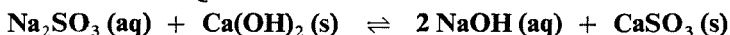


CHEMICAL EQUILIBRIUM OF THE HETEROGENEOUS REACTION



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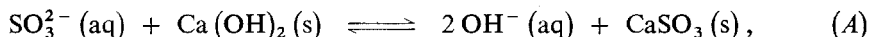
Received August 11th, 1975

The equilibrium of the reaction $\text{Na}_2\text{SO}_3(\text{aq}) + \text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons 2\text{NaOH}(\text{aq}) + \text{CaSO}_3(\text{s})$ was measured at temperatures from 298 K to 353 K in the range of sodium ion concentrations from 0.1 to 4.2 mol/kg. The degree of conversion of the sodium sulphite decreases considerably with the increase of the sodium ion concentration and with the temperature. Experimentally obtained values of the equilibrium ratio were correlated with a simple equation as a function of the ionic strength. The results of the equilibrium measurements were used to evaluate the heat of formation of the solid calcium sulphite and to estimate the standard entropy of the sulphite ion in an aqueous solution.

In connection with some technical problems the possibility of sodium sulphite conversion with calcium hydroxide was considered. As a first necessary condition for a rational appreciation of the feasibility of such a process appears evidently the knowledge of the equilibrium of the corresponding chemical reaction and its dependence on significant physico-chemical parameters, especially on temperature and concentration. Because the equilibrium study in this system was not yet carried out, the presented work is dedicated to this topic.

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 sulphite can be present as a hydrate. This reaction is characterized by the thermodynamic equilibrium constant K

$$K = (\text{OH}^-)^2(\text{CaSO}_3)/(\text{SO}_3^{2-})(\text{Ca}(\text{OH})_2), \quad (I)$$

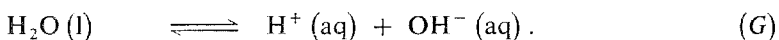
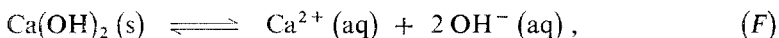
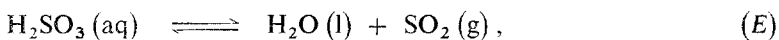
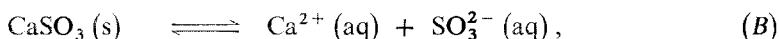
which under the assumption of the existence of both pure solid phases can be simpli-

fied to

$$K = (\text{OH}^-)^2/(\text{SO}_3^{2-}). \quad (2)$$

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

Adding solid calcium hydroxide to an aqueous solution of the sulphite, during the conversion process, the following elementary processes, in addition to reaction (A), are considered to occur in the system (under the assumption of total dissociation of the sulphite and the hydroxide in an aqueous solution)



These reactions are characterized by the thermodynamic equilibrium constants $K_B = (\text{Ca}^{2+})(\text{SO}_3^{2-})$, $K_C = (\text{H}^+)(\text{SO}_3^{2-})/(\text{HSO}_3^-)$, $K_D = (\text{H}^+)(\text{HSO}_3^-)/(\text{H}_2\text{SO}_3)$, $K_E = p_{\text{SO}_2}(\text{H}_2\text{O})/(\text{H}_2\text{SO}_3)$, $K_F = (\text{Ca}^{2+})(\text{OH}^-)^2$ and $K_G = (\text{H}^+)(\text{OH}^-)/(\text{H}_2\text{O})$.

According to the phase rule this system consists of four phases, namely the gas phase, liquid phase and two solid phases. Gibbs phase rule shows that the given system has two degrees of freedom. At a constant temperature one independent variable is therefore left. The activities of all species in the solution may be expressed as functions of equilibrium constants, activity of water and of the hydroxide ion activity. Denoting the hydroxide ion activity as $(\text{OH}^-) = b$ the following expressions for the activities of all species can be obtained:

