

THE APPLICATION OF THE LEAD SULPHATE ELECTRODE TO THE  
STUDY OF THE ABNORMAL BEHAVIOR OF UNI-BIVA-  
LENT SALTS IN AQUEOUS SOLUTIONS.

A STUDY OF THE HEAT EFFECT OF WITHDRAWING ONE GRAM  
ATOM OF CADMIUM FROM CADMIUM AMALGAM AS AP-  
PLIED TO THE CADMIUM CELL.

by

Clifford Ashton Altman.

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Clifford Ashton Altman Department of Chemistry

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The Application of the Lead Sulphate Electrode to the  
Study of the Abnormal Behavior of Uni-bivalent  
Salts in Aqueous Solutions.

This investigation was undertaken to obtain, if possible, some information concerning the abnormal behavior of the uni-bivalent salts in aqueous solutions.

If the generally accepted method of determining the ionization of a salt in a solution by measuring the electrical conductivity of the solution is used, it is found that the law of mass action does not apply, even approximately, to the reaction which represents the breaking up of a salt into its ions.

The law of mass action is stated as follows: "The product of the concentrations of the reacting substances when divided by the product of concentrations of the resulting substances--each concentration being taken as a factor as many times as molecules of that substance enter into the reaction--is always a constant." For example: if the law of mass action is applied in the case of the salt AB, which dissociates into  $A^+$  and  $B^-$  ions, the expression,

$$\frac{(A^+) \cdot (B^-)}{(AB)} = K,$$

would hold true.

The equilibrium between pure solute and the same molecular species in a saturated solution requires that the concentration of the undissociated substance in solution shall be constant. In a saturated solution, the product of the concentrations of the two ions would also be a constant. Thus the product of the concentrations of the ions reaches its maximum value in a saturated solution. This maximum value is called the solubility product and should be the same whether the salt is in solution alone or is in a solution of another salt.

For aqueous solutions of strong electrolytes less than 0.0001n, the law of mass action holds though the limit of certain non-aqueous solutions is much higher. Aqueous solutions of more than 0.0001n concentrations show a departure from the law which increases with the concentration. This deviation from the law also varies greatly with different types of salts. For example: uni-univalent salts are found to follow the mass action law much more closely than do uni-bivalent salts.

This phenomenon admits of three possible explanations.

That the undissociated part is the cause of the deviation from the law of mass action is indicated by the fact that for uni-univalent salts in solution the solubility product is very nearly constant. The law of mass ac-

tion demands that in a saturated solution the solubility product and the undissociated part shall both be constant, as is shown above.

The second explanation is that the bi-valent ion is extremely abnormal in its behavior causing the product of the ions to be at variance with the law.

The third possible explanation is that ionization takes place in steps giving rise to a considerable proportion of intermediate ion in the solution. For example: an intermediate ion  $\text{KSO}_4^-$  corresponding to the  $\text{HSO}_4^-$  ion in sulphuric acid might exist in a solution of potassium sulphate. The conductance of a solution of potassium sulphate would be the sum of the conductivities of the  $\text{K}^+$   $\text{KSO}_4^-$  and  $\text{SO}_4^{--}$  ions. In determining the ionization by the conductivity method the  $\text{KSO}_4^-$  ion would be calculated as  $\text{SO}_4^{--}$  ion. This would make the conductance much greater than corresponding electro-motive measurements would lead one to expect.

Measurements of the electro-motive force of concentration cells of uni-univalent salts have given means of further studying this problem. The Nernst equation enables us to calculate the electro-motive force of a concentration cell from the ion concentration. This equation is based upon the theory that the pressures of substances in solution follow the gas laws. The Nernst law as it applies to uni-univalent salts is as follows:

$$E = \frac{v}{n + v} \cdot 2 \cdot 0.0592 \left( \log \frac{C_1}{C_1'} - \log \frac{C_2}{C_2'} \right)$$

$v$  and  $n$  are the migration ratios of the ions.  $C$  is the solution pressure of the metal. As it is the same on both sides of the cell in a concentration cell of this kind, that is,  $C_1 = C_2$ , the equation simplifies to,

$$E = \frac{v}{n + v} \cdot 2 \cdot 0.0592 \log \frac{C_2}{C_1} .$$

A comparison of the calculated values for  $E$  obtained by the use of the foregoing formula with those obtained by experiment might be enlightening. Calculated and measured values of electro-motive forces obtained from uni-univalent salts in solution are very nearly concordant indicating that the concentrations are very closely a measure of the chemical or thermo-dynamic activities of the ions. In the more concentrated solutions the calculated values show a slight divergence in such a direction as to indicate that the concentration calculated from conductivity data increases slightly more rapidly than the chemical activity.

