3 = 80$.

*18. Winkler found that 1 part of oxygen combines with 4.737 parts of indium; the compound thus obtained was regarded as a monoxide until L. Meyer pointed out that in this case the metal would not fit in the natural system, but would do so if we assumed it formed a sesquioxide. Bunsen found its specific heat = 0.057. What is its atomic weight, and what position does it occupy in the system?

19. Marignac found that 5 grams of strontium chloride, containing 6 molecules of water of crystallisation, yielded 3.442 grams of strontium sulphate. Calculate the atomic weight of strontium.

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20. An unknown quantity of potassium bromo-aurate

(AuBr_3KBr) on being heated left 9.92441 grams of a mixture of metallic gold and potassium bromide. The mass on being treated with water left 6.19001 grams of gold. The solution of KBr required 3.38451 grams of silver for total precipitation by Stas' method, and afforded 5.89199 grams of silver bromide. These data afford 3 independent values for the atomic weight of gold which you are required to calculate. $\text{H} = 1$; $\text{O} = 15.96$; $\text{K} = 39.03$; $\text{Br} = 79.76$; $\text{Ag} = 107.66$. S. & A. D.

21. By dissolving 0.4442 gram of metallic cobalt in an acid, 177.4 c.c. of hydrogen at 10°C . and 750 mm. pressure are obtained. The specific heat of the metal is 0.107. Calculate the atomic weight of cobalt. S. & A. D.

22. The analysis of silver chromate, by Meineke, yielded $\text{Ag}_2\text{O} = 69.856$ per cent., $\text{Cr}_2\text{O}_3 = 22.930$ per cent., and $\text{O} = 7.228$ per cent. Calculate the atomic weight of chromium. $\text{Ag} = 107.66$; $\text{O} = 15.96$.

23. Dumas found that 2.399 grams of aluminium chloride required 5.802 grams of silver for the complete precipitation of the chlorine. Calculate the atomic weight of aluminium.

24. Dewar and Scott found that, after reducing 5.74647 grams of AgMnO_4 with SO_2 , the silver present required 3.00677 grams of KBr for its complete precipitation. Calculate the atomic weight of manganese. $\text{O} = 16$; $\text{Ag} = 107.93$.

25. Marignac found (i.) that 100 parts of crystallised barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) required 88.4067 parts of silver for complete precipitation. He also found (ii.) that 100 parts of the same salt gave 95.53 parts of barium sulphate. Calculate the atomic weight of barium from these numbers, on the assumption that the most probable ratios of Ag , Cl , O , H , and S , are as follows (Lothar Meyer and Seubert):— $\text{Ag} = 6.7456$; $\text{Cl} = 2.21586$; $\text{O} = 1$; $\text{H} = 0.06265$; $\text{S} = 2.005$. D. Sc. Lond.

26. As the result of 9 estimations, Classen found that 246.3384 grams of bismuth yielded 274.637 grams of bismuth oxide. Find the atomic weight of bismuth.

27. One litre of mercury vapour at the standard temperature and pressure weighs 8.923 grams. On heating 118.3938 grams of mercuric oxide, Erdmann and Marchand obtained 109.6308 grams of mercury. On the assumption that mercuric oxide is formed by the union of 1 atom of mercury with 1 atom of oxygen, what light do these facts throw on the atomic and molecular weights of mercury? S. & A. D.

CHAPTER XI.

SIMPLE CALCULATIONS IN GAS ANALYSIS.

DETAILS of the more elaborate calculations required in gas analysis are not given in this chapter ; a larger manual, such as Sutton's 'Volumetric Analysis,' must be consulted, if those are needed. There are, however, simple calculations, such as those involved in the estimation of the amount of oxygen in the air, or of carbon dioxide in coal gas, or other simple determinations, of which it is advisable to give examples.

The vessels used in gas analysis are very varied in design, but may be roughly divided into two classes—(i.) absorption vessels and (ii.) measuring tubes.

Gases cannot always be measured in absorption vessels, since these may not be convenient in shape, in which case they are always used in connection with a suitable measuring tube.

Measuring vessels may be graduated in two ways : (i.) They may have their length accurately divided into millimetres, and the volume corresponding to each division then determined independently, and a record kept. This method of calibration is necessary when the measurement takes place over mercury. (ii.) They may be marked out in lengths which correspond to definite volumes, such as the cubic centimetre ; as, for example, in Lunge's nitrometer, or the gas burette used with Hempel's absorption pipettes.

In the illustrations given, fig. 3 represents a graduated absorption-tube, for use over mercury. Fig. 5 is a graduated gas burette, such as is used with the ungraduated absorption vessel, fig. 6.

A eudiometer-tube (fig. 4) is similar in shape to fig. 3,

but is made longer, narrower, and stronger, because it has to withstand the stress of an explosion. It is provided with platinum wires that are fused into the top; these

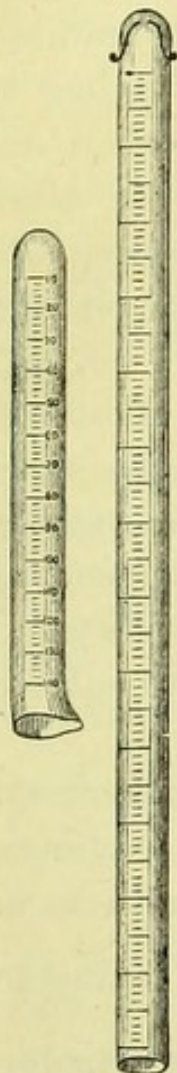


FIG. 3.



FIG. 4.

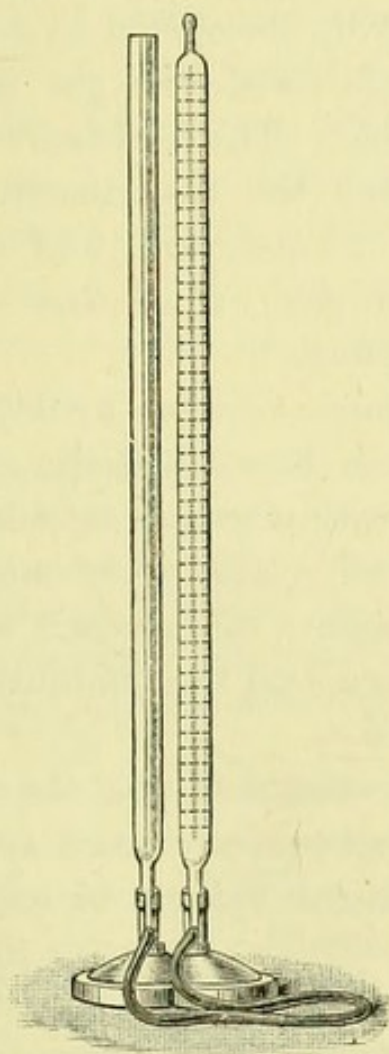


FIG. 5.

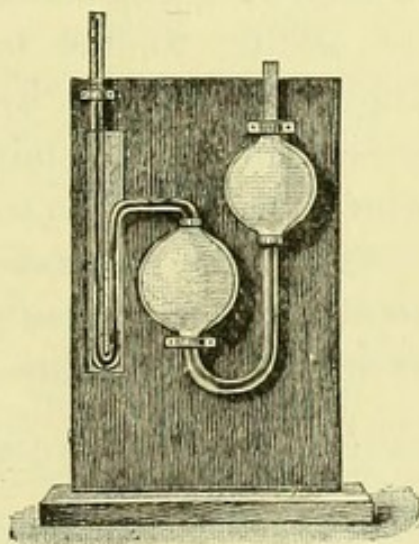


FIG. 6.

allow the passage of an electric spark with which to explode gaseous mixtures contained therein. Both the absorption-tube (fig. 3) and the eudiometer-tube (fig. 4) are graduated from the top downwards.

Every determination of the volume of gases over mercury requires four primary observations (Bunsen) :—

- (i.) The level of the mercury in the eudiometer.
- (ii.) The level of the mercury in the trough, measured on the etched divisions on the eudiometer.
- (iii.) The atmospheric temperature.
- (iv.) The barometric pressure.

Gases may be estimated either **directly** or **indirectly**. Thus oxygen, carbon monoxide, carbon dioxide, sulphur dioxide, hydrogen sulphide, nitric oxide, olefiant gas, and others, may be estimated directly by absorption—i.e. some suitable reagent, which will combine with the gas in question, is introduced into the tube. The difference between the volumes, before and after the experiment, gives, after suitable correction for temperature and pressure, the volume of the absorbed gas; from this its percentage amount can easily be calculated.

On the other hand, gases such as hydrogen, nitrogen, marsh gas, and others, can be estimated indirectly. For example, oxygen mixed with nitrogen may be determined by adding to the mixed gases, after measurement, a known volume of hydrogen; an electric spark is then passed through the mixture, and the diminution in volume which takes place is noted.

The different measurements of gas are then reduced to normal temperature and pressure; and since 2 volumes of hydrogen combine with 1 volume of oxygen to form water, $\frac{1}{3}$ of the corrected diminution of volume is due to the oxygen that was present in the mixture. The nitrogen is of course ascertained by difference.

Similarly a mixture of marsh gas and hydrogen may be analysed by exploding the measured gases with a known excess of oxygen. The carbon dioxide in the residual gases is absorbed and its volume ascertained. This amount, after reduction of all the measurements to normal temperature and pressure, gives the volume of marsh gas present, since marsh gas produces its own volume of carbon dioxide on combustion. The amount of hydrogen is found by difference.

In Hempel's apparatus the analysis of mixtures of gases, similar to those the analysis of which has just been

described, is performed by combustion over heated copper oxide or palladium, and the eudiometer is entirely discarded.

Since many of these operations are carried out with moist gas over mercury, and correction has to be made for the influence of varying pressure upon the gas, one frequent correction is due to the vapour pressure of water, or what is known as the tension of aqueous vapour.

The manner in which the tension of aqueous vapour affects the measurement of a gas may be shown by the following example :—

Example 1.—50 cubic centimetres of moist nitrogen are contained in an absorption tube over mercury. The mercury in the tube is 150 mm. above the level of that in the trough, the barometer stands at 760 mm., the temperature of the gas is 10° C., and the tension of aqueous vapour is 9.165 mm. at 10° C. Find the volume of the gas when dry at 760 mm. pressure.

It is evident that the gas, under the circumstances named, is not under atmospheric pressure, because there is a column of mercury 150 mm. in length, which is exerting pressure in an opposite direction to the atmosphere ; so that the pressure, apart from the question of the tension of aqueous vapour, is $760 - 150 = 610$ mm.

The manner in which the aqueous vapour further affects the result may be explained by the following illustration :—

If a drop of water is allowed to rise into the Torricellian vacuum of a barometer tube, at the temperature 10° C., the mercury in the tube will be depressed 9.165 mm. If also a drop of water is brought into a tube that contains a measured quantity of gas standing over mercury, it will be found, if the temperature is 10° C., that in this case also the mercury will be depressed 9.165 mm.