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

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

$$(\text{SO}_3^{2-}) = K_B b^2/K_F, \quad (5)$$

$$(\text{HSO}_3^-) = K_C K_B (\text{H}_2\text{O}) b / K_C K_F, \quad (6)$$

$$(\text{H}_2\text{SO}_3) = K_B K_G^2 (\text{H}_2\text{O})^2 / K_C K_D K_F, \quad (7)$$

$$p_{\text{SO}_2} = K_B K_E K_G^2 (\text{H}_2\text{O}) / K_C K_D K_F, \quad (8)$$

where, under the above named assumptions, the activities of solid substances will have values equal to one. At the same time the solution electroneutrality condition must be fulfilled, which can be expressed as follows:

$$[\text{Na}^+] + 2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{OH}^-] + 2[\text{SO}_3^{2-}] + [\text{HSO}_3^-]. \quad (9)$$

The general rigorous solution of equations (3) to (9), however, require except the knowledge of all equilibrium constants of reactions (B) to (G), also the knowledge of the activity coefficients of all species, their concentration dependences included. This way does not appear feasible for the insufficient knowledge of the activity coefficient course in concentrated solutions. Therefore an attempt is made to solve this problem approximately under the assumption that the solution behaves ideally. In this case $(x) = [x]$, which in combination with the previously mentioned equations results in the following relation

$$m_0 + 2K_F/b^2 + K_G[\text{H}_2\text{O}]/b = b + 2K_B b^2/K_F + K_G K_B [\text{H}_2\text{O}] b / K_C K_F, \quad (10)$$

where m_0 denotes the sodium ion molality. Table I shows that the last terms on both sides of equation (10) are of negligible values (10^{-8} to 10^{-14}), and therefore it is possible to simplify this equation without significant loss of accuracy to the form

$$2K_B b^4 / K_F + b^3 - m_0 b^2 - 2K_F = 0. \quad (11)$$

For a chosen sodium ion concentration at a given temperature it is possible to calculate from this equation the hydroxide ion equilibrium concentration, and from the system of equations (3) to (7) the complete equilibrium composition in the liquid phase, using the equilibrium constant values found in literature and shown in Table I. The described procedure yielded the dependence of the conversion degree of reaction (A) on the sodium ion concentration m_0 at 298 K, which is shown in Fig. 1 (curve 4). It can be seen that there is a considerable difference between the course of the calculated and experimental values, which indicates that the approximation of an ideal solution is insufficient in this case.

From the solubility product values of both solid phases present, it is further possible to estimate the equilibrium constant of equation (2). Using values found in literature (Table I), the equilibrium constant of reaction (A) at 298 K estimated in this way oscillates within a wide range from 57 to 327. A similar estimation can be accomplished with the aid of tabulated thermodynamic data on heats of formation

and on entropies of the reacting components. For the calculation heat of formation values from the standard source¹¹ were used, with the exception of calcium sulphite, where a verified estimation procedure was used¹². The standard entropy values of calcium hydroxide¹¹, the hydroxide ion¹¹ and of calcium sulphite¹³ formed also a relatively reliable base, with the exception of the standard entropy of the sulphite ion for which values found in literature are of considerable difference, $10.4 \text{ cal K}^{-1} \text{ mol}^{-1}$ (ref.¹¹) and $3 \pm 3 \text{ cal K}^{-1} \text{ mol}^{-1}$ (ref.¹⁴). According to these limits the values of the calculated equilibrium constant of reaction (A) oscillates within the range $6.7 \cdot 10^{-2}$ and 12.6. As follows from the foregoing analysis the equilibrium constant values calculated by various thermodynamical procedures and from diverse thermodynamic data, differ by several orders, so that for obtaining of more reliable data experiments have shown indispensable.

EXPERIMENTAL

Equilibrium Measurements

Measurements were performed at 298, 323 and 353 K and for approximately twelve sodium ion concentrations at every temperature. Weighed amounts of sodium sulphite and sodium hydro-

