

## CHEMICAL EQUILIBRIUM OF THE HETEROGENEOUS REACTION BETWEEN THE SOLID CALCIUM HYDROXIDE AND THE AQUEOUS SOLUTION OF THE SODIUM SULPHATE

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Received April 2nd, 1975

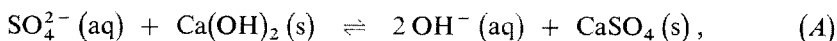
The equilibrium of the reaction  $\text{Na}_2\text{SO}_4(\text{aq}) + \text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons 2\text{NaOH}(\text{aq}) + \text{CaSO}_4(\text{s})$  was measured at temperatures from 25 to 80°C in the range of sodium ion concentrations from 0.06 to 2.0 mol kg<sup>-1</sup>. The equilibrium ratio  $K_m$  decreases considerably with the increase of the sodium ion concentration and with the temperature. The logarithm of the equilibrium ratio may be expressed with a good accuracy as a linear function of the square root of the ionic strength. The experimental values of equilibrium concentrations are in good agreement with the existing data of this system. The thermodynamic analysis of results has shown that the calcium sulphate formed is present in the system probably in the form of the dihydrate, and has qualified the published values of the solubility products of the calcium hydroxide and of the sodium sulphate which are consistent with the measured equilibrium data. The experimental values of  $K_m$  were correlated by means of a simple equation as a function of the ionic strength. From the results of the equilibrium measurements, the standard changes of enthalpy and of the Gibbs energy of reaction have been evaluated at a temperature of 25°C.

In connection with a study of the sodium sulphite conversion with calcium hydroxide, the feasibility of the sodium sulphate conversion with calcium hydroxide was considered as well. A necessary condition for a rational appreciation of such a process appears the knowledge of the equilibrium of the pertinent chemical reaction and its dependence on significant physico-chemical parameters, especially on temperature and concentration. With regard to the hitherto published data on this system<sup>1-3</sup>, the aim of this work consisted — besides the testing of the method — in the verification, extension and in a more precise determination of existing equilibrium data, and in obtaining the changes of the thermodynamic quantities associated with the reaction mentioned above.

### THEORETICAL

The position of the chemical equilibrium is most rapidly determined by calculation from available thermodynamic quantities. The considered type of reaction can be

expressed by the general equation



where the solid calcium sulphate can be present as a hydrate. This reaction is characterized by the thermodynamic equilibrium constant

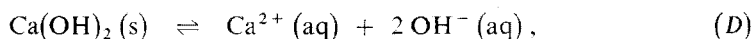
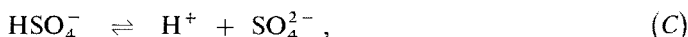
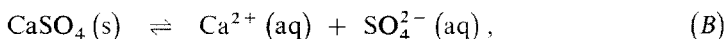
$$K = \frac{(\text{OH}^-)^2 \cdot (\text{CaSO}_4)}{(\text{SO}_4^{2-}) \cdot (\text{Ca}(\text{OH})_2)}, \quad (1)$$

(the parentheses denote activities) which under the assumption of the existence of both pure solid phases can be simplified to

$$K = \frac{(\text{OH}^-)^2}{(\text{SO}_4^{2-})}. \quad (2)$$

It can easily be shown that the equilibrium constant defined in this way is equal to the ratio of the true solubility products of the calcium hydroxide and of the calcium sulphate.

If solid calcium hydroxide is added to an aqueous solution of the sulphate in the conversion process considered above, the following elementary processes, in addition to the reaction (A), can take place in the system formed in this way (under the assumption of complete dissociation of the sodium sulphate and hydroxide in the aqueous solution):