In other words, water evaporates either into a vacuum or into space filled with other gases, the pressure it exerts

being the same in both cases and constant at the same temperature.

This is an illustration of Dalton's law of partial pressures, which may be stated as follows : In a mixture of gases at a given pressure, the pressure of each individual gas is not that of the mixture, but is directly proportional to its own volume at the total pressure ; so that if U is the total volume of a mixture, U' the volume of a constituent at the same pressure, P the total pressure, and P' the partial pressure of a constituent, then

$$U : U' :: P : P'.$$

In fact, the pressure of a mixture of gases is the sum of the partial pressures of its constituents.

Apply this law to the above case. There are 50 c.c. of gas at 610 mm. total pressure, and the partial pressure of one of the two constituents is known to be 9.165 mm. ; therefore the partial pressure of the other must be $610 - 9.165 = 600.835$ mm. ; and consequently the volume of the dry gas at 760 mm. will be, according to Chapter VI.,

$$50 \times \frac{600.835}{760} = 39.52 \text{ c.c.}$$

The volume of the water vapour at 760 mm. can also be found by the proportion $50 \times \frac{9.165}{760} = 0.6$ c.c.

Two other corrections must be applied in accurate analyses : (i.) A correction for the error introduced by the meniscus. Owing to capillarity, the top of the mercury column is always convex ; consequently if the volume of gas in the tube is only measured to the top of the curve, a small portion will escape measurement. This loss is counterbalanced by the addition of a small amount either to the volume, or to the mercury reading, the absorption-tube being graduated from the top downwards. (ii.) A correction for the expansion by heat of the mercury

columns, in the absorption-tube and in the barometer. This expansion renders the readings higher than they otherwise would be. The length of the columns must therefore be reduced to 0° C., and the following formula will serve for this :—

Let L_t be the length of the column of mercury in millimetres at the temperature t , and L_0 its length at 0° C. The coefficient of the expansion of mercury is 0.00018. Then

$$L_t = L_0 (1 + 0.00018 t), \text{ and } L_0 = \frac{L_t}{1 + 0.00018 t}$$

Since the principal difficulty in solving problems in simple gas analysis by absorption is due to the corrections necessary for the volume of the absorption vessel, the meniscus, and tension of aqueous vapour, the following worked-out example, due to Bunsen, will aid the student:—

Example 2.—Find the volume of dry air from the following analytical measurements of air saturated with moisture :—

Observation at the lower level of the mercury	= 565.9 mm.
" " upper level in the eudiometer	= 317.3 mm.
meter	<hr style="width: 100px; margin: 0 auto;"/>
Height of column to be subtracted from the barometer	$p = 248.6$ mm.
Volume in the table of capacity corresponding to division 317.3	$v = 292.7$
Correction for the meniscus	$m = 0.4$
Temperature of the air	$t = 20.2^\circ$ C.
Height of the barometer	$P = 746.9$ mm.
Tension of aqueous vapour	$T = 17.6^\circ$ mm.

V = corrected volume at 0° C. and 1 metre pressure.

$$V = \frac{(v + m)(P - p - T)273}{1000 (273 + t)} = \frac{(292.7 + 0.4)(746.9 - 248.6 - 17.6)273}{1000 (273 + 20.2)}$$

$$\therefore V = \frac{293.1 \times 480.7 \times 273}{1000 \times 293.2} = 131.2 \text{ c.c.}$$

Example 3.—450.96 c.c. of CO_2 free air are mixed with hydrogen, which increases the volume to 657.06 c.c. After

exploding the mixture there remain 374.73 c.c. of gas. Assuming the temperature and pressure to be normal at each measurement, calculate the percentage amount of oxygen in the air.

The diminution in volume after the explosion = $657.06 - 374.73 = 282.33$ c.c. One-third of this amount, 94.11 c.c., is due to the oxygen present in the air.

$$\therefore \text{The percentage present} = \frac{100 \times 94.11}{450.96} = 20.88.$$

QUESTIONS.

1. A mixture of equal volumes of nitrogen and oxygen, measured at 10° C. and 750 mm. pressure is saturated with moisture. Find—

(i.) The weight of water in 1 cubic metre of the moist gases.

(ii.) The partial pressures of the oxygen and nitrogen.

Tension of aqueous vapour at 10° C. = 9.165 mm.

2. The capacity of a room is 2,016 cubic feet. Find the weight of water vapour contained in it, if the barometric pressure is 730 mm., the temperature 20° C., and the air is saturated with moisture.

Tension of aqueous vapour at 20° C. = 17.391 mm.

3. From the following data you are required to give the volume of the dry gas at 0° C. and 760 mm. pressure:—

Observed volume of moist gas 68.6 cub. ins.

Height of barometer 738.5 mm.

Temperature 15.0° C.

Height of mercury in eudiometer above level

of mercury in trough 147.5 mm.

Tension of aqueous vapour at 15° C. 12.7 mm.

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4. Find the volume of air at 0° C. and 1 m. pressure from the following observations (Bunsen):—

Observation at the lower level of mercury 565.9 mm.

Observation at the upper level in eudiometer 310.7 mm.

The division 310.7 corresponds to a volume in

the table of capacity 286.0

Correction for the meniscus 0.4

Temperature of the air 20.2° C.

Height of the barometer 0.7474 m.

5. Calculate the percentage composition of air from the following analyses (Bunsen) :—

—	(i.)			(ii.)			(iii.)		
	Vol.	Press. mm.	Temp. C.	Vol.	Press. mm.	Temp. C.	Vol.	Press. mm.	Temp. C.
Air employed	809.6	500.1	1.7	839.0	523.6	3.4	856.2	547.5	6.4
After addition of hydrogen . . .	991.0	675.1	1.8	991.3	670.7	3.6	1010.5	694.5	6.4
After the explosion	823.9	504.1	2.1	801.6	485.4	3.6	811.2	502.8	6.2

6. Find the percentage composition of a mixture of nitrogen, oxygen, and carbon dioxide from the following results (Bunsen) :—

—	Vol.	Press. mm.	Temp. C.
Original gas	171.2	624.0	13.5
After absorption of carbon dioxide	167.3	619.6	13.5
After absorption of oxygen	147.0	605.8	13.9

7. In the eudiometrical analysis of a hydrocarbon gas the following numbers were obtained. Fill up the last column of corrected numbers, and give the molecular formula and name of the gas.

—	Observed Volume	Temp. C.	Difference of Mercury level, mm.	Height of Barometer mm.	Corrected Volume of dry gas at 0° C. and 1 m. pressure
Gas used (moist)	91.8	12.8°	623.1	752.7	
After admission of oxygen (moist)	535.1	12.9°	160.6	751.7	
After combustion (moist)	498.8	12.8°	194.0	751.1	
After absorption of CO ₂ (dry)	454.3	13.0°	237.2	741.5	

Tension of aqueous vapour at 12.8° C. = 11.0 mm.

“ “ “ 12.9° C. = 11.1 “

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8. A sample of air free from carbon dioxide, which measured 651.4 volumes at a pressure of 537.4 mm., and at a temperature of 4° C. was mixed with hydrogen and exploded. After the

addition of the hydrogen the bulk of the gas at 0° C. and 760 mm. was 657.06 volumes, and after explosion it measured 374.73 volumes. Calculate the percentage of nitrogen and oxygen present.

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9. The analysis of a gaseous mixture gave the following results:—

—	Observed Volume	Temp. C.	Barometer mm.	Height of Internal Column of Mercury mm.	Corrected Vol. at 0° C. and 1 metre pressure
Volume of gas employed (moist)	81.8	18.9°	740.2	476.3	
Volume after admission of oxygen (moist)	410.2	19.0°	740.3	153.7	
After combustion (moist)	366.2	19.0°	740.4	197.1	
After absorption of carbonic anhydride (dry)	341.4	18.0°	744.0	222.1	

Supply the numbers in the column headed 'Corrected Vol. at 0° C. and 1 metre pressure.'

Tension of aqueous vapour at 18.9° C. = 16.2 mm.

" " " 19.0° C. = 16.3 "

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10. Find the percentage amounts of the absorbable gases present in two samples of coal gas from the following results by Hempel's method:—

—	(i)	(ii)
Original volume of gas	66.4 cc	55.8 cc.
Volume after absorption of CO_2 by KOH	66.3 "	55.7 "
" " " C_2H_4 &c. by Br	63.0 "	52.9 "
" " " C_6H_6 by HNO_3	61.9 "	52.1 "
" " " O by alkaline pyrogallate	58.1 "	49.0 "
" " " CO by Cu_2Cl_2	54.0 "	45.5 "

Hydrogen, nitrogen, and methane are unestimated.

11. Find the percentage amounts of hydrogen, nitrogen, carbon monoxide, and carbon dioxide in heating gas, from the following analysis by Hempel's method (Winkler):—

Original volume of gas	97.7 c.c.
Volume after absorption of CO_2	85.7 "
Residual volume after absorption of CO	68.6 "
Of the residual volume were taken	59.3 "
Volume after addition of air to the 59.3 c.c.	98.8 "
Volume after combustion of the hydrogen	80.5 "

CHAPTER XII.

ABSORPTION OF GASES BY LIQUIDS.

Dalton and Henry's Law.—Gases dissolve in liquids, which have no chemical action upon them, in quantities, by weight, which are dependent upon the temperature and pressure at the time of experiment. For a constant temperature the volume of a gas dissolved by a liquid is constant, but the weight of the gas dissolved will vary in direct proportion to the pressure. The solubility of a gas decreases as the temperature rises.

The volume of a gas at t° C. and 760 mm. pressure, which is dissolved by 1 volume of a solvent, constitutes the **coefficient of absorption** of the gas for that solvent under the given conditions. For example, the following numbers are the absorption coefficients of the gases named for water at 0° C. and 760 mm. :—

Hydrogen	0.0193
Nitrogen	0.02035
Oxygen	0.04114
Nitrous oxide	1.3052
Carbon dioxide	1.7967
Hydrogen sulphide	4.3706
Sulphur dioxide	7.9789

Example.—Calculate the volume of nitrogen absorbed by 100 litres of water when exposed to air, at 0° C. and 760 mm. pressure, containing 79 per cent. nitrogen. Coeff. of sol. of nitrogen = 0.02.

According to definition, 1 volume of water will dissolve 0.02 volume of nitrogen at 0° C. 760 mm., but the partial pressure of the nitrogen in the air is $\frac{79}{100}$ of 760; therefore the amount dissolved by 1 litre of water, under these conditions, is $\frac{79}{100} \times 0.02 = 0.0158$ ls. nitrogen, or 100 litres will dissolve $0.0158 \times 100 = 1.58$ ls. nitrogen.

QUESTIONS.

