ON THE FICTITIOUS HEAT OF SOLUTION OF THALLOUS SULPHATE.

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If we construct the following two reversible cells and apply the Gibbs-Helmholtz equation to them, we obtain the following relations (1) and (2).

Thallium amalgam saturated 50%	saturated solution with solid thallous sulphate	Hg_2SO_4	Hg	Cell A.
Thallium amalgam saturated 50%	solution of thallous sulphate of any desired concentration	Hg_2SO_4	Hg	Cell B.

$$\text{for cell } A \qquad Q_A = nF\left\{E_A - T\left(\frac{dE}{dT}\right)_A\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots(1)$$

$$\text{for cell } B \qquad Q_B = nF\left\{E_B - T\left(\frac{dE}{dT}\right)_B\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots(2)$$

in which Q_A or Q_B represents the quantity of heat corresponding to the chemical reaction in cell A or in cell B when nF of electricity be allowed to pass reversibly through each cell. Now if nF of electricity be taken out of call A and be passed through cell B in the opposite direction, both being carried out in a reversible manner, the chemical change which takes place in the whole system is the dissolution of n equivalents of thallous sulphate in the unlimited quantity of the solution in cell B. The heat corresponding to this change is nothing but the so-called differential heat of solution $(Q)_T$ and is given by the difference of equations (2) and (1).

$$(Q)_T = Q_B - Q_A = nF\left[(E_B - E_A) - T\left\{\left(\frac{dE}{dT}\right)_B - \left(\frac{dE}{dT}\right)_A\right\}\right] \quad \cdots(3)$$

If the saturated solution without the solid salt be used in cell B then $(Q)_T$ must be equal to the fictitious heat of solution $(F)_T$ and equation (3) will be transformed into the following form as in this case $E_A = E_B$,

$$(F)_T = nFT\left\{\left(\frac{dE}{dT}\right)_A - \left(\frac{dE}{dT}\right)_B\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots(4)$$

Besides, the fictitious heat of solution is also derived from the following relation

$$\left(\frac{dE}{dT}\right)_A = \left(\frac{dE}{dT}\right)_B + \left(\frac{dE}{dC}\right)_T \frac{dC}{dT}$$

combining this with equation (4), we obtain

$$(F)_T = nFT\left(\frac{dE}{dC}\right)_T \frac{dC}{dT} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

The author had previously determined the fictitious heat of solution of thallous sulphate at 30°C. on the basis of relations (4) and (5) and the following values had been obtained.(1)

-14.73 cal./gr. (from equation (4))
-14.74 cal./gr. (from equation (5))

With the aid of equation (3) we can determine the differential heat of solution of an anhydrous salt at any desired concentration by measuring the

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(1) *Z. physik. Chem.*, **105** (1923), 155. The figures reported previously are corrected as given above owing to the alteration of the atomic weight of thallium.

electromotive forces and their temperature coefficients of cells *A* and *B*, but it is found to my reglet that equation (3) has a very limited scope of application, for the metal of the salt to be considered must show a well defined potential as the electrode, otherwise a large error can not be avoided in the result because equation (3) gives the differential heat of solution as a difference of two figures which are not far apart from each other. In the case of thallous sulphate, though thallium amalgam can show the very good constancy of potential, we can not determine the differential heat of solution in the wide range of concentration owing to its slight solubility, however, we can determine the differential heats of solution at several concentrations quite near to the saturation and then by the slight extrapolation the fictitious heat of solution may be evaluated and it might be without interest to compare the result with the previous one obtained by making use of equations (4) and (5).

Experimental.

The experimental methods had been described in the previous paper and will not be repeated here, only the results obtained being given in the following tables.

Cell *A*. (with the solid salt).

The figures shown in Table 1 were taken from the previous report.

TABLE 1.

Saturated solution, 5.826 gr. of Tl_2SO_4 in 100 gr. of solution at 30°C.