These reactions are characterized by thermodynamic equilibrium constants in the usual form:  $K_B = (\text{Ca}^{2+}) \cdot (\text{SO}_4^{2-})$ ,  $K_C = (\text{H}^+) \cdot (\text{SO}_4^{2-})/(\text{HSO}_4^-)$ ,  $K_D = (\text{Ca}^{2+}) \cdot (\text{OH}^-)^2$ ,  $K_E = (\text{H}^+) \cdot (\text{OH}^-)/(\text{H}_2\text{O})$ . This system consists of three phases, namely the liquid phase and two solid phases. According to the Gibbs phase rule the given system has two degrees of freedom. If the temperature is fixed, only one independent variable is left (*e.g.* the concentration). The activities of all species in the solution can be expressed as functions of equilibrium constants, activity of water, and of the hydroxyl ion activity which will be denoted as  $(\text{OH}^-) = b$ . The following expressions

for the activities of all species can be obtained:

$$(\text{H}^+) = K_E \cdot (\text{H}_2\text{O})/b, \quad (3)$$

$$(\text{Ca}^{2+}) = K_D/b^2, \quad (4)$$

$$(\text{SO}_4^{2-}) = K_B b^2/K_D, \quad (5)$$

$$(\text{HSO}_4^-) = K_B K_E \cdot (\text{H}_2\text{O}) \cdot b/K_C \cdot K_D, \quad (6)$$

where, under the assumptions given above, the activities of solid substances will be equal to one. Simultaneously, however, the condition of the solution electroneutrality is to be fulfilled, which can be expressed as follows

$$[\text{Na}^+] + 2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{OH}^-] + 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-]. \quad (7)$$

The general rigorous solution of the set of equations (3) to (7) requires, in addition to the knowledge of equilibrium constants of reactions (B) to (E), also the knowledge of the activity coefficients of all species, their concentration dependences included. This procedure, however, does not appear feasible for the insufficient knowledge of the activity coefficient course in concentrated solutions and, therefore, the problem will be solved approximately under the assumption that the solution behaves ideally, *i.e.*  $(X) = [X]$ . In this case the following equation is obtained from the relations given above

$$\begin{aligned} m_0 + 2K_D/b^2 + K_E(\text{H}_2\text{O})/b = \\ = b + 2K_B b^2/K_D + K_B K_E \cdot (\text{H}_2\text{O}) \cdot b/K_C K_D, \end{aligned} \quad (8)$$

where  $m_0$  denotes the molality of sodium ions. The last terms on both sides of Eq. (8) assume negligible values ( $10^{-9}$  to  $10^{-14}$ ), as it is evident from Table I, and therefore it is possible – under assumption of the unity activity of water – to simplify the given equation to the form

$$2K_B b^4/K_D + b^3 - m_0 b^2 - 2K_D = 0. \quad (9)$$

For a selected concentration of sodium ions  $m_0$  at a given temperature it is possible to calculate the equilibrium concentration of hydroxyl ions from this equation, and from the set of equations (3) to (6) under the assumption of ideal behaviour one can compute the complete equilibrium composition of the liquid phase, using the published values of equilibrium constants given in Table I. With maximum and minimum values of  $K_B$  and  $K_D$  the described procedure yielded the equilibrium

TABLE I  
Survey of Published Values of Reaction Equilibrium Constants

Value	Temperature, K	Ref.	Value	Temperature, K	Ref.
Constant $K_D$					
$5.47 \cdot 10^{-6}$	291.15	4	$1.20 \cdot 10^{-6}$	298.15	8
$2.5 \cdot 10^{-5}$	298.15	5	$2.37 \cdot 10^{-5}$	298.15	9
$4.9 \cdot 10^{-5}$	298.15	6	$2.33 \cdot 10^{-4}$	298.15	10
$2.1 \cdot 10^{-5}$	323.15	6	Constant $K_E$		
$4.3 \cdot 10^{-6}$	353.15	6	$1.008 \cdot 10^{-14}$	298.15	11
Constant $K_B$			$5.474 \cdot 10^{-14}$	323.15	11, 12
$6.10 \cdot 10^{-5}$	283.15	4	$25.18 \cdot 10^{-14}$	353.15	12
$2.33 \cdot 10^{-4}$	298.15	4	Constant $K_C$		
$4.04 \cdot 10^{-4}$	298.15	7	$1.20 \cdot 10^{-2}$	293.15	4

concentrations of reaction (A) in dependence on the concentration of sodium ions  $m_0$  at a temperature of 25°C, which are shown in Fig. 1. Using the published values given in Table I, the estimated equilibrium constant of reaction (A) at 25°C varies within wide limits from  $6 \cdot 10^{-2}$  to  $4 \cdot 10^1$ . A similar estimation can be carried out using the tabulated thermodynamic data on heats of formation and on the standard entropies of reactants<sup>13</sup>. The equilibrium constant calculated from these data amounts

