

It being now required that the composition of this slag should be represented by an analytical statement in the usual form, *i.e.*, summation by percentage, the procedure is obvious.

$$\begin{array}{rcl} \text{Silica} & = \frac{18000}{450} & = 40.00 \text{ per cent.} \\ \text{Alumina} & = \frac{9000}{450} & = 20.00 \text{ per cent.} \\ \text{Lime} & = \frac{16000}{450} & = 35.56 \text{ per cent.} \\ \text{Magnesia} & = \frac{2000}{450} & = 4.44 \text{ per cent.} \\ & & \hline & & 100.00 \text{ per cent.} \end{array}$$

These are simply proportions abbreviated, *e.g.*,

For silica,  $450 : 180 = 100 : 40$ , etc.

The process is too elementary for examples to be added.

#### DEDUCTION OF FORMULA FROM ANALYSIS.

**Problem IV.**—Given the analysis of a chemical compound, to derive its formula.

The analysis alone does not necessarily give us all the data for the formula. We may always obtain a provisional formula, which is correct as to *relative* numbers of atoms of the various elements.

In metallurgical cases, as we know all the ordinary compounds, and the valencies of the usual elements entering into such compounds, the provisional formula is almost invariably the correct one.

The subject is not enlarged upon, as much that is said under the heading of "Atomic and Molecular Weights" applies as well.

*Method.*—By dividing each percentage figure by the atomic weight of the element, we obtain numbers which stand in the numerical ratios of the respective numbers of atoms. Reducing these numbers to their lowest proportional terms, by G. C. D., we obtain the simplest expression for the provisional formula.

*Examples.*—(a) An oxide of iron contains: iron, 70 per cent.; oxygen, 30 per cent. Find its formula.

Divide each percentage by corresponding atomic weight.

$$\frac{70}{56} = 1.250 \text{ for iron; and } \frac{30}{16} = 1.875 \text{ for oxygen.}$$

(The decimal points may be omitted, provided attention be paid to the number of places, so as not to accidentally multiply one number by ten or more, so we call these numbers 1250 and 1875 respectively.)

But 1250 and 1875 are as 2 : 3.

*Ans.*  $\text{Fe}_2\text{O}_3$ .

It is evident that the arithmetical process is unable to answer the question "why not 4 and 6 as well as 2 and 3?" In fact several formulæ have been written in more than one way, *e.g.*,  $\text{Fe}_2\text{Cl}_6$  otherwise  $\text{FeCl}_3$ .

Evidently, in the above rule, we may have instead of "element" any subcompound or radical, if we choose so to state the analysis.

It is only in formulæ of exceptional complexity that the simplest ratio will not suggest itself at sight, when the first quotients have been obtained, so that we rarely have to apply the formal G. C. D. rule.

(b) A slag analyzes as below:

Silica ( $\text{SiO}_2$ ).....	48.39 per cent.
Ferrous oxide ( $\text{FeO}$ ).....	29.03 per cent.
Lime ( $\text{CaO}$ ).....	22.58 per cent.
	<hr/>
	100.00 per cent.

Find formula expressed as separate silicates of iron and lime. Applied as in the first example, we find as first quotients:

$$\text{SiO}_2 = \frac{48.39}{60} = .806. \quad \text{FeO} = \frac{29.03}{72} = .403. \quad \text{CaO} = \frac{22.58}{56} = .403.$$

No operation is needed to find the ratio 2 : 1 : 1.

There are then two molecules of silica, one each of the bases, hence formula:  $\text{CaOSiO}_2 + \text{FeOSiO}_2$ . ("Bisilicate."\*)

(c) A mineral contains:

Sodium.....	32.86 per cent.
Aluminum.....	12.86 per cent.
Fluorine.....	54.28 per cent.
	<hr/>
	100.00 per cent.

