ON THE REACTION OF HYDROGEN PEROXIDE WITH POTASSIUM PERMANGANATE IN PRESENCE OF SULPHURIC ACID.

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Brodie (Phil. Trans., 1850, **2**, 779) investigated the action of hydrogen dioxide upon potassium permanganate in the presence of sulphuric acid, and found that this reaction required three molecules of H_2O_2, whilst other chemists assert that the reaction takes place with five molecules of H_2O_2. In either case, correct equations are obtained.

$$2\,KMnO_4 + 3\,H_2SO_4 + 3\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 6\,H_2O + 8O$$
$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 10\,O.$$

This anomaly can be explained in the following way:

Let us write again the preceding equation without giving any determinate coefficient to the substances employed and obtained in the reaction, in fact, writing this equation in the most indeterminate way.

$$a\,KMnO_4 + b\,H_2SO_4 + cH_2O_2,$$

giving $$x\,K_2SO_4 + y\,MnSO_4 + z\,H_2O + t\,O.$$

The products employed for the reaction will give:

For $a\,KMnO_4$.	For $b\,H_2SO_4$.	For $c\,H_2O_2$.
$K = a.$	$H = 2b.$	$H = 2c.$
$Mn = a.$	$S = b.$	$O = 2c.$
$O = 4a.$	$O = 4b.$	

And the products of the reaction

For $x\,K_2SO_4$.	For $y\,MnSO_4$.	For $z\,H_2O$.	For $t\,O$.
$K = 2x.$	$Mn = y.$	$H = 2z.$	$O = t.$
$S = x.$	$S = y.$	$O = z.$	
$O = 4x.$	$O = 4y.$		

Giving the following equations :

$$a = 2x.$$
$$b = x + y.$$
$$4a + 4b + 2c = 4x + 4y + t + z \ldots\ldots\ldots\ldots (3)$$
$$a = y$$
$$2b + 2c = 2z,$$

from which

$$x = \frac{a}{2},\ y = a,\ b = x + y = \frac{3a}{2},\ z = b + c.$$

Substituting the values of b, x, y, z in equation (3), gives

$$4a + \frac{12a}{2} + 2\,c = 2a + 4a + t + b + c,$$

or

$$\frac{8a}{2} + 6a + 2\,c = 6\,a + \frac{3a}{2} + t + c.$$

and

$$\frac{8a}{2} - \frac{3a}{2} = t + c - 2\,c = t - c.$$

$$c = t - \frac{5a}{2}.$$

We have also

$$z = b + c = \frac{3a}{2} + t - \frac{5a}{2} = t - a.$$

Finally we obtain the following values:

$$x = \frac{a}{2},\ y = a,\ b = \frac{3a}{2},\ c = t - \frac{5a}{2},\ z = t - a.$$

As these results represent whole numbers, it is evident that the smallest value which can be given to a is 2, because

$$\frac{3a}{2} \text{ and } \frac{5a}{2}$$

represent whole numbers.

Taking $a = 2$, the other values become

$$a = 2,\ x = 1,\ y = 2,\ b = 3,\ c = t - 5,\ z = t - 2.$$

But c and z are whole and positive numbers, then necessarily t is greater than 5, otherwise $t - 5$ and $t - 2$ would be negative. As we must have $t > 5$, t must be then equal to all the whole numbers, beginning with 6.

Then

$$\begin{aligned} x &= 1. \\ y &= 2. \\ b &= 3. \\ a &= 2. \\ c &= 1, 2, 3, 4, 5, 6 \ldots \\ z &= 4, 5, 6, 7, 8, 9, 10 \ldots \\ t &= 6, 7, 8, 9, 10, 11 \ldots \end{aligned} \Bigg\} \textit{ad infinitum.}$$

If, now, we replace the indeterminate quantities used in the original equation by their values we have

$$2\,KMnO_4 + 3H_2SO_4 + H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 4\,H_2O + 6O.$$