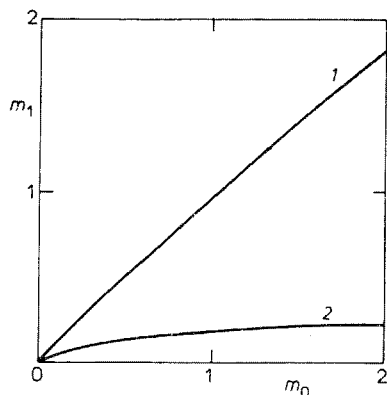


FIG. 1

Dependence of Equilibrium Concentration of Hydroxyl Ions  $m_1$  on Concentration of Sodium Ions  $m_0$  at Temperature of 298.15 K, Calculated under Assumption of Ideal Behaviour according to Eq. (9) for Following Values:  $K_B = 1.20 \cdot 10^{-6}$ ,  $K_D = 4.9 \cdot 10^{-5}$  (curve 1), and  $K_B = 4.04 \cdot 10^{-4}$ ,  $K_D = 2.5 \cdot 10^{-5}$  (curve 2)

to  $2 \cdot 10^{-1}$ , if the tabulated data of the calcium sulphate anhydride are used. As follows from the foregoing analysis, the values of the equilibrium constant calculated by various thermodynamic procedures and from different thermodynamic data, differ by several orders of magnitude, so that the experiments have shown indispensable to obtain more reliable data in a wider range of variables (temperature, solution concentration).

## EXPERIMENTAL

*Equilibrium measurements.* Measurements have been carried out at temperatures of 25, 50 and 80°C, and for approximately ten sodium ion concentrations at each temperature. Weighed amounts of sodium sulphate and sodium hydroxide were introduced into the equilibrium apparatus initially rinsed by a stream of pure nitrogen, then boiled and under a stream of nitrogen cooled distilled water was added. After complete dissolving of all components supported by permanent mixing the two components left — calcium sulphate and calcium oxide — were added. Thereafter the equilibrium apparatus was closed and immersed into a bath of constant temperature. At a temperature of 25°C, the equilibrium has been established during permanent mixing after 16 to 18 hours, and at temperatures of 50 and 80°C after 5 to 6 hours. Finishing the experiment, the mixing was stopped, and after sedimentation of the suspension (approximately after 5 minutes) the whole apparatus was turned by 45 degrees which caused the solution to flow on a fritted glass filter. The apparatus was then returned into the original position and pure nitrogen let in. The filtration rate through the fritted glass S2 was 0.3 to 1.0 ml/min. The filtration process and the sampling was practically identical with the same procedure described previously<sup>14</sup>. The position of equilibrium was obtained by a gradual approach from both sides of reaction (A).

*Equilibrium apparatus.* An equilibrium apparatus proved already during measurements of heterogeneous equilibria<sup>14</sup> was used. A vessel with a magnetic stirrer contained the suspension of solids of about 14 ml. The equilibrium apparatus was completely immersed in a bath of constant temperature kept with an accuracy of  $\pm 0.05^\circ\text{C}$  in the whole bath volume. Water or a mixture of water and glycerol was used as a thermostatic medium. The temperature was measured with standard thermometers graduated to  $0.02^\circ\text{C}$ .