Find its formula.

$$\text{Na} = \frac{32.86}{23} = 1.429. \quad \text{Al} = \frac{12.68}{27} = 0.4763. \quad \text{F} = \frac{54.28}{19} = 2.857.$$

\* *I.e.*, oxygen in  $\text{SiO}_2$  = twice oxygen in base. The relation is seen at a glance when the old "dualistic" form is retained.

These quotients readily give the ratios 3 : 1 : 6.  $\text{Na}_3\text{AlF}_6$ .

(d) A salt contains by analysis:

Sodium.....	16.20 per cent.
Tin.....	41.56 per cent.
Oxygen.....	16.90 per cent.
Water.....	25.34 per cent.
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	100.00 per cent.

Find formula. *Ans.*  $\text{Na}_2\text{SnO}_3, 4\text{H}_2\text{O}$ .

Taking the above formula what would be the exact corresponding analysis?

*Ans.*

Sodium.....	16.17 per cent.
Tin.....	41.73 per cent.
Oxygen.....	16.83 per cent.
Water.....	25.27 per cent.
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	100.00 per cent.

(e) Analysis:

Nickel.....	31.15 per cent.
Hydrogen.....	3.18 per cent.
Nitrogen.....	14.84 per cent.
Sulphur.....	16.95 per cent.
Oxygen.....	33.88 per cent.
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	100.00 per cent.

Find formula. *Ans.*  $(\text{NH}_3)_2\text{NiSO}_4$ .

(f) Analysis:

Phosphorus.....	24.62 per cent.
Oxygen.....	19.06 per cent.
Chlorine.....	56.32 per cent.
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	100.00 per cent.

Find formula. *Ans.*  $\text{P}_2\text{O}_3\text{Cl}_4$ .

Note that in this case our least quotient used as unity would give us a *fractional subscript*. We therefore double every number, with the above result.

(g) A compound yields by analysis:

Copper.....	29.54 per cent.
Iron.....	13.07 per cent.
Tin.....	27.53 per cent.
Sulphur.....	29.86 per cent.
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	100.00 per cent.

Find the formula. The quotients in this case can be read off into their simplest terms at sight. *Ans.*  $\text{Cu}_2\text{FeSnS}_4$ .

(h) Analysis:

Carbon.....	3.05 per cent.
Hydrogen.....	0.25 per cent.
Iodine.....	96.70 per cent.
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	100.00 per cent.

Find formula. *Ans.*  $\text{CHI}_3$ . (Iodoform.)

The last problem suggests a point important in practice. The principle is simple enough, but the working out of a formula by this method presupposes almost absolute accuracy in the analysis, a condition rarely present.

In cases of very simple composition, and of substances *whose atomic weights do not differ very largely*, ordinary analytical accuracy or even fair approximations would lead to correct formulæ. It is otherwise in complex formulæ, especially where there is great discrepancy (as in "h") between atomic weights of the constituents.

Let us suppose we have an analysis of pyrite, which reads as follows:

Iron.....	47.50 per cent.
Sulphur.....	52.50 per cent.
	<hr/>
	100.00 per cent.

the correct analysis being:

Iron.....	46.57 per cent.
Sulphur.....	53.43 per cent.
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	100.00 per cent.

The difference is quite outside of allowable error in an analysis of this character. Yet, if we apply the rule, we shall find the formula  $\text{FeS}_2$ , for our quotients will be 85 and 164, numbers far too close to the ratio of 1 : 2 to admit any other interpretation.

Let us next look at the analysis of iodoform. Hydrogen is not only the element of least atomic weight, but it has by far the least percentage in the composition, and is also the most difficult to determine with accuracy. Let the analysis read:

Carbon.....	3.10 per cent.
Hydrogen.....	.20 per cent.
Iodine.....	96.70 per cent.
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	100.00 per cent.

As to total error reckoned on the composition, the error in hydrogen is hardly more than  $\frac{1}{20}$  of that in the pyrite analysis. But as to the ratio, it puts it out very badly, giving as trial subscripts 258, 200 and 761 for C, H and I respectively, variation enough to throw doubt upon the identity of the numbers representing atoms of carbon and hydrogen, and in fact making the formula  $C_5H_4I_{15}$  look far more probable, *arithmetically speaking*, than  $CHI_3$ .