If, keeping $x = 1$, $y = 2$, $b = 3$, $a = 2$, we take the second values of c, z and t, we have

$$2\,KMnO_4 + 3\,H_2SO_4 + 2H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 5\,H_2O + 7O$$

and so on, from which we deduce the following simple relation :

$$\left.\begin{array}{l}\text{Taking a of } KMnO_4 \\ \text{“ \quad b of } H_2SO_4\end{array}\right\}\text{constant.}$$
$$\text{and c of } H_2O_2 \qquad \text{variable}$$

we obtain a quantity, t, of free oxygen depending upon the quantity c, (H_2O_2) employed, which as in weight t, oxygen liberated, is equal to c ; quantity of H_2O_2 used in the reaction, *plus 5*.

The study of this reaction shows that this result belongs to the class of indeterminate problems and consequently an infinity of solutions may be obtained, but only in certain positive relations once determined. The quantity x (K_2SO_4) and y $(MnSO_4)$ are dependent upon a $(KMnO_4)$ and b (H_2SO_4), and for these quantities the amount of H_2O_2 to be taken may vary from the minimum, $c = 1$ and for this, corresponding values for t and z are obtained.

If potassium dichromate is substituted for potassium permanganate, analogous results are obtained : the final products of the reaction will be potassium sulphate, chromium sulphate, water and oxygen.

We have

$$a\,K_2Cr_2O_7 + b\,H_2SO_4 + c\,H_2O_2,$$
$$\text{giving } x\,K_2SO_4 + y\,Cr_2(SO_4)_3 + z\,H_2O + t\,O,$$

from which we obtain

$$2a = 2x.$$
$$2a = 2y.$$
$$7a + 4b + 2c = 4x + 12y + z + t \ldots\ldots (3).$$
$$2b + 2c = 2z \ldots\ldots\ldots\ldots\ldots\ldots (4).$$
$$b = x + 3y.$$

giving the following values

$$a = x,\ x = y,\ z = b + c,\ b = 4a,\ a = \frac{b}{4}$$

Substituting the values of b and y in equation (3) gives

$$7a + 16a + 2c = 4a + 12a + z + t,$$

reducing and subtracting equation (4) we have

$$3a + c = t.$$
$$c = t - 3a.$$

But t being a whole and positive number we must have

$$t > 3a.$$

Equation (4) gives

$$b + c = 2z.$$
$$4a + c = z$$
$$c = z - 4a,$$

and $$z > 4a.$$

We have then the following values:

$$a = x,\ x = y,\ z = b + c,\ b = 4a,\ a = \frac{b}{4}$$

Giving to b its smallest value, 4, we find

$$a = 1$$
$$b = 4$$
$$x = 1$$
$$y = 1$$
$$\left.\begin{array}{l} c = 1,\ 2,\ 3,\ 4,\ 5,\ \ 6 \ldots \\ t = 4,\ 5,\ 6,\ 7,\ 8,\ \ 9 \ldots \\ z = 5,\ 6,\ 7,\ 8,\ 9,\ 10 \ldots \end{array}\right\} \textit{ad infinitum.}$$

Introducing these values in the original equation, gives

$$K_2Cr_2O_7 + 4\,H_2SO_4 + H_2O_2 = K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O + 4O$$

The other values of c, t and z will give

$$K_2Cr_2O_7 + 4\,H_2SO_4 + 2\,H_2O_2 = K_2SO_4 + Cr_2(SO_4)_3 + 6H_2O + 5O$$
$$K_2Cr_2O_7 + 4\,H_2SO_4 + 3\,H_2O_2 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 6O$$

and so on, from which we deduct the following simple relation :

$$\left.\begin{array}{lll}\text{Taking a of} & K_2Cr_2O_7 \\ \quad\text{“} \quad \text{b “} & H_2SO_4\end{array}\right\}\text{constant,}$$
$$\text{and} \quad \text{c “} \quad H_2O_2 \quad \text{variable,}$$

we obtain a quantity, t, of free oxygen depending upon the quantity c, (H_2O_2) employed, such as in weight t, oxygen liberated is equal to c, quantity of H_2O_2 used in the reaction, *plus 3.*

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