Temperature	Electromotive force (mean)	Calculated	Calc.—Obs.
27.5	1.05823	1.05811	− 0.00012
30.0	1.05889	1.05891	+ 0.00002
32.5	1.05972	1.05971	− 0.00001
35.0	1.06049	1.06051	+ 0.00002
37.5	1.06131	1.06131	0.0
40.0	1.06208	1.06211	+ 0.00003

The figures given in the third column were calculated by the following equation

$$E_A = 1.05891 + 0.000320\,(t-30).$$

Hence the temperature coefficient at 30°C. will be—

$$\left(\frac{dE}{dT}\right)_{A,\,30^\circ} = 0.00032\frac{\text{volt}}{\text{degree}}$$

Cell *B*.

(with unsaturated solution of thallous sulphate).

In the following tables C denotes the concentration of the solution expressed in number of grams of solute in 100 gr. of solution.

TABLE 2.

$C=2.283$

Temperature	Cell 1.	Cell 2.	Mean	Calculated	Calc.—Obs.
25.0	1.07777	1.07774	1.07775	1.07775	0.0
27.5	1.08007	1.08004	1.08005	1.08005	0.0
30.0	1.08236	1.08234	1.08235	1.08235	0.0
32.5	1.08469	1.08468	1.08468	1.08465	− 0.00003
35.0	1.08695	1.08693	1.08694	1.08695	+ 0.00001

The relation between the electromotive force and the temperature can be represented as follows:

$$E=1.08235+0.00092\ (t-30).$$

Hence

$$\left(\frac{dE}{dT}\right)_{2.823}=0.00092\frac{\text{volt}}{\text{degree}}$$

TABLE 3.

$C=3.059$

Temperature	Cell 1.	Cell 2.	Mean	Calculated	Calc.—Obs.
25.0	1.07028	1.07037	1.07033	1.07033	0.0
27.5	1.07251	1.07261	1.07256	1.07256	0.0
30.0	1.07475	1.07484	1.07479	1.07479	0.0
32.5	1.07697	1.07707	1.07702	1.07702	0.0
35.0	1.07918	1.07925	1.07922	1.07925	+ 0.00003

The following equation may be derived from the observed electromotive forces.

$$E=1.07479+0.000892\ (t-30)$$

which gives

$$\left(\frac{dE}{dT}\right)_{3.059}=0.000892\frac{\text{volt}}{\text{degree}}$$

TABLE 4.

$C = 5.110$

Temperature	Cell 1.	Cell 2.	Mean	Calculated	Calc.—Obs.
25.0	1.05751	1.05750	1.05750	1.05749	− 0.00001
27.5	1.05966	1.05963	1.05964	1.05964	0.0
30.0	1.06181	1.06177	1.06179	1.06179	0.0
32.5	1.06396	1.06393	1.06394	1.06394	0.0
35.0	1.06610	1.06606	1.06608	1.06609	+ 0.00001

The following equation describes the above data.

$$E = 1.06179 + 0.00086\ (t - 30)$$

Therefore

$$\left(\frac{dE}{dT}\right)_{5.110} = 0.00086 \frac{\text{volt}}{\text{degree}}$$

From the foregoing results we can compute the differential heat of solution of thallous sulphate at each concentration by substituting the numerical values for E_A, E_B, $\left(\frac{dE}{dT}\right)_A$ and $\left(\frac{dE}{dT}\right)_B$ in equation (3). The second column of the following table shows the differential heats of solution thus calculated ($nF = 2 \times 96494 \times 0.2389$) except the last two which are the fictitious heats of solution obtained in the previous investigation.

TABLE 5.

Differential heat of solution per 1 gr. of thallous sulphate.
Temperature 30°C.

Concentration of solution (gr./100 gr. solution)	Differential heat of solution (cal.)	Calculated
2.283	− 14.47	− 14.41
3.059	− 14.38	− 14.48
5.110	− 14.68	− 14.66
5.826	− 14.73 (fictitious heat − 14.74 of solution)	− 14.72 (extrapolated)

In such a narrow range of concentration the differential heat of solution may be considered to be a linear function of the concentration and the following equation was obtained by applying the method of least squares to the observed values.

$$(Q)_{30^\circ} = -14.21 - 0.088\ C$$

The calculated values based on this equation are expressed in the third column of the table. Now by extrapolating the concentration to the saturation ($C=5.826$), the fictitious heat of solution may be obtained which is given in the last line of the same column and is found to be in good agreement with the previous result.

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