In cases similar to this one, it is safer not to adopt the lowest ratio number as unity. This is in fact erroneous both in arithmetical principle and in chemical probability, *i.e.*, as regards greatest chance of analytical error. The latter consideration hardly belongs to a discussion of stoichiometric relations, but we may point out that a small percentage is more liable to proportional errors in laboratory manipulation.

Choose, then, for the standard of comparison (after the divisions have been made), an element whose determination is probably the most accurate in character, especially if its ratio number (quotient) be relatively large.

The subject of mineral analysis and of the determination of formulæ is not pursued further here, as it is thought to be hardly a fit topic for a text devoted to elements. It is, however, susceptible of considerable expansion, and advanced works on mineralogy discuss it at length.

Few examples are given under this heading, because Tables II and III are really problems and answers, which the student may take up and verify *ad libitum*. Obviously the data in them may be worked either way, *i.e.*, either the analysis assumed and the formula worked out, or vice versa.

As in the case of certain slag problems, treated in Part II, it is not essential for the working of a formula that the composition should be expressed *in the form of an analysis, summing to 100 per cent.* For if the expression for the composition indicates the *proper ratios* of the various elements, it is evident that these must come to the same simplified expression at last as the ratios expressed by the analysis.

Problem "f" above illustrates a case which may often occur. When reduction to lowest terms gives a fraction, multiply by a number which will clear of that fraction, raising, of course, subscript of every other element.

**Problem IV.** (a) *Other methods of solution.*—All the methods are based upon the division by atomic weights, but the quotients may be treated somewhat differently from above rule, which practically amounts in most cases to the division of all the quotients by the least one.

We may take any one quotient and write instead of it some number rich in factors, like 60 for example. Raise the other quotients in the same proportion. ( $q : 60 = q^1 : x$ ) Now divide by the highest common factor. This, however, is no great variant from the first method.

*Example (1).*—Analysis:

Nitrogen.....	6.32 per cent.
Platinum.....	43.92 per cent.
Chlorine.....	47.95 per cent.
Hydrogen.....	1.81 per cent.
	100.00 per cent.

Quotients : nitrogen = 0.451; hydrogen = 1.81; platinum = 0.225; and chlorine = 1.353. (Call chlorine 60.)

$$\frac{60}{1.353} = 44.35$$

Multiply each of the quotients by this number; we get at once (neglecting trivial discrepancies): N = 20; H = 80; Pt = 10; Cl = 60. Divide through by ten, and put the ammonium radical together, we get  $(NH_4)_2PtCl_6$ .

*Example (2).*—Cane sugar. Analysis:

Carbon.....	42.11 per cent.
Hydrogen.....	6.43 per cent.
Oxygen.....	51.46 per cent.
	100.00 per cent.

Quotients: C = 3.51; H = 6.43; O = 3.215. We see that the H is twice as large as the O. Remains only to get simple ratio between C and O. (Call the carbon 60.)

$$\frac{60}{3.51} = 17.1$$

Hence 60 : 55 = 12 : 11. Formula becomes then  $C_{12}H_{22}O_{11}$ .

It has also been suggested to throw the two numbers into a "continued" fraction, selecting the "convergent" which seems most reasonable.

**Problem IV.**—(b) Experimental data as aids to determination of formula.

Many physical and chemical data may be obtained which, though they will not change the *relative* number of atoms as given by the above method, may indicate what *multiple* of the provisional numbers must be taken to satisfy the facts.

Later the subject of vapor density will be taken up, and some mention will be made of the methods which deduce molecular weight from considerations of boiling point, freezing point (of solutions), and finally of vapor tension. These, however, are not strictly chemical. Another method remains, which we now explain and illustrate in a single example.

