

MEXICAN ASSAY RETURNS.

Mexico uses the metric system, and assays of ores for the precious metals are reported in grams to the metric ton (tonne).

As there are one million grams in a metric ton, one gram to the "tonne" is one millionth, or one ten-thousandth of one per cent.

Since one hundred per cent. in the Mexican system equals 1,000,000 grams, and one hundred per cent. in the United States system equals 29,167 ounces, we have:

$$\frac{1,000,000}{29,167} = 34.285$$

That is, any number of grams to tonne is 34.285 times corresponding "ounces to ton."

Hence, *given grams to tonne* in a Mexican report, *to find ounces to ton* in the United States system:

"Divide number of grams by 34.285."

We may also multiply by the reciprocal:

$$\frac{1}{34.285} = 0.029167$$

The latter has the advantage of presenting the same significant figures as the familiar number denoting ounces Troy in a ton, or milligrams in an assay ton.

To pass from ounces to grams it is only necessary to reverse the rule, using 34.285 as multiplier or 0.029167 as divisor.

Example.—Grams of metal to "tonne," 3679; how many "ounces to ton"? *Ans.* 107.3.

VOLUMETRIC ANALYSIS

By "Volumetric" analysis is meant analysis by means of solutions of certain reagents, whose exact chemical equivalence *per liter* (or other definite volume) is known.

The analytical operation is known as "titration."

The reagent is dropped from a graduated vessel (usually a burette) into a solution of the substance which is being estimated.*

It is necessary that some visible "end point" should mark the completion of the reaction. This "end point" may be the appearance of a color, or the vanishing of a color. It may be the cessation of the formation of a precipitate, or (as in acid-alkaline interaction) a change of color instead of appearance or disappearance. Finally, there may be no sufficient change visible in the solution under examination to warrant the designation of "end point" but the solution may be tested by the withdrawal of a small portion (on the end of a rod), which drop is then tested by another reagent, usually on a "spot plate" made for the express purpose of such tests.

Example.—In the titration of a ferrous solution by potassium bichromate, the true "end point," *i.e.*, the entire transition of the ferrous salt into the ferric form, cannot be recognized in the solution itself. When it is suspected that the "end" is near, a drop of the solution is withdrawn and touched to a drop of testing solution—"ferricyanide." Since ferrous salts give a blue color with potassium ferricyanide and ferric salts do not, the gradual lessening of the blue color in successive tests indicates the approach of the "end," and the failure to produce any color marks the true "end point."

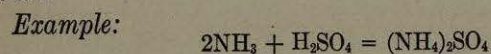
Other changes may be exemplified in the disappearance of the rich purple of "permanganate" in the iron and many other tests. The change of litmus from red to blue or vice

* In a few cases this may be reversed, the solution under examination being dropped into a previously measured amount of the reagent. The chemical principle is not affected. A few examples will be given of this procedure.

versa, the appearance of starch-iodine blue when the first excess of iodine has been liberated, and several others are familiar matters to the laboratory.

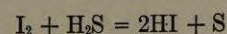
This brief indication of the ordinary procedure in volumetric analysis is all that can be said as to its practice. We are concerned entirely with its arithmetic, and shall give only such comments upon methods as are needed to explain the application of the proper calculations.

First, the student should understand that the reactions commonly encountered in volumetric analysis are interpreted by equations in exactly the same fashion as in all cases (viz: a great majority of all chemical reactions) where equations can be used at all.



This expresses the neutralization of ammonia by addition of sulphuric acid (or the reverse). If litmus had been added to the ammonia, the color at the moment the least excess of acid was present would "indicate" by turning to red. At this moment the equation is exactly satisfied.

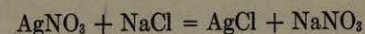
Example (starch added as indicator):



This equation may be satisfied by the addition of the iodine to the hydric sulphide or the reverse. If starch has been added in small but indefinite quantity, the color will appear in the first case or disappear in the last, marking in either case the completion of the equation.

We have already gone a little further into "operative" volumetric than was intended, the object being to impress upon the student the fundamental principle that the "end point" is just as much within the sphere of the chemical equation as in any case in gravimetric analysis. There are, in fact, cases in which even the operations themselves are *chemically* identical in volumetric and gravimetric.

Example:



If this were a gravimetric case the silver chloride would be separated out and weighed, if volumetric the exact point

of precipitation would be recognized by some suitable means. Precisely the same chemical reaction is involved in either case.

Volumetric solutions may be roughly classed under three heads. No matter how a solution is "made up," however, its relation to the substance with which it reacts is the same, the differences being merely matters of figures. To illustrate by arithmetic, the ratio of three to seven is the same as the ratio of one hundred and twenty-three to two hundred and eighty-seven. The first is rather easier to handle, and solutions bearing relations expressed by simple numbers are easier to figure on than more complex ones. As a safeguard against error, it is strongly recommended to "make up" solutions with simple relations, either chemical or numerical, to the substances tested.

First.—A solution may be made up in such a way that its numerical relation to the substance which is to be determined shall be irregular. Such solutions are called "arbitrary." They are sometimes made so at first, and allowed to remain unadjusted. Often, however, a solution which was "made up" in some simple relation changes by standing. It is then "restandardized," that is, its present relation to a given quantity of the substance in question is ascertained.

