

Citation:

E. Cohen, Experimental Determination of the Limiting Heat of Solution, in:
KNAW, Proceedings, 3, 1900-1901, Amsterdam, 1901, pp. 327-332

The equation of the indicated surface is

$$(ax + by + cz)(by + cz - ax)(cz + ax - by)(ax + by - cz) \\ - 16(x^2 \sin 2A + y^2 \sin 2B + z^2 \sin 2C) I R^2 u^2 + 16 I^3 u^4 = 0,$$

if x, y, z are the usual trilinear coordinates, u denotes the distance from the point to the plane of the triangle and a, b, c, A, B, C, I, R indicate as usual the sides, the angles, the area and the radius of the circumscribed circle of triangle ABC .

Chemistry. — “*Experimental Determination of the Limiting Heat of Solution*” (First Part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read September 29, 1900.)

1. When a substance is dissolved in any medium a quantity of heat appears which is generally called the “heat of solution”.

It has been shown, particularly by VAN DEVENTER and VAN DE STADT¹⁾, that this universal name may easily lead to confusion. They point out that a precise definition is necessary as the quantity of heat which is generated (for instance, when dissolving a salt in water) depends on the amount of substance already present in the solvent.

If equal quantities of a salt are successively introduced into pure water each quantity on dissolving will produce a different heat effect so that there really exists an unlimited number of different heats of solution which each depend on the concentration of the liquid into which the new quantity of the salt is introduced.

If a certain quantity of a salt is dissolved in a large amount of water so that the solution is so dilute, that on further dilution no heat is evolved, the heat effect accompanying the dissolving is called (by V. DEVENTER and V. D. STADT) the “*first heat of solution*” (calculated on 1 gram-molecule of salt) This is the quantity which is generally called the “*heat of solution*” and which has been determined for a large number of substances by BERTHELOT, THOMSEN and others.

This heat of solution is also called “*heat of solution in much water*” or “*heat of solution to extreme dilution*”.

¹⁾ Zeitschrift für phys. Chemie, 9. 34 (1892).

As the quantity of heat evolved during dissolution, depends on the concentration of the liquid employed, each fresh quantity of salt will cause a different heat effect until the solution has become saturated.

Each of these heats of solution excepting the last, is called an "*intermediate*" heat of solution. The sum of the *intermediate* heats of solution is called the "*integral*" or "*total*" heat of solution or also "*heat of solution to saturation*".

2. The last term of the integral heat of solution is particularly important theoretically. It represents the quantity of heat evolved when a salt (calculated per gram molecule) dissolves in its own saturated solution.

This quantity of heat is called "*fictitious*", *theoretical* or *ideal* heat of solution also "*last or limiting heat of solution*". It is this factor which plays a great part in the thermodynamics of solutions; we refer to the expressions given by V. D. WAALS¹⁾, VAN 'T HOFF²⁾, LE CHATELIER³⁾ and BAKHUIS ROOZEBOOM⁴⁾ for the relation between the solubility and temperature.

LE CHATELIER and BAKHUIS ROOZEBOOM already pointed out and REICHER and VAN DEVENTER demonstrated experimentally that there can exist a great difference between the first and the limiting heat of solution and that they may even have a different sign⁵⁾.

That these quantities coincide in the case of substances which are but little soluble, will be easily understood.

3. Only the „first heat of solution” is accessible to determination by a direct calorimetric method. The other heats of solution may be calculated from the heats of dilution, by means of HESS' law, then from the table of the heats of dilution of solutions of different concentrations and from the first heat of solution the heat effect may be calculated with which increasing quantities of salt dissolve in a definite volume of water, and from this the heat of solution of the last quantity may be obtained by extrapolation.

1) Zittingsversl. Kon. Akad. van Wetensch., 28 Febr. 1885.

2) VAN 'T HOFF, Lois de l'Equilibre chimique etc. Kongl. Svenska Vetenskaps Akad. Handl. 21. 17 (1886). OSTWALD'S-Klassiker 110. Translation by BREIDIG, S. 55.

