That is, the difference in atomic weights is to the atomic weight of chlorine, as the actual loss of weight is to the actual weight of chlorine.
The result is the same as by the more direct method.
(l)

$$
\begin{aligned}
& \mathrm{RO}+2 \mathrm{HCl}=\mathrm{RCl}_{2}+\mathrm{H}_{2} \mathrm{O} \\
& \mathrm{FeS}_{2}+\mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{FeSO}_{4}+\mathrm{H}_{2} \mathrm{~S} \\
& \mathrm{RCl}_{2}+\mathrm{H}_{2} \mathrm{~S}=\mathrm{RS}+2 \mathrm{HCl}
\end{aligned}
$$

In the above equations, RO and FeS weigh each one gram. The equations are all "in chain," i.e., the $\mathrm{H}_{2} \mathrm{~S}$ from one gram of FeS just precipitates RS from the original one gram of RO.

Use "approximate" atomic weights, i.e., $\mathrm{Fe}=56$, etc. Deduce atomic weight of $R$ without the use of equation or proportion.
Solution.-The molecular weights of RO and FeS must be equal. But since the molecular weight of FeS is 88 that of RO must also be 88 .
Then RO̊ $-0=\mathrm{R}$. That is, $88-16=72=$ atomic weight of $R$.
( $m$ ) Eleven grams of a sulphide RS when oxidized to $\mathrm{RSO}_{4}$ now weigh nineteen grams. Find the atomic weight of R. ( $\mathrm{S}=32$.)
Solution.-The oxygen weighs 8 grams. Hence the sulphur weighs 4 grams. This leaves 7 grams for the weight of the " $R$."
Or

$$
\begin{gathered}
8: 64=7: 56 \\
\text { At. wt. of } R=56
\end{gathered}
$$

(n) One gram of phosphorus produces 2.2903 grams $\mathrm{P}_{2} \mathrm{O}_{5}$. What is the atomic weight of phosphorus?

Solution. $2.2903-1 .=1.2903=$ weight of oxygen.
Molecular weight of five atoms of oxygen $=5 \times 16=80$.

$$
\begin{gathered}
1.29: 1=80: x \quad x=62 \\
\frac{x}{2}=\text { at. wt. of phosphorus }=31
\end{gathered}
$$

$(o)^{*}$

$$
\begin{array}{ll}
\mathrm{RS}+2 \mathrm{O}_{2} & =\mathrm{RSO}_{4} \\
\mathrm{RSO}_{4}+\mathrm{BaCl}_{2} & =\mathrm{RCl}_{2}+\mathrm{BaSO}_{4} \\
\mathrm{RCl}_{2}+2 \mathrm{AgNO}_{3} & =2 \mathrm{AgCl}+\mathrm{R}\left(\mathrm{NO}_{3}\right)_{2} \\
\mathrm{R}\left(\mathrm{NO}_{3}\right)_{2}(\text { ignited }) & =\mathrm{RO}+\mathrm{N}_{2} \mathrm{O}_{5} \\
\mathrm{RO}+\mathrm{H}_{2} & =\mathrm{R}+\mathrm{H}_{2} \mathrm{O}
\end{array}
$$

The metal " R " from the last reaction weighs 1.815 . The $\mathrm{BaSO}_{4}$ weighs 7.7042.

Find (1) atomic weight of "R;" (2) weight of RS; (3) weight of RO ; (4) weight of AgCl ; (5) volume of hydrogen gas; (6) volume of oxygen gas.
Answers. (1) 55 ; (2) 2.873 ; (3) 2.343 ; (4) 9.4631 ; (5) 0.7392 liter; (6) 1.4784 liters.
(p) $\mathrm{KClO}_{3}=\mathrm{KCl}+\mathrm{O}_{3}$. Having assumed this equation let us suppose atomic weights of potassium and chlorine to be unknown, but that of silver to be known (say 108). Call weight of $\mathrm{KClO}_{3}$ " $a$." Loss on ignition $\left(\mathrm{O}_{3}\right)=$ " $b$." The chlorine in the residue is precipitated as AgCl whose weight is " $c+d$." Silver is now separated and weighed as metallic silver " $d$," leaving weight of chlorine as "c."
Required the atomic weights of chlorine and potassium.
Since "atomic and actual weights are in equal ratio" we have:

$$
d: c=108: x \quad x=\frac{108 c}{d}=\text { at. wt. chlorine }
$$

We have also the actual weight of the potassium, viz: $a-b-c$.
If then the atomic weight of the potassium be called " $y$ " we have:

$$
b: a-b-c=48: y \quad y=48 \frac{(a-b-c)}{b}
$$

(q) *A dyad metal " $R$ " is dissolved in acid:

$$
\mathrm{R}+\mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{RSO}_{4}+\mathrm{H}_{2}
$$

Weight of the metal, one gram. Volume of the hydrogen, 0.3425 liter.

