[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

THE DETERMINATION OF REACTION AFFINITY IN SYSTEMS OF SOLID SALTS

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1. A Thermodynamic Relation for Partially Saturated Solutions[1]

If π_0, π_1, ... indicate the chemical potentials of the components K_0, K_1, ... , and n_0, n_1, ... indicate the number of gram molecules of each in a homogeneous solution, the Gibbs equation for this solution reads

$$n_0 d\pi_0 + n_1 d\pi_1 + \ldots\ldots = 0 \qquad (1)$$

If the potentials π_2, π_3, ... are held constant, $d\pi_2 = d\pi_3 = \ldots = 0$, and consequently Equation 1 becomes merely

$$n_0\, d\pi_0 + n_1 d\pi_1 = 0 \qquad (2)$$

Equation 2 is applicable to homogeneous mixtures of K_0, K_1 . . . when saturated with the pure solid components K_2, K_3, . . . It has often been applied to simple binary mixtures. According to the above, however, it retains its validity when the binary mixture is saturated with an arbitrary number of solid substances while the concentration n_1/n_0 varies.

In order to define n_0 and n_1 in a solution saturated with other substances K_2, K_3 . . . . it is necessary to remove the latter from the solution so far as is stoichiometrically possible. The solution will then consist stoichiometrically of K_0 and K_1 only. This is also true if one or several of the saturating substances are molecular compounds of K_0 or K_1.

By means of Equation 2 it is possible to calculate, from vapor pressure measurements of the solvent, the free energy change of reaction of solid salts. The principle of this method is described in section 2.

2. The Principle of the Affinity Measurement

Where the reaction, in the solid state, is the formation of a double salt from its components as $A + B \longrightarrow AB$, the affinity of the process equals the chemical potential of A in the solid system A + AB minus the potential of A in the solid system B + AB. Representing these systems by (1) and (2), respectively, the affinity may, therefore, be expressed, $\pi = \pi_{A\,(1)} - \pi_{A\,(2)}$, or $\pi = \pi_{B\,(2)} - \pi_{B\,(1)}$. With water present as a solvent, when the amount of A in the solution is gradually changed from saturated solution (1) to saturated solution (2) while equilibrium with the solid AB is maintained, we have, $\pi = -\int_1^2 d\pi_A$, where $d\pi_A$ indicates the increase in chemical potential for A in the solution corresponding to a small increase in n_A. Introducing equation (2), we obtain

$$\pi = \int_1^2 \frac{n_0}{n_A}\, d\pi_0 \qquad (3)$$

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[1] J. N. Brönsted, *Kgl. Dansk. Vid. Selsk. Medd.*, 1, Nr. 5 (1918).

where n_0 refers to the solvent. In order to integrate this expression, π_0 must therefore be known as a function of n_0/n_A from (1) to (2). Or, since $\pi_0 = RT\ln p_0$, we must know the vapor pressure of the solution over this interval. It is of value to note in the construction of this vapor pressure curve that, contrary to the case of simple binary mixtures, $d\pi_A/dn_A$ is finite for $n_A = 0$, owing to the existence of A in solutions containing only AB in a stoichiometrically pure state.

If the reaction considered is one between four solid salts, $A + B \longrightarrow C + D$, the affinity is measured by a method which is entirely similar, the stable salt pair $C + D$ fulfilling the function of the double salt in the example considered above, and (1) and (2) therefore corresponding to the two triads $A + C + D$ and $B + C + D$, respectively. The affinity is therefore obtained by integration of Equation (3) between these two limits on the basis of vapor pressure measurements in a solution saturated with $C + D$, the amount of A or B varying from one triad solution to the other.

To test this relation experimentally, a distinction must be made between two possible cases, which may be called the congruent and the incongruent, respectively.[2] When a saturated solution of $A + AB$ and $B + AB$ may be made by means of positive amounts of these respective salts, the solution is congruent. If, however, the solution saturated with $B + AB$ can be made by positive quantities of A and AB, the solution is incongruent, and a saturated pure double salt solution will be unstable.