TABLE I
Survey of Published Values of Reaction Equilibrium Constants

Symbol	Value	Temperature K	Reference
K_G	$1.008 \cdot 10^{-14}$	298	(2)
	$5.474 \cdot 10^{-14}$	323	(2)
	$25.180 \cdot 10^{-14}$	353	(1)
K_C	$6.31 \cdot 10^{-8}$	298	(3)
	$(7.1 \pm 0.6) \cdot 10^{-8}$	298	(4)
	$3.58 \cdot 10^{-8}$	323	(5)
	$3.105 \cdot 10^{-8}$	353	(5)
K_B	$1.27 \cdot 10^{-7}$	291	(7)
	$4.4 \cdot 10^{-7}$	298	(6)
	$1.7 \cdot 10^{-7}$	303	(8)
	$1.33 \cdot 10^{-7}$	323	(8)
	$0.39 \cdot 10^{-7}$	353	(8)
K_F	$5.47 \cdot 10^{-6}$	291	(9)
	$2.5 \cdot 10^{-5}$	298	(10)
	$4.9 \cdot 10^{-5}$	298	(8)
	$2.1 \cdot 10^{-5}$	323	(8)
	$4.3 \cdot 10^{-6}$	353	(8)

xide were introduced into the 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 sulphite and calcium oxide — were added. The equilibrium apparatus was closed and immersed into a bath of constant temperature, where during permanent mixing a constant composition established after 17 to 20 hours. The position of the equilibrium was obtained by gradual approach from both sides of reaction (4). Finishing the experiment, the mixing was stopped. After sedimentation of the suspension (approx. 5 min), the whole apparatus was turned by 45 degrees, which caused the solution to flow on a fritted glass filter. The apparatus was then turned into the original position and the inert gas let in and allowed to flow through. The filtration velocity through the fritted glass S2 was about $0.3-1.0 \text{ cm}^3 \text{ min}^{-1}$. The filtration process and the sampling was practically identical with the same procedure described already previously¹⁵.

Equilibrium Apparatus

An equilibrium apparatus proved already during measurements of heterogeneous equilibria previously was used. A vessel with a magnetic stirrer contained the suspension of solid substances of about 14 cm^3 . The equilibrium apparatus was completely immersed in a bath at constant temperature held with an accuracy of 0.05 K in the whole bath volume. As a thermostatic medium water or a mixture of water and glycerol was used. The temperature was measured with standard thermometers with a scale division of 0.02 K.

Chemicals

Water — for the preparation of equilibrium mixtures boiled distilled water was used, which was cooled under the atmosphere of nitrogen. Sodium sulphite — was a colourless commercial reagent of analytical grade (Lachema) containing 0.06 mol per cents of sodium carbonate and about one per cent moisture. Sodium hydroxide — was a granulated commercial reagent of analytical grade (Lachema) with a minimum content of 97 per cent sodium hydroxide. Calcium oxide — was a commercial reagent of analytical grade (Lachema) with a minimum content of 97.5 per cent calcium oxide. Calcium sulphite — was prepared from calcium carbonate and sulphur dioxide which was taken off from a pressure tank and purified in gas washing bottles with concentrated sulphuric acid. The suspension of calcium carbonate was saturated with gaseous sulphur dioxide until complete dissolving of the solid. The pure solution of the calcium hydrosulphite was then saturated with hydrogen and heated to 333 K. The precipitated calcium sulphite hemihydrate was filtered and washed with hot boiled water and finally with methylalcohol. The solid was dried in a desiccator with phosphor pentoxide for one week. The content of calcium sulphite was determined by the conventional iodometric titration method. One kilogramme of sample contained 7.735 mol of calcium sulphite. Calcium carbonate — was prepared by precipitation of a calcium chloride solution at 323 K with an ammonium carbonate solution in moderate excess. The preparation was filtered, washed and dried first at laboratory temperature and then in a drier at 393 K. The remaining chemicals used were of analytical grade.

Analytical Procedures

The initial sample volume of the equilibrium solution used for the analysis was about $10-12 \text{ cm}^3$. The samples for the analysis were weighed. All volumetric vessels were calibrated and the amounts of titration agents were converted to masses. The titration standard solutions were also prepared on the base of masses, with the exception of the iodometry.

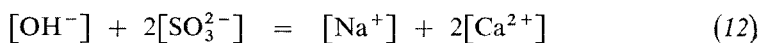
Determination of the hydroxide ion concentration (datum A). The sulphite ions present in the solution were oxidized to sulphate ions by a six per cent solution of hydrogen peroxide. After decomposition of the peroxide excess, catalyzed by elementary silver originating from silver monoxide¹⁶, the alkalinity of the sample was determined by titration with a 0.05N solution of sulphuric acid under permanent mixing and continuous boiling to remove carbon dioxide. Phenol red served as an indicator. The standardization of the sulphuric acid was accomplished by the same procedure with 0.05M standard solution of potassium hydrocarbonate.