This method consists in the substitution in the compound under discussion of a fraction of one of its constituents.

Take acetic acid. Its provisional formula would be found to be  $\text{CH}_2\text{O}$ . That is, this is the simplest possible expression of the *relative* numbers of C, H, and O atoms.

But it is found that one *fourth* of the hydrogen can be replaced by silver, and that the simplest formula obtainable for silver acetate is:  $\text{AgC}_2\text{H}_3\text{O}_2$ . Also, chlorine may be substituted for one, two or three-fourths of the hydrogen. The conclusion is inevitable that there are not less than *four* atoms of hydrogen in the original body, hence we multiply the provisional formula by two, obtaining as the probable true formula the expression:  $\text{C}_2\text{H}_4\text{O}_2$ .

#### EXCESS AND DEFICIENCY.

**Problem V.**—Given actual weights of certain elements or compounds, whose chemical relations are known, find which of the two is in chemical excess over the other, and by what weight or proportion.

This finds its application both in manufacturing chemistry and in metallurgy—in the latter, both in furnace work and wet processes (*e.g.*, chlorination and cyaniding).

The problem is at once recognized as the same in principle as those in which we are required to find weights which shall be *chemically* equivalent to certain other weights, of different substances. The only way to ascertain what is the excess or deficiency of a given element is to carry out the same principle, and compare the weights thus obtained. The “excess” is then

ascertained by the somewhat obvious method of subtracting one from the other.

Some of the illustrations are metallurgical, others more general.

*Examples.*—(a) We find in an ore  $\text{SiO}_2$ , 40 per cent.;  $\text{Al}_2\text{O}_3$ , 20 per cent. We are calculating on a “singulo” basis, which here indicates  $(\text{Al}_2\text{O}_3)_2(\text{SiO}_2)_3$ . What is the percentage of silica in excess of the formula?\*

A rough computation is often made to determine which of the elements is in excess. In the present case the question has already indicated that it is the silica.

We make the usual proportion. Find by this means the chemical requirement of either silica or alumina, using the given percentages just as though they were actual weights.† Begin, then, with the alumina, and use “approximate” atomic weights.

$$\begin{array}{l} 2\text{Al}_2\text{O}_3 : 3\text{SiO}_2 = \text{lbs. alumina} : \text{lbs. SiO}_2 \text{ required} \\ 204 : 180 = 20 : 17.64 \end{array}$$

Silica in the ore 40 per cent. Required, 17.64 per cent. Excess,  $40 - 17.64 = 22.36$  per cent.

(b) Taking the results of the last problem as a basis, what weight of pure limestone  $\text{CaCO}_3$ , ( $\text{CaO} = 56$ ) would satisfy the silica excess on singulo formula, *i.e.*,  $2\text{CaO}, \text{SiO}_2$ ?

(NOTE.—To calculate for  $2\text{CaO}$  we must figure from  $2\text{CaCO}_3$ .)

$$\begin{array}{l} \text{SiO}_2 : 2\text{CaCO}_3 = \text{SiO}_2 \text{ excess} : \text{Req. limestone.} \\ 60 : 200 = 22.36 : 74.53. \text{ Answer.} \end{array}$$

*Proof:* The 74.53 lbs. limestone yield 41.74 lbs.  $\text{CaO}$ . (Problem III.) 41.74 lbs. limestone require 22.36 lbs. silica, on the given formula, that is, the exact excess as previously computed. (Operations omitted.)

Other illustrations of “excess” problems in slag calculations are given in the second part. We here annex a few general cases.

\* Explanations of the terms “singulo,” etc., in slag problems, will be found in the second part, under calculations referring chiefly to furnace charges.

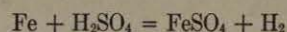
† In the metallurgical part we assume the standard weight, in figuring, of 100 lbs. This makes lbs. and percentages into identical figures, and often prevents error or confusion.

Evidently we can figure as above in percentage, and, if necessary, translate into “actual weights” afterwards.