Find atomic weight of " R." Ans. 65.4.
$(r)$ *Vapor of phosphorus oxychloride weighs 6.8529 grams per liter. What is the molecular weight? Ans. 153.5.
(s) MnS contains 36.83 per cent. sulphur. What is atomic weight of manganese?

$$
36.83: 63.17=32.06: 55
$$

( $t$ ) One gram of a dyad metal is dissolved and precipitated as RS. The sulphur in this is determined as $\mathrm{BaSO}_{4}$ whose weight is 2.3346 grams.
What is the atomic weight of the metal? Ans. 100.
(u) One gram of $\mathrm{R}\left(\mathrm{NO}_{3}\right)_{2}$ ignited, leaves 0.45 gram RO . What is atomic weight of " R."

$$
\mathrm{R}+16: \mathrm{R}+124=0.45: 1.00 \quad \mathrm{R}=72.38
$$

(v) 2 RO is converted into $\mathrm{R}_{2} \mathrm{X}$ without change of weight. What is the atomic weight of " X "?

Ans. Twice that of oxygen.
(w) From one gram of " $R$ " is derived $0.9614 \mathrm{R}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$. Find atomic weight of $R$.

Ans. 137.
(x) One gram of $\mathrm{RSO}_{4}$ is converted into $\mathrm{R}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$, which is not weighed, but is converted into $\mathrm{Mg}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ which weighs 0.6895 gram. What is the atomic weight of $R$ ? (Use " approximate" weights, $\mathrm{Mg}=24$, etc.)

Ans. 65.
(y) Oxide $\mathrm{M}_{2} \mathrm{O}$ of a monad metal being converted into bromide goes from 75 grams to 435 grams. What is atomic weight?

Ans. 7.
(z) $\mathrm{MCl}=8.2016 . \quad \mathrm{AgCl}=15.7707$. At. wt. of $\mathrm{M}=39+$
RAOULTS LAW.
"One molecule of a compound dissolved in 100 molecules of a liquid lowers the freezing point of the liquid by $0.62^{\circ}$ Centigrade."
The figure $0.62^{\circ}$ is nearly, but not quite a constant for all cases. The limitations of this law are very great, and it may be said without going into any general discussion, that it does not apply to aqueous solutions of inorganic salts.
If $P=$ weight of the substance dissolved and $L=$ weight of solvent.
$M=$ molecular weight of solvent and $m=$ molecular weight of substance dissolved.
$E=$ reduction in freezing point, in degrees Centigrade, then:

$$
\frac{P}{L}: \frac{m}{100 M}=E: 0.62^{\circ}
$$

or, translating the formula, we see that by comparing the observed reduction in temperature $(E)$, with the constant $0.62^{\circ}$, we deduce ratio between numbers of molecules. Since we are supposed to know the molecular weight of the solvent ( $M$ ) and since all the other numbers are data of the experiment, we solve for $m$ :

$$
m=\frac{P \times 62 \times M}{L \times E}
$$

Examples.-(a) To 780 grams benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right.$, molecular weight $=78$ ) add 124.6 grams anthracene (established formula is $\mathrm{C}_{14} \mathrm{H}_{10}$ ).

Observed depression of temperature on freezing $=4.34^{\circ} \mathrm{C}$.

$$
\begin{aligned}
& P=124.6, L=780, M=78, E=4.34 \\
& m=\frac{124.6 \times 62 \times 78}{780 \times 4.34}=178 .
\end{aligned}
$$

Analysis of anthracene is C, 94.38 ; H, 5.62. Empirical formula easily deduced as $\mathrm{C}_{7} \mathrm{H}_{5}$, molecular weight as 89 , corrected by above to $\mathrm{C}_{14} \mathrm{H}_{10}$ molecular weight $=178=89 \times 2$.

MOLECULAR WEIGHTS DETERMINED FROM FREEZING AND BOILING POINTS OF SOLUTIONS.
Raoult's rule is defective in that it assumes a constant depression of freezing point for various solvents. It is retained, however, though no further examples are given under it.
The following rules for determination of molecular weights of a certain class of substances apply both to depression of freezing point and raising of boiling point. As the "constant" in these cases varies for each solvent, a table is appended of the values of the constant for a few of the more important solvents.
(A) From depression of freezing point.