Determination of the sulphite ion concentration (datum B). Sulphite ions were determined iodometrically. Because in the case of low sodium ion concentrations the sulphite ion concentration was also low, it was necessary to use 0.01N volumetric solutions. A 0.01M potassium iodate solution served as a standard. The concentrations of potassium iodate (2×10^{-5} mol cm⁻³) and of the hydrochloric acid (pH < 1.5) were chosen in such a way, to allow a reliable amperometric titration¹⁷. The sample of the equilibrium solution was added from a gravimetric pipette¹⁵ to a solution of iodine formed from an acidified solution of potassium iodate and iodine. The sample amount taken for the analysis was of a volume to consume approximately one half of the iodine set free. The excess of the iodine was titrated amperometrically with a 0.01N sodium thiosulphate solution with a voltage of 20 mV between platinum electrodes. The indication sensitivity of the used pointer galvanometer Metra was about $1.0 \cdot 10^{-2}$ cm³ per scale difference in the vicinity of the titration stop. The 0.01N sodium thiosulphate solution was prepared from redistilled water and its standardization was controlled at least once in 14 days. The standardization accuracy was within the limits of the indication accuracy, that is about 0.2 per cent. The sulphite ion concentration in equilibrium mixtures with sodium ion molalities higher than 0.8 was determined by direct iodometry. The liquid sample was introduced from the gravimetric pipette directly into a 0.05M iodine solution acidified with hydrochloric acid. The excess of iodine was determined by titration with a 0.05N sodium thiosulphate solution.

Determination of the total sodium and calcium concentration (datum C). The total contents of sodium and calcium have been determined by an acidimetric titration as hydroxides. After the sulphite oxidation and successive hydroxide ion titration with sulphuric acid¹⁶ a neutral solution formed in which the sulphate ions were replaced by hydroxide ions using a column with a strongly basic anionic exchange resin. The hydroxide ions set free were determined by titration with sulphuric acid under continual boiling using phenol red as an indicator. The ion exchange column possessed a total effective hydroxide ion exchange capacity of $8.3 \cdot 10^{-3}$ mol. It was regenerated by a 1M sodium hydroxide solution and washed by decarbonized water.

Determination of the calcium ion concentration (datum D). Calcium was determined by complexometric titration using a 0.01N 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



in which the hydrogen and hydrosulphite ion concentrations have been omitted, the following relation is obtained

$$A + 2B = 2C \quad (13)$$

It can be seen that the four analytical determinations are not independent. The analytical datum

C served as a control and as a criterium 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. Higher values of $2C$ indicated significant oxidation of sulphite ions.

RESULTS AND DISCUSSION

The thermodynamic equilibrium constant K of reaction (A) expressed by equations (1), respectively (2), can be rewritten into the form

$$K = K_m K_\gamma, \quad (14)$$

in which the equilibrium ratio K_m , defined as

$$K_m = m_{\text{OH}^-}^2 / m_{\text{SO}_3^{2-}} \quad (15)$$

represents a measurable quantity. K_γ is a correction factor expressing the nonideal solution behaviour, defined as

$$K_\gamma = \gamma_{\text{OH}^-}^2 / \gamma_{\text{SO}_3^{2-}} \quad (16)$$

The measurement results are shown in Tables II and III. Table II shows the complete composition of the equilibrium mixtures at 298, 323 and 353 K and Table III the experimental values of the equilibrium ratio K_m in dependence on the sodium ion molality m_o at 298, 323 and 353 K. The value of the equilibrium ratio K_m was obtained by measurements from both sides of reaction (A) and the values found in this way were controlled by preparing an 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 was experimentally verified that the equilibrium ratio K_m is independent of the ratio of the calcium hydroxide and calcium sulphite amounts present in the solid phase.