(c) Add one gram CaO to one gram H<sub>2</sub>SO<sub>4</sub>. (1) Which is in excess? (2) How much CaSO<sub>4</sub> formed? (3) How much left over of the substance which is in excess?

Ans. (1) CaO. (2) 1.38 + grams. (3) 0.4286 CaO excess.

(d) One lb. of iron is dissolved in two lbs. of sulphuric acid. What weight of iron will it still dissolve?



Ans. 0.1428 lb. iron.

(e) One lb. of iron and one lb. of sulphuric acid. How much iron remains unacted on? Ans. 0.4286 lb.

(f) 10 lbs. H<sub>2</sub>SO<sub>4</sub> dissolves 3 lbs. iron. How many lbs. of zinc will it now dissolve? Ans. 3.15.

(g) A mineral analyzes:

SiO <sub>2</sub> .....	41.6 per cent. (Si = 28)
CaCO <sub>3</sub> .....	50.0 per cent. (Ca = 40)
MgCO <sub>3</sub> .....	8.4 per cent. (Mg = 24)

After combining with the lime and magnesia according to the formulæ, CaSiO<sub>3</sub> and MgSiO<sub>3</sub>, what percentage of silica will remain in excess? Ans. 5.6 per cent.

(h) 9.8 grams H<sub>2</sub>SO<sub>4</sub> precipitate 23.3 BaSO<sub>4</sub> from a solution of BaCl<sub>2</sub>. The solution still contains 20.8 BaCl<sub>2</sub>. What was deficit in the H<sub>2</sub>SO<sub>4</sub> added? Ans. 9.8 grams.

(i) One lb. of zinc, one of iron and one of lime (CaO), are dissolved in ten lbs. of sulphuric acid. How much of the latter remains free? Ans. 4.99 lbs.

Use approximate weights in all of the above problems. Other examples of excess and deficiency will be found later. They involve gas volumes, hence can hardly be logically inserted before that topic has been treated.

#### ATOMIC AND MOLECULAR WEIGHTS.\*

**Problem VI.**—Given the analysis of a compound in which the atomic weight of one element is unknown, to determine the "weight" of that one.

All the variants of this problem include analytical data in

\* Problems under this heading which involve "gas volumes" should be omitted until that subject has been mastered. It has been found impossible to maintain an absolutely "logical" sequence in every detail.

some form. The student should realize that such data *taken by themselves* do not always furnish the means for solution of the problem.

Theoretical chemistry is no part of this manual, but some explanation is demanded of the data needed to establish atomic weights. This is a mere outline to enable the student to perceive the limitations of analysis *alone* in the general solution of these problems.

The reader is supposed to be acquainted with the usual definitions of "atom" and "molecule," and to understand "Avogadro's rule."

The compound called "marsh-gas" is to be analyzed. The combining weight of hydrogen is here assumed as unity.

The analysis will show carbon 75 per cent., hydrogen 25 per cent.

Were this all, we might reasonably call the combining weight of carbon three, having assumed that of hydrogen as one. For the actual weight of the carbon is three times that of the hydrogen.

$$\frac{75}{25} = 3$$

We next analyze olefiant gas, finding carbon 85.71, hydrogen 14.29.

$$\frac{85.71}{14.29} = 6$$

Since, then, we have exactly *six* times as much carbon as hydrogen, the evidence for at. wt. of carbon = 6 seems to be as good as for 3.

Acetylene gas, again, gives the composition, carbon 92.31, hydrogen 7.69. Twelve times as much carbon as hydrogen.

$$\frac{92.31}{7.69} = 12$$

Dropping the special illustration, it is seen at once that analysis of itself may be quite inadequate to answer the question of atomic weight, or, as called above, "combining" weights.

If the atomic theory be admitted, then the "atomic weights" are the relative weights of the atoms. Here it may be well to remind the student that we regard an "atom" as the smallest particle whose chemical action we recognize, and warn him to throw

aside all objections, whether ignorant or merely pedantic, which are founded upon the Greek words from which "atom" is derived.