1. The coefficient of solubility of oxygen in water is 0.04, and of nitrogen 0.02. Calculate the composition of the gas dissolved by water freely exposed to an atmosphere containing 25 per cent. oxygen and 75 per cent. nitrogen.

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*2. What is Dalton and Henry's law of solubility of gases? 100 c.c. of water at 10° C. will dissolve 118 c.c. of CO₂; how much CO₂ is dissolved by a litre of water at 10° C. when shaken up with air containing 0.05 per cent. of CO₂?

3. Twenty litres of water are exposed to a gaseous mixture which contains hydrogen 20, oxygen 50, and nitrogen 30 per cent. What weight of each gas will be absorbed, supposing that the total pressure is 720 mm.?

4. A quantity of water is freely exposed to a mixture of equal volumes of oxygen and nitrous oxide. Calculate the percentage composition of the dissolved gases.

CHAPTER XIII

DETERMINATION OF THE MOLECULAR WEIGHTS OF COMPOUNDS. VAPOUR DENSITY DETERMINATIONS, RAOULT'S LAW, &c.

JUST as the equivalent or combining weight of an element is seldom its atomic weight, so also the empirical formula of a compound is very frequently not its molecular formula, and, consequently, does not represent its molecular weight.

It has been already stated in Chapter III. page 13, that the vapour density of a compound is half its molecular weight; if, then, the vapour density of a compound is determined, it furnishes one means of establishing the

weight of the molecule. There are, however, many non-volatile substances to which that method is inapplicable. These bodies may be inorganic or organic, basic, neutral, or acid in their properties.

In the case of bases such as strychnine, quinine, and others of like properties, use has been made of the fact that their chlorides form a double compound with platinum chloride, which is similar in constitution to that formed by ammonium chloride. The amount of platinum in such a compound, taken along with other considerations, such as its basicity, can be used to measure the molecular weight of a substance.

In the case of acids their silver, barium, or lead salts may be employed in a corresponding manner.

There are many bodies to which none of these methods are applicable, and until 1882 their molecular weights could only be ascertained very approximately. In that year F. M. Raoult showed that, if in the same quantity of any solvent equivalent molecular proportions of different compounds are dissolved, a like depression of the freezing-point of the solvent is obtained.

Recently E. Beckmann and, independently, H. W. Wiley have shown that when an alteration takes place in the boiling-point of a liquid, in which another substance is dissolved, the increase in temperature is also a function of the molecular weight of the dissolved body. Both these methods, but especially Raoult's, are now used for the determination of molecular weights.

DETERMINATION OF VAPOUR DENSITIES.

There are three methods at present in use, though not to an equal extent, viz.—those due to Hofmann, Dumas, and Victor and Carl Meyer respectively.

The three methods differ in principle.

In the Hofmann process the volume of vapour, produced by the volatilisation of a known weight of substance, is measured.

Dumas finds first the weight of an unknown quantity of vapour and afterwards ascertains its volume.

V. and C. Meyer measure the volume of air displaced in the volatilisation of a known weight of material.

Hofmann's Method.—The apparatus (fig. 7) consists of a graduated and calibrated vapour-tube A, of about 200 c.c.

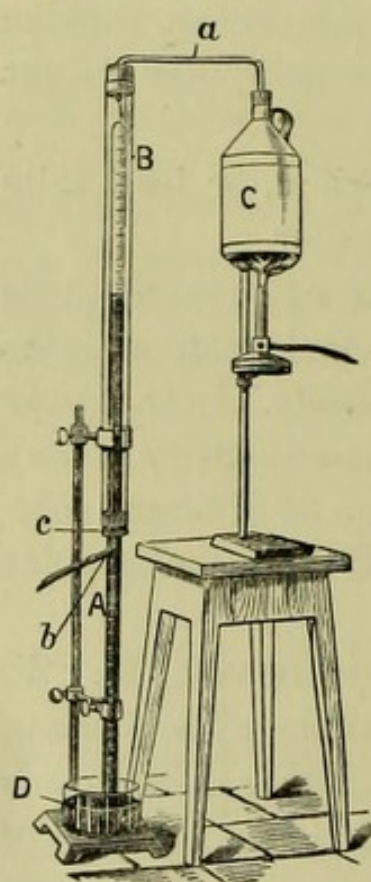


FIG. 7.

capacity, which is surrounded in part by the glass jacket B; this is fixed tightly over it by means of a perforated cork *c*. The jacket is connected with the boiler *c* by a tube *a*, through which steam, or other vapour from a liquid of known boiling-point can be blown, and the lower tube *b* is connected with a condenser. By this means that part of A which is jacketed by B can be kept at a constant temperature. A stoppered tube of known weight, sufficiently small for insertion up the tube A, is also required.

When commencing the operation, the vapour-tube A is carefully filled with mercury, free from bubbles of air, and then inverted over mercury in the trough D. It is next covered with the jacket B, and the stoppered tube after being carefully filled and weighed, is inserted in the mouth of the vapour-tube A. It at once rises to the surface of the mercury, and the diminished pressure is probably sufficient to loosen the stopper, partially vaporise its contents, and depress the mercury: and the vaporisation is completed by the steam or other vapour blown in through *a*. As soon as the tem-

perature is constant, and the mercury no longer descends, the following observations are made :—

The volume of the vapour	= V
The temperature of the vapour	= t
The height of the mercury column in the tube A	= p mm.
The barometric pressure	= P mm.

Besides these data the following are also necessary :—

The weight of substance taken	= W ₁
The weight of a volume of hydrogen, measured under the experimental con- ditions, equal to that of the vapour	= W

$$\text{The vapour density (V.D.) then} = \frac{W_1}{W}.$$

Example 1.—0.338 gram of carbon tetrachloride yielded 109.8 c.c. of vapour at 99.5° C. The barometer stood at 746.9, and the height of the mercury above that in the tray was 283.4 mm. Find the vapour density of the compound.

Here

$$W_1 = 0.338 \text{ gram.}$$

$$\begin{aligned} W &= V \times 0.0000896 \times \frac{P-p}{760} \times \frac{273}{273+t} \\ &= 109.8 \times 0.0000896 \times \frac{746.9-283.4}{760} \times \frac{273}{273+99.5} = 0.004397 \text{ gm.} \end{aligned}$$

The vapour density of the compound—

$$\text{V.D.} = \frac{W_1}{W} = \frac{0.338}{0.004397} = 76.86.$$

There are several corrections which require to be applied if the highest accuracy is desired. These can be ascertained by reference to a larger text-book. There is, however, one which may be mentioned here, viz. that for the expansion of the mercury column by heat, of the mercury columns

of the barometer—this correction also applies to Dumas' and Meyers' methods—and of the vapour tube. The formula given in the chapter on gas analysis (p. 65), for the reduction of the barometer to 0°C ., also serves in this case.

Thus, in the example given, if the mean temperature of the column of mercury is 50°C ., the following correction gives the length at 0°C . :—

$$L_0 = \frac{283.4}{1 + 0.00018 \times 50} = 283.14;$$

and this number must be substituted for the number 283.4 in the preceding calculation.

Dumas' Method.—The principal piece of apparatus required in this method is a thin glass bulb (fig. 8), of about 200–300 cubic centimetres capacity, which has its neck

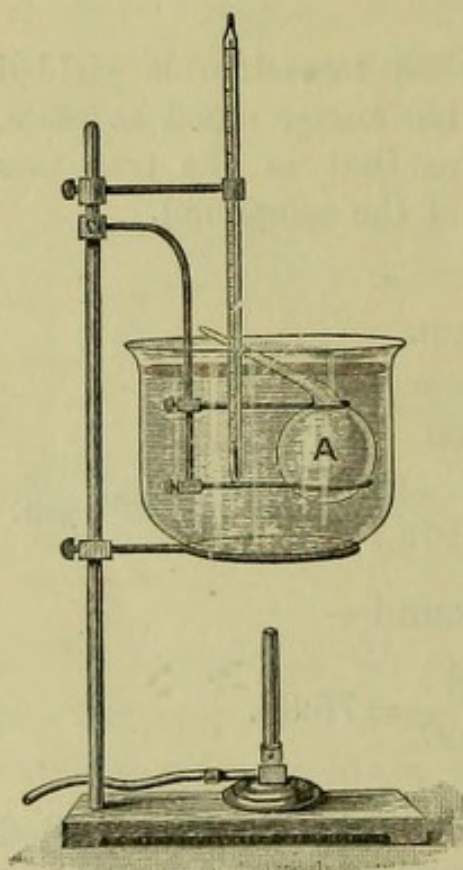


FIG. 8.

drawn out, at the end, into a capillary tube. This bulb is carefully dried and weighed, and 10–20 c.c. of the substance to be tested, are introduced into it in the liquid condition. This may be done by gently warming the bulb so as to expel part of the air and then dipping its neck into some of the liquid, and as the bulb cools this is drawn up into it.

The bulb is then clamped down, by some such arrangement as shown in the figure, in a bath of liquid of considerably higher boiling-point than that of the substance the vapour density of which is required. A thermometer is also fixed in the bath. The bath is next heated to a temperature

20–30° higher than the boiling-point of the substance, which then volatilises and drives all, or most, of the air out of the vessel, which is thus filled with the vapour, the density of which is required.

When the rush of vapour from the bulb ceases, its mouth is carefully sealed by a blowpipe flame. The globe is then carefully dried, cooled, and weighed. The end of the neck is afterwards broken off under mercury or water, which at once, either almost or entirely, fills the bulb. The mercury or water is afterwards measured and the capacity of the globe thus obtained. The following observations are necessary in order to calculate the vapour density of the substance :—

The weight of the bulb	= w_1
The temperature of the bath	= T
Barometric pressure at time of sealing	= P mm.
The apparent weight of the bulb and vapour	= w_2
Barometric pressure at second weighing	= p mm.
Temperature at second weighing	= t
Capacity of the globe in c.c.	= C

Then if the real weight of the vapour = W_1 and the weight of same volume of hydrogen at the temperature and pressure of sealing the globe = W ,

$$\text{V.D.} = \frac{W_1}{W}.$$

Now W_1 , the true weight of the vapour, is equal to $w_2 - w_1$ (which gives the apparent weight) plus the weight of the volume of air displaced by the bulb during weighing. This weight of air is found by the expression

$$C \times 0.001293 \times \frac{p}{760} \times \frac{273}{273 + t}$$

where 0.001293 is the weight in grams of 1 c.c. of normal air ; so that

$$W_1 = w_2 - w_1 + \left(C \times 0.001293 \times \frac{p}{760} \times \frac{273}{273 + t} \right).$$

In many works this weight of air is subtracted from the weight of the bulb (w_1), on the assumption that it is vacuous, the temperature and pressure at the time having, of course, been noted. The method given, however, is more correct, although the ultimate result is the same.