Table III shows an evident dependence of the equilibrium ratio K_m on the sodium ion molality m_o , which according to equation (14) is caused by the concentration dependence of the quantity K_γ . Describing this dependence with the aid of the Debye-Hückel law, the following expression can be obtained from equation (14) after rearrangement

$$\log K_m = c - aI^{1/2}, \quad (17)$$

where the parameter value a depends according to theory only on the temperature. Parameter c is equal to $\log K$ and according to equation (17) 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 good approximation as a linear function at all temperatures according to equation (17). The parameters c and a of this equation have been therefore evaluated for every temperature by the method of least squares and a survey of the c and a values obtained in this way is shown in Table IV. The last column of this table shows the relative average deviation of ΔK_m , which characterizes the reproduction of experimentally obtained equilibrium ratio values by equation (17) with the above mentioned c and a parameters.

A remarkable aspect of these results is the fact, that equation (17) reproduces the experimentally obtained dependences very well, although the measurements were performed in a concentration range lying a great deal beyond the range where

TABLE II

Liquid Phase Composition Found Experimentally in Equilibrium Mixtures At 298·15, 323·15 and 353·15 K

				Molality			
Na ⁺	OH ⁻	SO ₃ ²⁻	Ca ²⁺	Na ⁺	OH ⁻	SO ₃ ²⁻	Ca ²⁺
298·15							
0·1177	0·1199	0·0012	0·0046	1·0826	0·8516	0·1182	0·0012
0·2363	0·2282	0·0043	0·0025	1·1773	0·9061	0·1410	0·0014
0·3934	0·3686	0·0137	0·0019	1·5203	1·0827	0·2169	0·0028
0·4926	0·4555	0·0225	0·0018	2·0971	1·3076	0·3829	0·0015
0·5982	0·5328	0·0324	0·0015	3·0834	1·5502	0·7494	0·0035
0·8333	0·6932	0·0621	0·0013	3·7151	1·6666	0·9999	0·0015
323·15							
0·108	0·109	0·001	0·003	0·997	0·758	0·117	0·000
0·206	0·196	0·004	0·001	1·498	1·013	0·236	0·001
0·402	0·362	0·017	0·000	2·015	1·169	0·415	0·000
0·486	0·429	0·024	0·001	3·000	1·394	0·788	0·000
0·509	0·443	0·031	0·000	3·977	1·507	1·228	0·000
0·811	0·656	0·073	0·000	4·046	1·577	1·215	0·002
353·15 K							
0·116	0·109	0·002	0·000	1·580	0·972	0·297	0·000
0·213	0·200	0·006	0·000	2·035	1·066	0·485	0·000
0·423	0·369	0·024	0·000	2·127	1·145	0·482	0·001
0·614	0·508	0·053	0·000	2·567	1·203	0·669	0·000
0·831	0·644	0·089	0·000	3·122	1·289	0·909	0·000
1·029	0·749	0·140	0·000	3·798	1·384	1·204	0·000

the limiting Debye–Hückel law is valid. The inability to apply the Debye–Hückel law in this case is well demonstrated by the value of the parameter a for which theory suggests a value approximately three times higher than the one obtained from experiment. Therefore it is necessary to regard equation (17) 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 extrapolated to zero ionic strength (the logarithm of which is equal to parameter c) needs not to correspond to the thermodynamic equilibrium constant of reaction (A). For performing such an extrapolation, it would be necessary to perform the measurements at low

TABLE III
Experimental Values of the Equilibrium Ratio K_m In Dependence on Temperature and on the Sodium Ion Molality m_0

m_0	K_m	m_0	K_m	m_0	K_m
298·15 K		323·15 K		353·15 K	
0·118	11·81	0·108	10·10	0·116	7·58
0·236	12·06	0·206	9·13	0·213	7·01
0·393	9·91	0·402	7·78	0·423	5·62
0·493	9·22	0·486	7·68	0·614	4·87
0·598	8·76	0·509	6·33	0·831	4·67
0·833	7·74	0·811	5·92	1·029	4·02
1·083	6·14	0·997	4·91	1·580	3·19
1·177	5·82	1·498	4·34	2·035	2·34
1·520	5·40	2·015	3·30	2·127	2·72
2·097	4·47	3·000	2·47	2·567	2·17
3·083	3·21	3·977	1·85	3·122	1·83
3·715	2·78	4·046	2·05	3·798	1·59