*Chemicals.* For the preparation of equilibrium mixtures boiled distilled water was used, which was cooled under a stream of nitrogen. The sodium sulphate was an anhydrous commercial reagent of analytical grade (Spolek pro chemickou a hutní výrobu). The sodium hydroxide was a pelleted commercial reagent of analytical grade (Lachema) with a minimum content of 97 per cent NaOH. The calcium oxide was a commercial reagent of analytical grade (Lachema) with a minimum content of 97.5 per cent CaO. The calcium sulphate in most experiments was a commercial reagent of analytical grade (Spolek pro chemickou a hutní výrobu). Pulverized gypsum or a sample prepared by a heterogeneous reaction between a sodium sulphate solution and a calcium hydroxide suspension in a molar ratio of 3 : 1 were used in isolated cases. The remaining chemicals used were of analytical grade.

*Analytical procedures.* The total sample volume of the equilibrium solution used for analysis was about 10 to 12 ml. The samples for the analysis were weighed. All volumetric vessels were calibrated and the amounts of titration agents were converted to mass basis. The titration standard solutions were prepared also on the mass basis.

*Determination of the hydroxyl ion concentration* (datum  $A = [\text{OH}^-]$ ). The total alkalinity of the sample was determined by titration with a 0.025M solution of sulphuric acid under continu-

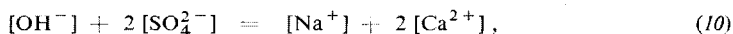
ous boiling to remove carbon dioxide. Phenol red served as an indicator. The precise concentration of sulphuric acid was determined in the same way with a 0.05M standard solution of potassium hydrogen carbonate.

*Determination of the sulphate ion concentration* (datum  $B = [\text{SO}_4^{2-}]$ ). The total content of the sulphate ion was determined gravimetrically as barium sulphate according to the classical method of Hints and Weber. The sample was acidified with diluted hydrochloric acid using methyl orange and heated to boiling. The precipitation was carried out at once with a hot solution of  $\text{BaCl}_2$ . The precipitated barium sulphate was left over night to recrystallize. The following day the precipitate was filtered through a hard filter ("blue tape"), washed, and after drying burned with the filter and ignited.

*Determination of the total sodium and calcium ion concentration* (datum  $C = 1/2 [\text{Na}^+ + \text{Ca}^{2+}]$ ). The total contents of sodium and calcium were determined by an acidimetric titration as hydroxides. In the neutral solution formed after the hydroxyl ion titration with sulphuric acid (determination  $A$ ), an ion exchange of sulphate ions for hydroxyle ions was carried out using a column with a strongly basic anion exchanger (Ionenaustauscher III, Merck). The hydroxide formed was determined by titration with sulphuric acid under continuous boiling using phenol red as an indicator. The column possessed a total effective capacity of  $8.3 \cdot 10^{-3}$  mol of sodium ions. It was regenerated with a 1M solution of the NaOH and washed with decarbonized water.

*Determination of the calcium ion concentration* (datum  $D = [\text{Ca}^{2+}]$ ). Calcium was determined by complexometric titration using a 0.01M solution of the disodium salt of ethylenediaminetetraacetic acid. Methylthymol blue served as an indicator diluted 1 : 100 with potassium chloride. The complexometric agent was standardized using zinc (99.99 per cent) dissolved in nitric acid (1 : 1).

From the data obtained by analysis and from the electroneutrality condition of the solution, which under the omission of the hydrogen and hydrogen sulphate ions can be expressed by the equation



the following relation is obtained

$$A + 2B = 2C. \quad (11)$$

Therefrom it can be seen that the four determinations are not independent. The analytical datum  $C$  served as a check determination and as a criterion of the measurement accuracy. The agreement of  $(A + 2B)$  with  $2C$  within the limits of one to two relative per cents was considered as satisfactory.

