THERMODYNAMIC STUDIES ON ZINC IODIDE AND MERCUROUS IODIDE.[1]

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I. The Fictitious Heat of Solution of Zinc Iodide. As is well known, the fictitious heat of solution of an anhydrous salt can be determined by the following thermodynamic relations, existing between the temperature coefficients of the electromotive forces, $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$, of the reversible cells with and without solid salt.[2]

$$(Q)_T = T\left[\left(\frac{dE}{dT}\right)_A - \left(\frac{dE}{dT}\right)_B\right] n \cdot 23074 \cdots\cdots (1)$$

$$(Q)_T = T\left(\frac{dE}{dC}\right)_T \left(\frac{dC}{dT}\right) n \cdot 23074 \cdots\cdots\cdots\cdots (2)$$

The authors have determined the fictitious heat of solution of zinc iodide with the aide of formula 1. In the case of zinc iodide, formula 2 is not suitable for this purpose, owing to the experimental difficulties in determining the temperature coefficient of solubility of zinc iodide as it has been known to be exceedingly small.

The following cells were constructed and their electromotive forces were measured at several temperatures, the results are shown in tables 1 and 2.

Zn amalgam 10%	Zinc iodide, saturated solution, Hg_2I_2 solid salt	Hg……Cell A.
Zn amalgam 10%	Zinc iodide, saturated solution, Hg_2I_2	Hg……Cell B.

(1) This is the abstract of a paper which will be published in *The Science Reports of the Tôhoku Imperial University.*

(2) E. Cohen, and others, *Z. Physik. Chem.* **93**, (1918), 43; **94**, (1920), 210; **105**, (1923), 155.

TABLE 1.

Cell A, with solid salt.

Temperature degree	Electromotive forces		
	Observed (mean) volt	Calculated volt	Calc.—obs.
20.00	0.52358	0.52358	0.00000
22.50	0.52391	0.52395	+0.00004
25.00	0.52429	0.52429	0.00000
27.50	0.52461	0.52462	+0.00001
30.00	0.52489	0.52492	+0.00003
32.50	0.52519	0.52521	+0.00002
35.00	0.52551	0.52548	−0.00003

TABLE 2.

Cell B, without solid salt.

Temperature degree	Electromotive forces		
	Observed (mean) volt	Calculated volt	Calc.—obs.
20.00	0.52278	0.52300	+0.00022
22.50	0.52350	0.52356	+0.00006
25.00	0.52415	0.52415	0.00000
27.50	0.52478	0.52477	−0.00001
30.00	0.52543	0.52543	0.00000
32.50	0.52612	0.52612	0.00000
35.00	0.52685	0.52685	0.00000

By the method of least square the following equation was obtained for the cell A and the electromotive forces calculated are given in the third column of Table 1.

$$E=0.52429+0.0001336\ (t-25)-0.000001496\ (t-25)^2$$

which gives

$$\left(\frac{dE}{dT}\right)_{A,\,298}=0.0001336 \quad \text{volt/degree.}$$

The electromotive forces of the cell B can be expressed by the equation:

$$E=0.52415+0.0002427(t-25)+0.0000027(t-25)^2$$

and the calculated values are given in the third column of Table 2. From the above equation we obtain,

$$\left(\frac{dE}{dT}\right)_{B,\,298} = 0.0002427 \text{ volt/degree.}$$

Substituting these numerical values for $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$ in the formula 1, we can calculate the fictitious heat of solution of zinc iodide, thus

$$(Q)_{298} = 298.1(0.0001336 - 0.0002427)46148 = -1500 \text{ cal./mol.}$$

II. The Heat of Formation of Zinc Iodide. The heat of formation of zinc iodide can be determined by applying Gibbs-Helmholtz's equation to the Cell A, in combination with the heat of formation of mercurous iodide. If the figure 14200 cal. (Nernst,[1] Bernoulli[2]) be taken as the heat of formation of mercurous iodide (HgI), the heat of formation of zinc iodide will be :

$$2Hg + I_2 = Hg_2I_2 \; ; \; \Delta H_{298} = -28400 \text{ cal.}$$
$$Zn + Hg_2I_2 = ZnI_2 + 2Hg \; ; \; \Delta H_{298} = -22360 \text{ cal.}$$

The heat change in drawing an atom of zinc out of the amalgam being null, hence

$$Zn + I_2 = ZnI_2 \; ; \; \Delta H_{298} = -50760 \text{ cal.}$$

This value is found to be a little larger than that obtained by T. J. Webb[3] as the result of his study on the cell : Ag | AgI, ZnI_2 | Zn amalgam.