3) Recherches expérimentales et théoriques sur les équilibres chimiques. Extrait des Annales des Mines, livraison Mars—Avril 1888, p 138. (Paris, DUNOD).

4) Rec. des Trav. chim. des Pays-Bas 8, 123, (1889).

5) Zeitschrift für phys. Chemie 5, 559 (1890).

It will be easily seen that the accuracy of such a calculation will leave much to be desired and this is why, thus far, the limiting heat of solution is but approximately known in a few instances.

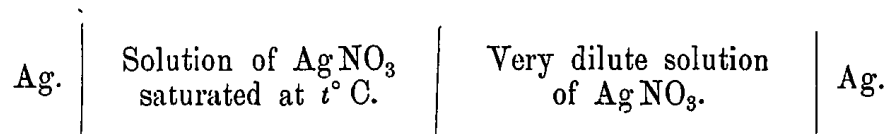
4. I now wish to describe two methods for the determination of the limiting heat of solution which do not differ in principle although at present for certain experimental reasons the second method is preferable to the first.

In both cases, two electrical measurements and a calorimetric one (which in many cases has already been executed by BERTHELOT or THOMSEN) lead to the knowledge of the desired heat factor which we will call L_f .

5. In order to be better understood we will choose a definite example and make it our object to determine the limiting heat of solution (L_f) of AgNO_3 say at t° .

FIRST METHOD.

We construct a galvanic cell according to the following scheme:



In view of the future determination of the temperature-coefficient of the cell, the solid phase will *not* be introduced into the saturated solution but a clear saturated solution will be employed.

The mechanism of this cell during the passage of the current is now, according to known principles, as follows:

When one gram-ion of silver dissolves in the weak solution, the concentration of silver in that solution is increased by 1 gram-ion; but at the same time, if $(1-n_1)$ is the migration constant of the silver, $(1-n_1)$ gram-ions of silver will have passed from the dilute into the saturated solution.

The increase in the dilute solution therefore amounts to n_1 gram-ions.

The saturated solution has, of course, become correspondingly poorer in silver.

At the same the NO_3 -ions have been displaced in the opposite direction. If n_1 is their migration constant, then n_1 gram-ions of NO_3 have passed from the saturated to the diluted solution, therefore, during the passage of 96540 Coulombs, n_1 gram-ions of Ag and n_1

gram-ions of NO_3 have been transferred from the saturated to the dilute solution.

6. As the cell described is a reversible one we may apply the equation of GIBBS and VON HELMHOLTZ.

$$E_e = \frac{E_c}{n\epsilon_0} + T \frac{dE}{dT}.$$

As n is here = 1 we get:

$$E_c = \epsilon_0 \left(E_e - T \frac{dE}{dT} \right).$$

We may imagine the heat effect of the change which takes place in the cell during the passage of 96540 Coulombs as occurring in two stages:

- 1st. Withdrawal of n_1 AgNO₃ from the solution saturated at t° ; heat effect $-n_1 L_f$.
- 2nd. Solution of n_1 AgNO₃ in the extremely dilute solution; heat effect $n_1 W_1$ (representing by W_1 the first heat of solution).

We thus get:

$$E_c = \epsilon_0 \left(E_e - T \frac{dE}{dT} \right) = -n_1 L_f + n_1 W_1$$

or

$$L_f = W_1 - \frac{\epsilon_0}{n_1} \left(E_e - T \frac{dE}{dT} \right).$$

If now the E.M.F. of the cell is determined at t° and also the temperature coefficient at that temperature, then all the quantities on the right hand side of the equation are known and consequently L_f , which we desired to determine.