If the solution of $w$ grams of a substance in 100 grams of a liquid lowers freezing point $T^{\circ}$, then molecular weight will equal

$$
\frac{K \times w}{T}
$$

In this formula $K$ is a constant differing for each liquid.
Example.-Constant for benzene being 50, solution of 2 grams of nitrobenzene in 100 grams benzene lowered freezing point by 0.8 Centigrade.

$$
K=50 . \quad \mathrm{w}=2 . \quad \mathrm{T}=0.8 . \quad \text { Mol. } \mathrm{wt} .=\frac{50 \times 2}{0.8}=125
$$

Nitrobenzene has the formula $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NO}_{2}$ according to usual statement. This would give 123 as molecular weight. Since the question in regard to molecular weight is usually whether a certain trial number deduced from analysis, or a multiple of same is the true figure, the approximation 125 settles the determination in favor of the formula as given.
Analysis would in this case evidently give us 123 as lowest possible figure, since nitrogen appears to the extent of but one atom. In the case under Raoult's rule, the "empirical" figure is doubled.
(B) From raising of boiling point.

If the solution of $w$ grams of a substance in 100 grams of a liquid raises boiling point $t^{\circ} \mathrm{C}$, then molecular weight $=$

$$
\frac{L \times w}{t}
$$

In this formula, " $L$ " is a constant differing for each liquid, like " $K$ " in the freezing case.
Example.-Constant for ether being 21.1, solution of 3.533 grams iodine in 100 grams ether, raised boiling point $0.296^{\circ}$ Centigrade.

$$
L=21.1 . \quad w=3.533 . \quad t=0.296 . \mathrm{mol} . \mathrm{wt} . \quad=\frac{3.533 \times 21.1}{0.296}=252
$$

The doubled atomic weight of iodine approximates 254 , hence the above determination would lead to the adoption of that figure.
(These rules and the table below are taken with some slight change from Lupton's Chemical Arithmetic, London, 1907. They have little to do with strictly stoichiometric work, and are inserted more as reference matter than for working examples.)

| Solvents. | K. | L. |
| :---: | :---: | :---: |
| Water | 18.5 | 5.2 |
| Acetic acid | 39 | 25.3 |
| Benzene | 50 | 26.7 |
| Carbon disulphide | .... | 23.7 |
| Chloroform |  | 36.6 |
| Alcohol |  | 11.5 |
| Ether | .... | 21.1 |
| Acetone . | .... | 16.7 |

## COMPUTATION OF GAS VOLUMES.

Gas volumes are most readily computed in the metric system. After setting forth the method, however, based upon the crith as the weight unit and the liter as the volume unit, we shall show how to compute from pounds and cubic feet.
The unit weight assumed for gas calculations is the "crith" which represents the weight of one liter of hydrogen gas under normal conditions of temperature and pressure, viz: $0^{\circ} \mathrm{C}$., and 760 mm . barometer.

Expressed in grams this weight is 0.089873 . Since the adoption of oxygen as 16 , it has been suggested that a crith based upon a hypothetical gas one-sixteenth of the density of oxygen would be the proper unit.

The weight of one liter of oxygen is 1.42961 in grams. One sixteenth of this is 0.08935 . The purpose of this work, however, not being to discuss refinements of scientific precision, we shall adopt the approximate figure of 0.09 gram-nine-hundredths of a gram.
Dividing unity by this figure we get 11.11 as the number of criths in one gram. Hence:

To convert grams into criths, multiply by 11.11 or divide by 0.09 . To convert criths into grams, multiply by 0.09 or divide by 11.11 . The calculations will be slightly in error, because our "crith" is too heavy. Practically this is of no moment whatever. In any operation, whether for lecture demonstration or manufacturing process, the error is so slight that the average "shortage" of product as compared with theory will far exceed it.
The first thing for the student to remember in the symbolism for gases, is that equal numbers of molecules* occupy equal volumes (Avogadro's rule). Just as the symbols for elements do not indicate the atomic weights, but carry them "understood," so the symbolism for gases indicates their relative volumes only in the light of the "rule" of Avogadro. Equal numbers of symbolic molecules indicate equal volumes.
Take the following gas formulæ:
$\mathrm{H}_{2}: \mathrm{HCl}: \mathrm{NH}_{3}: \mathrm{CH}_{4}: \mathrm{PF}_{5}: \mathrm{CO}: \mathrm{CO}_{2}: \mathrm{COCl}_{2}: \mathrm{C}_{2} \mathrm{H}_{4}: \mathrm{CH}_{3} \mathrm{Cl}$
Each of these expressions indicates one molecule. The volumes of all the expressions are equal. $\dagger$ This volume relation is just as fully borne out in actual operations, involving actual volumes, as are the weight relations we have hitherto discussed. A coefficient multiples the volume just as it does the weight. We shall call the molecular expression two volumes.