In pursuing the study of this question for uni-bivalent salts, P. V. Faragher<sup>1</sup> made some measurements of cells of the type:  $\text{Hg}, \text{Hg}_2\text{SO}_4, \text{K}_2\text{SO}_4(\text{C}), \text{K}_2\text{SO}_4(\text{C}_2), \text{Hg}_2\text{SO}_4, \text{Hz}$ . Each cell was made up by shaking the solution of  $\text{K}_2\text{SO}_4$  with mercurous sulphate and mercury. To eliminate possible error the cells were shaken for different lengths of time varying from a few minutes to more than a day. A series of measurements of these cells was made to see if the cells

1. Abstract of thesis submitted to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Boston, 1913).

had a reproduceable electro-motive force. The initial value of the electro-motive force was quite reproduceable but in each case variations began almost immediately. After the cells stood for a day or two, the electro-motive force of each of the cells seemed to come to a constant value which was nearly a millivolt lower than that of the cells freshly made up. A cell made by simply putting the solution of  $K_2SO_4$  into a half cell containing dry mercurous sulphate and mercury without any shaking came to the same constant value as that of those that were shaken.

The change in electro-motive force was thought to be due to some slow establishment of an equilibrium in the solution. Analyses were made of fresh solutions and those which had stood for several hours. The mercury was precipitated with potassium chloride as mercurous chloride. The solution was titrated with a standard solution of sodium hydroxide using phenolphthalein as an indicator. The results of the different analyses were identical. Also partially hydrolyzed mercurous sulphate was shaken with N/10  $K_2SO_4$  solution to which a slight excess of sulphuric acid had been added. The results corresponded exactly with those of the other analyses. These facts show that the equilibria involved in these reactions are soon reached and are in no way to be considered as responsible for the changes in electro-motive force.

The cells made up with N/100  $K_2SO_4$  showed the same variations as those with N/10  $K_2SO_4$ . Cells were made up of various concentrations of  $K_2SO_4$  as in the preliminary experiment and measured immediately against a N/10 mercurous sulphate cell which had become constant. The comparative values for each of the cells other than the N/10 were corrected to the values they would have had if the N/10 one had been freshly made up when used as a reference electrode. The potentials obtained from these measurements were plotted as ordinates against the logarithms of the total sulphate ( $2K^+ + SO_4^{--} + 2H^+ + SO_4^{--} + 2Hg^+ + SO_4^{--}$ ) as abscissas lie on a line which is only slightly convex downward, but which is very much steeper than the curve given by the Nernst equation. The above results are equivalent to the statement that the ratio

$$\frac{(SO_4^{--})_{0.1}}{(SO_4^{--})_{(C_1)}}$$

as derived from conductance measurements is too large. Take, for example, the case where  $(C_1) = 0.01$ , the ratio

$$\frac{0.71 \times 0.103}{0.854 \times 0.013} = 6.60.$$

A freshly prepared N/100 cell when compared with a N/10 cell also freshly prepared gave a difference in potential of 30.2 millivolts. If this value is substituted in the Nernst equation, the true value of the ratio is found to be 4.91.

This phenomenon is capable of being explained in one of the two ways already suggested. Either the sulphate ion is very abnormal in its behavior or the potassium sulphate does not ionize directly into potassium as ion and sulphate. The conductance measurements assume that the conductance is all due to the potassium and sulphate ions. Since the chemical activity does not increase as rapidly as the concentration, it seems probable that there may be present in the solution other ions, such as  $\text{KSO}_4^-$ , which affect the conductance but do not affect the electro-motive force, because the electrodes used are reversible with respect to the sulphate ion. Such other ions in the solution would affect the E. M. F. measurements only insofar as they affected the concentration of the sulphate ions.