The latter case, which is the simplest experimentally, is illustrated by Fig. 1, n, the number of moles of A per mole of water, being taken as abscissas and p, the vapor pressure of the saturated solution, being ordinates. The point AB on this diagram corresponds to a solution saturated with double salt and points $AB + B$ and $AB + A$ to saturation with each of the indicated solid systems. Starting with the solution saturated with $AB + B$ and evaporating off water, p will remain constant as long as two solid phases are present, but will finally begin to fall when all solid B has been converted into solid AB. On further evaporation of water the pressure will fall until $AB + A$ is reached, when solid A will separate and p will again become constant. When the original amounts of AB, B and water are known, and the amount of water evaporated has been determined, a curve for vapor pressure as a function of concentration between $AB + B$ and $AB + A$ may be constructed of the type necessary for the calculations outlined above.

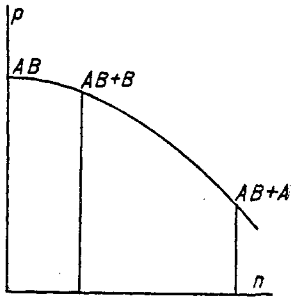

Fig. 1.

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[2] Meyerhoffer, *Sitz. Akad. Wiss. Wien*, **104**, IIb (1895); Meyerhoffer and Saunders, *Z. physik. Chem.*, **28**, 471 (1899).

In the congruent case, which has been treated experimentally in this communication, much the same reasoning applies. Here, however, the evaporation of water from a single solution containing AB + B will be insufficient to give the desired solution saturated with AB + A. From Fig. 2 it may be seen that a determination of the concentration–vapor pressure function involves, in this case, the evaporation of water from two separate solutions saturated with AB which contain small amounts of A and B, respectively. Here p will fall increasingly with increasing concentration of A or B until the two points A + AB and B + AB are reached, where constancy of p will in each case be attained. A knowledge of the amount of water, double salt and single salt present, and of the vapor pressure of each of the two solutions is therefore necessary in order that the affinity may be computed for the double salt.

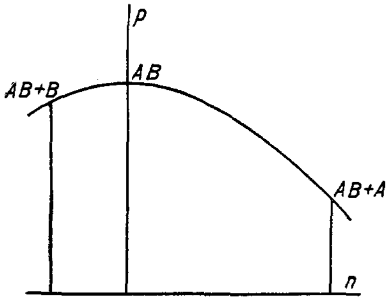

Fig. 2.

3. Apparatus and Procedure

The apparatus used is illustrated in Fig. 3. It consisted, in essence, of two flasks A and B, a condensing bulb M, and a manometer H, these being connected by a system of stopcocks which enabled each part of the apparatus to be evacuated separately. A Gaede pump, the connection for which only is shown in the drawing, was used for evacuation. The flasks, mounted together on a strong support which gave them a motor-driven horizontal agitation of about 3 cm., were connected to the bulb M and the mano-

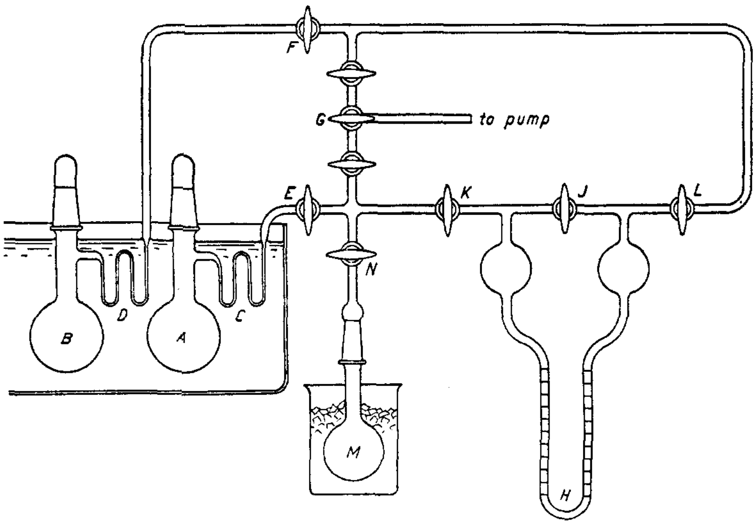

Fig. 3.