## RESULTS AND DISCUSSION

The thermodynamic equilibrium constant  $K$  of the reaction ( $A$ ) expressed by Eq. (1) or (2) can be rewritten into the form

$$K = K_m K_\gamma, \quad (12)$$

in which the equilibrium ratio  $K_m$ , defined as

$$K_m = m_{\text{OH}^-}^2 / m_{\text{SO}_4^{2-}} \quad (13)$$

represents a measurable quantity and  $K_\gamma$  is a correction factor expressing the nonideal behaviour of the solution, defined as

$$K_\gamma = \gamma_{\text{OH}^-}^2 / \gamma_{\text{SO}_4^{2-}} \quad (14)$$

The results of measurements are shown in Tables II and III. Table II shows the complete liquid phase composition of the equilibrium mixtures and Table III gives the experimental values of the equilibrium ratio  $K_m$  in dependence on the sodium ion concentration  $m_0$  at temperatures 25, 50, and 80°C. The value of the equilibrium ratio  $K_m$  was obtained by measurements from both sides of reaction (A) and the

TABLE II  
Liquid Phase Compositions (molalities) Found Experimentally in Equilibrium Mixture

Na <sup>+</sup>	OH <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	OH <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>
298.15 K				1.0047	0.1209	0.4612	0.0177
				1.0160	0.1219	0.4693	0.0175
0.0619	0.0533	0.0202	0.0164	1.5120	0.1316	0.7149	0.0196
0.1094	0.0667	0.0353	0.0156	1.5122	0.1328	0.7188	0.0192
0.2140	0.0911	0.0783	0.0160	1.9920	0.1373	0.9628	0.0211
0.4233	0.1173	0.1637	0.0128	2.0641	0.1411	0.9998	0.0218
0.4947	0.1244	0.1980	0.0151	2.0662	0.1390	1.0038	0.0218
0.6387	0.1355	0.2652	0.0142	353.15 K			
0.7941	0.1478	0.3476	0.0158				
0.8187	0.1502	0.3529	0.0163				
0.9885	0.1551	0.4394	0.0164	0.0971	0.0396	0.0436	0.0147
1.2520	0.1648	0.5686	0.0209	0.1176	0.0435	0.0515	0.0147
1.4710	0.1689	0.6828	0.0177	0.2123	0.0543	0.0935	0.0140
1.9685	0.1802	0.9326	0.0202	0.2131	0.0550	0.0931	0.0144
1.9902	0.1776	0.9424	0.0201	0.3067	0.0617	0.1374	0.0149
				0.4213	0.0680	0.1939	0.0150
				0.5049	0.0742	0.2350	0.0152
				0.5098	0.0754	0.2350	0.0158
				0.8426	0.0876	0.4000	0.0178
				1.0088	0.0886	0.4861	0.0186
				1.0234	0.0909	0.4960	0.0190
				1.0439	0.0909	0.5009	0.0181
				1.0573	0.0933	0.5087	0.0190
				1.9227	0.1039	0.9458	0.0236
				2.0267	0.1083	1.0045	0.0220
				2.0637	0.1071	1.0118	0.0214
323.15 K							
0.0845	0.0498	0.0400	0.0244				
0.1033	0.0550	0.0422	0.0172				
0.2009	0.0702	0.0813	0.0158				
0.2133	0.0710	0.0859	0.0153				
0.3890	0.0896	0.1649	0.0152				
0.4981	0.0979	0.2173	0.0159				
0.5126	0.0988	0.2255	0.0157				
0.8032	0.1138	0.3660	0.0170				
0.8152	0.1161	0.3682	0.0170				

TABLE III

Experimental Values of Equilibrium Ratio  $K_m$  in Dependence on Temperature and on Concentration of Sodium Ions  $m_0$

298·15 K		323·15 K		353·15 K	
$m_0$	$K_m \cdot 10^2$	$m_0$	$K_m \cdot 10^2$	$m_0$	$K_m \cdot 10^2$
0·0619	14·097	0·0845	6·209	0·0971	3·597
0·1094	12·598	0·1033	7·168	0·1176	3·668
0·2140	10·608	0·2009	6·063	0·2123	3·154
0·4233	8·397	0·2133	5·861	0·2131	3·249
0·4947	7·821	0·3890	4·821	0·3067	2·772
0·6387	6·923	0·4981	4·410	0·4213	2·385
0·7941	6·284	0·5126	4·325	0·5049	2·343
0·8187	6·397	0·8032	3·535	0·5098	2·416
0·9885	5·474	0·8152	3·660	0·8426	1·918
1·2520	4·778	1·0047	3·169	1·0234	1·666
1·4710	4·179	1·5120	2·423	1·5523	1·414
1·9685	3·480	1·9920	1·957	1·9227	1·141
1·9902	3·346	2·0662	1·925	2·0637	1·134