Take the last equation given. Suppose that the solution is the salt (NaCl) and that having an "arbitrary" solution, *i.e.*, one made up by some rough guess, or quite at random, we find by experiment that 40 c.c. of it precipitates 0.096 gram silver. If we do not care to make the relation any simpler, we make a record usually placed on the bottle containing the solution, and reading something as follows:

$$\begin{aligned} \text{"NaCl solution.} \quad 1 \text{ c.c.} &= 0.0024 \text{ gram metallic silver."} \\ & \left(\text{for } \frac{.096}{40} = 0.0024 \right) \end{aligned}$$

We shall give very few problems devoted to the relations and calculations resulting therefrom, of irregularly related solutions. They may be what is called "good practice," but they are on the whole poor laboratory practice, to be avoided when possible. If no other argument avails, the single one that the less calculation the less liability to error, seems to be final.

Always try, then, to secure either "simple factor" solutions (see below), or "normal," the latter term including deci-, centi-, and any other submultiple of "normal." It is usually easy to secure a simple solution from a complex one (the terms being used of course in a purely arithmetical sense), and several problems are devoted to this point alone.

Second.—A solution may easily be so adjusted that a given volume of it bears a simple relation to a given weight of the substance "sought." Such solutions are called "simple factor" solutions.

Example.—A solution of potassium permanganate may be so made up that one c.c. equals exactly 0.01 gram of iron. Then, if we take for analysis one gram of the iron ore, each c.c. of the solution used indicates one per cent. of iron.

Suppose that in making up the solution it is made stronger than this. The procedure will now be to ascertain its exact strength in relation to a certain weight of iron, and then (usually by dilution) to reduce the solution to the required strength.

Let original strength be such that one gram of iron in solution requires only 70.5 c.c. of the permanganate for end reaction. Instead of keeping the solution as it is, and labelling it with the proper factor, as in the case of the silver solution above, we add to 70.5 c.c. of it 29.5 c.c. of water, thus making the 100 c.c. which will exactly correspond to 1 gram of iron.

To "make up" a liter of it we should take 705 c.c. and add 295 of water. Or, if we have a liter of the strong solution, and want to know how much water to add:

$$705 : 295 = 1000 : 418.4$$

that is, add to each liter of the solution, as it stands, 418.4 c.c. of water.

These "simple factor" solutions are very easy to calculate from, indeed in most cases there is no calculation required since the number of c.c. used gives the result in identical figures. They are most used in those cases, very numerous in technical work, in which a certain solution is employed for one determination, as, for example, a solution of sulphuric acid in gas testing, for determination of ammonia only.

Third.—We may make a "normal" solution. This being an important convention, its theory will be set forth in considerable detail. We shall use the common abbreviation of "N" for normal, and in case of solutions which are submultiples of normal (tenths and hundredths), the fraction is prefixed. Thus N solution of HCl reads "normal solution of hydrochloric acid." Thirty c.c. of $\frac{1}{10}$ N. Na_2CO_3 reads "Thirty cubic centimeters of deci-normal solution of sodium carbonate."

"Cubic centimeter," however, is almost invariably "c.c.," even in speaking, in the laboratory.

A deci-normal solution is one-tenth the strength of a normal, a centi-normal is one-hundredth, and so forth.

There are three theories of "normal" solutions, but as one of them is now decidedly paramount, we shall use it alone, and to save the student we shall not even describe the "make-up" of the others.

The "normal" is based on the atomic weight of hydrogen. It might as well be based on the atomic weight of almost any other element, without making any difference in either theory or practice.

One liter of a normal solution contains or is equivalent to the atomic weight of hydrogen taken in grams.

Example.—One liter of "normal" KOH contains 1.008 gram hydrogen.

It also contains 16 grams of oxygen and 39.1 grams potassium.

Generally, the "normal" solution of any element will contain the "atomic gram weight" of that element, if the same be a monad, *i.e.*, "equivalent," atom for atom, to hydrogen. Certain special exceptions will be later noted.

Illustrations of the "normal" principle:

Take the acid HCl. Its molecular weight is 36.468, *i.e.*,

H.....	= 1.008
Cl.....	= 35.460
	36.468

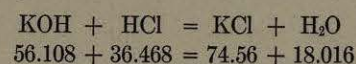
Take the molecular weight in grams, then one liter of the N solution contains 36.458 grams of the compound HCl.

Next take the alkali KOH:

K.....	= 39.10
O.....	= 16.00
H.....	= 1.008
	56.108

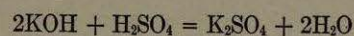
The molecular weight in grams will be 56.108 grams, contained in one liter.

These two compounds react as follows:



Unless the student understands far less of the theory of chemical reactions than we have assumed at the outset, he will see at once that *one liter* of the one solution will exactly satisfy (in this case, "neutralize") *one liter* of the other. Necessarily, then, *any* volume of the one will exactly satisfy the same volume of the other.

Next take the acid H_2SO_4 . Its molecular weight is 98.086. If we take 98.086 grams to a liter, however, we shall evidently have twice as much hydrogen (H_2) as in the last case. In order that the H here may be replaced by K as in that case, we should have to write the equation:



Evidently, in comparing the solutions, it is seen that it would take *two* volumes of the KOH solution to satisfy *one* of the H_2SO_4 . So to get the "N" for the latter we must divide by two, thus:

$$\frac{98.086}{2} = 49.043^*$$

It is very important that the student should appreciate from the start the consequences of this conventional make-up of solutions. The "balance" is not only between certain solutions prepared with reference to one another, but subsists between *any* two which have been prepared on the normal basis.