Considerations which bear upon the determination of atomic weights, aside from proportions by weight (analysis), are in part:

(1) Variant proportions between two elements in a series of compounds containing those elements only. (Law of multiple proportions.)

(2) Substitution of one element for another, wholly or in part, in a compound.

(3) Vapor Density, if the compound can be obtained as a gas.

(4) Specific heat of the element under investigation.

(5) Place of the element in the periodic system.

Several of these will receive attention in the course of the presentation of problems. Full discussion of them is out of place in a manual chiefly devoted to arithmetical computation.

In many of the problems the formula is assumed to begin with, in which case the calculation of the atomic weight of one element becomes a mere matter of "proportion." Every instructor in chemistry knows how difficult it is to prevent students from "taking for granted" what they see in print. Hence, although the determination of atomic weights is work only for an advanced specialist, it is thought important to place the limitations of the purely analytical method clearly before the mind of the reader.

The more advanced student is warned, however, that it is the conclusions and not the philosophy of theory that we present.

Atomic weights being purely relative, we must have some basis of comparison, and this must be found in some one of the elements themselves.

Were the ratio of oxygen to hydrogen exactly sixteen to one, as was so long assumed, we should doubtless to-day use hydrogen as unity in this scale of relative weights.

Various reasons, however, urge the use of oxygen taken as sixteen, as the basis. The arguments which have finally prevailed in this usage do not belong here.

In some solutions relating to atomic weights, and in many cognate problems, we have shown complete operations, in others we have simply given the answers, while in a few cases we have partly indicated the method, leaving something to the device of the student.

#### VAPOR DENSITIES OF ELEMENTS AND COMPOUNDS.

The atomic weights of certain elements being known, it does not follow that we can immediately announce the molecular weight of a compound of such elements, even when we have the analysis of the compound. Under the head of calculations of gas volumes will be found the general laws regulating the relation of molecular weights as deduced from the density of compound substances, when in the gaseous condition.

It is probable that certain elements have different molecular weights under different conditions. It is hardly credible that the two conditions of phosphorus, "white" and "red," have the same molecular weight; the same may be said of the three conditions of carbon. Oxygen and sulphur have also been cited as probable cases of variation. On the other hand, these differences may vanish under high temperatures, and it is difficult to see how they can be proved by physical experiment.

Hydrogen, oxygen, nitrogen, chlorine (below 800° C.), bromine, iodine, sulphur (above 1000° C.), selenium, tellurium and potassium have vapor densities such that, *taking density of hydrogen = 1*, the numbers correspond with respective atomic weights. Their "double densities" ( $O_2 = 32$ , etc.) are double their atomic weights, and *probably* express their molecular weights. These molecules would then contain each two atoms. Density of mercury and cadmium as vapor is half atomic weight (when D. of hydrogen = 1). The inference is that their atomic and molecular weights are equal.

Densities of the vapors of arsenic and phosphorus are twice their atomic weights, taking the same unit of comparison, we infer that their molecules are respectively  $As_4$  and  $P_4$ .

As to the molecular weight of compounds, if we assume the "Avogadro" rule the density gives us the molecular weight at once. There are many compounds which cannot be vaporized, and their molecular weights, so far as present means of determination go, remain unknown.

It follows, that the formulæ by which we express these compounds may be nothing more than the true formula reduced to its *simplest arithmetical ratio of elements*. We have, for example, no means of proving that ferrous sulphate, which we write

FeSO<sub>4</sub>, may not have a much more complex constitution than indicated by this formula.

Acetylene gas and benzene have absolutely the same analysis. But the densities are 26 and 78 respectively (H<sub>2</sub> = 2). The analyses show that the ratio of carbon to hydrogen by weight is as 12 : 1, hence we write the molecule of the first one as C<sub>2</sub>H<sub>2</sub> and of the latter as C<sub>6</sub>H<sub>6</sub>.