If potassium sulphate ionizes into  $\text{K}_2\text{SO}_4 = \text{K}^+ + \text{KSO}_4^-$  to any extent instead of into  $2\text{K}^+ + \text{SO}_4^{--}$  ions there is less of the  $\text{KSO}_4^-$  ion in the more dilute solution as it is fair to assume that  $\text{KSO}_4^-$  ions also dissociate into  $\text{K}^+$  and  $\text{SO}_4^{--}$  ions. It has been shown for other salts that ionization is more nearly complete the more dilute the solution. Accordingly the primary assumption upon which the calculations obtained by using the Nernst equation are based, viz: that only potassium and sulphate ions are responsible for the conductance of a solution of  $\text{K}_2\text{SO}_4$ , would be more nearly true the more dilute the solution under consideration. As

the solution becomes more concentrated, the error in the ratio

$$\frac{(\text{SO}_4^{--}) C_2}{(\text{SO}_4^{--}) C_1}$$

would become greater. The error in the numerator would always be greater than that in the denominator as the greater concentration is always in the numerator and the ratio is always positive. This would explain why the chemical activity lags behind the concentration. It would also explain why the divergence between experimentally obtained data and calculated values gradually increases with the concentration.

The present investigation was undertaken with a view to making similar measurements using a lead, lead sulphate electrode in place of the mercury, mercurous sulphate electrode used in the foregoing experiments. It was hoped that the difficulties experienced with the mercurous sulphate might be avoided by this substitution. As pure lead electrodes of exactly the same potential are very difficult to prepare, a lead amalgam was used with the idea of removing the difficulty. The complete cell used was of the type: lead amalgam,  $\text{PbSO}_4$ ,  $\text{K}_2\text{SO}_4(C_1)$ ,  $\text{K}_2\text{SO}_4(C_2)$ ,  $\text{PbSO}_4$ , lead amalgam. This electrode should be reversible with respect to the sulphate ion and so should give a measure of the activity of that ion.

The first problem was to see if the electrode, lead amalgam,  $\text{PbSO}_4$ ,  $\text{K}_2\text{SO}_4$ , was reproduceable to give a definite value. It was necessary also to see if this definite value would remain constant with lapse of time.

The work was started by making a half cell of the type: lead amalgam,  $\text{PbSO}_4$ ,  $\text{N}/10 \text{ K}_2\text{SO}_4$ . This kind of an electrode was compared with another just as nearly like it as it was possible to make one. The first measurements of the electrodes when freshly made up showed no difference of potential. However, in each trial a rapid change took place and in a few minutes there was always a difference of potential. This difference became as large as a tenth of a volt in some measurements. The same  $\text{N}/10$  potassium sulphate electrode was measured against a normal calomel electrode. It was also measured against other electrodes of different concentrations of  $\text{K}_2\text{SO}_4$  varying from  $0.5\text{N}$  to  $\text{N}/100$ . There was no uniformity in the measurements.

It was thought that these changes in potential might come from some kind of hydrolysis of the lead or from lead sulphate. Solutions of several ages were taken for analysis. Tests were made of solutions which were freshly made up and of those which had stood for various lengths of time, some even as much as a week. Such indicators as litmus, phenolphthalein, and methyl-orange failed to show any

evidence of the presence of either hydrogen or hydroxyl ions.

A second attempt was made to measure the potentials by using the same solutions of potassium sulphate replacing the lead amalgam by lead strips coated with lead sulphate. The whole electrode was prepared in the following manner: Two large pieces of lead foil were dipped into a solution of  $K_2SO_4$ , through which a current was passed for an hour. This oxidized the anode to lead peroxide. The two pieces of lead foil, still in the solution of  $K_2SO_4$ , were then connected by a wire and set aside for twenty-four hours. This process formed very thin coats of lead sulphate over the lead foil. These pieces of foil coated with lead sulphate were then cut into smaller strips to be dipped into the different solutions of  $K_2SO_4$ . In this experiment all of the solutions of  $K_2SO_4$  were saturated by adding pure lead sulphate to them. Two strips which had been cut from the same larger piece of foil, when dipped into solutions of  $K_2SO_4$  of the same concentration, gave no potential difference at first. They did not remain at the same potential, however, very long, but soon drifted apart. The changes in potential observed were similar to those obtained in the original experiment, but they did not take place as rapidly.

As the cells did not remain constant in any case

and were not reproduceable, the experiment was abandoned.

A Study of the Heat Effect of Withdrawing One Gram  
Atom of Cadmium from Cadmium Amalgam As  
Applied to the Cadmium Cell.