* These first examples have been carried to third decimal place because at. wt. of H has a figure in that place. In all future cases, however, we shall carry expressions to second place only, carrying if necessary from third place. Thus for the three substances above we shall write, $\text{HCl} = 36.47$; $\text{KOH} = 56.11$ and $\text{H}_2\text{SO}_4 = 98.09$. Normal to liter for the latter would be $\text{H}_2\text{SO}_4 = 49.04$.

Whether hydrogen or halogen, metal or radical, one liter, consequently one c.c., of any one \equiv one liter of any other. (The sign \equiv is used to signify "is equivalent to.") Also, any volume of an "N" sol. of a given element will carry the same weight of that element as the same volume of any other "N" solution which carries the same element, even though in a different combination.

This being both fundamental and important, an example follows.

Example. Normal solution of silver, one liter contains: silver 107.88 grams.

Normal solution of NaCl , one liter contains: Na, 23.0 grams; and Cl, 35.46 grams.

"N" solution of BaCl_2 . According to system explained this must be $\frac{208.30}{2} = 104.15$, containing chlorine, 35.46 grams. Thus one c.c. of either the sodium or barium chlorides ("N") will exactly precipitate (satisfy equation) one c.c. of the ("N") silver solution.

By both principle and illustration, then:

1 c.c. of any "N" solution \equiv 0.001008 gram hydrogen.

1 c.c. of any halogen acid will contain 0.001008 hydrogen.

1 c.c. of any chloride will contain 0.03546 chlorine.

1 c.c. of any acid ("N") will exactly neutralize 1 c.c. of any N alkali.

1 c.c. of any element ("N") will contain $\frac{1}{1000}$ of the atomic gram weight of that element, if a monad; $\frac{1}{2000}$ if dyad, $\frac{1}{3000}$ if triad. (See below.)

The student who has grasped the principle of this method of adjusting solutions needs no further illustrations.

We here give a table of the more common normal solutions. Many substances are too strong as full normals, and in such cases it is usual to employ the deci-normal " $\frac{1}{10}$ N" and often the centi-normal, " $\frac{1}{100}$ N."

The student should distinguish between normal solutions proper, and the so-called normal solutions which are often said to be "normal to each other." It is evident that two solutions may be arbitrarily made up in such a way that *any volume of the one shall be equivalent to an equal volume of the other*. This implies nothing as to any relation between volume and atomic weight.

VOLUMETRIC NORMAL SOLUTIONS. WEIGHTS PER LITER.		
Compound or element.	Atomic or molecular wt.	Grams per liter.
KOH.....	56.11	56.11
NaOH.....	40.01	40.01
NH ₃	17.03	17.03
CaO.....	56.09 (÷ 2)	28.05
BaO.....	153.37 (÷ 2)	76.69
K ₂ CO ₃	138.20 (÷ 2)	69.10
Na ₂ CO ₃	106.00 (÷ 2)	53.00
HCl.....	36.47	36.47
HBr.....	80.93	80.93
HNO ₃	63.02	63.02
H ₂ SO ₄	98.09 (÷ 2)	49.04
H ₂ C ₂ O ₄	90.02 (÷ 2)	45.01
H ₃ PO ₄	98.06 (÷ 3)	32.69
Ag.....	107.88	107.88
I.....	126.92	126.92
Ba.....	137.37 (÷ 2)	68.69
Al.....	27.10 (÷ 3)	9.03
NaCl.....	58.46	58.46
BaCl ₂	208.29 (÷ 2)	104.15
AlCl ₃	133.48 (÷ 3)	44.49

The second decimal places are hardly worth considering as a rule. If over five, carry 1 to first place, *e.g.*, AlCl₃ = 44.49. Call it 44.5.

Take any substance in the table, it is evident that to get the quantity in one c.c. we have only to divide by 1000.

Example:

Sodium carbonate, Na₂CO₃: One liter "N" contains 53.0 grams.
 One liter $\frac{1}{10}$ N contains 5.30 grams.
 One liter $\frac{1}{100}$ N contains .530 gram.
 One c.c. N contains .0530 gram.
 One c.c. $\frac{1}{10}$ N contains .00530 gram.
 One c.c. $\frac{1}{100}$ N contains .000530 gram.

Since then any volume of "N" solution satisfies the same volume of "N" solution of any other substance, the same must be good as between the $\frac{1}{10}$, $\frac{1}{100}$ or any other equalized relations to normal.

The student should now find it easy to "set up" for himself any number of illustrations, with these "type" cases before him. The practical use of normal solutions and their subdivisions belongs to laboratorial instruction.

We have still to consider a class of solutions which cannot be brought strictly within the rules for normal cases. There are compounds whose "normal" for one reaction is not the same as for another, that is, it may be a "normal" in the one case and an "irregular" for another. The relation between the two cases may easily be calculated, but the irregularity remains. One of the most familiar of all volumetric reagents, potassium permanganate, comes under this class. It is also obvious that variant valence under different conditions destroys the strict rule for the "make-up" of normals.

In the case of "permanganate" as well as of several other common compounds, solution is rarely or never "made up" by weighing out a figured portion of the solid. Or rather, this is done as a mere approximation, and the solution is carefully tested ("standardized") afterward.

These special cases introduce no confusion in the subject. A few problems will show how to "convert" a solution for one element into a solution for another, simply by the calculation of a factor to be used in each analysis.

Even this might be dispensed with, if we chose to take the trouble to apply such a factor to the solution itself, instead of to the label.

See problem for deduction of manganese factor, using "permanganate," from the already known factor for iron.