We cannot entirely pass over the phenomenon of substitution, as affecting the determination of structure or at least molecular weight, but its full consideration belongs to general chemistry.

Take, then, the case of methane, CH<sub>4</sub>. It can be so treated that one-fourth, never less, of its hydrogen can be replaced by chlorine. Also, two-fourths, three-fourths and all four-fourths can be replaced, and in each case the weight of the displaced hydrogen is to the weight of the substituted chlorine as 1 : 35.5. Unless we are to throw aside the atomic theory entirely, we must conclude that each of these replacements is of one atom of hydrogen by one of chlorine. This, then, forms another and often a very important method of securing evidence as to the probable number of atoms in a molecule, and may serve to correct the "empirical" formula derived from analysis alone.

*Examples.*—(a) Glucinum has now attributed to it the atomic weight of 9.1 and its oxide has the formula GIO. Formerly its oxide was written Be<sub>2</sub>O<sub>3</sub>. As this threw it out of line in the Periodic System, experiments on its specific heat showed its formula to be as now adopted.

The composition of the oxide is: Gl, 36.25 per cent.; O, 63.75 per cent. What would be the atomic weight under the older formula?

*Solution.*—This and all other problems of its kind may be best stated under the form of a simple proportion.

$$\begin{aligned} \text{O}_3 : \text{Gl}_2 &= \text{O}_3 : 2x \\ 63.75 : 36.25 &= 48 : 27.29 \quad x = 13.64 \end{aligned}$$

(b)\* A gas analyzes:

Carbon.....	92.31 per cent.
Hydrogen.....	7.69 per cent.
Total.....	100.00 per cent.

\* These and other problems marked with \* should be omitted as already indicated, until section on "gas volumes" has been mastered.

One liter of this gas weighs 3.4821 grams. Find its molecular weight and formula.

$$\begin{aligned} x : 22.4 &= 3.4821 : 1 \\ x &= \text{molecular weight} = 78 \end{aligned}$$

From the analysis we have:

$$92.31 : 7.69 = 12 : 1$$

Hence the atoms are present in the ratio 1 : 1. Dividing 78 by 13\* we get quotient of 6, hence formula may be assumed as C<sub>6</sub>H<sub>6</sub>.

(c) A gas analyzes the same as in (b) but a liter of it weighs 1.1607 grams. Find molecular weight and formula.

*Solution.*—The same proportion indicates molecular weight as 26. Dividing as before by 13 (12 + 1) we get 2. Formula C<sub>2</sub>H<sub>2</sub>. These, although not problems for the finding of atomic weights, serve to illustrate a very closely related topic.

(d) Specific heat of copper is 0.0952.

An oxide of copper analyzes:

Copper.....	88.83 per cent.
Oxygen.....	11.17 per cent.
	100.00 per cent.

What is the atomic weight of copper?

The proportion gives us:

$$11.17 : 88.83 = 16 : x$$

According to this analysis, with no limiting data, we should conclude that the atomic weight of copper might well be 127.2, that being the value of  $x$ .

Following the law of Dulong and Petit, this number, multiplied by the specific heat, should give a product of about 6. However,  $127.2 \times 0.0952 = 12.1 +$  or fully double the average "atomic heat." This indicates that we should divide our result by two, assigning the metal an atomic weight of 63.6, with formula for this oxide Cu<sub>2</sub>O. This is confirmed by the analysis of cupric oxide (CuO), and by various other data.

\* I.e., C(12) + H(1).

(e)  $MCl_2$  weighs "a."  $MBr_2$  weighs "b." What is the atomic weight of M? (Cl = 35.5. Br = 80.)

$$\text{Answer.} \quad \frac{160a - 71b}{b - a}$$

The student should work out the "why" of this formula. See next problem.

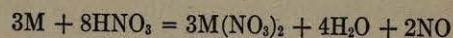
(f)  $MCl_2$  weighs 3.78 grams.  $MBr_2 = 6.45$  grams. Find atomic weight of M. Note that the formula, *i.e.*, valence of M, is assumed in these cases.