The value of W is given by the expression

$$C \times 0.0000896 \times \frac{P}{760} \times \frac{273}{273 + T}$$

Example 2.—Calculate the vapour density of hexane from the following data:—

Weight of globe, 23.449 grams

Weight of globe and vapour at 15.5° C., 23.720 grams

Temperature of sealing, 110° C.

Capacity of globe, 178 c.c.

According to the formula given.

$$W_1 = 23.720 - 23.449 + \left(178 \times 0.001293 \times \frac{273}{273 + 15.5} \right) \\ = 0.48878 \text{ gram ;}$$

$$W = 178 \times 0.0000896 \times \frac{273}{273 + 110} = 0.011368 \text{ gram ;}$$

$$\therefore \text{V.D.} = \frac{W_1}{W} = \frac{0.48878}{0.011368} = 42.99.$$

In case, as sometimes happens, the whole of the air is not expelled by the vapour, the residual volume is measured ; and this must be subtracted from the volume C in the expressions for both W and W_1 .

Meyers' Method.—The apparatus used in this process consists of a vapour-tube A (fig. 9), which is slightly enlarged at the upper end to receive a cork ; the lower end is blown into an elongated bulb of about 150 c.c. capacity, at the bottom of which are placed a few fragments of asbestos. A capillary tube a , is attached to it near the top, and the whole is fitted, by means of a cork, into a wide glass tube B , which serves both as boiler and steam jacket.

When making a determination the tube A, is first thoroughly dried, then fitted into its outer envelope, corked, and the mouth of the capillary tube immersed in the water of the vessel c. The water, or other liquid, in the envelope B, is then boiled; and this heats the air in the vapour-tube, which expands, and part of it escapes in bubbles from the mouth of *a*. When these cease to come off, thus indicating that the air in A has reached a constant temperature, the graduated tube, D, is filled with water and brought over the mouth of the capillary tube.

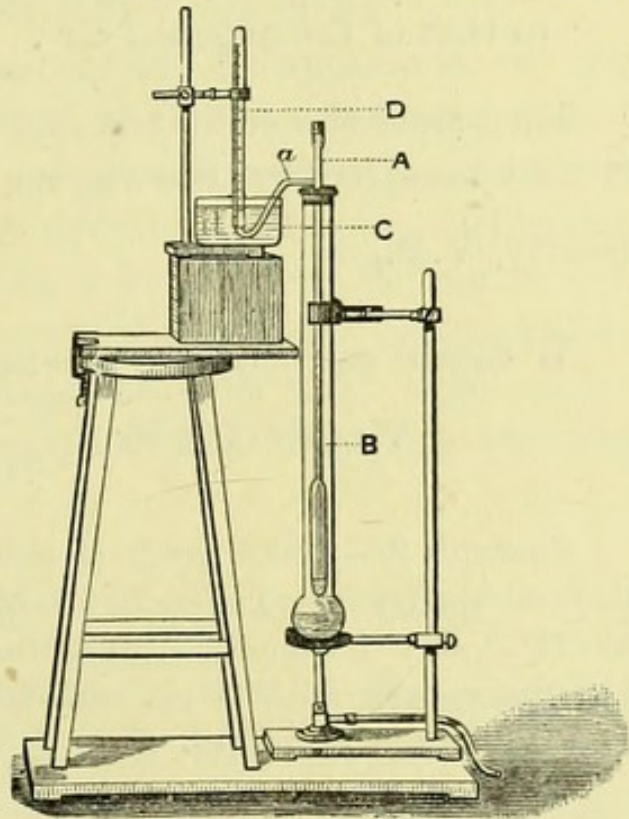


FIG. 9.

A small stoppered tube, such as is used in the Hofmann method, is now filled with the substance to be tested, weighed, and quickly dropped into the tube A, the cork of which is rapidly withdrawn and replaced. The vaporisation of the compound commences at once, and the vapour drives a portion of the air over into the graduated tube D.

When the expulsion of air ceases, the tube D is removed and immersed in a deep vessel of water, so as to obtain the air in it, at a definite temperature. The volume of air is read off when the levels of the water in the tube and in the vessel are coincident.

The following observations are then made :—

Volume of the expelled air	= V
Temperature of measurement of the air	= <i>t</i>
Barometric pressure	= P mm.
Tension of aqueous vapour at <i>t</i> °	= T mm.

Besides these are required the following data :—

The weight of substance taken = W_1

The weight of a volume of hydrogen equivalent
to that of the expelled air = W

Then since the volume of the expelled air is equivalent to that occupied by the vapour in the tube, the vapour

density, V.D., = $\frac{W_1}{W}$.

W can be calculated by the expression,

$$V \times 0.0000896 \times \frac{P-T}{760} \times \frac{273}{273+t}$$

Example 3.—0.1008 gram of chloroform on vaporisation in Meyers' apparatus expelled 22 c.c. of air. Temperature of the air 16.5° C.; barometric pressure, 707.5 mm.; tension of aqueous vapour at 16.5° C. = 13.54 mm. Find the vapour density of the chloroform.

Here

$$W_1 = 0.1008$$

$$W = 22 \times 0.0000896 \times \frac{707.5 - 13.54}{760} \times \frac{273}{273 + 16.5} = 0.001697$$

$$\text{V.D.} = \frac{W_1}{W} = \frac{0.1008}{0.001697} = 59.38.$$

The specific gravity of a vapour may be found by any of the three methods given, if (i.) the weight of the hydrogen in the expressions which give W , is replaced by an equivalent weight of air: or (ii.) the number which represents the vapour density is divided by 14.44, which is the sp. gr. of air referred to hydrogen.

When the vapour density of a substance has been determined by any of the three preceding methods, and its empirical formula is known, it is easy to fix its molecular formula.

For example, while the three hydrocarbons acetylene (C_2H_2), benzene (C_6H_6), and styrolene (C_8H_8) have the

same empirical formula, CH , the vapour density differs in each case, being 13, 39, or 52, according to which hydrocarbon is present; the molecular weight must therefore be settled in accordance with the vapour density.

Also, if in the experimental determination of the vapour density of a compound, the number obtained should differ slightly from that calculated from other data, yet it would still control the molecular formula. Thus for example if the number $50\frac{1}{2}$ were obtained for the vapour density of styrolene, there could be no doubt whatever that its true molecular formula would be that which most nearly gave a molecular weight of 101 ($50\frac{1}{2} \times 2$)—viz. that yielded by $\text{C}_8\text{H}_8 = 104$.

MOLECULAR WEIGHT OF AMMONIUM BASES.

It has already been said that many nitrogen bases form double compounds with platinum chloride, and that the platinum present is a measure of the molecular weight. The following example will illustrate the method of calculation :—

Example 4.—Calculate the molecular weight of quinine from the following datum :—100 grams of the double platinum compound (having the general formula $2\text{RHCl} + \text{PtCl}_4$, where R is a monad radicle) yield 26.85 grams of platinum.

Since in the general formula $2\text{RHCl}, \text{PtCl}_4$ there is one atom of platinum, it will be readily understood that the following proportion will yield the molecular weight of the compound :—

$$\left\{ \begin{array}{l} \text{Weight of Pt} \\ \text{found} \end{array} \right\} : \left\{ \begin{array}{l} \text{the atomic weight} \\ \text{of Pt} \end{array} \right\} :: 100 : \left\{ \begin{array}{l} x, \text{ the molecular} \\ \text{weight of the} \\ \text{compound} \end{array} \right\}$$

$$26.85 \quad : \quad 195 \quad :: 100 : \quad x$$

$$\therefore x = \frac{195 \times 100}{26.85} = 726.2.$$

But by the terms of the question

$$\begin{aligned} 2\text{RHCl}, \text{PtCl}_4 &= 726 \cdot 2 \\ \therefore 2\text{R} &= 726 \cdot 2 - (2\text{HCl}, \text{PtCl}_4) \\ \therefore \text{R} &= \frac{726 \cdot 2 - 410}{2} = 158 \cdot 1; \end{aligned}$$

which is the molecular weight of quinine, on the assumption that it is monobasic.

MOLECULAR WEIGHT OF ACIDS.

The determination of the molecular formula of an acid by analysis of its silver, or other metallic salt, may be illustrated by the following question :—

Example 5.—An acid anhydride containing 47·1 per cent. of carbon, 5·8 per cent. of hydrogen, and 47·1 per cent. of oxygen, yields in contact with water a monobasic acid the silver salt of which contains 64·68 per cent. of metal. What is the molecular formula of the acid ?

The empirical formula of the substance is obtained, in the usual manner, yielding the following ratios :—

$$\begin{aligned} \text{C} &= 47 \cdot 1 \div 12 = 3 \cdot 92 \\ \text{H} &= 5 \cdot 8 \div 1 = 5 \cdot 80 \\ \text{O} &= 47 \cdot 1 \div 16 = 2 \cdot 94 \end{aligned}$$

These ratios lead to the formula $\text{C}_4\text{H}_6\text{O}_3$.

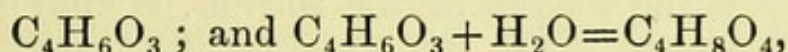
The silver salt of the acid contains 64·68 per cent. of silver ; since it is monobasic the molecule will contain 108 parts of silver ; and consequently the following proportion gives the molecular weight of the salt :—

$$\begin{array}{l} \left\{ \begin{array}{l} \text{The percentage} \\ \text{amount of Ag} \end{array} \right\} : \left\{ \begin{array}{l} \text{the atomic weight} \\ \text{of Ag} \end{array} \right\} :: 100 : \left\{ \begin{array}{l} x, \text{ the molecular} \\ \text{weight of the} \\ \text{salt} \end{array} \right\} \\ 64 \cdot 68 : 108 :: 100 : x \\ x = \frac{108 \times 100}{64 \cdot 68} = 166 \cdot 9. \end{array}$$

But this molecular weight, less the difference between the atomic weights of silver and hydrogen, gives the molecular weight of the acid itself, i.e.

$$166.9 - (108 - 1) = 59.9.$$

Now the organic substance under consideration possesses the formula



which corresponds to a molecular weight 120. But the molecular weight found for the acid is 59.9, and therefore the formula $C_4H_8O_4$ must be halved, so as to bring its molecular weight into conformity with that experimentally determined.

MOLECULAR REDUCTION OF FREEZING-POINTS.

RAOULT'S LAW.

Raoult has shown, by numerous experiments:—

(i.) That all substances, solid, liquid, or gaseous, when dissolved in a liquid which can be solidified, lower the point of solidification.

(ii.) In the case of the solvents examined, the molecular lowering of the freezing-point, due to the solution of different substances, approximates to one of two values, one of which is double the other.

These numbers vary with the nature of the solvent. The higher of these pairs of values is the more common, and is designated the **normal**, and the lower is termed the **abnormal** value. The mean values are for water 47-37 and 18.15, for acetic acid 39 and 18, for benzene 49 and 24, for nitrobenzene 72 and 36, and for ethylene dibromide 117 and 58.