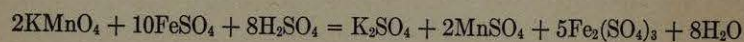
Although it somewhat invades the province of laboratory instruction, we may here slightly enlarge upon the remark made above as to method of obtaining an original "standard" solution whether normal or not. Certain solutions may be made with far greater accuracy by original "weighing out" of their required quantity, others may preferably be "standardized" after the make-up, and several can be obtained by the latter procedure only.

Examples.—(1) Silver. No comparison of a silver solution with another one can rival the accuracy of making an original silver solution by weighing out pure silver to the required amount and then dissolving it.

(2) Caustic potash (KOH). Any solution of KOH made by weighing out would be considered as a mere approximation, owing (a) to probable impurities, (b) to the great difficulty of weighing so hygroscopic a substance accurately.

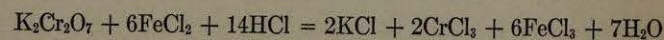
(3) Hydrochloric acid (HCl). Here we have the third case. We cannot weigh the gas, so we can get an accurate solution only by comparisons with others.

The following equations, nearly all of which are very familiar ones, will show how the calculation of the "normal" may have to vary from the set rule indicated above.



Since we have here $2\text{KMnO}_4 = 10\text{FeSO}_4$ we see that the "normal" quantity for KMnO_4 must be $\frac{1}{5}$ of its molecular weight.

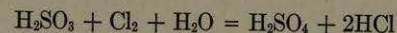
Practically, this solution is made by adjustment with metallic iron or an iron salt (ferrous-ammonium sulphate) and very commonly as a "simple factor solution" so that its normal value enters little into consideration.



Since one molecule of the chromate acts upon six molecules of the ferrous salt, take one-sixth of the formula weight of the former.

The reactions of oxalic acid show that both its hydrogen atoms are replaced in ordinary interchange, hence we take one-half its "weight" as the normal. Similarly for all ordinary di-basic acids.

Sulphurous acid may be estimated from its reaction with chlorine.



Hence normal quantity is:

$$\frac{\text{H}_2\text{SO}_3}{2} \text{ or } \frac{\text{SO}_2}{2}$$

Iron in changing from ferrous to ferric uses (theoretically or actually) only "one-half" of an oxygen atom. The expression is of course absurd in a theoretical sense, but useful in illustration. Thus:

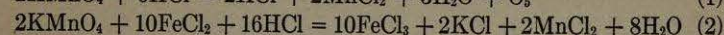
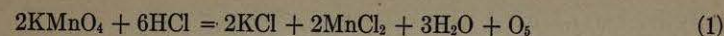


The "O" being regarded as derived from an oxidizing agent (say KMnO_4), we see that in this relation we must take the atomic weight of iron as "normal."

Using 56 as atomic weight of iron, let us ask as a problem:

"Permanganate" solution, standard for iron per c.c. being 0.0056,

Required, "available" oxygen per c.c., according to following equations:



Solution:

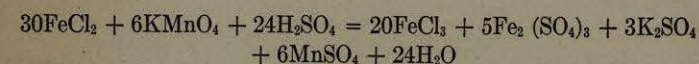
$$560 : 80 = 0.0056 : x \quad x = 0.0008 = \text{available "O" per c.c.}$$

What is standard of the above solution for CaO ?

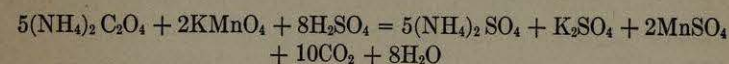
$$\text{Ans. } \frac{.0056}{2} = 0.0028$$

Let the student study the following equations carefully. The first one, showing oxidation of ferrous chloride by permanganate, will assist him in understanding why ferrous salts, considered as reducing agents, have their molecular weights (gram) as "normals" instead of half that weight.

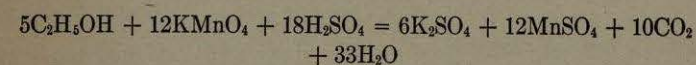
3. Oxidation of ferrous chloride:



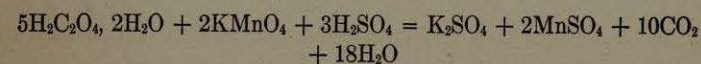
4. Oxidation of ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$:



5. Oxidation of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$:



6. Crystallized oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$:



With these as types any case of permanganate oxidation may be solved.

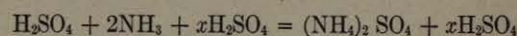
We have finally to mention volumetric analysis by means of two solutions. For convenience these should be "normal to each other," if not made up to strict at. wt. normal. Obviously, any two strict N solutions are also "normal to each other."

In almost every case in practice the operation of a two-solution method consists in taking a fixed amount of one of them, subjecting it to whatever chemical reaction the particular

analysis calls for, and then, with the other solution, determining the amount of the chemical change which has taken place. Technically, we are said to "titrate back" in using the second solution.

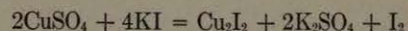
Examples. (1) In the analysis of illuminating gas, ammonia is determined by a process outlined as follows: A measured amount of the gas is made to pass through a solution of sulphuric acid, whose standard and volume are accurately known. Care is taken that the amount of acid shall be *more* than equivalent to any probable ammonia present in the volume of gas used. Now the acid is "titrated back" with an alkaline solution (it may be an ammonia solution as well as any other), which titration evidently determines how much of the acid was left *over and above the amount neutralized by the ammonia* in the gas. Subtracting this amount from the original quantity taken, we have the data for figuring the amount of ammonia present in the gas.