When the materials of a voltaic cell react, they lose a certain amount of chemical energy. Zinc has a greater tendency to go into solution as ion in sulphuric acid than copper. The replacement of copper by zinc in a solution of their sulphates is attended by a loss of free energy. If this free energy is not made use of, it is converted into heat and lost. When a reaction takes place with any facility in the ordinary chemical way, the heat produced by it is called the heat of reaction. It may be measured by making the reaction take place in a calorimeter. This process offers great experimental difficulties and is otherwise impracticable. There is, however, an indirect method of determining the heat of reaction which is quite easy. Helmholtz showed that it is quite possible to establish a relationship between the chemical energy and the electrical energy produced by a cell in action. It was supposed at one time that all the energy produced by the heat of reaction could be made available as electrical current. If

this were the case, the following statement would be true: heat of reaction = work produced = electrical energy, or, in symbols,  $Q = W = EF$ . In the case of some reactions this statement is not far wrong, but in most cases it is somewhat in error.

If we take a cell of a completely reversible type, we can deduce a formula by means of a reversible cycle. A reversible cell is one which after it has delivered current for a time can be completely restored to its initial condition by passing a current through it in the opposite direction. Its electro-motive force and internal resistance are not affected by the passage of a slight current through it in either direction.

In deducing this formula, let us suppose the electrical energy produced to be less than the fall of internal energy. (The electrical energy in some cases is greater than the fall of internal energy, for example, when the temperature coefficient of a cell is positive.) Then the cell in working will give out  $(Q - EF)$  as heat at constant temperature. Let the temperature be raised slightly to the temperature  $T + dT$  and kept constant at that temperature. Now let the same quantity of electricity ( $F$ ) be sent through the cell in the opposite direction. If the electro-motive force of the cell has been diminished by the amount  $dE$  because of the change in temperature, the work done on the

cell will be  $F(E - dE)$  and the amount of heat absorbed will be  $Q - F(E - dE)$ , provided the heat of reaction has not changed with the slight change in temperature. The system may then be cooled to its original temperature, thus completing the cycle. The external work done by the system is  $F(E - dE) - FE = -FdE$ . The quantity of heat  $(Q - FE)$  was transferred from the temperature  $T + dT$  to the temperature  $T$ , so the work done, according to the second law of thermo-dynamics, is  $\frac{dT}{T}(Q - FE)$ , which also is equal to the external work. Therefore  $\frac{dT}{T}(Q - FE) = -FdE$ , or

$$Q = F\left(E - T\frac{dE}{dT}\right).$$

From this relation it can be seen that if the cell has no temperature coefficient the heat of reaction will be exactly equal to the electrical work produced. If the temperature coefficient is positive, the electrical energy will be greater than the heat of reaction and if the temperature coefficient is negative, the electrical energy will be less than the heat of reaction.

The object of this experiment was to find out the heat effect of withdrawing one gram atom of cadmium from cadmium amalgam as it is used in the cadmium cell. To this end six cadmium amalgam cells were made. Of these, two were made with 14% cadmium amalgam; two, with 12 1/2% cadmium amalgam; and two, with 10% cadmium amalgam. The cells were all

of this type: cadmium amalgam for one electrode, and pure cast cadmium for the other, in a solution of  $\text{CdSO}_4$ . Three separate experiments were performed with apparatus alike in all respects except the percentages of the cadmium amalgams which were used. The same cadmium electrodes were used in all three experiments. Also the solution of  $\text{CdSO}_4$  was of the same concentration in all three cases.

For each experiment two cells were made up as nearly alike as possible. The amalgams were prepared by weighing the mercury and cadmium to a tenth of a milligram and then gently heating them together to form the amalgam. Parts of the same lot of amalgam were used in each case to make the cells that were alike. The pure cadmium electrodes were dipped into a solution of cadmium sulphate, connected by a wire, and allowed to stand for some time in order to bring them to the same potential. This ideal condition of zero potential difference between the two electrodes was not reached, but a difference as small as .45 millivolt was reached. This difference was used each time as a correction when absolute potentials were taken.

Two cells as nearly alike as it was possible to make them were placed together in a bath at  $25^\circ \text{C}$ . When they had come to the temperature of the bath, the electromotive force of each cell was taken and also the cells were set in opposition and the difference of potential measured.

One cell was then placed in a bath at 30° C. Its electro-motive force was measured and then the difference between the one at 30° C. and the one at 25° C. was taken. The cells were then interchanged and the same readings taken again. These different measurements were taken as a check and the results were very satisfactory.

The same measurements were then repeated in all their details with the cells made up of 12 1/2% amalgam and with those containing the 10% amalgam.