Let A represent the **coefficient of lowering**, i.e. the depression of freezing-point produced by the solution of 1 gram of substance in 100 grams of solvent, M the mole-

cular weight of the substance dissolved; and T the **molecular coefficient of lowering**, i.e., the depression of freezing-point produced by the solution of one gram-molecule of the substance; then $T = MA$.

The method consists in determining the freezing-point of the solvent, first without, and then with the addition of the substance, the molecular weight of which is required. Then if P is the weight of the solvent, P' that of the substance dissolved, and K the experimentally found lowering of the freezing-point, the coefficient of lowering, A , is found by the proportion :

$$\left. \begin{array}{l} P' : 1 \\ 100 : P \end{array} \right\} :: K : A$$

$$\therefore A = K \frac{P}{P' \times 100}$$

The value of T is found for each solvent, by noting the depression of freezing-point produced by substances of known molecular weight. If then the value of T is known, and that of A is experimentally found for a substance of unknown molecular weight; the molecular weight, $M = \frac{T}{A}$.

Example 6.—12.616 grams of dextrose were dissolved in 92.25 grams of water. The freezing-point of the water was depressed 1.45°C . $T = 19$. Find the molecular weight of dextrose.

By the formula given, $M = \frac{T}{A}$; and

$$A = K \frac{P}{P' \times 100} = 1.45 \times \frac{92.25}{12.616 \times 100} = 0.106$$

$$\therefore M = \frac{19}{0.106} = 179.$$

This number corresponds sufficiently closely to that yielded by a body with the molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$.

MOLECULAR INCREASE OF BOILING-POINT.

The formulæ which serve for the calculations required in the determination of molecular weights by Raoult's method, will also serve for the calculation of those obtained by Beckmann and Wiley's process, if A is taken as the coefficient of rise, and T as the molecular coefficient of rise of temperature.

This method however is not so useful as Raoult's, because the value of T is a much smaller number, and errors of experiment are consequently more serious in their effects.

QUESTIONS.

1. Calculate the vapour density of a substance by Hofmann's method. Weight of substance used, 0.1366 gram. Volume of vapour, 101.9 c.c. Temperature of vapour, 140° C. Height of mercury column, 503.5 mm. Barometer, 730.9 mm. at temperature of 24.7° C.

The coefficient of expansion of mercury is 0.00018.

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2. Find the vapour density of the following bodies, from the data given by Thorpe :—

—	(i.)	(ii.)	(iii.)	(iv.)
Weight of liquid in grams	0.1322	0.0512	0.0769	0.2018
Volume in c.c.	84.2	80.78	69.77	106.7
Temperature in degrees C.	109.1	99.6	99.60	122.5
Barometer in millimetres .	762.2	749.1	749	744.2
Height of column of mercury in millimetres . .	393	482	493.4	240.3

3. Describe Hofmann's process for determining vapour densities, indicating its advantages or otherwise, over the other methods in use. Calculate a V.D. (air = 1) made according to the above method from the following :—

Weight of substance = 0.0518 gram. Barometer = 752.5 mm.

Volume of vapour = 25.5 c.c. Height of column of mercury = 484 mm. Temperature of vapour = 100° C. Temperature of air = 15° C.

Coefficient of expansion of mercury for 1° C. = 0.00018.

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4. Find the vapour density by Dumas' method of the following bodies, from the data given:—

—	(i.)	(ii.)	(iii.)	(iv.)
Weight of bulb in grams	—	—	19 8945	36·6709
Weight of bulb and vapour in grams	—	—	20 3015	37·1615
Difference between weight of air and vapour	0·2512	0·2897	—	—
Barometer at sealing, mm.	—	—	758·1	{ 763·9 at 18° C.
Temperature of sealing, C.	259°	259°	205°	98·1°
Barometer at second weighing, mm.	—	—	751	{ 764·2 at 17° C.
Temperature of second weighing, C.	9°	12°	15°	20·8°
Volume of globe in c.c.	99·8	115·3	112	178
Residual air in c.c.	0·6	1·3	2	—

5. Required the molecular weight, and the vapour density (air = 1) of thallium chloride from the following data:—

Volume of bulb = 337 cubic centimetres. Temperature = 828° C. Bar. = 760 mm. Weight of residual chloride of thallium = 0·8899 gram. Tl = 203·6. Cl = 35·37.

S. & A. D.

6. Calculate the vapour densities of the following bodies, from data obtained by V. Meyer's method:—

—	(i.)	(ii.)	(iii.)
Weight of substance taken in grams	0·198	0·0585	0·0715
Temperature of the water in degrees C.	13·5°	16°	20°
Height of the barometer in mm. reduced	766·5	732·7	773·5
Tension of aqueous vapour in mm.	10·35	—	17·391
Volume of air obtained in c.c.	38·85	9·8	23
	S. & A. D.	S. & A. D.	—

7. Calculate the molecular formula and vapour density of a hydrocarbon from the following numbers:—

(i.) Combustion analysis. 0·1237 gram of substance taken gave 0·4282 gram CO₂, and 0·0626 gram H₂O.

(ii.) Vapour density by Victor Meyer's method. Barometer 718·3 mm. Tension of vapour 11·91 mm. Temperature of air in tube 14° C.

Weight of substance taken 0·16175 gram. Volume of air displaced 16·2 c.c. S. & A. D.

8. 0.2705 gram substance gave 0.9305 gram CO_2 and 0.1487 gram H_2O . A vapour density determination by V. Meyer's method gave:—Weight of substance, 0.0846 gram. Temperature of water 23°C . Barometer (reduced) 749.5 mm. Tension of aqueous vapour at 23°C . 20.9 mm. Volume of air obtained 9.15 c.c. Required the molecular formula of the body.
S. & A. D.

9. Calculate the molecular formula and vapour density of a hydrocarbon from the following numbers:—

(i.) Combustion analysis. Substance taken 0.1310 gram $\text{CO}_2 = 0.4505$. $\text{H}_2\text{O} = 0.0705$.

ii.) Vapour density, by Meyers' method. Substance taken 0.1105 gram.

Temp. 17.5°C . Barometer 754.1 mm.

Volume of air 13.2 c.c. Tension of aqueous vapour 14.882 mm.
S. & A. D.

10. A hydrocarbon which has the vapour density 50 gave the following numbers on analysis:—

0.3500 gram gave 1.0754 grams CO_2 , and 0.5050 gram H_2O . Calculate the formula of the body.
S. & A. D.

11. Caffeine is a base, and, like ammonia, its hydrochloride forms with platonic chloride a double chloride. This contains 24.6 per cent. of metal. What is the molecular weight of caffeine?
S. & A. D.

* 12. Calculate the formula of the base whose platinum chloride gives the following analyses:—

(i.) 0.3435 gram salt gave 11.8 c.c. nitrogen at 16°C . and 757 mm. pressure.

(ii.) 0.410 gram gave 0.458 gram CO_2 , and 0.1555 gram H_2O .

(iii.) 0.383 gram gave 0.1045 gram Pt, and 0.4612 gram AgCl .

13. Calculate the molecular weight of strychnine when 0.4515 gram of its platino-chloride yields 0.0815 gram of platinum.

14. The platino-chloride of cinchonine contains 27.61 per cent. of platinum. Calculate its molecular weight on the assumption that it is dibasic.

15. 0.571 gram of a monobasic acid gave on combustion 1.4362 grams of carbon dioxide and 0.2547 gram of water; 0.2143 gram of the silver salt of this acid gave 0.101 gram of

silver. Give the formula and the percentage composition of the acid. S. & A. D.

16. The silver salt of a certain organic acid contains 63.1 per cent. of silver. Calculate the molecular weight of the acid, on the assumption that it is tribasic. B. Sc. Lond.

17. Determine the molecular weight of a dibasic acid from the following data :—

Crucible + lid + Ag salt	16.7935
Crucible + lid + Ag	16.5775
Crucible + lid	16.2625

18. Determine the molecular weight of a dibasic acid given that :—

1.233 grams of the barium salt, after heating in a crucible with concentrated sulphuric acid, gave 1.131 grams of barium sulphate.

19. Determine the coefficient of depression and the molecular weights of the following substances from the data given : (i. to vi.) by Brown and Morris, (vii.) by S. & A. D.

	(i.) Dextrose	(ii.) Cane Sugar	(iii.) Mannitol	(iv.) Maltose	(v.) Arabinose	(vi.) Raffinose	(vii.) Anhydrous Magnesium Sulphate
Weight of substance taken, in grams	8.3704	13.052	7.5382	10.499	4.1355	8.2225	6
Weight of water taken, in grams	94.86	91.98	95.09	93.68	97.45	94.51	100
Corrected depression of freezing-point, in degrees Centigrade	0.94°	0.835°	0.835°	0.665°	0.54°	0.31°	0.958°
Value of T	19	19	19	19	19	19	37

20. Taking 56.7 grams of acetic acid freezing at 16.52°, and taking methyl acetate in successive quantities as follows :— (i.) 0.0725 gram, (ii.) 0.0970 gram, (iii.) 0.0821 gram, (iv.) 0.1192 gram, the freezing-points after each addition are observed to be (i.) 16.452°, (ii.) 16.363°, (iii.) 16.282°, (iv.) 16.177° respectively. What is the molecular weight of methyl acetate found from each observation ? (T = 39.) S. & A. D.

21. Determine the coefficient of rise, and the molecular

weights of the following bodies, from data given by H. W. Wiley. ($T = 8\ 968$.)

—	(i.) Potassium Bromide	(ii.) Potassium Iodide	(iii.) Potassium Nitrate	(iv.) Potassium Dichro- mate	(v.) Sodium Nitrate	(vi.) Oxalic Acid
Weight of sub- stance taken, in grams	6	9	6	18	6	6
Weight of water taken, in grams	150	150	150	150	150	150
Rise of tempera- ture, in degrees Centigrade	0.29°	0.33°	0.33°	0.38°	0.42°	0.20°

22. The solution of 1.065 grams iodine in 30.14 grams ether produced a rise of the boiling-point of 0.296° C. Find the molecular weight of iodine if $T = 21.04$.

CHAPTER XIV.

CALORIFIC POWER AND CALORIFIC INTENSITY.

CALORIFIC POWER.

THE calorific power of a substance is a term which expresses its total heat-evolving power during combustion. This power is measured by the number of grams of water raised from 0° C. to 1° C. by the combustion, in oxygen, of 1 gram of the substance. This definition uses the gram as unit of weight, and Centigrade degrees; but the pound or ounce and Fahrenheit degrees might be employed if desired.

It is not within the scope of this work to describe the apparatus and methods of ascertaining the calorific power of a substance, these can be found by referring to works on physics. It is convenient however to append the calorific power of a few substances, i.e. the number of units of heat evolved by the combustion of 1 gram of them.