The reaction might be written thus:

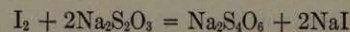


That is, if we had taken $x + 1$ molecules of H_2SO_4 and 2 molecules of ammonia, we would still have to determine the " x " unsaturated molecules of the acid. The convenience of having the two solutions related by some very simple factor, or better, having them normal "*inter se*," needs no demonstration.

(2) In the "iodide" method for copper, the following equations define the reaction:



Then,



This is a case in which one solution (KI) need not be known. It is added in excess, but only so much of its iodine as corresponds to Cu_2 is liberated. The "hypo" solution which determines the iodine (2nd equation) is of course known in its relation to iodine, consequently to copper according to first equation.

"To avoid mistakes in calculating absolute strength of one solution from another, observe which is the stronger, and be sure that the calculated strength corresponds with this observation: the *stronger* solution is used in *smaller* volume than the

weaker, when the two solutions are compared." (Prof. Horace L. Wells, "Chemical Arithmetic," p. 117.)

The error indicated is of precisely the same nature as may be made in determining volumes of gases according to changes in temperature or pressure. Inversion of fractions or logic is a common error. I have seen a student, after a careful but "inverted" calculation, deliberately dilute a solution already too weak.

When many determinations of the same kind are to be made and only regular "normals" are at hand, it lessens the computations to take, instead of ordinary fractions of a gram, or whole grams of the substance for analysis, *weights which have such a relation to the N solution that the reading in c.c. shall give the required percentage directly.* The "relation" is absolutely simple, however, and our problems open with illustrations of the principle, which is often used in gravimetric analysis also.

MISCELLANEOUS PROBLEMS IN VOLUMETRIC ANALYSIS.

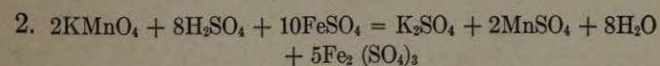
1. Having $\frac{1}{10}N$ acid solution, prepared for alkaline determinations, it is required to find the weights of various substances to be taken for determinations in order that *each c.c.* of the acid used shall indicate *one per cent.* of the constituent "sought."

Constituent sought.	Weights of substance to be taken.
Nitrogen (N).....	0.1401 gram
Ammonia (NH_3).....	0.1703 gram
Sodium carbonate (Na_2CO_3).....	0.530 gram
Potassium carbonate (K_2CO_3).....	0.691 gram
Sodium oxide (Na_2O).....	0.310 gram
Potassium oxide (K_2O).....	0.471 gram
Sodium hydroxide (NaOH).....	0.4001 gram
Potassium hydroxide (KOH).....	0.5611 gram
Calcium carbonate (CaCO_3).....	0.5005 gram
Calcium oxide (CaO).....	0.2805 gram
Barium carbonate (BaCO_3).....	0.9870 gram
Barium hydroxide ($\text{Ba}(\text{OH})_2$).....	0.8571 gram

If the solution is full normal, take ten times these weights.

If the solution is $\frac{1}{10}N$ take one-tenth of these weights.

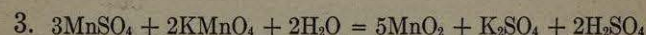
The student may now easily solve any parallel case.



This is the ordinary reaction of "permanganate" on ferrous salts.

Required: Weight of permanganate per liter, if each c.c. of the solution equals 0.01 gram of iron, or, taking 1 gram for analysis, each c.c. = 1 per cent.

Solution.—The relation is 10Fe to 2KMnO₄, numerically, 559 : 316.3. *Ans.* 5.658 grams per liter.



This is the equation for determination of manganese by the "permanganate" method. Having a solution of KMnO₄ standardized for iron, what factor is required for application when the same solution is to be used for manganese?

Solution.—Compare the equation with that in example 2 above. We see that in the first case 2KMnO₄ = 10FeSO₄; and in the second, 2KMnO₄ = 3MnSO₄. Take the exact figures for atomic weights (Fe = 55.84, Mn = 54.93), we have:

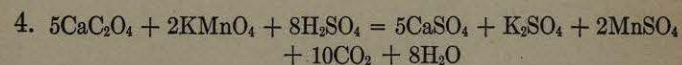
$$55.84 \times 10 = 558.4 \text{ and } 54.93 \times 3 = 164.79$$

If our iron "standard" is represented by unity (for example, 1 c.c. = 1 per cent.), then we may write:

$$558.4 : 164.79 = 1 : 0.295$$

Then 1 c.c. of the solution would indicate 0.00295 manganese, if the adjustment for iron had been 1 c.c. = 0.01 gram.

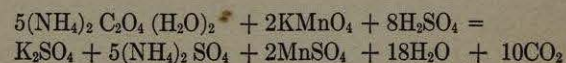
Ans. Factor = 0.295.



Equation of determination of lime (CaO) by "permanganate."

As in (2) above, having iron solution, determine "factor" to be used when same is to be used for CaO. We have 10Fe = 5CaO. Hence we need take only one-half of the iron indication, as the approximation of atomic weight of iron is so close to molecular weight of lime. (Fe = 56, CaO = 56 approx.) Thus, if 1 c.c. = 0.01 iron, then 1 c.c. = 0.005 lime.