III. The Free Energy of Formation and the Entropy of Mercurous Iodide. E. Cohen and his co-workers[4] expressed the electromotive force of the cell : Cd amalgam | CdI_2, Hg_2I_2 | Hg as follows

$$E_1 = 0.41886 + 0.0003642\,(t-30) - 0.0000003\,(t-30)^2.$$

Hence

$$\left(\frac{dE_1}{dT}\right)_{298} = 0.0003672 \text{ volt/degree.}$$

The temperature coefficient of the cell : Cd | solution | Cd amalgam has been given by the expression[5]

$$\left(\frac{dE_2}{dT}\right)_{298} = -0.000244 \text{ volt/degree.}$$

Then the entropy change ΔS_{298} corresponding to the reaction : $Hg_2I_2 + Cd = CdI_2 + 2Hg$ may be calculated thus :

$$\Delta S_{298} = 2F\left\{\left(\frac{dE_1}{dT}\right)_{298} + \left(\frac{dE_2}{dT}\right)_{298}\right\} = 5.68 \text{ entropy units.}$$

from which the entropy of mercurous iodide may be evaluated, as the entro-

(1) Nernst. *Z. physik. Chem.*, **2** (1888), 23.
(2) Bernoulli, *Helvetica Chim. Acta*, **2** (1919), 720.
(3) Webb, *J. Phys. Chem.*, **27** (1923), 448.
(4) *Z. physik. Chem.*, **94** (1920), 210.
(5) Gerke, *Chem. Rev.*, **1** (1925), 377.

pies[1] of Hg, Cd and CdI_2 are known to be $S_{Hg}=17.8$, $S_{Cd}=11.8$ and $S_{CdI_2}=38.7$,

$$S_{Hg_2I_2}=56.8 \text{ entropy units.},$$

which is quite consistent with the value $S_{Hg_2I_2}=56.76$, calculated with the aid of the formula proposed by Latimer[2] for the entropy of solid salt:

$$S_{298}=\tfrac{3}{2}\cdot R \ln A-0.94 \ (A \text{ being atomic weight}).$$

The entropy change and the free energy change in the formation of mercurous iodide will be:

$$2Hg+I_2=Hg_2I_2\ ;\ \Delta S_{298}=-5.4 \text{ entropy units},$$

$$(S_{I_2}=2\times 13.3)$$

$$2Hg+I_2=Hg_2I_2\ ;\ \Delta F_{298}=\Delta H_{298}-T\Delta S_{298}=-26790 \text{ cal.}$$

IV. The Free Energy of Formation of Zinc Iodide. This can be calculated as follows:

$$Zn+Hg_2I_2=ZnI_2+2Hg\ ;\ \Delta F_{298}=-2EF=-24195 \text{ cal.}$$

$$2Hg+I_2=Hg_2I_2\ ;\ \Delta F_{298}=-26790 \text{ cal.}$$

Hence

$$Zn+I_2=ZnI_2\ ;\ \Delta F_{298}=-50985 \text{ cal.}$$

This result may be compared with that obtained by the entirely different process. The electromotive force of the cell involving the reaction $Zn+2AgI=ZnI_2+2Ag$, has been given by T. J. Webb[3]: $E=0.3987$.

Hence

$$Zn+2AgI=ZnI_2+2Ag\ ;\ \Delta F_{298}=-2EF=-18400 \text{ cal.}$$

and

$$Ag+\tfrac{1}{2}I_2=AgI\ ;\ \Delta S_{298}=3.4 \text{ entropy units.}[4]$$

$$Ag+\tfrac{1}{2}I_2=AgI\ ;\ \Delta H_{298}=-15100 \text{ cal.}[3]$$

$$Ag+\tfrac{1}{2}I_2=AgI\ ;\ \Delta F_{298}=\Delta H-T\Delta S=-16114 \text{ cal.}$$

so that

$$Zn+I_2=ZnI_2\ ;\ \Delta F_{298}=-50628 \text{ cal.}$$

The agreement is fairly satifactory.

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(1) Lewis-Randall, "Thermodynamics," 1923; Webb, *J. phys. Chem.*, **29** (1925), 816.
(2) *J. Am. Chem. Soc.*, **43** (1921), 818.
(3) *J. Phys. Chem.*, **27** (1923), 448.
(4) Lewis-Randall, loc. cit.