of the calcium carbide, it having been obtained for our use by the payment of the express charges only.

My thanks are due to Messrs. McElroy, Ewell, and Runyan for assistance in the preparation of the gas and in reading the polariscope.

INDIRECT ANALYSIS.

BY EDWARD K. LANDIS.

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IN investigating this subject the author was struck with the difference in the formulas given in the text-books and on trying some of the cases found the results did not agree. Supposing that the old atomic weights used in the formulas were the cause of the trouble, it was thought best to derive a formula in such a manner that it would apply equally if the present weights should be modified, and it is given herewith, trusting that it may be useful to many chemists in cases where a separation of the two elements is difficult or tedious.

It will apply to any case where the atomic weights of the two elements are not the same, and the greater the difference between the atomic weights the greater the accuracy. Unfortunately, nickel and cobalt cannot be determined in this manner, but many other elements can be. This method is especially convenient for sodium and potassium, and probably more accurate than the separation with platinum chloride.

FIRST METHOD.

Data given:

Weight of mixture.

Weight of common constituent.

Let x = weight of salt with greatest per cent. of common constituent.

Let y = weight of salt with least per cent. of common constituent.

Let a = amount of common constituent in one part of x.

b = " " " " " " " " y.

W = weight of mixture.

w = " " common constituent.

To find x and y:

$$
\begin{aligned}
&x+y=W, \qquad x=W-y,\\
&ax+by=w,\\
&a(W-y)+by=w,\\
&aW-ay+by=w,\\
&by-ay=w-aW,\\
&(b-a)y=w-aW,\\
&y=\frac{w-aW}{b-a},\\
&x=\frac{w-bW}{a-b}.
\end{aligned}
$$

$a-b=$ difference of coefficients of x and y.

Therefore, to find x or y, multiply the weight of mixture by the coefficient of the other salt. Find the difference between this and the weight of common constituent, and divide this result by the difference of the coefficients.

SECOND METHOD.

Same data as before and same symbols, except that here

$a=$ molecular weight of x.
$b=$ " " " y.

If all the common constituent were combined with y we should have a greater weight than W, and if combined with x less than W. In either case call this W'.

$$
\text{Then } \frac{b}{a}x+\frac{b}{b}y=W'
$$

$$
\frac{a}{a}x+\frac{b}{b}y=W,
$$

$$
\text{Subtracting } \frac{b-a}{a}x=W'-W,
$$

$$
x=\frac{a(W'-W)}{b-a},
$$

$$
b-a : W'-W=a:x.
$$

Rule.—Calculate the weight if common constituent were all combined with one of the salts. Find the difference between this and the weight of the two salts. Then the difference of the molecular weights is to the difference found as the molecular weight of the salt causing the difference is to the amount of that salt.

As an illustration let us take two grams sodium chloride and one gram potassium chloride with the following data :

$$\begin{aligned} Cl &= 35.45 \\ Na &= 23.05 \\ K &= 39.11 \\ KCl &= 47.5456 \text{ per cent chlorine.} \\ NaCl &= 60.598 \quad \text{''} \quad \text{''} \end{aligned}$$

FIRST METHOD.

$W = 3,$

$w = 1.687416,$ $\qquad x = NaCl,$

$a = 0.60598,$ $\qquad y = KCl,$

$b = 0.475456,$

$$x = \frac{w - bW}{a - b} = \frac{1.687416 - 1.426368}{0.130524} = 2,$$

$$y = \frac{w - aW}{a - b} = \frac{1.81794 - 1.687416}{0.130524} = 1.$$

Crookes gives the following formula :

Let $W =$ weight of mixed chlorides.

$C =$ " " chlorine.

$NaCl = C \times 7.6311 - W \times 3.6288.$

$KCl = W \times 4.6288 - C \times 7.6311.$

Using the data above this gives $NaCl = 1.9904$, $KCl = 1.0096$.

The above formula should read

$NaCl = 7.6311\ C - 3.6288\ W$ to be perfectly clear, otherwise it means that C is multiplied by 7.6311, W subtracted from the product and the result multiplied by 3.6288, which would not give the answer.