5. Nineteen c.c. of KMnO₄ are required to oxidize 0.225 gram of ammonium oxalate, (NH₄)₂C₂O₄ + 2H₂O. Required the "standard," *i.e.*, weight per c.c., for iron. Use Fe = 56, etc.



Compare again with the equation for iron. That is, compare reaction of 2KMnO₄ with oxalate and with iron, and deduce the relation of the two latter, on the principle that things equal to the same thing are equal (here equivalent) to each other. We have the old relation of 10Fe = 2KMnO₄, also 5 of the "oxalates" equal to the same.

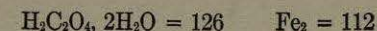
$$5 \text{ "ox." } : 10\text{Fe} = 1 : x; \text{ i.e., } 800 : 560 = 1 : 0.7$$

Ratio therefore is 0.7. Now by terms of the problem $\frac{2.25}{1.9} = 0.0118$, that is, 1 c.c. of KMnO₄ = 0.0118 oxalate, multiply this by the ratio just found: $0.0118 \times 0.7 = 0.00826$.

Ans. 1 c.c. = 0.00826 metallic iron.

6. Taking a liter of the permanganate solution of example 5, how much water must we add to make 1 c.c. equivalent to 0.005 iron? *Ans.* 652 c.c.

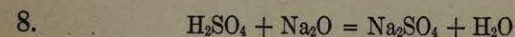
7. See equation of reaction between crystallized oxalic acid and permanganate, under oxidation equations above. Fix standard for iron titration by oxalic acid. (Iron at 56 at. wt.)



$$\frac{112}{126} = \frac{8}{9}$$

Hence if we wish to "standardize" a solution for iron by means of the acid,

$$\frac{8 \times \text{oxalic indication}}{9} = \text{indication for iron}$$



If ten c.c. of H₂SO₄ precipitate five grams BaSO₄, how much water must be added to one liter, so that 1 c.c. equals 0.1 gram Na₂O? *Ans.* 329 c.c.

9. 5.3 grams sodium carbonate require 176 c.c. of a $\frac{1}{2}N$ solution of acid to neutralize. What is percentage of impurities in the sample? *Ans.* 12 per cent.

(The 5.3 is one-tenth of the 53 grams, or weight for 1 liter normal. If pure it would have neutralized 100 c.c. of normal acid, or 200 c.c. of $\frac{1}{2}$ normal. As it lacks 24 c.c., per cent. of impurities is evidently $\frac{1}{2}$ of 24 = 12.)

10. 1 gram of nitrogenous organic matter is treated with "soda-lime," which brings the nitrogen into form of ammonia,

and the NH_3 is received into normal H_2SO_4 (100 c.c.). The latter is now "titrated back" with N alkali, of which 87 c.c. are required. What per cent. of nitrogen in the substance?

Solution.—The amount of nitrogen in 1 c.c. normal NH_3 is 0.014, which would of course neutralize 1 c.c. N acid. But it equals 13 c.c. normal acid, hence the amount of NH_3 is $0.014 \times 13 = 0.182$. ($100 - 87 = 13$.)

Ans. 18.2 per cent. nitrogen.

11. Using same solutions as in the last example, if we desire that each c.c. of the acid consumed by NH_3 shall equal 1 per cent. of nitrogen in the substance, what weight of the organic matter should we take to start with? See example 1.

Ans. 1.4 grams.

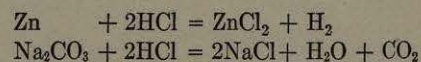
12. We "make up" haphazard a solution of permanganate, and standardize with 0.5 gram of iron wire, which contains 99.7 per cent. iron.

It takes 42.6 c.c. of this solution to react. We want a solution of which 1 c.c. = 0.005 Fe. How much water do we add to one liter of this solution? (Total volume 2.34 liters, subtract original liter.)

Ans. 1.34 liters.

13. Solutions of Na_2CO_3 and HCl are equivalent ("normal to each other"). 100 c.c. of the acid acting on zinc evolve 100 c.c. of hydrogen. How many c.c. of the Na_2CO_3 will evolve 100 c.c. of CO_2 gas when acted on by excess of any acid?

The equations are:



Ans. 100 c.c.

(For the relative amounts of the reagents in equal volumes, since they are mutually equivalent, is Na_2CO_3 and 2HCl .)

14. Wishing to get a silver solution with 0.01 gram of the metal in each c.c., and having only silver nitrate at hand, how much of this salt must be weighed out to make one liter of the desired solution?

Ans. 15.7454 grams.



Use nearest whole numbers for at. wts. In testing a spring water we make a solution of iodine, 25.4 grams to liter. Of this we place 100 c.c. in vessel and add the spring water under test. Of the latter 625 c.c. are required for the end reaction

(disappearance of the starch-iodine blue). What volume of H_2S gas in one liter of this water? Use the "22.4" rule after getting weight of the gas.

Ans. 358 c.c.

16. Two acid solutions intended to be each normal to a certain alkaline solution are respectively too strong and too weak. Of the strong, 70 c.c. neutralize 100 c.c. of the alkaline solution, while it requires 115 c.c. of the weak for the same volume (100 c.c.) of alkali.

We are now to mix the two acid solutions, mixture to be one liter in volume, so as to get a solution exactly "normal" to the alkaline solution.

Here is a good chance for "rational" arithmetic.

(1) As to the strong, it is obvious that if we add 30 c.c. of water to 70 c.c. of it, we get 100 c.c. of correct strength.

(2) As to the weak, it may be regarded in the light of 100 c.c. of correct strength, plus 15 c.c. of water.