If the expression for the element alone, 0 for example, indicates one volume, then any expression of a molecule indicates two volumes. It is true that it is theoretically incorrect to

[^0]write a single symbol in a great majority of cases. But in numberless cases they will continue to be so written by persons who are in a hurry, and have not the fear of the theorist before their eyes. For these the " two-volume" convention is best adapted.
The "density" of a gas we shall consider as expressed by the same figure as its molecular weight. (Oxygen $=32$, hydrogen $=2.016, \mathrm{CO}=28$, etc.)
As there are thousands of persons who have learned that the "density" of a gas is one-half of its molecular weight, it may be well to point out here that the whole matter is purely conventional. Any set of numbers might serve as expressions for density so long as they were in the proper ratios expressing the experimental facts.
While hydrogen was accepted as "unity," there was no small convenience in taking its density as unity and comparing all other densities on that basis. However, the convention of (practically) doubling the old densities has obtained almost universal acceptance, presenting the advantage of giving one set of numbers instead of two. The anomaly of a scale of comparison without any "unit" (i.e., numerical unit) does not make any difficulty. We have no numerical unity any longer in the table of atomic weights, since we base everything on $0=16$.
Together with the adoption of the molecular weight figures as expressions for density, came also in some texts the usage of calling the molecular volume "one" (type) volume. Here again all is mere convention. Nevertheless, there is great convenience sometimes in conventions, and as there is no practical reason to prevent us from calling the molecular volume "two" instead of one, and as the "two-volume" convention seems to the author to greatly facilitate comprehension of the subject in presentation to beginners, we retain it, albeit it is of little consequence whether we do or not in a text of this kind.
However, it seems easier to remember that one volume of nitrogen and three of hydrogen combine to make two of ammonia than that one-half a volume of the first and one and a half of the second combine to form one volume. All fractions disappear under the two-volume idea, whether in combination or in decomposition. Nor can the author see any force in the criticism that there is "inconsistency" between this convention and the adoption of the molecular weight figure for density.

We call the molecular expression, then, two type volumes, as already set forth. Let us now translate an equation into volumetric relations:

$$
\mathrm{C}_{2} \mathrm{Ca}+2 \mathrm{H}_{2} \mathrm{O}=\mathrm{Ca}(\mathrm{OH})_{2}+\mathrm{C}_{2} \mathrm{H}_{2}
$$

Acetylene from "carbide." Assume concrete volumes, viz: 1 vol. = 1 liter. Put the equation into criths, as to weight, or into liters as to volume, the results are the same. The molecular weight of the gas is 26 ; there will be 26 criths of it, and 2 liters of the gas. But since we have a concrete weight for one term all the others follow (problems I and II). We shall have 64 criths of the carbide, 36 criths of water.

Compare now the relation of the weight of the carbide to the volume of the acetylene. On the theoretical side we note that (in this particular case) one molecule of the first gives two "type volumes" of the second. Taking actual weight of the one and actual volume of the other, we see that relation of molecular weight to number of type volumes is the same as the relation of crith weight to liter volumes.

In this illustration we have made actual and theoretical figures coincide. The student is recommended to "invent" other cases, and prove that the application is quite general.
Although we prefer the " 22.4 " method to be later introduced, we have given precedence to the "crith" as the older method of solution of problems of this nature, and proceed to put it into a formal "rule" with examples.

Deduction of Gas Volumes from Equations Expressing Weights.
Problem VII.-(a) Given the equation for the production of a gas, and the weight of any one of the solid compounds entering the reaction, to deduce the volume of the gas. Weights given in grams.
(We call the solid, or liquid, substance the "first" and the gas the "second.")
Following the illustration already given we have the rule:
AS the molecular weight of the first
IS TO the type-volume of the second;
SO IS the weight in criths of the first
TO the volume in liters of the second.

It is not necessary that the known quantity should be the solid by weight. It is quite the same problem if we assume the volume of the gas and seek the weight of the compound or element which we are to use in its production.
Examples.-(a)

$$
\mathrm{KClO}_{3}=\mathrm{KCl}+\mathrm{O}_{3} \text { (type volumes }=3 \text { ) }
$$

We take 100 grams of potassium chlorate, how many liters of oxygen shall we obtain? ( 100 grams $=1111$ criths.)