value obtained in this way was checked by preparing the supposed equilibrium mixture in which the composition changed during the experiment only within the limits of experimental errors. The equilibrium ratio  $K_m$  represents therefore a true equilibrium quantity. It has been verified experimentally that the equilibrium ratio  $K_m$  is independent of the ratio of the calcium hydroxide and calcium sulphate amounts present in the solid phase and of the provenance of the calcium sulphate.

Table III shows an outstanding dependence of the equilibrium ratio  $K_m$  on the sodium ion concentration  $m_0$ , which according to Eq. (12) is caused by the concentration dependence of the quantity  $K_s$ . Describing this dependence in the first approximation with the aid of Debye-Hückel's law, the following expression can be obtained from Eq. (12) after rearrangement

$$\log K_m = c - aI^{1/2}, \quad (15)$$

where the value of the parameter  $a$  depends according to theory only on the temperature; the parameter  $c$  according to Eq. (15) represents the value of the equilibrium ratio  $K_m$  extrapolated to zero ionic strength. The dependence of the equilibrium ratio logarithm on the square root of the ionic strength can be expressed with a very good approximation as a linear function at all temperatures in agreement with Eq. (15). The parameters  $c$  and  $a$  of this equation have been evaluated by the method



of least squares for each temperature and a survey of the parameter values obtained in this way is given in Table IV. The last column of this table shows the relative average deviation,  $\Delta K_m$ , with which Eq. (15) reproduces the experimentally found values of the equilibrium ratio, if the above mentioned values of the parameters  $a$  and  $c$  are used.

A remarkable aspect of this result is the fact, that Eq. (15) reproduces the experimentally found dependences very well, although the measurements were performed in a concentration range lying a great deal beyond the validity range of the limiting Debye-Hückel's law. The nonapplicability of Debye-Hückel's law in this case is well demonstrated by the value of the parameter  $a$  for which theory suggests a value approximately two times to three times higher than the one obtained from experiment. Therefore, Eq. (15) is to be regarded as an empirical correlation function the simple form of which is probably caused by a mutual compensation of far more complex dependences of activity coefficients of both ions on the ionic strength. Thus not even the limiting value of the equilibrium ratio  $K_m$  extrapolated to zero ionic strength (the logarithm of which is equal to the parameter  $c$ ) needs not to correspond exactly to the thermodynamic equilibrium constant of reaction (A). To perform such an extrapolation, it would be necessary to dispose of data measured at such low ionic strength values, where the limiting Debye-Hückel's law is valid. In principle, however, this procedure is not possible, because of the existence of a minimum ionic strength of the solution at which reaction (A) can still take place, and this minimum ionic strength value is determined by the solubilities of both solid phases at zero sodium ion concentration. For instance at 25°C the value of this minimum ionic

TABLE IV  
Values of Parameters in Eq. (15) and Relative Average Deviation of Equilibrium Ratio  $K_m$  or  $K'_m$

Temperature, K	$c$	$a$	$\Delta K_m, \%$
Reaction (A)			
298·15	-0·7143	0·4418	$\pm 2\cdot24$
323·15	-0·9965	0·4051	$\pm 2\cdot06$
353·15	-1·2786	0·3848	$\pm 3\cdot02$
Reaction (F)			
298·15	-0·7257	0·4107	$\pm 2\cdot58$
323·15	-1·0119	0·3705	$\pm 2\cdot30$
353·15	-1·2933	0·3510	$\pm 3\cdot35$

strength is equal to  $0.109 \text{ mol kg}^{-1}$  and lies therefore outside the range of the validity of the limiting Debye-Hückel's law.