Hydrogen to water	34,462	Turpentine	10,852
Carbon	8,080	Anthracite	8,000
Sulphur	2,220	Alcohol	7,183
Phosphorus	5,747	Ether	9,027
Carbon monoxide	2,403	Carbon bisulphide	3,401
Cyanogen	5,195	Zinc	1,301
Marsh gas	13,063	Iron	1,576
Olefiant gas	11,858	Tin	1,144
Benzene	9,915	Antimony	961
Petroleum	11,400	Silicon	7,830

Whether burnt in oxygen or air the calorific power of a body is an invariable quantity ; but, where the body is a compound, this quantity is not necessarily the sum of the calorific powers of its elements. It is in general less than the calculated amount, olefiant gas being an exception to this rule. This is accounted for by the fact that a certain amount of energy must be considered as being utilised in undoing the work of combination.

It also is customary to assume that, in a compound containing carbon, hydrogen, and oxygen, only the **excess of, or available** hydrogen, produces heat ; i.e. the oxygen in the compound is looked upon as being already combined with the hydrogen : if there is more than enough hydrogen to satisfy it, the excess is available for producing thermic effect. If there is not enough hydrogen, then a certain proportion of the carbon is also combined, and only the residue will produce heating effect.

As an example illustrating this point, take the following :—

Example 1.—Calculate the calorific power of dry wood, from the following percentage composition :—

Carbon	51.00
Hydrogen	6.24
Oxygen	41.50
Nitrogen	1.00

99.74

By definition its calorific power is the amount of heat produced by the combustion of 1 gram. Now 1 gram of wood contains 0.415 gram of oxygen which combines with 0.0518 gram of hydrogen to form water.

The available hydrogen therefore = $0.0624 - 0.0518 = 0.0106$ gram. Now 1 gram of hydrogen yields 34,462 heat units; and 1 gram of carbon gives 8,080 heat units; therefore 1 gram of wood has the following calorific power:—

Heat evolved by available	
hydrogen	$= 0.0106 \times 34462 = 365.29$
Heat evolved by the carbon	$= 0.51 \times 8080 = 4120.80$
	Total calorific power = 4486.09

CALORIFIC INTENSITY.

The calorific intensity of a body must be clearly distinguished from its calorific power. The latter is the amount of heat given off during combustion; while the former is the theoretical temperature to which the products of combustion can be raised from 0° C.

The calorific intensity will vary according as the combustion takes place in oxygen, or air. The rule for calculating the calorific intensity of a substance may be stated thus:—

Divide its calorific power by the sum of the weights of the products of combustion and of the residual substances multiplied by their respective specific heats.

Example 2.—Calculate the calorific intensity of hydrogen when burnt in oxygen and air respectively. Assume the initial temperature to be 0° C. and the pressure 760 mm.

The calorific power of hydrogen is 34,462. This number includes the amount of heat given out by the water vapour (produced during the combustion of the hydrogen)

during its reduction from steam at 100° C. to water at 100° C., and, since the latent heat of steam is 537, that number of heat units per gram of water will be evolved. Now since 1 gram of hydrogen yields 9 grams of water, and as in calculating its calorific intensity the steam is no longer considered as condensed to water, the number 34,462 must be reduced by $537 \times 9 = 4833$.

Again, there is more heat, per degree, required to raise the water produced from 0° – 100° C., than is required afterwards to raise it from 100° – t° C., because the specific heat of water (page 52) is greater than that of steam, in the proportion of 1 to 0.4805. The difference between these values, from 0° – 100° C., must therefore be deducted from the 34,462 heat units. Since there are 9 grams of the product, water, this difference equals

$$(1 - 0.4805)100 \times 9 = 467.55.$$

The number of heat units remaining is therefore :

$$34462 - (4833 + 467.55) = 29161.45.$$

This number divided by 9×0.4805 gives the theoretical temperature of each gram of product ; i.e.

$$\left. \begin{array}{l} \text{Calorific intensity of hy-} \\ \text{drogen burnt in oxygen} \end{array} \right\} = \frac{29161.45}{9 \times 0.4805} = 6743.5^{\circ} \text{ C.}$$

If the hydrogen had been burnt in air, there would have been not only the steam to raise to a high temperature, but also the residual nitrogen, of specific heat 0.244. Since there are in the air nearly 3.35 grams by weight of nitrogen for every gram of oxygen ; and 8 grams of oxygen are required to burn 1 gram of hydrogen ; there will be $8 \times 3.35 = 26.80$ grams of nitrogen to be heated along with the steam. Introducing these figures the calorific intensity or theoretical temperature, T , of hydrogen burnt in dry air becomes—

$$\frac{29161.45}{(9 \times 0.4805) + (26.8 \times 0.244)} = 2659.8^{\circ} \text{ C.}$$

To calculate the calorific intensity of hydrogen the following numbers are consequently necessary :—

Total heat of combustion of unit weight of hydrogen	= 34462
Deduction for heat rendered latent in transforming water into steam, per unit of hydrogen	= 537×9
Specific heat of steam	= 0.4805
Deduction for difference between specific heat of water and steam	= $(1 - 0.4805)100 \times 9$
Specific heat of nitrogen	= 0.244
Weight of nitrogen per unit of oxygen	= 3.35

and the calorific intensity, T, for hydrogen when burnt in air is :—

$$T = \frac{34462 - \{(1 - 0.4805)100\} + 537\} 9}{(9 \times 0.4805) + (26.8 \times 0.244)} = 2659.8^\circ \text{C.}$$

The calculation of the calorific intensity of hydrogen, is a good example of the method employed in such determinations. If the products of combustion are all gases the calculation is much simpler, since the corrections rendered necessary by the latent heat of the vapours, and varying specific heats of the same substance in the liquid and gaseous form, are eliminated.

The calculated calorific intensity is after all only a theoretical quantity. It is based on the assumption that the specific heats of the products of combustion and residual substances are constant at all temperatures ; this is not true, since the specific heats of gases generally increase as the temperature rises. The dissociation of the compound gases at a high temperature also limits it.

In practice too there is also a considerable amount of

heat lost from such causes as radiation, excess of air, or imperfect combustion; and the temperature will also depend in part on the physical condition, freedom from moisture, inert substances present, and the products of combustion of the substance under consideration.

On the other hand it will be noticed that in the above calculations no account is taken of any heat possessed by the fuel and air before combustion; this of course would increase the ultimate temperature.

It should be noted that all the calculations, both in calorific power and calorific intensity, are made on the assumption that the pressure remains constant at 760 mm.

QUESTIONS.

1. Calculate the amount of water which can be raised 50° C. by the combustion of 3 grams of (i.) carbon, (ii.) carbon monoxide, (iii.) phosphorus, and (iv.) silicon respectively.

2. Taking their calorific powers as the sum of those of their constituents, calculate the calorific power of (i.) ethylene, (ii.) marsh gas, and (iii.) acetylene.

3. Calculate the calorific powers of the following substances from their percentage composition:—

—	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Ash
(i.) Beech wood . . .	50.08	6.23	41.61	0.93	—	—
(ii.) Oak wood . . .	50.64	6.03	42.05	1.28	—	—
(iii.) Welsh coal . . .	80.61	6.01	1.50	1.44	3.5	6.94
(iv.) Newcastle Hartley coal . . .	81.81	5.50	2.58	1.28	1.69	7.14
(v.) Wigan cannel . . .	79.23	6.08	7.24	1.18	1.43	4.84
(vi.) Derbyshire coal average . . .	79.68	4.94	10.28	1.41	1.01	2.65

4. Calculate the calorific intensity of (i.) carbon monoxide and (ii.) marsh gas when burnt in oxygen.¹

5. Calculate the calorific intensity of (i.) marsh gas, (ii.) benzene, (iii.) alcohol, (iv.) ether, and (v.) turpentine when burnt in air.

¹ Specific heat of water = 1, nitrogen = 0.2440, carbon dioxide = 0.2164, steam = 0.4805.

ANSWERS.

CHAPTER I.

1. 1,575 mm.
500 "
5 "
2. 10,005·6 ms.
0·15 "
5 "
3. 3,750 sq. cm.
4. 1,500,000 c.c.
5. 1,050,000 sq. cm.
9,500 "
6. 1·05 sq. ms.
19·6578 "
2·753002 "
7. 750,000 sq. mm.
600 "
100,500 "
8. 0·152394 m. 152·394 mm.
0·380987 " 380·987 "
2·37744 ms. 2,377·44 "
9. 81·2875 sq. dcm.
10. 200 gms.
18 "
11. 2,100 cgms.
190 "
15,650 "
12. 100,000 c.c.
500 "
15,000 "
500,000 "
13. 19·635 sq. cm.
44·178 "
346·36 "
14. 1,767·15 gms.
15. 4·4 pints
16. 9·0869 ls.
17. 1·6 oz. per gallon

18. 12·5 gms. per litre
19. 9·72 gms.
20. 4·536 kilos. 4536 gms.
21. 123·458 ounces
22. 250 gals.
23. 721·47 g als. 3,235·43 ls.
24. 50·967 ls.
25. 220·1 gals.
26. The diameter = 3 cm.

CHAPTER II.

1. 216° R. -4° R. 15·6° R.
74·6° R. -5·7° R.
-14·2° R. -22·6° R.
2. 59° F. 14° F. -49° F.
527° F. -13° F. 19·4° F.
3. -20° C. -0·5° C.
-17·7° C. 143·8° C.
-25° C. 9·5° C. 240° C.

CHAPTER III.

1. 279·6 gms.
2. 42·50 "
3. 10·5 "
4. 1·5
5. 0·826
6. 0·657
7. 0·644
8. 1·505
9. 0·826
10. 1·183
11. 1·0042
12. 2·707
13. 8·530
14. 11·296

15. 0.831
 16. 0.888
 17. 2.615
 18. 11.1

CHAPTER IV.

1. Potassium	28.68	
Hydrogen .	0.73	
Sulphur .	23.57	
Oxygen .	47.06	
	<hr/>	
	100.00	
	<hr/>	
2. Sodium .	16.08	
Carbon .	4.20	
Oxygen .	72.73	
Hydrogen .	6.99	
	<hr/>	
	100.00	
	<hr/>	
3. Calcium .	39.68	
Phosphorus .	18.45	
Oxygen .	38.10	
Fluorine .	3.77	
	<hr/>	
	100.00	
	<hr/>	
4. Nitrogen .	25.93	
Oxygen .	74.07	
	<hr/>	
	100.00	
	<hr/>	
5. Calcium .	33.20	
Silicon .	23.24	
Oxygen .	43.15	
Hydrogen .	0.41	
	<hr/>	
	100.00	
	<hr/>	
6. Hydrogen .	1.77	
Calcium .	17.66	
Silicon .	24.72	
Oxygen .	49.45	
Potassium .	4.30	
Fluorine .	2.10	
	<hr/>	
	100.00	
	<hr/>	

7. Copper .	43.65	
Phosphorus .	14.32	
Oxygen .	40.65	
Hydrogen .	1.38	
	<hr/>	
	100.00	
	<hr/>	
8. Chromium .	55.32	
Oxygen .	42.55	
Hydrogen .	2.13	
	<hr/>	
	100.00	
	<hr/>	
9. Aluminium .	5.70	
Potassium .	8.23	
Sulphur .	13.50	
Oxygen .	67.51	
Hydrogen .	5.06	
	<hr/>	
	100.00	
	<hr/>	
10. Chromium .	9.53	
Oxygen .	14.65	
Lead .	75.82	
	<hr/>	
	100.00	
	<hr/>	
11. Carbon .	77.42	
Hydrogen .	7.53	
Nitrogen .	15.05	
	<hr/>	
	100.00	
	<hr/>	
12. Carbon .	33.80	
Hydrogen .	1.41	
Nitrogen .	19.72	
Oxygen .	45.07	
	<hr/>	
	100.00	
	<hr/>	
13. Calcium .	38.83	
Phosphorus .	18.06	
Oxygen .	41.94	
Carbon .	1.16	
	<hr/>	
	99.99	
	<hr/>	

CHAPTER V.