meter system by the long, thin-walled glass tubes, or springs, C and D, sufficiently elastic to permit the agitation. They were immersed to their necks in a thermostat giving a temperature of 19.93 ± 0.01°. The rest of the apparatus was at room temperature, care being taken to prevent the condensation of water vapor on the walls of the tubes. Flask A contained the solution the vapor pressure change of which with changing concentration was under observation. Flask B contained a saturated reference solution of constant vapor pressure. The saturating component used in all experiments in this communication was ammonium chloride. The spring C and the stopcock E were made of as large a bore as possible to permit the ready passage of water into the condensing bulb M.

In operating the apparatus the oil in the manometer, β-bromonaphthalene, was first carefully freed from air by warming and prolonged evacuation. The flasks were then appropriately filled and freed from air by prolonged evacuation and agitation. The remainder of the system was then evacuated with the stopcocks E and F closed. After about five minutes the solutions had come to temperature equilibrium after evacuation, and the stopcocks in the bridge G were closed and, with K, J and L open, E and F were opened. J was then closed and the difference of level in the manometer H read with a lens and recorded when it had become constant. The process of evacuation and measurement was repeated to constancy of the vapor pressure difference between the two solutions, when air had adequately been removed from the system. With K closed, about 2 cc. of water was then transferred from A into the ice-cooled bulb M by distillation. N was then closed and M weighed to determine the quantity of water transferred, after which M was dried and reattached to the apparatus. With E and K closed M was again evacuated, and the pressure difference between the two solutions again determined. Thus, by successive small increments, the concentration of the single salt in the saturated double salt solution was made to approach saturation. Finally a point was reached where the solid single salt separated from the solution and further evaporation of water caused no further decrease in vapor pressure. When this point was clearly established the experiment was discontinued and the contents of the flask A were analyzed by one of several methods given hereinafter in order to find the amount of water present at the start. If the solution became inconveniently thick, the experiment was discontinued before the double point had been reached and more water and weighed single salt were added. The process of measurement and concentration was then repeated. From the data so obtained was calculated the vapor pressure of the solution as a function of its concentration.

A few precautions deserve brief note. Obviously, for instance, the apparatus must not be evacuated during the progress of a determination since this would entail an indeterminate loss of water. Again, after the removal of water by condensation there was, in the presence of much solid salt, a lag in the attainment of equilibrium which often necessitated a wait of two hours. Finally, the stopcocks K and L were kept closed when the apparatus was not in use to prevent the solution of water in the oil of the manometer H.

4. Measurements

Preliminary experimentation having demonstrated that carnallite was unsuitable for the purposes of measurement, the double salt $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ was finally selected as having convenient properties. Measurements were made with and without NaCl as an additional saturating component of constant potential. The following reference points were then determined.

The saturated ammonium chloride solution used throughout in the reference flask B had a vapor pressure, at 19.93°, of 12.32 cm. of oil or 13.65 mm. of mercury. The last of these two figures is based on a pycnometric determination of the density of β-bromonaphthalene, which showed it to be 0.1108 that of mercury at room temperature.

The vapor pressures of the saturated points of the systems under investigation were found to be:

Saturating salts	p, mm. of Hg
$CuCl_2 \cdot 2H_2O + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	11.80
$NH_4Cl + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	13.63
$CuCl_2 \cdot 2H_2O + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NaCl$	10.80
$NH_4Cl + CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NaCl$	12.11
$CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	14.75
$CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O + NaCl$	12.73

These points serve as the integration limits for the equation developed above. The concentrations of the salts at the various points were determined analytically, as described below.

The purity of the salts prepared commercially for analytical purposes was found sufficient for the experiments. Proof of this is, of course, the constancy of the double-point vapor pressures on the evaporation of successive increments of water. That the double salt (which was prepared from its single constituents recrystallized together from solution in stoichiometric proportions), the ammonium chloride and the copper chloride contained, in the solid state, no more than their theoretical amount of crystal water was demonstrated by gravimetric analysis to 0.1%.