In all cases the electro-motive force of the individual cells containing the amalgams of different percentage were practically the same. The average of a large number of measurements was 0.0465 volt at 25° C.

The heat of reaction was calculated from the equation

$$Q = n(E - T \frac{dE}{dT}).$$

The results of the three experiments are given in the following table: The withdrawal of cadmium from the amalgam requires the absorption of heat, so all of the heat of this reaction is negative when calculating the heat effect of the whole cadmium cell.

% of Cadmium in Amalgam	Average Difference of E. M. F. Both cells at 25°	Average Difference of E. M. F. Cell I at 25° Cell II at 30°.	Average Difference per degree $\frac{dE}{dT}$	Heat of Reaction Q
	volts	volts	volts	joules
14	0.000475	0.00111	-0.000222	21 764
12.5	0.00049	0.001095	-0.000219	21592
10	0.00051	0.00115	-0.000230	22118

Average value of Q  
21824

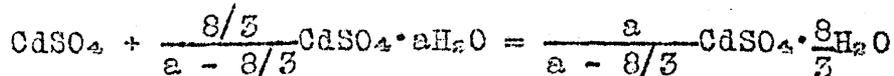
(2)<sup>1</sup> The second part of the heat effect of the cell is: the cadmium set free reacts with the  $\text{Hg}_2\text{SO}_4$  to form  $2\text{Hg} + \text{CdSO}_4$ .

Heat of formation of  $\text{CdSO}_4 = 219,900$  calories

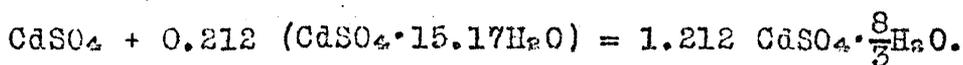
Heat of formation of  $\text{Hg}_2\text{SO}_4 = 175,000$  calories

Difference  $= 44,900$  calories

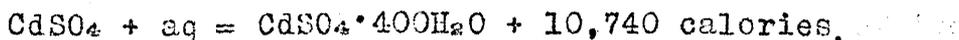
(3) The  $\text{CdSO}_4$  withdraws water from the saturated solution to form the hydrate  $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ . The latter process follows the equation



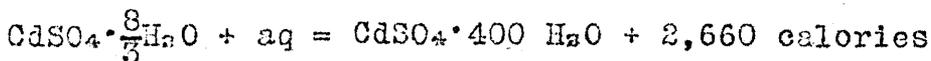
where  $a$  is the number of mols of water to one of salt, in the saturated solution. At  $18^\circ$   $a = 15.17$ , so that the formation of the hydrate is according to the equation



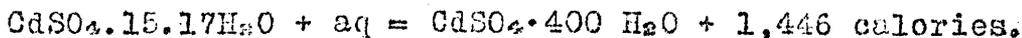
The heat of solution of the anhydrous salt to the dilution of 400  $\text{H}_2\text{O}$  is



of the hydrate



and the heat of dilution



The total production of heat in the above reaction is therefore

$$10,740 + (.212 \times 1,446) - (1.212 \times 2,660) = 7,825$$

calories. Adding together quantities of heat (2) and (3)

1. Data for reactions (2) and (3) are taken from Lehfeldt's *Electro-Chemistry*, pp. 189-190.

we get

$$44,900 + 7,825 = 52,725 \text{ calories}$$

$$52,725 \times 4.184 = 220,600 \text{ joules.}$$

Deducting the heat effect of withdrawal of cadmium from the amalgam we get 198,766 joules

$$F(E - T \frac{dE}{dT}) = 198,766 \text{ joules.}$$

$\frac{dE}{dT}$  is  $-0.0000354$  volt per  $1^\circ$ . (Lehfeldt).

$$E_{20^\circ} = \frac{198,766 - (295 \times 0.0000354 \times 2 \times 96,600)}{2 \times 96,600} = 1.0184 \text{ volt.}$$

This value is more nearly that given by the Bureau of Standards (1.0185 volt at  $20^\circ$  C.) than the one given by Lehfeldt who uses the value  $1.0186^1$  volt at  $18^\circ$  C.

The results of this experiment, when introduced into similar calculations of the potential of the unsaturated cadmium cell, fail to give a temperature coefficient of practically zero, which the experiments on the cells show. Apparently some other datum is at fault in this calculation, since the results for the saturated cell give results in agreement with experiment.

1. Attributed by Lehfeldt to Jaeger and Wachsmuth.