1. Na_2HPO_3 .
2. CH_2O .
3. $\text{CH}_4\text{N}_2\text{S}$ (NH_4CNS).
4. AgNO_2 .
5. $\text{C}_2\text{H}_4\text{O}$.
6. C_7H_8 .
7. $\text{C}_4\text{H}_5\text{N}_2\text{O}$.
8. LiKSO_4 .
9. CuHAsO_3 .
10. $\text{Na}_2\text{H}_2\text{Cl}_4$.
11. PbB_2O_4 , H_2O .
12. $\text{Ca}_3\text{P}_2\text{O}_8$.
13. Na_3SbS_4 , $9\text{H}_2\text{O}$.
14. CaO , 2SiO_2 , $2\text{H}_2\text{O}$.
15. $3(\text{MgFe}''\text{O})$, 4SiO_2 , H_2O .
16. $(\text{CaMg})\text{CO}_3$.
17. 5CaO , $2(\text{AlFe}'''\text{O})_2$, 6SiO_2 .
18. $5(\text{NaK})_2\text{O}$, $6(\text{Fe}''\text{MnCaMg})\text{O}$,
 $6(\text{Fe}'''\text{O})_2$, 28SiO_2 .
19. $2(\text{AlFe}'''\text{O})_2$, $(\text{NaKLi})_2\text{O}$,
 10SiO_2 .
20. Na_2O , 2BeO , 6SiO_2 , H_2O .
21. Na_2O , Al_2O_3 , 6SiO_2 .

CHAPTER VI.

1. 126.25 c.c. 113.75 c.c.
109.58 c.c.
2. 322.81 vols.
3. 24.683 ls.
4. 276.49 ls.
5. 42.6° C.
6. 11.384 ls.
7. 229.01 ls.
8. 0.0714, or 71.4 ls. more and
0.0625, or 62.5 ls. less resp.
9. 256.6 vols.
10. 52.63 mm.
11. -26.62° C.
12. -71.9° C.
13. 1252.74 mm.
14. 879° C.
15. 650.6.

CHAPTER VII.

1. 2.232 ls.
2. 4.96 ls.
3. 19.936 gms.
4. 6,200 c.c. oxygen ;
12,400 c.c. hydrogen.

5. 94.11 gms.
6. 27.7 gms.
7. 19.13 gms. CO_2
11.73 gms. H_2O .
8. (i.) 83.70 ls.
(ii.) 139.50 ls.
9. 1,569.9 c.c.
10. 1.43 ls.
11. 285.93 ls.
12. (i.) 10 mgms.
(ii.) 20 mgms.
13. 735 tons.
14. 538.01 gms.
15. 119.657 tons.
16. 6.221 gms.
17. 2.388 gms.
1,000 c.c.
18. 131.25 gms. HNO_3 .
327.06 gms. HCl .
19. 44 gms. CO_2 formed ;
16 gms. O remaining.
20. 0.0009344 kilo. Zn.
0.001408 kilo. H_2SO_4 .
18.95 c.c. @ 735 mm., or
0.5170 of the volume.
21. 436.25 c.c.
22. 11.899 gms. air.
2.024 ls. CO_2 .
4.049 ls. H_2O (steam).
15.233 ls. N.
23. 59.62 gms.
78.92 ls.
24. 160 ls. air.
33.6 ls. CO_2 .
25. 1,184.67 c.c.
706.39 c.c.
26. 12.9 gms.
27. 694.46 c.c.
28. 3.550 ls.
29. 52.5 gms. 45.204 ls.
30. 2.779 ls.
31. 11.836 tons.
32. 7.168 gms.
33. 46.958 gms.
34. 39.183 gms.
3.9183 gms. less.

CHAPTER VIII.

1. 79.5 ls.
2. 28 vols. H., 79 vols. N., and
107 vols. of gas remaining.

3. (i.) 1,000 c.c.
(ii.) 1,500 c.c.
4. (CH₄) 4 ls. O required,
2 ls. CO₂ formed.
(C₂H₄) 6 ls. O required;
4 ls. CO₂ formed.
(C₂H₆) 7 ls. O required;
4 ls. CO₂ formed.
5. The gas was carbon monoxide.
6. 22.4 ls. CO₂. 11.2 ls. N.
7. 400 c.c. H.
8. (C₂H₄) 1,500 vols. O required;
1,000 vols. CO₂ formed.
(C₂H₂) 1,250 vols. O required;
1,000 vols. CO₂ formed.
(C₂N₂) 1,000 vols. O required;
1,000 vols. CO₂ formed.
(CH₄) 1,000 vols. O required;
500 vols. CO₂ formed.
9. 9.52 ls.
10. (i.) 10 ls. (ii.) 10 ls.
(iii.) 671.88 cc.
11. 83.3 c.c.
12. 690.47 ls.

CHAPTER IX.

1. 36.295 per cent. H₂O.
2. 60.492 per cent. Cl.
3. 5.732 per cent. Al.
4. 45.476 per cent. H₂O.
5. 41.425 per cent. CO₂.
6. 0.929 per cent. Fe₂O₃.
7. 48.176 per cent. K.
8. 26.288 per cent. PbO.
9. 6.616 per cent. Na₂O.
10. CaO 1.3169
BaO 1.1831
-
- 2.5000
-
11. 93.816 per cent. C.
6.109 per cent. H.
-
- 99.925
-
12. 88.20 per cent. C.
11.80 per cent. H.
-
- 100.00
-

13. CH₂O.
14. 69.387 per cent. Cl.
15. 43.985 per cent. NaCl.
56.015 per cent. KCl.
-
- 100.000
-
16. 3.728 per cent. S.
17. 76.978 per cent. AgBr.
18. 5.204 per cent. Pb.
19. 3.7759 per cent. Fe₂O₃.
23.7378 per cent. Al₂O₃.
20. 36.255 c.c. = 3.6255 per cent.
CO₂.
21. 61.155 per cent. NO₃.
22. 4.023 gms.
23. 0.1648 gms.
24. 40.8 gms.
25. 32.359 per cent. Cl.
26. 32.849 per cent. Na₂O.
27. 34.536 per cent. Sb.
28. 99.546 per cent. K₂Cr₂O₇.
29. 36.801 per cent. B₂O₃.
30. 33.518 per cent. N.

CHAPTER X.

1. (i.) 5.394. (ii.) 5.859.
(iii.) 5.27.
2. The atomic heat = 4.392 at
20° - 1040° C. and = 5.507
at 985° C. The former
number would lead to 18
as the atomic weight of
carbon.
3. (i.) 6.384. (ii.) 6.520.
(iii.) 6.474.
4. (i.) 67.01. (ii.) 77.10.
(iii.) 113.87. (iv.) 118.30.
(v.) 196.92. (vi.) 15.68.
5. (i.) 0.9428. (ii.) 0.170.
(iii.) 0.1067. (iv.) 0.079.
(v.) 0.0837.
6. 52.059.
7. 107.959.
8. 40.05.
9. 72.69.
10. 69.82.
11. 12.06.
12. (i.) 48.06. (ii.) 47.99.
(iii.) 47.93. (Thorpe.)

13. (i.) 26.975 (ii.) 27.06.
 14. 15.95.
 15. 28.347. (Thorpe.)
 16. 140.221.
 17. 149.995.
 18. 113.688.
 19. 87.367.
 20. (i.) Au : KBr = 196.90.
 (ii.) Au : Ag = 196.92.
 (iii.) Au : AgBr = 196.92.
 21. 58.711.
 22. 51.976.
 23. 27.46.
 24. 55.43.
 25. (i.) 136.921.
 (ii.) 136.491.
 26. 208.923. (Classen.)
 27. Atomic weight = 200.17.

Molecular weight is the same as the atomic weight.

CHAPTER XI.

1. 9.38 gms.
 Partial pressure of N and O, each 370.417 mm.
 2. 981.50 gms.
 3. 49.48.
 4. 131.26. (Bunsen.)
 5. (i.) N 79.073 ; O 20.927, per cent. (ii.) N 79.081 ; O 20.919, per cent. (iii.) N 79.108 ; O 20.892, per cent. (Bunsen.)
 6. N 83.24 ; O 13.80 ; CO₂ 2.96, per cent.
 7. Butane, C₄H₁₀. 10.399, 296.35, 260.19, 218.69.
 8. N 79.269 ; O 20.731, per cent.
 9. 21.26, 218.71, 180.43, 167.15.
 10. (i.) (ii.)
 per cent. per cent.
 CO₂ 0.15 0.17
 C₂H₄ 4.96 5.01
 C₆H₆ 1.65 1.43
 O 5.72 5.55
 CO 6.17 6.27

11. H	14.43
N	55.77
CO	17.49
CO ₂	12.28
	<hr/>
	99.97
	<hr/>

CHAPTER XII.

1. O 40 ; N 60, per cent.
 2. 0.59 c.c.
 3. H 0.00655 gms. O 0.5587 gms. N 0.1451 gms.
 4. O 3.055 ; N 96.945, per cent.

CHAPTER XIII.

1. 75.98.
 2. (i.) Ethidene chloride, 49.29 ;
 (ii.) Propionitrite, 27.48 ;
 (iii.) Heptane, 49.94 ;
 (iv.) Picoline, 46.77.¹
 (Thorpe.)
 3. 6.09.
 4. (i.) Myristuol, 82.29.
 (ii.) Menthol, 82.20.
 (iii.) Vanadium tetrachloride, 96.20.
 (iv.) Chloroform, 59.97.
 5. V.D. 8.24 (air = 1). TiCl = 238.97.
 6. (i.) 59.99. (ii.) 73.15.
 (iii.) 37.42.
 7. V.D. = 126. C₂₀H₁₄.
 8. V.D. = 116.7. C₁₈H₁₂.
 9. V.D. = 102.2. C₁₆H₁₂.
 10. C₇H₁₆.
 11. 191.3.
 12. Mol. wgt. = 154.17. C₉H₁₄NO = 152.
 13. 335.13. C₂₁H₂₂N₂O₂ = 334.
 14. 296.13. C₂₀H₂₄N₂O = 308.
 15. C₇H₆O₂. C = 68.59
 H = 4.96
 O = 26.45

 100.00

¹ There is evidently either an error in the data given or in the answer. Calculated from data given the answer is 46.12.