The four sets of measurements, which are summarized below, were then made. Actual readings of vapor pressure and concentration have been omitted in the interests of space conservation, the figures in the several tables having been obtained from curves constructed in each case from separate concordant series of observations. The initial amounts of double and single salts, which were always weighed before their introduction, and the different methods of obtaining the initial water content are recorded in each case to give a complete picture of the measurements.

In the tables Δp signifies the difference in vapor pressure, in cm. of oil, between the solution under observation and the saturated ammonium chloride reference solution, gH_2O indicates the number of grams of water present in the solution at each reading, p indicates the vapor pressure of the solution in mm. of mercury, $\log_{10} p$ the logarithm of this quantity, and n_1/n_0 the ratio of moles of single salt to moles of solvent at each vapor pressure.

Determination I.—Copper chloride, 4.826 g.; double salt, 9.63 g.

The amount of water present at the double point was found to be 9.77 g. by adding a weighed quantity of water to the salt–water mixture after the conclusion of the determination, and analyzing the resulting solution for ammonium content by distillation and for chlorine content by a standard silver nitrate solution.

TABLE I

RESULTS OF DETERMINATION I

Δp	H_2O, g.	p	$\log_{10} p$	m_1/m_0
−1.67	2.64	11.80	1.0719	0.1931
1.45	2.97	12.04	1.0806	.1709
1.14	3.48	12.39	1.0930	.1464
0.87	3.98	12.69	1.1035	.1280
.63	4.48	12.95	1.1123	.1136
.32	5.23	13.30	1.1239	.0958
.11	5.98	13.53	1.1312	.0853
+ .12	6.98	13.78	1.1393	.0731
.41	8.48	14.10	1.1492	.0598
.55	9.48	14.26	1.1541	.0539
.74	11.98	14.47	1.1605	.0426
.81	14.48	14.55	1.1629	.0352
.85	16.98	14.59	1.1641	.0300
.87	19.48	14.61	1.1647	.0262
.88	21.98	14.63	1.1653	.0232
..	...	14.75	1.1688	0

Determination II.—Ammonium chloride, 0.9153 g.; double salt, 9.96 g. The amount of water present at the double point was found to be 8.10 g. by saturating a solution with ammonium chloride and double salt and analyzing for ammonium and chlorine concentration as in Determination I. From these data the weight of water present when the double point is reached with 0.9153 g. of ammonium chloride was calculated. In this determination, therefore, the weight of double salt present during the vapor pressure measurements played no part since it was saturated throughout.

TABLE II

RESULTS OF DETERMINATION II

Δp	H_2O, g.	p	$\log_{10} p$	n_1/n_0
−0.02	8.10	13.63	1.1345	0.1193
+ .25	9.38	13.93	1.1439	.1029
.47	10.88	14.17	1.1514	.0888
.55	11.88	14.26	1.1541	.0814
.65	13.38	14.37	1.1575	.0722
.74	15.88	14.47	1.1605	.0610
.81	18.38	14.55	1.1629	.0526
.85	20.88	14.59	1.1641	.0463
.89	23.38	14.64	1.1656	.0415
.92	25.88	14.67	1.1664	.0374
.96	28.38	14.71	1.1676	.0341
..	...	14.75	1.1688	...

Determination III.—Sodium chloride, 18.13 g.; copper chloride, 11.147 g.; double salt, 4.940 g.; 10.33 g. of water was present at the double point. In this case, owing to the large amount of sodium chloride present, chemical methods were out of the question and the flask A (Fig. 3) was cut from the apparatus at C and weighed when a determination was finished. It was then emptied, dried and reweighed. These data permit the calculation of the desired quantity.

