LXV.—*On the Measurement of the Electromotive Forces produced by the combination of Cadmium and Iodine in Presence of Water.*

By A. P. LAURIE, B.A., B.Sc.

IN the March number of the *Philosophical Magazine* for this year, I published a paper on the "Electromotive Forces developed by the Combination of Zinc and Iodine." Instead of completing those experiments, I have taken up the reaction between cadmium and iodine on account of the greater ease with which cadmium iodide is manipulated. The following is an account of my preliminary experiments on this reaction, and the results which I think may be deduced from them.

As is well known, cadmium and iodine combine in the presence of water to form cadmium iodide, which dissolves. Just at the moment of combination there is a difference of electric potential

between the cadmium and the iodine atom, which we can measure by an arrangement which I shall presently describe. This difference of potential is modified by the surrounding conditions. In the first place, we may consider that it is made up of two parts, due respectively to the combination of the cadmium and iodine, and to the solution of the resulting molecule in the water.

Let us first consider that part which is due to the solution of the resulting molecule. If we imagine the reaction to be going on, we evidently have cadmium iodide accumulating in the water present, until at last we may suppose that the water becomes saturated with the salt. When this state is reached, it is evident that there is no further difference of potential between the salt and the water, that this factor of the whole difference of potential has disappeared. No doubt then this portion of the difference of potential has been diminishing from the beginning of the reaction, but it may diminish in two ways. If on the one hand there are any definite compounds formed between the salt and the water, we should expect on passing through the strength of solution corresponding with such a compound to have a sudden change in the difference of potential. If on the other hand no such compounds are formed, but the difference of potential between the salt and the water is a continuous function of the salt already in solution, we should expect the potential to fall off along a continuous curve, flattening as we approached a saturated solution.

Let us now consider the other part of the reaction, namely, the combination of the cadmium and iodine. The cadmium remains a solid metal throughout the reaction, and we may therefore suppose it to be uninfluenced by changes in the solution. The iodine is very slightly soluble in pure water, but is increasingly soluble as the amount of cadmium iodide in solution is increased. There is probably then a difference of potential between the iodine and the cadmium iodide, this difference of potential diminishing as the amount of iodine present in a given solution is increased, and finally disappearing when the solution is saturated with iodine. This difference of potential must evidently diminish the difference of potential due to the combination of the cadmium and iodine, as the iodine has to be torn from its solution in cadmium iodide. We may, however, consider that when the solution is saturated with iodine, the iodine is then free to combine with the cadmium.

We should expect then that if we increase the amount of iodine present in a given solution, the difference of potential will increase between the cadmium and iodine, and in this case also it will increase in jumps if we pass through any compounds of cadmium iodide and iodine; but if there are no such compounds, the difference of potential

between the cadmium and iodine will increase along a continuous curve, the increase, however, becoming less rapid as we approach the saturation of the solution with iodine.

We can, however, diminish this difference of potential in another way. If we suppose a given solution to be saturated with free iodine, and we then add more solid cadmium iodide so as to increase the amount of cadmium iodide in solution, we shall immediately diminish this difference of potential, because we are now no longer dealing with a liquid saturated with iodine; the liquid is capable of dissolving a great deal more iodine, and consequently a difference of potential has been set up between the iodine and the cadmium iodide.

I have explained in my Zinc-Iodine paper how, by integrating such a curve as one of those above described, we can obtain a measure of the whole electrical energy produced by the reaction, so that I need not enter into it here. With a view to measuring these differences of potential I have devised the following voltaic cell.

A cadmium plate and a platinum wire are immersed in a solution of cadmium iodide containing a little free iodine. On connecting the cadmium and platinum plates a current passes through the cell, the cadmium combining with the free iodine to form cadmium iodide, which dissolves in the water present. It is hardly necessary to explain that it is the free iodine round the *platinum* wire which is used for this combination. On connecting this cell with a Thomson quadrant electrometer, I could measure its electromotive force against a Latimer Clark cell, the electrometer reading to 0.005 of a volt. In every case two cells in series were used, and the Latimer Clark has been kindly tested for me by Professor Ayrton against his standard. Its E.M.F. at 10° C. is 1.433 volts (the temperature at which the experiments were made). Commercial cadmium and polished electro-cadmium were used. They gave the same deflection on the electrometer.