The experimental values of equilibrium concentrations given in Table II are in a good agreement with the course given graphically by Bittrich and Leibnitz<sup>2,3</sup> nor are they at variance with the results of Neumann and Karwat<sup>1</sup> who performed the equilibrium measurements at different temperatures, namely at 15, 40, 70, and  $100^\circ\text{C}$ . Further on, it is evident from Table II that the dependence of the calcium content on the sodium ion concentration  $m_0$  in the equilibrium mixture at temperatures of 25 and  $50^\circ\text{C}$  passes through a rather flat minimum at the molality of  $m_0 \approx 0.7$ , and this fact is in agreement with the experimental findings published previously<sup>2</sup>.

Since the dependence of the equilibrium ratio  $K_m$  on the ionic strength has been determined experimentally on three temperature levels, it is possible to draw some thermodynamic conclusions from the resulting temperature dependences. By rearrangement of Eq. (12) and by its differentiation with respect to the reciprocal value of temperature at constant pressure and at constant ionic strength the following equation is obtained

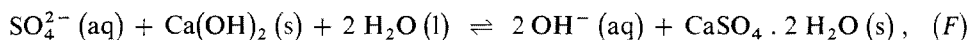
$$\left(\frac{\partial \ln K_m}{\partial T^{-1}}\right)_{P,I} = \left(\frac{\partial \ln K}{\partial T^{-1}}\right)_P - \left(\frac{\partial \ln K_\gamma}{\partial T^{-1}}\right)_{P,I} \quad (16)$$

The values of the differential quotient on the left hand side of this equation can be obtained from the  $\log K_m$  vs  $1/T$  dependences at various ionic strengths. The slopes of the straight lines obtained in this way vary only negligibly with the ionic strength, which according to Eq. (16) indicates a very slight dependence of the last term of this equation on the ionic strength. By extrapolation of these slopes to zero ionic strength it is therefore possible to obtain a rather reliable value of the first term on the right hand side of Eq. (16) and consequently also a relatively good value of the heat of reaction. The enthalpy change of reaction (A) has been determined in this way as  $-4.93 \text{ kcal mol}^{-1}$  with the probable error within the limits of  $\pm 0.1 \text{ kcal mol}^{-1}$ . This value of the heat of reaction differs from the value  $+0.4 \text{ kcal mol}^{-1}$  calculated from known thermodynamic data<sup>13</sup> by  $5.3 \text{ kcal mol}^{-1}$ . By extrapolation of the equilibrium ratio to zero ionic strength according to Eq. (15) the standard change of the Gibbs energy of reaction (A) at a temperature of  $298.15 \text{ K}$  will be obtained as

$$\Delta G^0 = +0.97 \text{ kcal mol}^{-1} .$$

According to the discussion following Eq. (15), the actual value of  $\Delta G^0$  will lie near this value or shall be somewhat lower. By calculation from tabulated thermodynamic data<sup>13</sup> it is possible to obtain a value of  $\Delta G^0 = +0.7 \text{ kcal mol}^{-1}$ .

The described treatment of results of the equilibrium measurements has been performed on the basis of reaction (A), *i.e.* for the case that an anhydrous calcium sulphate is being formed in the reaction. Taking into account the complexity even of the constituting binary system<sup>15</sup> CaSO<sub>4</sub>—H<sub>2</sub>O it is not possible to predict safely the degree of hydration of the calcium sulphate being formed. In addition to the anhydrous salt, it is possible to consider the formation of the dihydrate as the other extreme, and in this case reaction (A) is transformed to



the equilibrium constant of which is given by the expression

$$K' = (\text{OH}^-)^2 / (\text{SO}_4^{2-}) \cdot (\text{H}_2\text{O})^2. \quad (17)$$