$\frac{30}{15} = 2$. That is, $115 \times 2 = 230$ c.c. of the weak, added to 70 c.c. of the strong, will make correct mixture, 23 to 7. Divide the liter into 30 parts, taking twenty-three of the weak and seven of the strong.

Ans. Strong, $233\frac{1}{3}$ c.c. Weak, $766\frac{2}{3}$ c.c.

17. Same problem. The "weak" acid, however, is weaker, as it takes 117 c.c. instead of 115.

Ans. Strong, 253.19 c.c. Weak, 746.80 c.c.

18. Wanted iodine solution, of which 1 c.c. shall equal 1 c.c. of H_2S gas.



We have weighed out 0.576 gram of iodine, what volume of solvent must be used? One liter of H_2S gas weighs 1.518 grams.

Ans. 50.8 c.c. = vol.

For 1 liter of it would contain 11.34 of iodine.

19. Wanted solution of "permanganate" of which 1 c.c. shall equal 0.01 gram of iron. We have a solution of which 20 c.c. = 0.24 iron. How much water to be added to a liter of this for the required strength?

Ans. 200 c.c.

20. One gram of silver is dissolved and made up to 1 liter. We want a solution of NaCl which shall be "normal" to it. Trial solution of the salt precipitates 0.0015 AgCl for each c.c. How much water must be added to one liter of the salt solution?

Ans. 129 c.c.

21. Chlorine is determined in water by solution of silver nitrate, using Ag_2CrO_3 as indicator. (That is, the highly colored silver chromate does not appear until all the AgCl is precipitated.)

For the silver solution 0.1 gram of metallic silver is dissolved in 1 liter. 6 c.c. of this solution bring end reaction with 100 c.c. of the water. How many parts chlorine in a million parts of water?

Solution.—Weight of silver used in the reaction = 0.0006.

$$107.88 : 35.46 = 0.0006 : 0.000197 \text{ (in 100 c.c.)}$$

Ans. Chlorine, 1.97 parts to million.

22. Taking above problem, and still using 100 c.c. of the water for analysis, we want a solution of silver such that *each* c.c. shall indicate 1 part in 1 million of chlorine. What weight of silver must we take for one liter of solution?

Solution.—In 100 c.c. (also grams) of the water, 1 part in million equals .0001.

$$35.46 : 107.88 = .0001 : .000304$$

Ans. For 1 liter take 0.304 gram Ag.

23. Solutions of NH_3 and H_2SO_4 are normal "to each other." 50 c.c. of the H_2SO_4 precipitate 1 gram of BaSO_4 . How much NH_3 is there in 1 c.c. of its solution? (Approximate at. wts.)

Ans. 0.00292 gram in one c.c.

24. Wanted, solution of H_2SO_4 of which 1 c.c. \equiv 0.001 of NH_3 . 100 c.c. of a trial solution precipitate 0.711 BaSO_4 . How much water must be added to 1 liter of the H_2SO_4 solution. (Approx. at. wts.)

Ans. 36 c.c. water to one liter.

25. 1 c.c. of HCl solution \equiv 0.010796 gram silver. 40 c.c. of same solution \equiv 24 c.c. of an alkalin solution. (Exact at. wts.)

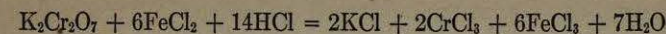
Taking 0.5305 of impure Na_2CO_3 for analysis, we acidulate it with 100 c.c. of the HCl , boil off CO_2 gas remaining, and then "titrate back" excess of acid with the NH_3 solution, of which 9 c.c. are required.

What is per cent. of sodium carbonate in the sample?

Ans. 85 per cent.

Let the student, in verifying this, pay attention to the relation to "normal" as shown by figures of the first data.

26. Wanted, 1 liter of solution of $\text{K}_2\text{Cr}_2\text{O}_7$, 1 c.c. to \equiv 0.01 iron.



What weight of $\text{K}_2\text{Cr}_2\text{O}_7$ must be taken? (Exact at. wts.)

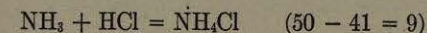
The 1 liter must be \equiv 10 grams iron ($0.01 \times 1000 = 10$).

Ans. 8.7805 grams.

27. 1 c.c. of a $\frac{1}{10}$ *N* solution of HCl \equiv 1.582 c.c. of NH_3 . To what weight of Na_2CO_3 is 1 c.c. of this NH_3 equivalent? Note that we do not have to recur to the HCl in getting answer.

Ans. 0.003353 gram.

28. 1 gram of organic substance is taken for determination of nitrogen. NH_3 from the nitrogen is received in 50 c.c. *N* solution of HCl , which is now "titrated back" with *N* sol. of NH_3 , using 41 c.c. of same. What is percentage of nitrogen?



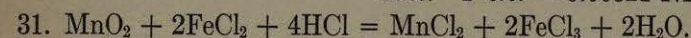
Ans. 12.6 per cent.

29. If 10 c.c. H_2SO_4 precipitate 0.1631 BaSO_4 , what weight of NH_3 \equiv 1 c.c. of the acid? (Approx. wts.)

Ans. 0.00238 gram.

30. Same as above, but 50 c.c. H_2SO_4 precipitate 1.1 BaSO_4 .

Ans. 1 c.c. \equiv 0.00321 NH_3 .



Half a gram of iron dissolved in excess of hydrochloric acid, with one gram of manganese ore. Upon titration we find 0.285 iron. Using approx. wts., what per cent. of MnO_2 in the ore?