The method employed was to make up various solutions containing varying amounts of cadmium iodide and free iodine, and then place them in the cell and measure the E.M.F. produced. In this way we measure the E.M.F. produced by the combination of an infinitely small quantity of cadmium and iodine under definite conditions, and so determine a point on one of our curves.

A very brief description of each group of experiments will be sufficient after the above explanation.

Firstly, I tested the effect of diminishing the amount of free iodine present, the cadmium iodide in solution remaining the same. The results are given in curve and Table A. The experiments were not made so carefully as those that follow, but are sufficient to show that the E.M.F. is a continuous function of the free iodine present, and

that the curve flattens off as we approach saturation with iodine as we should expect. There is no indication of a compound.

TABLE A.

E.M.F. of cadmium cells.	Grams of free iodine in 1 c.c. of a 1 per cent. cadmium iodide solution.
1·087	0·0032
1·081	0·0016
1·067	0·0008
1·063 (?)	0·0004
1·050	0·0002
1·045	0·0001
1·039	0·00005

Milligrams of free iodine in 1 c.c. of solution.

Secondly, I tested the effect on the E.M.F. of the cell of increasing the amount of the cadmium iodide present. Each solution was saturated with iodine with the view of having the iodine free to combine with the cadmium in each case, so that I could measure the changes in the difference of potential between the cadmium iodide and the water alone. The results are given in curve and Table B. There is no indication of a compound between the cadmium iodide and the

water, but the curve is continuous, flattening as we approach saturation.

TABLE B.

E.M.F. of cadmium cells.	Grams of cadmium iodide in 100 grams of water.	Grams of free iodine in 1 c.c. of the solution.
1.119	0.1	0.0008
1.087	1.0	0.0032
1.081	5.0	0.0071
1.072	11.4	0.0095
1.057	30.0	0.0113
1.046	50.0	0.0151
1.036	70.0	0.0202
1.034	81 sat. at 10° C.	0.0300

Thirdly, I tested the effect of increasing the amount of cadmium iodide present, keeping the amount of iodine present constant. The results are given in curve and Table C. Here we have two effects, one superposed on the other. Firstly, the gradual diminution of the difference of potential between the cadmium iodide and the water, which is shown by curve B. Secondly, the diminution in the difference of potential between the cadmium and the iodine, due to the effect on the iodine of the increasing amount of cadmium iodide in solution. Evidently any number of curves, starting from different points along curve B and lying below it, could be drawn for different constant amounts of free iodine present. These experimental results then bear out the description of the probable variations in E.M.F. given at the beginning of the paper.

TABLE C.

E.M.F. of cadmium cells.	Grams of cadmium iodide in 100 grams of water.
1.084	0.1
1.060	0.49
1.045	1.1
1.025	5.1
1.018	0.0
1.008	20.0
1.001	30.0
0.994	40.0
0.985	50.0
0.980	60.0
0.975	70.0
0.974	80.0
0.974	81.0

We have next to consider the effect of change of temperature on the electromotive force of the cell. The importance of such measurements has been sufficiently explained in my Zinc-Iodine paper, where I

have given an account of Professor Helmholtz's work on this subject. It is sufficient to state here that we can obtain a measure of the difference between the electrical energy produced during a reaction, and the whole heat set free by the reaction, if we measure the variations in E.M.F. caused by variations in temperature.

The calculation is made by means of the following formula :—

$$T \frac{de}{dt} = J \cdot dQ,$$

where de is the variation of E.M.F. caused by altering the absorbed temperature T by the amount dt ; and dQ is the difference between the electrical energy and the heat produced by the reaction. I have then, applying this formula, made some experiments to settle the following question. When a salt is dissolved in water, the heat set free or absorbed is made up of two parts, the heat of solution of the salt in water, and the latent heat of liquefaction of the salt. It is usually assumed that when a salt is *formed* in presence of water, as in the combination of cadmium and iodine, that this latent heat enters into the thermal result, that the salt is formed in the *solid* state and then dissolved: I have obtained some evidence that the salt is formed in the liquid state. Iodide of zinc sets free heat on dissolving in water. Iodide of cadmium absorbs heat on dissolving in water. Nevertheless, both salts give similar curves as representing their E.M.F. of solution in water. This naturally suggests the question whether the latent heat of liquefaction enters into the energy set free when the salt is *formed* in presence of water, or to put it in another way, whether the salt is *formed in the solid* or *formed in the liquid state*, when the metal and iodine combine.