7. A single remark remains to be made: the dilute solution must be so chosen that W_1 is really practically the first heat of solution. If it is made too dilute, the accuracy with which E and $\frac{dE}{dT}$ can be determined (for instance by POGGENDORFF's compensation method) becomes too small as the resistance would become unduly great. At the same time any (small) heat of dilution would be

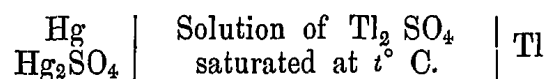
neglected. It is therefore, in any case as well to keep within certain limits¹⁾.

It is, of course, obvious that as a rule, electrodes which are reversible in regard to the anion may also be employed. This method is not likely to be used at present because the migration constants in concentrated solutions and their dependance on the temperature have been studied so little n_1 for saturated solutions of AgNO_3 being quite unknown.

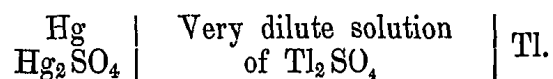
SECOND METHOD.

8. This method which, as already explained, quite corresponds in principle with the first one, is capable of being realised experimentally.

We take for instance the case that the limiting heat of solution of thallos sulphate is to be determined and construct a cell according to the following scheme:



connected in opposition to:



When 2×96540 Coulombs have passed through this combination, 1 gram-molecule of Tl_2SO_4 has been transferred from the saturated to the dilute solution.

In the equation

$$E_c = \frac{E_c}{n\varepsilon_0} + T \frac{dE}{dT}$$

$n = 2$ therefore

$$E_c = 2 \varepsilon_0 \left(E_c - T \frac{dE}{dT} \right),$$

¹⁾ When the saturated and the diluted solutions differ very much in degree of dissociation, there will exist a difference between the ionisation-heats at the electrodes in those solutions. Provisionally, we only know that difference will be very small. Still, a numerical determination would be interesting, in which OSTWALD's equation (Zeitschr. f. phys. Chemie 11, 501, 1893) might be a guide.

whilst further

$$E_c = -L_f + W_1,$$

in which L_f represents the limiting heat of solution and W_1 the first heat of solution of Tl_2SO_4 , therefore:

$$-L_f + W_1 = 2\varepsilon_0 \left(E_e - T \frac{dE}{dT} \right)$$

or

$$L_f = W_1 - 2\varepsilon_0 \left(E_e - T \frac{dE}{dT} \right).$$

The right hand side of the equation contains again only known quantities if the E.M.F. of the cell and its temperature coefficient at T° have been determined. W_1 may be borrowed from the table of BERTHELOT or THOMSEN¹⁾.

The advantage of this method over the first lies in the fact that migration is excluded here and that we therefore, avoid the difficulty that the migration constants of concentrated solutions are not known.

I hope to describe the measurements in a future communication.

Amsterdam, Chem. University Lab., Aug. 1900.

Botanics. — “Contributions to the knowledge of some undescribed or imperfectly known Fungi” (3^d Part)²⁾. By Prof. C. A. J. A. OUDEMANS.

56. ASCOCHYTA RHEI Ellis et Everhart, Proc. Acad. Sc. Philad. 1893, p. 160 (= Phyllosticta Rhei Ell. Ev. ante annum 1893); Sacc. Syll. XI, 525, forma *caulincola* Oud. — On the stem and branches of *Rheum Rhaponticum*. — Nunspeet, Oct. 2, 1899; Mr. BEINS.

Maculae nunc nigrescentes, tunc vero pallescentes, irregulariter limitatae. Perithecia numerosissima, congesta, $\frac{1}{10}$ — $\frac{1}{8}$ mill. in diam., epidermide velata, depressa, membranacea, vertice perforata. Sporulae hyalinae, cylindratae, ad polos rotundatae, biloculares, non aut vix constrictae, $7-14 \times 3.5-4 \mu$.

57. ASCOCHYTA PSAMMAE Oud. n. sp. — On the leaves of *Psamma littoralis* (= Calamagrostis arenaria = Ammophila arundinacea = Psamma arenaria). — Dunes of Scheveningen, Sept. 1891.

¹⁾ See note on pag. 331. The same remarks also apply here.

²⁾ For 2nd Part see these Proceedings p. 230.