Molecular weight of $\mathrm{KClO}_{3}=122.5$. Place "abstract" numbers in first member, as usual; that is, the "molecular" weight and the "type" volumes.

$$
122.5: 3=1111: x . \quad x=27.2 \text { (liters of oxygen) }
$$

(b) $\mathrm{NH}_{4} \mathrm{Cl}+\mathrm{KOH}=\mathrm{KCl}+\mathrm{H}_{2} \mathrm{O}+\mathrm{NH}_{3}$ (type volumes $=2$ )

Required, four liters of ammonia gas, what weight of ammonium chloride?

$$
\begin{aligned}
& 53.5: 2=x: 4 \quad\left(\mathrm{NH}_{4} \mathrm{Cl}=14+4+35.5=53.5\right) \\
& x=107 \text { criths. } \quad 107 \times .09=9.63=\text { Answer in grams. } \\
& \text { (c) } \quad \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{NaHSO}_{4}+\mathrm{HCl}(2 \text { type volumes })
\end{aligned}
$$

Given twelve grams of common salt $(\mathrm{NaCl})$, how many liters of hydrochloric acid gas $(\mathrm{HCl})$ ?

Molecular weight of $\mathrm{NaCl}=58.5 . \quad 12$ grams $=133.33$ criths

$$
58.5: 2=133.33: x . \quad x=4.558 \text { (liters of } \mathrm{HCl} \text { ) }
$$

(d) $\mathrm{NH}_{4} \mathrm{NO}_{3}=\mathrm{N}_{2} \mathrm{O}+2 \mathrm{H}_{2} \mathrm{O}\left(2\right.$ type vols. of $\mathrm{N}_{2} \mathrm{O}, 4$ of $\left.\mathrm{H}_{2} \mathrm{O}\right)$

Given three liters of $\mathrm{N}_{2} \mathrm{O}$ gas, what weight was taken of ammonium nitrate?

> (Molecular weight of $\mathrm{NH}_{4} \mathrm{NO}_{3}=14+4+14+48=80$ ) $\quad 80: 2=x: 3 . \quad x=120$ criths $=10.8$ grams

If it be required to figure cubic feet of gas, given weights in pounds, this can be readily done by suitable transformation of the above rule.*
One pound contains 5040 criths. If, then, we raise the criths of the rule to pounds, we must also multiply the liters by 5040 .

[^1]However, as we want cubic feet, we must divide this number by 28.32 the number of liters in one cubic foot. The quotient is (very closely) one hundred and seventy-eight.
This forms a new kind of "unit of gas volume." To show exactly what it means we may put it thus:
"A crith has the same relation to a liter as a pound has to 178 cubic feet." Or, better, "A crith is to a pound as a liter is to 178 cubic feet."
It may be convenient to name this volume of gas. Let us call it a "pound-volume," 178 cubic feet.
Now the rule becomes:
"As the molecular weight of the first is to the type volume of the second, so is the weight in pounds of the first to the volume in pound-volumes of the second." (We then multiply number of "pound-volumes" by 178 to get cubic feet.)

Examples.-(a)

$$
\mathrm{CaOCl}_{2}+\mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{CaSO}_{4}, \mathrm{H}_{2} \mathrm{O}+\mathrm{Cl}_{2}(2 \text { type volumes })
$$

Take 100 lbs . of bleaching powder and find volume of chlorine gas.
(Molecular weight of $\mathrm{CaOCl}_{2}=40+16+71=127$.)
$127: 2=100: x . \quad x=1.574$ (pound-volumes)
$1.574 \times 178=280+\quad$ Answer, 280 cubic feet
(b) We are to inflate a balloon with fifty thousand cubic feet of hydrogen gas.

$$
\mathrm{Zn}+\mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{ZnSO}_{4}+\mathrm{H}_{2}(2 \text { type volumes })
$$

How many pounds of zinc must be used? (Atomic weight of $\mathrm{Zn}=65$.)

First, divide 50,000 by 178 , giving the number of "poundvolumes."
$50,000 \div 178=280.9$. The usual proportion follows:

$$
65: 2=x: 280.9 \quad x=9129 \text { (pounds of zinc) }
$$

In the above problems on gas volumes it is tacitly assumed that the volumes are taken under the "normal" conditions, viz: $0^{\circ} \mathrm{C}$. for temperature and 760 mm . barometer. Students are often perplexed by having questions put to them involving at once the chemical and physical conditions. This is all right at the last, but it is better to master principles separately and unite their calculation afterward.

All conditions being given, viz: chemical equation, temperature and barometer, the computation of volume as above comes first. Then follow the corrections for thermometer and barometer, one after the other.

The " 22.4 " Method.
A method of calculating gas volumes in relation to weight without the use of the "erith," is found in the fact that the molecular weight* of any gas taken in grams occupies twenty-two and four-tenths (22.4) liters. Using this figure we obtain results somewhat more accurate than with our crith of 0.09 gram. The latter, being too heavy, will give weights too high and volumes too low, though not by any serious amount.

The " 22.4 " liter figure is derived from the weight of 1.4296 grams for one liter of oxygen. It is amply close for any practical application. In using it we do not have to transform grams into criths or the reverse.

Each method has its advantages. The crith has perhaps been more used, but it is hard to see why it should be considered better or easier than the "two volume" to be now explained.