16. 192.47.
 17. 150.11.
 18. 119.00.
 19. Coef. of depression :—
 (i.) 0.1065. (ii.) 0.0588.
 (iii.) 0.1052. (iv.) 0.0596.
 (v.) 0.1272. (vi.) 0.0356.
 (vii.) 0.1596.
 Mol. wgt. :—(i.) 178.3.
 (ii.) 322.8. (iii.) 180.3.
 (iv.) 310.6. (v.) 149.3.
 (vi.) 533.8. (vii.) 231.8.
 20. (i.) 73.33. (ii.) 74.26.
 (iii.) 72.71. (iv.) 74.35.
 21. Coef. of rise :—(i.) 0.0725.
 (ii.) 0.055. (iii.) 0.0825.
 (iv.) 0.0316. (v.) 0.105.
 (vi.) 0.05.
- Mol. wgt. :—(i.) 123.6.
 (ii.) 163.0. (iii.) 108.7.
 (iv.) 283.2. (v.) 85.4.
 (vi.) 179.3. (Wiley.)
22. 251.1.

CHAPTER XIV.

1. (i.) 484.8. (ii.) 144.1.
 (iii.) 344.8. (iv.) 469.8.
 2. (i.) 11,848. (ii.) 14,675.
 (iii.) 10,109.
 3. (i.) 4,401. (ii.) 4,360.
 (iii.) 8,597. (iv.) 8,432.
 (v.) 8,216. (vi.) 7,720.
 4. (i.) 7,066. (ii.) 7,002.
 5. (i.) 2,373. (ii.) 2,674.
 (iii.) 2,418. (iv.) 2,581.
 (v.) 2,621.

APPENDIX.

A MORE general method of calculating the results of the indirect determinations, of which example 4, page 43, is a type, is by means of simultaneous equations. Thus, taking the example mentioned :

Let x = the amount of KCl (mol. wgt. 74.5) in the mixed chlorides,
 and y = " " NaCl (mol. wgt. 58.5); then since there are
 1.449 gms. of the chlorides—

$$(i.) \quad x + y = 1.449.$$

These chlorides contain 0.7739 gm. Cl; therefore

$$(ii.) \quad \frac{35.5}{74.5}x + \frac{35.5}{58.5}y = 0.7739.$$

Multiplying equation (i.) by $\frac{35.5}{74.5}$ and subtracting equation (ii.) from the result, we obtain

$$y \left(\frac{35.5}{74.5} - \frac{35.5}{58.5} \right) \left(\frac{35.5}{74.5} \times 1.449 \right) - 0.7739;$$

$$\therefore y = 0.6401 \text{ gm. NaCl.}$$

The amount of KCl = $1.449 - 0.6401 = 0.8089$ gm. From these numbers the percentage composition can then be calculated.

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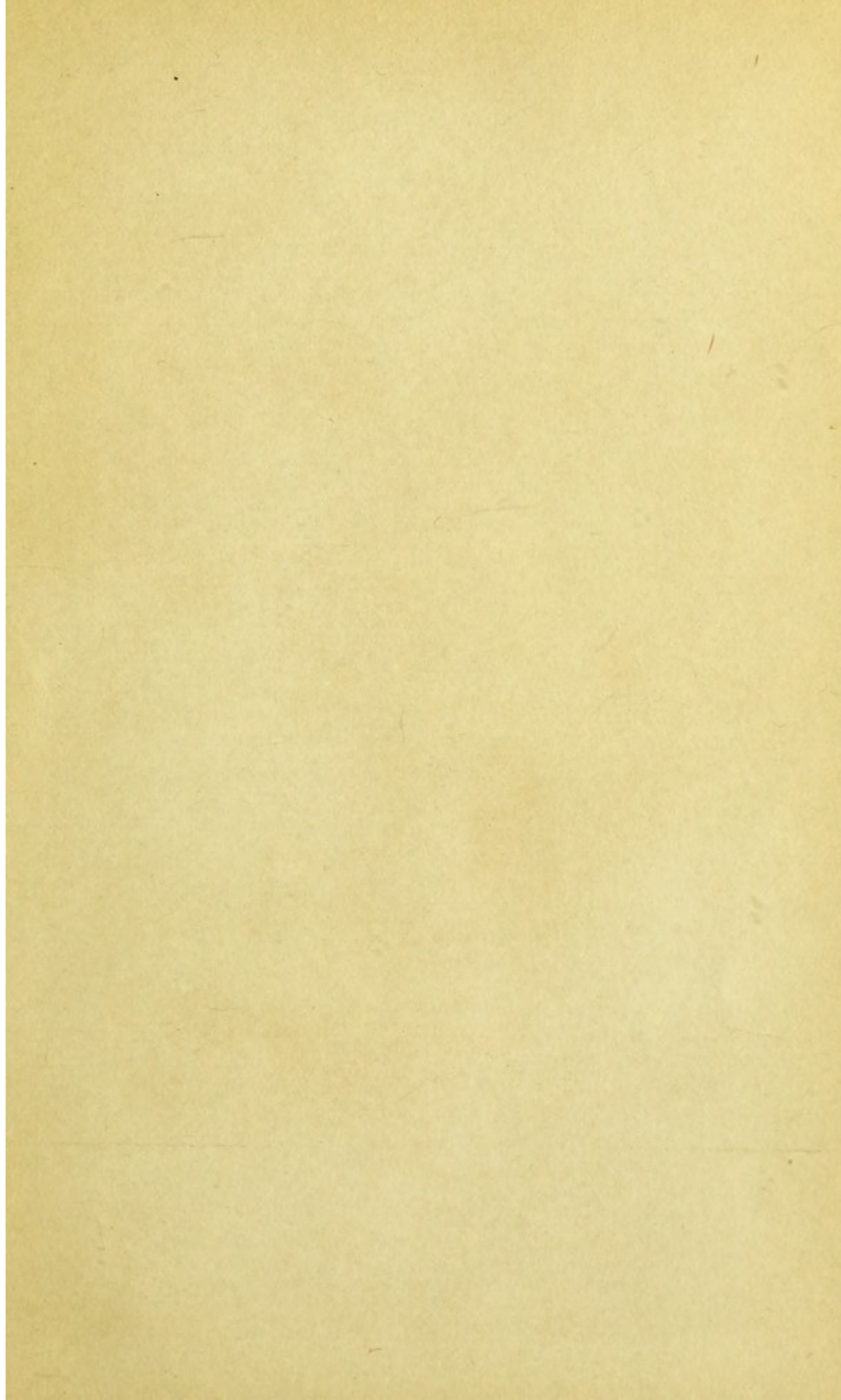
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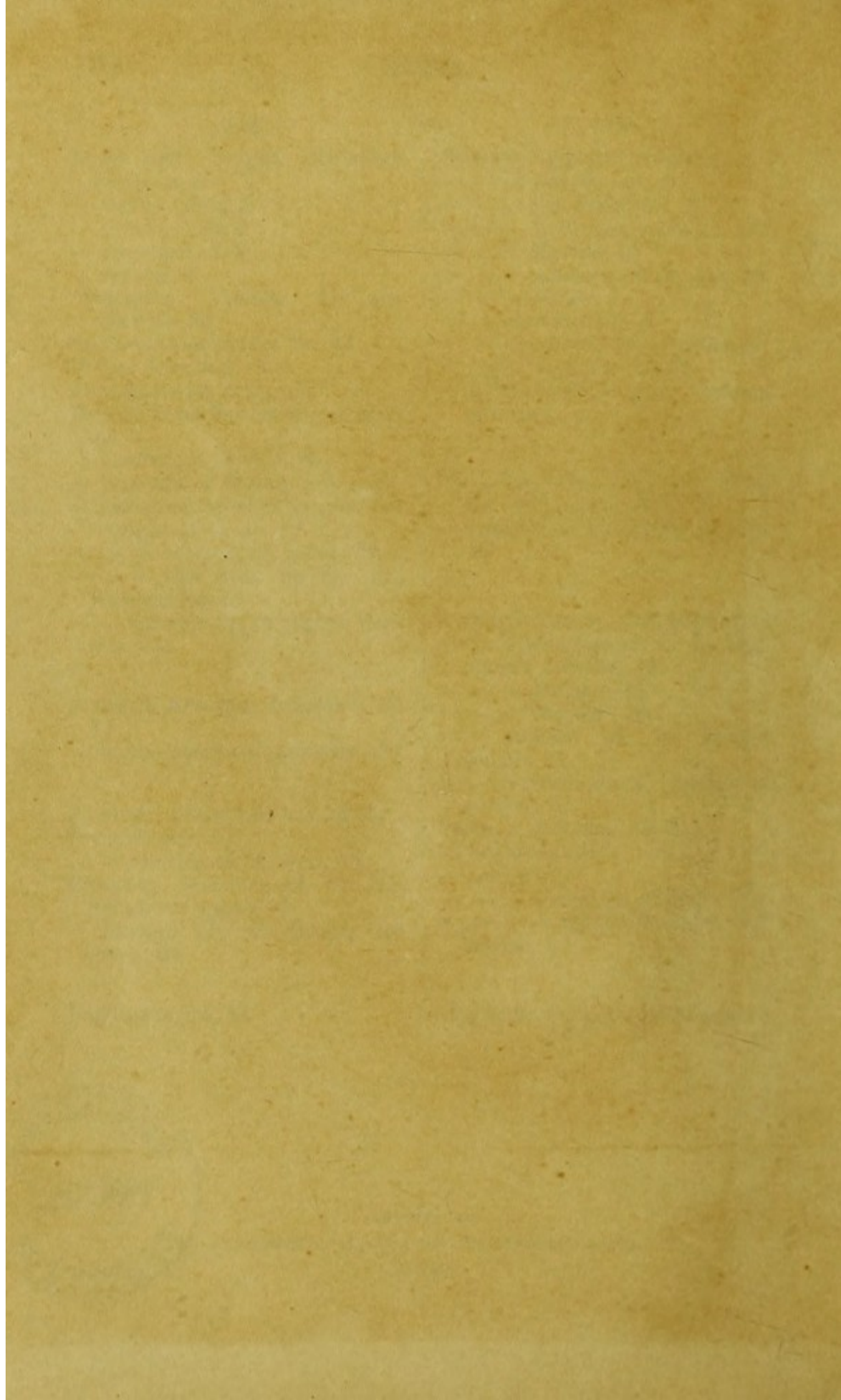


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