If, as I suppose, the salt is formed in the liquid state, and the latent heat of liquefaction does not enter into the energy set free during the reaction, we should expect that in a cell in which solid salt was separated by the passage of the current, there would be a considerable rise of E.M.F. due to the heat set free by the passage of the salt, when formed, from the liquid to the solid state. If there was no rise in E.M.F., and the curves B and C show that there is none, then we should have to suppose that this latent heat appeared as heat in the cell.

This then is a point for experiment by the application of the above formula. I have found the measurement of temperature effect very troublesome, as the iodine rapidly attacks the cadmium at high temperatures, and have had therefore to use a cadmium-silver iodide cell. This consists of a cadmium plate and silver wire coated with silver iodide, immersed in a cadmium iodide solution. I have used five or six cells in series, placed inside an ordinary hot water oven. I first

experimented on cells containing dilute cadmium iodide. This cell showed no variation on the electrometer on being raised through 40°C ., showing that its E.M.F. does not vary 0.00002 volt per degree Cent. I next experimented on cells containing saturated solution of cadmium iodide. I detected a slight diminution in E.M.F. on raising them through 40°C ., but not enough for measurement. These two sets of experiments may be taken as showing that practically the whole of the energy set free by the reaction between cadmium and iodine appears as electrical energy. Thirdly, I experimented on cells containing a large excess of solid salt, so that the solution should be saturated throughout the whole range of temperature, and consequently the passage of a current would separate solid cadmium iodide. I immediately obtained a very considerable diminution of E.M.F. on warming the cell. I found it impossible to measure it accurately, as for various reasons both the E.M.F. of the cells and the temperature effect kept varying.

A very laborious series of experiments ultimately enabled me to detect the causes of these fluctuations, but not to remedy them with the apparatus at my disposal. I therefore only give a rough approximation to this temperature effect at present. It is about 0.00037 volt per degree C. This means that in a cell in which the passage of the current causes the separation of *solid* salt there is set free about 4000 heat-units for every gram-molecule of cadmium iodide. The value of the electrical energy set free in heat-units by the formation of the solution $\text{CdI}_2, 400\text{H}_2\text{O}$, is about 2000 heat-units. Consequently, if the theory described above is correct, we should expect an absorption of heat of about 2000 heat-units on dissolving cadmium iodide in water ($\text{CdI}_2, 400\text{H}_2\text{O}$). This result is much too high, as Thomsen gives the value 1000 heat-units as the amount of heat absorbed. As already explained, the value given for the temperature effect is a very rough approximation, so that I think this result, as far as it goes, distinctly supports the above explained theory that when a salt is *formed* in presence of water, the latent heat of liquefaction does not enter into the energy set free.

Before concluding this paper I wish to draw attention to a point of some interest. On looking at curve B or C, it is obvious that a trace of salt, as little as 0.1 per cent., has a marked effect on the E.M.F. of the cell. This can hardly be explained on the usual theory of molecular compounds, unless we are prepared to write as one molecule $\text{CdI}_2, 20000\text{H}_2\text{O}$. Some other explanation must be found, but whatever this may be, the result is noteworthy as showing the enormous distance, compared to its molecular diameter, to which the molecule is able to influence the difference of potential between the water and the next molecule of salt which is going to dissolve.

Whether or no there is any limit to this can only be decided by experiments made with water prepared with the utmost care. Ordinary distilled water cannot be considered as sufficiently pure, but on trying it I obtained an E.M.F. higher than any given on Table B.

There is another subject on which the curves probably have an important bearing, namely, partial double decomposition between two salts in solution, but I have not yet sufficient experimental evidence to justify me in explaining their importance in this direction. In conclusion, I must explain that all experimental details have been omitted from this paper, but will probably be published elsewhere.