Bailey's Chemists Pocket Book (3rd edition) gives the following :

$$NaCl = \Big((C \times 2.1029) - W\Big) \times 3.6288.$$

Using the same data this gives $NaCl = 1.990277$ instead of 2.0.

SECOND METHOD.

Calculating Cl to KCl.

$$Cl = 1.687416,$$
$$W = 3,$$
$$\frac{1.687416}{0.475456} = 3.549047 \text{ KCl},$$
$$3.549047 - 3.0 = 0.549047,$$
$$\frac{0.549047 \times 58.5}{74.56 - 58.5} = \text{NaCl} = 2.$$

Calculating Cl to NaCl.

$$\frac{1.687416}{0.60598} = 2.7846 \text{ NaCl},$$
$$3.0 - 2.7846 = 0.2154,$$
$$\frac{0.2154 \times 74.56}{74.56 - 58.5} = \text{KCl} = 1.$$

The author hopes that this may prove the accuracy of the method and that it may be extensively used.

The preceeding applies to mixtures of two substances only; now let us consider the case of three. If we have iodine, bromine and chlorine in the same liquid, how are we to arrive at the amounts of each? We may consider two cases, one given in Woodward's Chemical Arithmetic and the other in Crookes' Select Methods, the second being exactly the opposite of the first. Three equal portions of a liquid containing chlorine, bromine and iodine are taken. No. 1 is precipitated with silver nitrate and precipitate of silver iodide, silver bromide and silver chloride weighed. No. 2 is precipitated in the same manner, but digested with potassium bromide until all chlorine is replaced by bromine, then weighed. No. 3 is likewise precipitated and digested with potassium iodide until entirely converted into silver iodide, then weighed. In Crookes' example the iodine is replaced by bromine and the bromine by chlorine. In the first case the weights increase, and in the second they decrease.

Now suppose we try to derive a formula for each of these cases, beginning with Woodward's and using the same data as before, also $Ag = 108$, $I = 127$, $Br = 80$.

Woodward's Chemical Arithmetic.

Mixture of silver iodide, silver chloride and silver bromide.

$$\begin{aligned}
&\mathrm{AgI} + \mathrm{AgBr} + \mathrm{AgCl} = W,\\
&\mathrm{AgI} + \mathrm{AgBr} + \mathrm{AgBr} = W',\\
&\mathrm{AgI} + \mathrm{AgI} + \mathrm{AgI} = W''.
\end{aligned}$$

Let $x = \mathrm{AgCl}$, $a =$ molecular weight.

$y = \mathrm{AgBr}$, $b =$ " "

$z = \mathrm{AgI}$, $c =$ " "

$$x + y + z = W,$$

$$\frac{b}{a}x + y + z = W',$$

$$\frac{c}{a}x + \frac{c}{b}y + z = W'',$$

$$x = \frac{a(W' - W)}{b - a},$$

$$y = \frac{b(W'' - W')}{c - b} - \frac{b(W' - W)}{b - a},$$

$$z = W' - \frac{b(W'' - W')}{c - b}.$$

Crookes', same data :

$$\begin{aligned}
&\mathrm{AgI} + \mathrm{AgBr} + \mathrm{AgCl} = W,\\
&\mathrm{AgBr} + \mathrm{AgBr} + \mathrm{AgCl} = W',\\
&\mathrm{AgCl} + \mathrm{AgCl} + \mathrm{AgCl} = W'',
\end{aligned}$$

$$x + y + z = W,$$

$$x + y + \frac{b}{c}z = W',$$

$$x + \frac{a}{b}y + \frac{a}{c}z = W'',$$

$$z = \frac{c(W - W')}{c - b},$$

$$y = \frac{b(W' - W'')}{b - a} - \frac{b(W - W')}{c - b},$$

$$x = W' - \frac{b(W' - W'')}{b - a}.$$

FIRST METHOD.