TABLE IV
Parameter Values in Eq. (17) and the Relative Average Deviation of the Equilibrium Ratio K_m

Temperature, K	c	a	$\Delta K_m, \%$
298·15	1·2259	0·3690	$\pm 3·58$
323·15	1·1208	0·3716	$\pm 4·36$
353·15	1·0104	0·3631	$\pm 5·26$

ionic strength values, where the limiting Debye–Hückel law is valid. 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. In this case of zero sodium ion concentration, the solubility of both solid phases present, determines this minimum ionic strength value. For instance at 298 K this value is equal to 0.079 mol/kg and lies therefore outside the range in which the limiting Debye–Hückel law is valid. Further it is interesting that not even the application of the advanced form of the Debye–Hückel law¹⁸ does lead in comparison with equation (17) to better results.

Equation (17) together with Table IV represent a description of the studied system in a condensed form, but for practical purposes a description in terms of conversion degree or equilibrium ratio dependences on the sodium ion concentration is more useful. From a simple balance consideration follows a relation for the equilibrium ratio

$$K_m = 2m_0x^2/(1 - x), \quad (18)$$

where the conversion degree x of reaction (A) is defined as

$$x = m_1/m_0. \quad (19)$$

Denoting the hydroxide ion concentration as m_1 , the sulphite ion concentration as m_2 and the calcium ion concentration as m_3 it is possible to rewrite the solution electroneutrality condition, expressed by equation (12) into the form

$$m_0 = m_1 + 2m_2 - 2m_3. \quad (20)$$

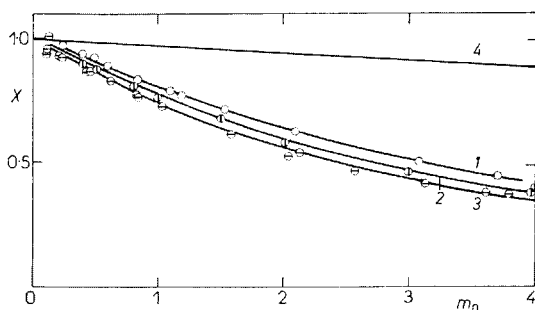


FIG. 1

Influence of the Sodium Ion Concentration m_0 on the Conversion Degree of Reaction (A)

Circles denote experimental values; 1 298.15 K; 2 323.15 K; 3 353.15 K; curves calculated from equation (22). Curve 4 is calculated under the assumption of ideal behaviour from equation (11) for published values of the equilibrium constants $K_F = 2.5 \cdot 10^{-5}$ and $K_B = 4.4 \cdot 10^{-7}$.

From Table II it follows apparently that the calcium ion molality m_3 is by three orders of magnitude smaller than the hydroxide ion concentration m_1 and could influence the calculation of the conversion degree x to some extent only at 298 K and at ionic strength of the solution lower than 0.5. This reason led therefore to the omission of the calcium ion concentration m_3 . The ionic strength is under this assumption given by

$$I = (m_0/2)(3 - x). \quad (21)$$

The dependence of the conversion degree x on the sodium ion concentration m_0 results by combining equations (17), (18) and (21) in the form

$$c - (a/\sqrt{2})\sqrt{[m_0(3 - x)]} = \log 2m_0 + 2 \log x - \log(1 - x), \quad (22)$$

which is shown in Fig. 1. Equation (22) reproduces experimental data with relative average deviations Δx equal to 0.9, 1.1 and 0.9 per cent at 298, 323 and 353 K. The dependence of the equilibrium ratio K_m on sodium ion molality m_0 , which is shown in Fig. 2, can be obtained by successive solution of equations (18) and (22). The dependence calculated in this way reproduces experimental data with a relative average deviation ΔK_m , shown in Table IV for all three temperatures.