Further on, the following relations are valid for the equilibrium ratio  $K'_m$  and for the correction factor  $K'_\gamma$ :

$$K'_m = m_{\text{OH}^-}^2 / m_{\text{SO}_4^{2-}} \cdot x_{\text{H}_2\text{O}}^2 \quad (18)$$

and

$$K'_\gamma = \gamma_{\text{OH}^-}^2 / \gamma_{\text{SO}_4^{2-}} \cdot \gamma_{\text{H}_2\text{O}}^2, \quad (19)$$

if a pure liquid at a pressure of one atmosphere is selected as the standard state for water and a hypothetical ideal onemolal solution for ions. The correlation of the equilibrium ratio  $K'_m$  has been performed with the use of Eq. (15) and a survey of the values obtained is given in Table IV. It is evident from this table that the values of the parameters  $a$  and  $c$  and the average relative deviation  $\Delta K'_m$  do not differ significantly from the results of the first alternative. The enthalpy change of reaction (F) has been determined as  $-4.97 \text{ kcal mol}^{-1}$  from the temperature dependence of the logarithm of equilibrium ratio  $K'_m$ . This value differs from the value  $-3.6 \text{ kcal mol}^{-1}$  calculated from thermodynamic data<sup>13</sup> by  $1.4 \text{ kcal mol}^{-1}$  and this deviation lies already within the limits of errors of the determination of heats of formation of the calcium hydroxide and calcium sulphate. The standard change of the Gibbs energy at a temperature of  $298.15 \text{ K}$  has been ascertained as  $+0.99 \text{ kcal mol}^{-1}$  also by extrapolating the equilibrium ratio to zero ionic strength. According to the discussion following Eq. (15) the actual value of  $\Delta G^0$  will lie near this value or will be somewhat lower.

Extrapolating the logarithm of the equilibrium ratio  $K'_m$  to zero ionic strength, the minimum value of the thermodynamic equilibrium constants  $K'$  is obtained as  $1.9 \cdot 10^{-1}$  which should be equal to the ratio of the true solubility products. From this value of  $K'$  it is possible to conclude that the most probable values of solubility products of the calcium hydroxide and of the calcium sulphate at  $25^\circ\text{C}$  are given in the sources<sup>6,10</sup>.

## REFERENCES

1. Neumann B., Karwat E.: Z. Elektrochem. Angew. Phys. Chem. 27, 114 (1921).
2. Bittrich H. J., Leibnitz E.: J. Prakt. Chem. (4), 3, 126 (1956).
3. Bittrich H. J., Leibnitz E.: J. Prakt. Chem. (4), 6, 4 (1958).
4. D'Ans J., Lax E.: *Taschenbuch für Chemiker und Physiker*, p. 852. Springer, Berlin 1943.
5. Mecke P.: Zement 24, 764/5 (1935).
6. Stephen H., Stephen T.: *Solubilities of Inorganic and Organic Compounds*, Vol. 1, Part 1. Pergamon Press, London 1963.
7. Hill A. E.: J. Amer. Chem. Soc. 59, 2242 (1937).
8. Singh D.: J. Sci. Res. Banaras Hindu Univ. 6, 131 (1955); ref. Bjerrum J., Schwarzenbach G., Sillen L. G.: *Stability Constants*, Part II.: *Inorganic Ligands*. Chem. Soc., London 1958.
9. Latimer W. M., Hicks J. F. G., jr, Schutz P. W.: J. Chem. Phys. 1, 620 (1933).
10. Hulett G. A., Allen L. E.: J. Amer. Chem. Soc. 24, 674 (1902).
11. Harned H. S., Owen S. D.: *The Physical Chemistry of Electrolytic Solutions*. Reinhold, New York 1958.
12. Čůta F.: *Analytická chemie odměrná*, p. 74. Academia, Prague 1956.
13. Rossini F. D., Wagman D. D., Evans W. H., Levine S., Jaffé I.: *Selected Values of Chemical Thermodynamic Properties*. Natl. Bur. Standards Circular 500, Washington 1952.
14. Mareček J., Erdős E.: This Journal 35, 1017 (1970).
15. *Gmelins Handbuch der Anorganischen Chemie*, 8. Auf., Calcium, Teil (B), Bd. 28, p. 708. Verlag Chemie, Weinheim 1961.

Translated by the author (E. E.).