Table III

Results of Determination III

Δp	H_2O, g.	p	$\log_{10} p$	n_1/n_0
−2.57	10.33	10.80	1.0334	0.1140
2.22	12.58	11.19	1.0488	.0937
1.93	15.08	11.51	1.0611	.0783
1.71	17.58	11.75	1.0700	.0612
1.54	20.08	11.94	1.0770	.0587
1.46	21.58	12.03	1.0803	.0546
1.42	22.58	12.08	1.0821	.0522
1.32	25.08	12.19	1.0860	.0469
1.26	27.58	12.25	1.0882	.0427
1.22	30.08	12.30	1.0899	.0392
1.18	32.58	12.34	1.0913	.0362
1.13	35.08	12.40	1.0934	.0336
1.09	37.58	12.44	1.0948	.0314
..	...	12.73	1.1048	...

Determination IV.—Sodium chloride, 19.40 g.; ammonium chloride, 1.5096 g.; double salt, 4.843 g. The amount of water present at the double point, 31.19 g., was ascertained exactly as in Determination III.

Table IV

Results of Determination IV

Δp	H_2O, g.	p	$\log_{10} p$	n_1/n_0
−1.39	6.50	12.11	1.0832	0.0782
1.25	8.23	12.26	1.0885	.0618
1.15	9.73	12.37	1.0923	.0523
1.08	10.73	12.45	1.0952	.0464
1.01	12.23	12.53	1.0980	.0416
0.93	14.73	12.62	1.1011	.0345
.89	17.23	12.66	1.1024	.0295
.88	19.73	12.67	1.1028	.0258
.87	22.23	12.68	1.1031	.0229
.87	24.73	12.68	1.1031	.0206
.87	27.23	12.68	1.1031	.0187
..	...	12.73	1.1048	...

5. Computation of the Affinity of Formation

The results given in the tables of the preceding section permit the calculation of two values for the affinity of formation of the double salt $CuCl_2\cdot$-

$2NH_4Cl\cdot 2H_2O$, one in the presence of sodium chloride as a saturating component of constant activity, and the other in its absence. The necessary integration is most easily effected by throwing Equation (3) into the form

$$A = \frac{RT}{0.4343}\int_0^n \frac{\mathrm{d}\log p}{n}$$

where $n = (n_1/n_0)$. Then Determinations I and III may be integrated by the relationship

$$\log p_0 - \log p = \alpha n^2 + \beta n^3$$

and Determinations II and IV by the expression

$$\log p_0 - \log p = \alpha n^2$$

where α and β are constants for each determination and p_0 refers to the saturated double salt solution. The values for these constants are:

Detn. no.	I	II	III	IV
α	7.05	2.4	10.7	3.75
β	−22.5	...	−46.0	..

Integration yields the following results

Detn. no.	I	II	III	IV
A in cal.	1960	767	2060	785

The two concordant values for the affinity of formation follow directly

$$A_{(\text{abs. NaCl})} = 2A_{\text{ii}} + A_{\text{i}} = 3494 \text{ cal.}$$
$$A_{(\text{pres. NaCl})} = 2A_{\text{iii}} + A_{\text{iv}} = 3630 \text{ cal.}$$

The average value for the affinity of formation of one molecule of double salt from its solid components, that is, the change in free energy by the reaction

$$CuCl_2\cdot 2H_2O_{\text{solid}} + 2NH_4Cl_{\text{solid}} \longrightarrow CuCl_2\cdot 2NH_4Cl\cdot 2H_2O_{\text{solid}}$$

is 3560 cals.

Summary

1. A thermodynamic relationship for the dilution affinities of partially saturated solutions has been advanced.

2. The change in vapor pressure with changing concentration of single salt in the systems $CuCl_2\cdot 2NH_4Cl\cdot 2H_2O + CuCl_2\cdot 2H_2O$, $CuCl_2\cdot 2NH_4Cl\cdot 2H_2O + NH_4Cl$, $CuCl_2\cdot 2NH_4Cl\cdot 2H_2O + CuCl_2\cdot 2H_2O + NaCl$, and $CuCl_2\cdot 2NH_4Cl\cdot 2H_2O + NH_4Cl + NaCl$, saturated with double salt and NaCl, has been determined by means of a differential tensimeter of novel design.

3. The validity of the principle desired has been demonstrated within experimental error, a free energy of formation of 3560 cal. being found for the double salt in question.

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