Let us take an actual gas for the explanation. $\mathrm{CO}_{2}$ has the molecular weight of 44 . Then 44 grams of it will occupy 22.4 liters.

Calculate this by the approximate "crith" of 0.09 gram. One liter of $\mathrm{CO}_{2}$ weighs 22 criths. $22.4 \times 22=492.8$ criths.
$492.8 \times 0.09=44.35$ grams, instead of 44 grams. That is, the weight comes out a little over, as it must, our "crith" having been taken ("for short") a little too large. It is evident, however, that the error is not material in any ordinary case.
We call the expression for one molecule of gas "two volumes," i.e., as before, two "type" volumes. We may now easily construct a rule for ascertaining gas volumes from weights. Let us assume the equation:

$$
\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{NaHSO}_{4}+\mathrm{HCl}
$$

If, in this equation, the units of atomic weight were grams, we should have 58.5 grams of NaCl and 22.4 liters of HCl .

[^2]Take 100 grams of the salt. Find the corresponding volume of hydrochloric acid gas. Evidently the proportion must be:

Mol. wt. of $\mathrm{NaCl}:$ Mols. $\times 22.4$ of $\mathrm{HCl}=$ wt. of salt : $x$ (liters of gas) 58.5
$1 \times 22.4$
$=100$
Problem VII.-(b) Equation being given, to find volume of gas directly from gram weights known.
Rule: As molecular weight of first substance
Is to 22.4 times number of molecules of second:
So is weight in grams of first
To volumes in liters of second.
As before, "first" substance means the one whose weight is either given or required, "second" substance gas whose volume is either given or required. Either can be the unknown. Problems (b) and (d), below, exemplify the case in which the gas is the known quantity.
The above illustrative problem worked by the "crith"method:

$$
58.5: 2=1111: 37.98 \text { (liters) }
$$

Weight being a trifle too great, volume comes out slightly too small.

For problems of this kind the method seems better than the "crith" way. The latter, however, is too generally used to be omitted.

Examples under the " 22.4 " method for gas volumes:
(a) $\quad \mathrm{CaCO}_{3}+2 \mathrm{HCl}=\mathrm{CaCl}_{2}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$

Take 125 grams calcium carbonate, what volume of carbon dioxide gas?
Molecular weight of $\mathrm{CaCO}_{3}=100$. Molecules of $\mathrm{CO}_{2}=1$.

$$
\begin{gathered}
\mathrm{CaCO}_{3}: \mathrm{CO}_{2}=\mathrm{CaCO}_{3}: \mathrm{CO}_{2} \\
100: 1 \times 22.4=125: x=28 \text { liters } \\
\text { 4) } \frac{5}{112.0} \\
\frac{28.00}{}
\end{gathered}
$$

(Substitute 4 and 5 for 100 and 125. Similar simplifications are often possible, and the student should be on the lookout for them.)
(b) Same equation as (a), above. We want 100 liters of carbon dioxide, what weight in grams shall we take of calcium carbonate?

$$
\begin{array}{rl}
\mathrm{CaCO}_{3}: \mathrm{CO}_{2} & =\mathrm{CaCO}_{3}: \mathrm{CO}_{2} \\
100: 1 \times 22.4 & =x: 100 \\
-204 & 4643
\end{array}
$$

$10,000 \div 22.4=446.43=$ grams of calcium carbonate
(c) $\mathrm{MnO}_{2}+2 \mathrm{NaCl}+2 \mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{MnSO}_{4}+\mathrm{Na}_{2} \mathrm{SO}_{4}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{Cl}_{2}$
(Evolution of chlorine gas from manganese dioxide, common salt and sulphuric acid.)
Take 435 grams of the manganese oxide. What volume of chlorine?

$$
\begin{aligned}
\mathrm{MnO}_{2}: \mathrm{Cl}_{2} & =\mathrm{MnO}_{2}: \mathrm{Cl}_{2} \\
87: 1 \times 22.4 & =435 \quad: x=128 \text { liters. }
\end{aligned}
$$

Note that $\mathrm{Cl}_{2}$ is one molecule of chlorine.

$$
\text { (d) } \quad \mathrm{C}_{2} \mathrm{Ca}+2 \mathrm{H}_{2} \mathrm{O}=\mathrm{Ca}(\mathrm{OH})_{2}+\mathrm{C}_{2} \mathrm{H}_{2}
$$

Evolution of acetylene gas by action of water on calcium carbide.
We want 1000 liters of acetylene; how many grams of carbide must we take?

$$
\begin{gathered}
\mathrm{C}_{2} \mathrm{Ca}: \mathrm{C}_{2} \mathrm{H}_{2}=\mathrm{C}_{2} \mathrm{Ca}: \mathrm{C}_{2} \mathrm{H}_{2} \\
64: 22.4=x \quad: 1000 \\
(x=2857)
\end{gathered}
$$

Let $v$ be the volume in liters, and $w$ the weight in grams of any mass of gas we have the general relation:

$$
\text { . } 22.4: v=\text { m.w. : } w
$$

Hence, to find weight of a given volume of gas, multiply volume by molecular weight, and divide by 22.4.*
To find volume of a given weight of gas, multiply weight by 22.4* and divide by molecular weight.