Solution.—Since 0.285 iron is unchanged, 0.215 entered the reaction, as per equation. We have $\text{Fe}_2 \equiv \text{MnO}_2$, hence:

$$112 : 87 = 0.215 : 0.167$$

Ans. 16.7 per cent. MnO_2 .

32. Analysis of coal gas for ammonia. 1 c.c. H_2SO_4 \equiv 0.56 NaOH (gram). Into 50 c.c. of the acid pass whatever quantity of gas is required by test, then titrate back with the NaOH solution, using 14 c.c.

What volume of the acid was neutralized by the NH_3 ?

Ans. 25 c.c.

33. 11.9922 grams silver are made up to 1.1111 liters in solution. What is now the relation to "normal" of this solution?

Ans. $\frac{1}{10}$ normal.

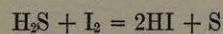
34. Two solutions are of equal volume. One contains 6.4935 grams of NaCl, the other 94.3167 of AgNO₃. What is their numerical relation in the "normal" adjustment?

Ans. The silver solution is five times the salt. That is, if the silver is N the salt is $\frac{1}{5}$ N.

35. We have KMnO₄ solution of which 1 c.c. \equiv 0.02 Fe. Take 2.5 grams for analysis, and use 80.5 c.c. of this solution, what is the per cent. of iron in the ore?

Ans. 64.4 per cent.

36. We have a solution of iodine, made by weighing out the solid, and containing 4 grams to the liter. Taking 100 c.c. of this, we pour in the water which is under examination for its contents of H₂S gas, and get end reaction at 850 c.c. of the water.

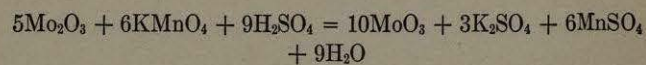


What *volume* of H₂S gas in 1 liter of the water?

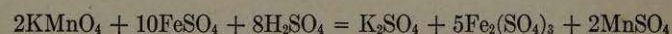
Ans. 0.0414 liters.

37. Phosphorus can be precipitated as (NH₄)₃PO₄ + 12MoO₃. The relationship to be considered is P \equiv 12MoO₃; numerically 31 : 1728.

Solution of the "yellow precipitate" being reduced, the MoO₃ becomes Mo₂O₃ (*i.e.*, 2MoO₃ becomes Mo₂O₃) and titration with permanganate gives following equation (use approx. wts. throughout. Fe = 56, etc.):



Compare this with the equation:



If we seek a relation from an already made solution of KMnO₄ adjusted for iron, to one for phosphorus, according to these ratios (or say we want a "factor" to pass from the iron to the phosphorus relation for the KMnO₄ solution) we calculate as follows: In the first equation 6KMnO₄ \equiv 10MoO₃, while in the second equation (since 2KMnO₄ \equiv 10 Fe), 6KMnO₄ \equiv 30Fe. Putting equivalents to same, as equivalents to each other, we have 10MoO₃ \equiv 30Fe. This reduced to its lowest terms becomes MoO₃ \equiv 3Fe, or, numerically, 144 molybdic anhydride \equiv 168 iron.

Returning now to the first comparison, *i.e.*:

$$\text{P} : 12\text{MoO}_3 = 31 : 1728$$

we see that 31 grams phosphorus corresponds to $\frac{168}{144} \times 1728$ grams metallic iron, easily reducible to the ratio:

$$\text{Fe} : \text{P} = 1 : 0.01538$$

That is, a KMnO₄ solution which for a given volume \equiv 1 Fe, corresponds to only 0.01538 phosphorus in the titration for phosphorus as given in the first equation in this section.

The figures (ratio) may of course be made to apply to either weights or percentages, according to circumstances.

38. Permanganate is so adjusted that 1 c.c. = 0.01 iron. From one gram of ore the yellow precipitate is obtained, reduced and titrated with the permanganate solution. It takes 15 c.c. for the reaction, what is the percentage of phosphorus in the ore?

$$\text{Solution:} \quad 1 : 0.01538 = 15 : 0.2307$$

Ans. 0.2307 per cent.

39. Permanganate solution, 1 c.c. = 0.013 iron. Take 5 grams of iron ore for phosphorus, we find by titration with KMnO₄ of the yellow precipitate that it requires 45 c.c. for end reaction. What per cent. of phosphorus in the ore?

Ans. 0.1799 per cent.

40. Mn₂P₂O₇ contains 50 per cent. of phosphoric anhydride (P₂O₅). A certain weight of this substance being taken and dissolved, phosphorus is obtained as the molybdate precipitate ("yellow ppt.") the latter dissolved and titrated with KMnO₄ sol. of such strength that 1 liter = 40.31 grams iron.

It takes 1 liter of the KMnO₄ solution to react. What weight of the phosphate was taken?

Ans. 2.84 grams.

41. 10 c.c. H₂SO₄ precipitate 0.124 BaSO₄. 10 c.c. NH₃ \equiv 14 c.c. HCl. 100 c.c. of the HCl precipitate 2 grams of AgCl.

Which is the stronger, the H₂SO₄ or the NH₃ solution? How many c.c. of water must be added to 1 liter of the stronger to equalize the solutions?

Ans. The NH₃ is the stronger. Add 0.8383 liter to 1 liter.

NOTE.—Some of the problems above have been computed with "weights" of 1907. (Mn. = 55, Ag = 107.93, etc.) The differences in answers are trivial.