Here  $a = 3.78$ ;  $b = 6.45$ .  $b - a = 2.67$ , etc.

M works out very easily to 55.

The method being quite general may be applied to any similar case.

(g) A metal is acted on by nitric acid, supposed equation being:



(This equation is intended merely for an exhibit of relation of metal to product. Relation of nitric acid to dissolved metals is highly irregular.)

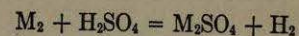
Weight of "M" = 1 gram, nitrate = 2 grams. Find atomic weight of "M." Ans. 124.

(h)\* A metal "X" acts on water.  $2X + 2H_2O = 2XOH + H_2$

Weight of "X" used = 10 grams. Hydrogen evolved = 4.8692 liters. Find atomic weight of "X."

$$X_2 : 22.4 = 10 : 4.8692. \quad X_2 = 46. \quad X = 23.$$

(i)\* A gram of metal is dissolved in acid, liberating 930 c.c. (at 18° C. and 750 mm.) of hydrogen. Find atomic weight of "M," assuming equation:



Form of solution. Call the volume of the gas reduced to "normal" conditions "V," then we have:

$$V : 1 = 22.4 : x \left( \text{atomic weight} = \frac{x}{2} \right)^*$$

(j) One gram of silica ( $SiO_2$ ) is derived from 2.8179 grams silicon tetrachloride ( $SiCl_4$ ). Find atomic weight of silicon. (Cl = 35.45.)

*Solution.*  $2.8179 - 1 = 1.8179$ ; this represents excess of  $Cl_4$  over  $O_2$ . The theoretical side is,  $Cl_4 = 141.8$  and  $O_2 = 32$ . Difference = 109.8. Hence:

$$\begin{array}{rclcl} \text{Diff. in mol. wts. : mol. wt. of } O_2 & = & \text{Diff. in wt. : wt. of } O_2 \\ 109.8 & : & 32 & = & 1.8179 = 0.5298 \end{array}$$

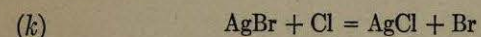
$SiO_2$  weighed 1 gram, silicon weighs  $1 - 0.5298 = 0.4702$ .

Finally,

$$\begin{array}{rcl} O_2 : Si & = & O_2 : Si \\ 5298 : 4702 & = & 32 : 28.4 \end{array}$$

Atomic weight of silicon = 28.4.

(Carefully note use of the *difference* between atomic weights for a datum.)



This equation represents displacement of bromine by chlorine.

Suppose atomic weight of bromine to be unknown. We have the following data. Weight of silver bromide 1.6910. Weight of silver chloride 1.2904. (Loss of weight in the replacement, 0.4006.) Find the atomic weight of bromine.

Composition of  $AgCl$  being known, we find weights of silver and chlorine to be, respectively, 0.9714 and 0.3190. Subtracting weight of silver from weight of silver bromide:  $1.6910 - 0.9714 = 0.7196 =$  weight of bromine.

Nothing remains except to put the two weights into proportion with their atomic weights, that of bromine being the unknown term.

$$\begin{array}{rclcl} \text{Weight of chlorine : weight of bromine} & = & \text{at. wt. Cl} & = & \text{at. wt. Br} \\ 3190 & : & 7196 & = & 35.45 = 79.97 \end{array}$$

The above problem might also be solved by using the difference in atomic weight as in (j), just above. Thus we have a loss of 0.4006 and this is obviously the *excess of weight of bromine above chlorine*. This difference is wholly due to the excess of the atomic weight of bromine over that of chlorine, it being evident that the difference in actual weights must be proportional to the difference in atomic weights. We know the weight of the chlorine (0.319) and the atomic weight of chlorine (35.45). Now call the atomic weight of bromine "x," we have:

$$x - 35.45 : 35.45 = 0.4006 : 0.319$$