Examples.-(a) Find weight of 49.4 liters of sulphuretted hydrogen gas.
(Molecular weight $2+32=34$ )
$49.4 \times 34=1679.6 . \quad 1679.6 \div 22.4=75$ grams
(b) Find volume of 237.72 grams of chlorine gas. $237.72 \times 22.4=5324.928 . \quad 5324.9 \div 71=75$ liters (Molecular weight of chlorine $=35.5 \times 2=71$ )
*The reciprocal of 22.4 is 0.04464 . It can be used as multiplier instead of 22.4 as divisor, and vice versa.

These measurements are not absolutely accurate, although close. Just as in the laws of volume under variations in heat and pressure, careful observation shows slight discrepancies, so the various gases do not show absolute accord with the " 22.4 " rule. But the differences are trivial, and for practical applications may be said not to exist.

Conversion of Molecular-gram Method into English Weights and Volumes.

This conversion is easier than with the "crith," because of an accidental relation between gram, ounce, liter and cubic foot.
A liter holds one thousand grams of water. A cubic foot holds one thousand ounces of water (998.4).
We have then the convenient fact that grams and liters are related just as are ounces and cubic feet.*

Thus, substituting ounces for grams, and cubic feet for liters, we may continue to use the number 22.4, with close approximation to exact results.

That is: 22.4 cubic feet of any gas weighs " $M$ " ounces.
"M" stands for the molecular weight of the gas considered.
Example.-(a) Calcium carbide, 94 per cent. pure, is to generate acetylene gas. Wanted 1000 cubic feet of gas, what weight of carbide must be taken?

Equation is:

$$
\begin{aligned}
& \mathrm{CaC}_{2}+2 \mathrm{H}_{2} \mathrm{O}=\mathrm{Ca}(\mathrm{OH})_{2}+\mathrm{C}_{2} \mathrm{H}_{2} \\
& \mathrm{CaC}_{2}: \mathrm{C}_{2} \mathrm{H}_{2}=\text { ounces : cubic feet. } \\
& \left.\begin{array}{r:c:c}
64 & 22.4= & x
\end{array}\right) \quad 1000 .
\end{aligned}
$$

(b) Coal contains 80 per cent. carbon. How many tons of it produce ten million cubic feet $\mathrm{CO}_{2}$ gas. How many cubic feet of air are consumed in the burning?

The equation of the reaction is:

$$
\begin{aligned}
& \mathrm{C}+\mathrm{O}_{2}=\mathrm{CO}_{2} \\
& \mathrm{C}: \mathrm{CO}_{2}=\text { ounces carbon : cubic feet } \mathrm{CO}_{2} \\
& 12: 22.4=\quad x \quad: \quad 10,000,000
\end{aligned}
$$

*I am unable to state who first pointed out this relation to me. It is given in the "Metallurgical Calculations" of Prof. J. W. Richards, who rediscovered it. It does not seem to be mueh known.
It is also given in Professor Wells' "Chemical Arithmetic."
5

Call oxygen 21 per cent. of the air by volume. Dividing the ounces obtained by 32,000 we get 167.4107 tons carbon, or, dividing by 0.80 (for coal), 209.263 ( 209 tons and 526 lbs .). The oxygen $\left(\mathrm{O}_{2}\right)$ is of same volume as the carbon dioxide $\left(\mathrm{CO}_{2}\right)$, hence the air is obtained by dividing that figure by 0.21 .

Ans. $47,619,047$ cubic feet.
209.263 tons.
(c) Ninety thousand cubic feet of hydrogen gas are required by the equation:

$$
\mathrm{Fe}+\mathrm{H}_{2} \mathrm{SO}_{4}=\mathrm{FeSO}_{4}+\mathrm{H}_{2}
$$

How many pounds of iron must be taken?

$$
56: 22.4=x: 90,000 . \quad x=225,000
$$

This 225,000 being in ounces we divide by 16 , getting:

$$
\text { Ans. } 14,062 \mathrm{lbs} \text {. }
$$

(d) A blast furnace, in a given time, blows in a million cubic feet of air. How many tons of carbon will this burn to carbon dioxide gas?