Because the dependence of the equilibrium ratio K_m on the ionic strength was experimentally obtained on three temperature levels, it is possible to draw some thermodynamic conclusions from the resulting temperature dependences. By rearrangement of equation (14) and by its successive differentiation with respect to the reciprocal temperature value under constant pressure and constant ionic strength

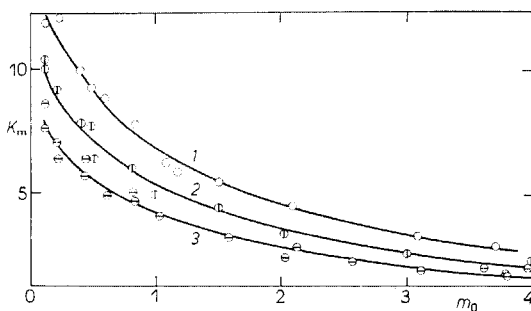


FIG. 2

Dependence of the Equilibrium Ratio K_m on the Sodium Ion Concentration m_0

Circles denote experimental values; 1 298.15 K; 2 323.15 K; 3 353.15 K; curves corresponding to values obtained by solution of equations (18) and (22).

the following equation results

$$\left(\frac{\partial \ln K_m}{\partial (1/T)}\right)_{P,I} = \left(\frac{\partial \ln K}{\partial (1/T)}\right)_P - \left(\frac{\partial \ln K_\gamma}{\partial (1/T)}\right)_{P,I} \quad (23)$$

The value of the differential quotient on the left hand side of this equation can be obtained from dependences of $\log K_m$ on $1/T$, with the ionic strength as a parameter. The slopes of the obtained straight lines change only negligibly, which according to equation (23) 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 equation (23) and consequently also a relatively good value of the reaction heat. This procedure served to determine the heat of reaction as $-1.89 \text{ kcal mol}^{-1}$ with the probable error of $\pm 0.02 \text{ kcal mol}^{-1}$. With the aid of this value and from known thermodynamic data¹¹ it is consequently possible to determine the heat of formation of calcium sulphite as

$$\Delta H_f^0 = -277.0 \text{ kcal mol}^{-1}.$$

This value differs from the predicted value $-276.3 \text{ kcal mol}^{-1}$ merely by $0.7 \text{ kcal} \cdot \text{mol}^{-1}$. This deviation lies securely within the limits of accuracy of the estimation¹² given with $\pm 1.5 \text{ kcal mol}^{-1}$.

Finally it is possible to obtain from the measured results some information about the entropy. By extrapolation of the equilibrium ratio to zero ionic strength according to equation (17), one arrives at the following value of the standard change of Gibbs function at 298 K

$$\Delta G^0 = -1.67 \text{ kcal mol}^{-1}.$$

According to the discussion following equation (17), the actual ΔG^0 value will lie near this value or shall be somewhat lower. From this Gibbs function value and from the heat of reaction, it is thus possible to determine the standard entropy change of reaction (A) at 298.15 as

$$\Delta S^0 = -0.74 \text{ cal K}^{-1} \cdot \text{mol}^{-1}.$$

From this value and from the standard entropy of calcium hydroxide¹¹, of the hydroxide ion¹¹ and of calcium sulphite¹³ one obtains for the standard entropy of the sulphite ion the value

$$S^0(\text{SO}_3^{2-}, \text{aq}, 298.15 \text{ K}) = +1.7 \text{ cal K}^{-1} \text{ mol}^{-1}$$

which, because of the above mentioned reasons, can be in reality also somewhat lower. The value determined by this procedure agrees with the value given by Conway¹⁴

$$S^0(\text{SO}_3^-, \text{aq}, 298.15 \text{ K}) = 3 \pm 3 \text{ cal K}^{-1} \text{ mol}^{-1},$$

but differs remarkably from the value given by Rossini¹¹.

The following conclusions result from the performed work:

1) Conversion of sodium sulphite with calcium hydroxide to sodium hydroxide allows to obtain conversion degrees up to 90 per cent at lower sodium ion concentrations, however the attainable conversion degree decreases remarkably with the increase of sodium ion concentrations and with the increase in temperature. The logarithm of the reaction equilibrium ratio is expressed with good accuracy by a linear function of the square root of the ionic strength.

2) The thermodynamic analysis of results confirmed the heat of formation value of solid calcium sulphite, predicted already formerly, and has also shown, which of both remarkably differing sulphite ion entropy values is more probable.

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Translated by the author (E. E.).