Woodward's Example :

$W = 27.19$, $W' = 30.87$, $W'' = 36.83$, $a = 143.45$, $b = 188$, $c = 235$.

$$x = \frac{143.45 \times 3.68}{44.55} = 11.8495 \text{ AgCl} = 2.9282 \text{ Cl}$$

$$y = \frac{188 \times 5.96}{47} - \frac{188 \times 3.68}{44.55} = 8.3105 \text{ AgBr} = 3.5363 \text{ Br},$$

$$z = 30.87 - \frac{5.96 \times 188}{47} = 7.03 \text{ AgI} = 3.799 \text{ I}.$$

Crookes' Example:

$W = 15.57$, $W' = 14.69$, and $W'' = 12.20$,

$$z = \frac{235 \times 0.88}{47} = 4.4 \text{ AgI},$$

$$y = \frac{188 \times 2.49}{44.55} - \frac{188 \times 0.88}{47} = 6.9877 \text{ AgBr},$$

$$x = 14.69 - \frac{188 \times 2.49}{44.55} = 4.1823 \text{ AgCl}.$$

SECOND METHOD.

Woodward's Example:

$$\text{AgCl} + \text{AgBr} + \text{AgI} = 27.19,$$
$$\text{AgBr} + \text{AgBr} + \text{AgI} = 30.87,$$
$$\text{AgI} + \text{AgI} + \text{AgI} = 36.83,$$
$$30.87 - 27.19 = 3.68,$$
$$44.55 : 3.68 = 143.45 : x = 11.8495 \text{ AgCl}.$$

Now 11.8495 AgCl = 15.5295 AgBr = 19.41187 AgI,

$$27.19 - 11.8495 = 15.3405,$$
$$36.83 - 19.41187 = 17.41813.$$

Therefore AgBr + AgI = 15.3405,

$$\text{AgI} + \text{AgI} = 17.41813,$$
$$17.41813 - 15.3405 = 2.07763,$$
$$47 : 2.07763 = 188 : x = 8.3105 \text{ AgBr}.$$

Adding the AgCl and AgBr thus found and subtracting their sum from 27.19, we get AgI = 7.03.

Comparison of results:

	Woodward.	First method.	Second method.
Cl	2.92	2.9283	2.9283
Br	3.51	3.5363	3.5363
I	3.69	3.799	3.799

Crookes' Example:

$$AgCl + AgBr + AgI = 15.57,$$
$$AgCl + AgBr + AgBr = 14.69,$$
$$AgCl + AgCl + AgCl = 12.20,$$
$$15.57 - 14.69 = 0.88,$$
$$47 : 0.88 = 235 : x = 4.4 \text{ AgI}.$$

Now $4.4 \text{ AgI} = 3.52 \text{ AgBr} = 2.68586 \text{ AgCl}$,

$$15.57 - 4.4 = 11.17,$$
$$12.20 - 2.68586 = 9.51414.$$

Therefore $AgCl + AgBr = 11.17$,

$$AgCl + AgCl = 9.51414,$$
$$11.17 - 9.51414 = 1.65586,$$
$$44.55 : 1.65586 = 188 : x = 6.9877 \text{ AgBr}.$$

Adding the AgI and AgBr thus found and subtracting their sum from 15.57, we get 4.1823 AgCl.

Comparison of results:

	Crookes.	First method.	Second method.
AgI	4.4	4.4	4.4
AgBr	6.998	6.9877	6.9877
AgCl	4.172	4.1823	4.1823

It will readily be seen that the first method requires less work than the second, and has the advantage of giving any of the three without the necessity of finding the others.

No originality is claimed for the foregoing, but the matter has been put in such a shape that it may be applied to any case, and any atomic weights may be used, thus making its application universal. In special cases it may be condensed by finding the factors by which to multiply the weights directly instead of multiplying by one number and dividing by another, but it was thought best to give the entire work as a help to those not conversant with algebra.

The writer would like to impress upon chemists the importance of giving the atomic weights and factors used in all calculations, so that their figures may be checked and errors avoided. As the atomic weights vary, important work may be recalculated and thus retain its value.