$$
\mathrm{C}+\mathrm{O}_{2}=\mathrm{CO}_{2}
$$

Air contains 21 per cent. by volume of oxygen, so we figure on 210,000 cubic feet of the latter.

$$
\begin{aligned}
12: 22.4= & x: 210.000 \quad x=112,500 \text { (ounces) } \\
& \frac{112,500}{32,000}=3.516 \text { tons }
\end{aligned}
$$

- Examples under Gas Volume Computation, by either Crith or Molecular Volume.
These problems have been computed by the molecular ( 22.4 liter) method in nearly every case. The student is nevertheless recommended to check occasionally by the "crith" method. He must remember, however, that the latter, when 0.09 gram is used as value of the crith, will give slight variants, i.e., as the weight is too great the volume sought will be either too great or too small according to the conditions of the problem.

1. A liter of gas weighs 1.1607 grams. Analysis of the gas is as follows:
Carbon
92.31 per cent.
(Data indicate $\mathrm{C}_{2} \mathrm{H}_{2}$ ) $\qquad$ 100.00 per cent.

It burns to $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$. Equate the reaction, and calculate total weight of the products of combustion. State also volume of carbon dioxide produced.
$2 \mathrm{C}_{2} \mathrm{H}_{2}+5 \mathrm{O}_{2}=4 \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \quad$ Weight of products $=4.8321$ grams
Volume of $\mathrm{CO}_{2}$ is shown directly, being twice that of the $\mathrm{C}_{2} \mathrm{H}_{2}$.
2. $\mathrm{H}_{2}+\mathrm{O}=\mathrm{H}_{2} \mathrm{O}$. 1000 liters of hydrogen and 400 of oxygen are exploded by the spark. When temperature is reduced again to "normal" $\left(0^{\circ} \mathrm{C}\right.$.) what gas remains and what volume of it?
Answer. No calculation is necessary. Read answer directly from data.
3. Same data, but temperature throughout is $100^{\circ}$. What are now the gases and volumes?

Ans. Same for hydrogen. 800 liters steam.
4. What is the weight of 100 liters of nitrogen?

Ans. 125 grams.
5. Illuminating gas has the following volumetric analysis:

| Carbon mono | 20 per cent. |
| :---: | :---: |
| Hydrogen | 30 per cent. |
| Methane ( $\mathrm{CH}_{4}$ ) | 40 per, cent. |
| Ethylene ( $\mathrm{C}_{2} \mathrm{H}_{4}$ ) | 10 per cent. |
| Total | 100 per cent. |

Equate the consumption of this gas in burning to water and carbon dioxide. Find how many cubic feet of air are required to burn 1000 cubic feet of the gas. (First find how many liters of oxygen are required.)
(200) $\mathrm{C} 0+0=\mathrm{CO}_{2} \ldots \ldots \ldots$. Oxygen required, $100 \mathrm{cu} . \mathrm{ft}$.
(300) $\mathrm{H}_{2}+\mathrm{O}=\mathrm{H}_{2} \mathrm{O} \ldots \ldots \ldots$. Oxygen required, $150 \mathrm{cu} . \mathrm{ft}$.
(400) $\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \ldots$. Oxygen required, 800 cu . ft.
(100) $\mathrm{C}_{2} \mathrm{H}_{4}+3 \mathrm{O}_{2}=2 \mathrm{CO}_{2}+2 \mathrm{H}_{2} \ldots \ldots$ Oxygen required, $300 \mathrm{cu} . \mathrm{ft}$.

Total oxygen required ........................... $1350 \mathrm{cu} . \mathrm{ft}$.
If atmospheric air contains 21 per cent. oxygen by volume, then:

$$
\frac{1350}{0.21}=6428=\text { cubic feet of air required. }
$$

For $\mathrm{CO}_{2}$ gas : $\mathrm{CO}(200)$ produces....... $\mathrm{CO}_{2} \ldots 200$ $\mathrm{CH}_{4}(400)$ produces........ $\mathrm{CO}_{2} \ldots 400$ $\mathrm{C}_{2} \mathrm{H}_{4}(100)$ produces ...... $2 \mathrm{CO}_{2} \ldots 200$


[^0]:    * We are little concerned as to whether this is or is not the true theoretical interpretation of the facts. Since it is a "working hypothesis" and does not lead us astray in stoichiometric work, it amply serves our purpose. $\dagger$ I.e., if the expressions occur in the same equation or in related equations.

[^1]:    *A very simple method of using ounces and cubic feet will be found at the close of this chapter.

[^2]:    * The student's attention is called to the molecular weights of elementary gases: $\mathrm{H}_{2}=2 ; \mathrm{O}_{2}=32$, etc. Explanation belongs to theoretical chemistry.

