

## SOLID-GAS EQUILIBRIUM IN THE BINARY SYSTEM SODIUM HYDROGEN SULPHATE-WATER\*

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Received August 24th, 1973

An investigation has been made of the equilibrium of hydration of sodium hydrogen sulphate in the temperature interval from 15 to 50°C by a direct measurement in a flow apparatus. From measured equilibrium decomposition pressures, the changes of the thermodynamic functions accompanying this reaction and the values of the enthalpy of formation, the free enthalpy of formation and the absolute entropy of  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$  at 298.15 K were determined.

In connection with a technologic problem of investigating the nature and the behaviour of deposits in a pipeline used during a manufacturing process for the transport of cooled and washed gaseous chlorine<sup>1</sup>, a need has arisen of a knowledge of the solid-gas equilibrium between sodium hydrogen sulphate, which constitutes a major part of these deposits, and water vapour. The data in the literature are uncomplete and they are not always consistent. There are no published data for the temperatures around 20°C. We decided, therefore, to investigate this equilibrium especially in the interval of lower temperatures and to determine the changes of thermodynamic functions accompanying this reaction.

In the binary system  $\text{NaHSO}_4\text{-H}_2\text{O}$ , there exists the monohydrate  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ , which is stable even above the melting point of water<sup>2</sup>. In the temperature range from the melting point of water to the melting point of this monohydrate (60.7°C) (ref.<sup>3</sup>), three phases can exist in a solid-gas equilibrium (the gas, the anhydrous salt, and the monohydrate):



The equilibrium constant  $K_a$  of this reaction is given by the expression

$$K_a = P^{-1} , \quad (\text{I})$$

\* Part VI in the series Chemical Equilibria in Heterogeneous Systems; Part V: This Journal 39, 917 (1974).

where  $P$  denotes the equilibrium vapour pressure of water in atm. The standard state for water was chosen as pure water in the ideal gaseous state at unit fugacity and at the temperature of the system. Because of the low values of pressure, the effect of pressure on the activities of pure solids was neglected.

In order to investigate the equilibrium of the reaction (A), a dynamic method using a flow apparatus has been chosen; in this arrangement, the gas phase moves through a bed containing the solid substances. In reactions with change in the number of gaseous molecules — such as the above-mentioned one — the attainment of equilibrium can be checked by measuring the pressure. The advantage of the dynamic methods is their applicability even in the case of low equilibrium pressures, a relatively quick attainment of equilibrium if there is a good contact between the phases and the fact that the equilibrium value sought may be approached from both sides.

### EXPERIMENTAL

*Substances used.* In preliminary experiments it was found that the available specimens of sodium hydrogen sulphate of analytical grade purity from different sources did not yield quite reproducible results during the measurements although the X-ray analysis did not show the presence of any admixtures in these specimens. For the final measurements, a sample of analytical grade purity was therefore purified by recrystallization from an aqueous solution of sulphuric acid in a way recommended in the paper of Ingraham and coworkers<sup>3</sup>. The monohydrate of sodium hydrogen sulphate obtained in this way showed diffraction lines in accordance with theoretical values<sup>4</sup>. The chemical analysis made afterwards led to the following deviations (in per cent by weight) in the content of individual components of this sample from the theoretical values: sodium +0.43; hydrogen +0.007; water +1.15. Nitrogen from a cylinder has been used as the carrier gas; it was the purest commercially obtainable nitrogen, declared as "nitrogen for bulbs". The remaining reagents were altogether of analytical purity and redistilled water was used throughout the experiments.

*Apparatus.* The block diagram of the equilibrium flow apparatus used is shown in Fig. 1. The inert carrier gas either without any conditioning or after being passed through a drying tower or, eventually, after being saturated to a certain degree with water vapour, was led through a reactor bed consisting of a mixture of sodium hydrogen sulphate and its monohydrate held at a predetermined temperature. The water vapour contained in the gas leaving the reactor was absorbed in drying absorbers; its absolute amount in the gas passed through was determined by weighing. The flow of nitrogen from a cylinder (1) was adjusted with the help of a needle valve (2) and of a pressure stabilizer (3) filled with an aqueous solution of zinc chloride (50 per cent of  $ZnCl_2$  by weight). The pressure of the carrier gas in the first section of the apparatus was measured by a manometer (4). The carrier gas was then led through one of the two parallel branches: either directly to the flowmeter (6) or to the drying tower (5) filled with magnesium perchlorate. The gas flow rate was measured by a capillary flowmeter (6), with an accuracy better than one per cent. The function of this flowmeter and its calibration have been described in a previous communication<sup>5</sup>. The flowmeter was filled with dioctyl phthalate and its temperature was periodically checked. The reactor was placed in a water thermostat, the temperature of which was maintained constant within the limits of  $\pm 0.05^\circ C$ . In this section of the apparatus, there were again two parallel branches; the first one was used for introducing the gas leaving the flowmeter directly into the reactor (8), the second one for introducing it first into the saturator (7) and then into the

reactor. The attachment of another tube allowed the carrier gas to bypass the reactor. The saturator was a glass washing bottle having a volume of approx. 100 ml provided with a sintered plate S 1 and filled to about one half with redistilled water. The reactor was a cylindrical glass vessel provided with an external glass coil which served to introduce the carrier gas. The packing of the reactor consisted of sodium hydrogen sulphate monohydrate mixed with glass balls to prevent caking; the thickness of this layer was about 7 cm.

The pressure in the apparatus behind the reactor was measured by a manometer (9). In the end section of the apparatus, the gas line was again divided into two parallel branches. One of them led to the analytical section while the other was open to the atmosphere. The whole gas line behind the reactor was electrically heated to prevent accidental condensation of water vapour. The analytical section (10, 11) consisted of two U-tubes connected in series and filled with magnesium perchlorate mixed with glass balls. The vapour pressure of water above this drying agent is  $6 \cdot 10^{-3}$  Torr. The amount of water absorbed was determined from the difference of weights before and after each experiment. In preliminary experiments it was found that there was an increase of weight in the first absorber only; for the final series of experiments, therefore, only one absorber was used.

*Procedure.* Before each experiment, the reactor section had first been brought to the desired temperature and than it was swept out with nitrogen after disconnecting the absorber. After the pressure drops and temperatures along the apparatus and the rate of flow of the carrier gas had reached constant values, the measurement of the gas flow through the reactor and the absorbers was made at precisely measured time intervals. The measurements were made at temperatures from 15 to 50°C. The first part of testing the apparatus consisted in checking the per cent saturation of the carrier gas with water vapour in the saturator. It was found that at lower temperatures,

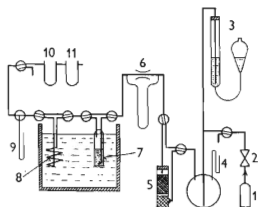


FIG. 1

## Experimental Flow Apparatus

For description see the text.

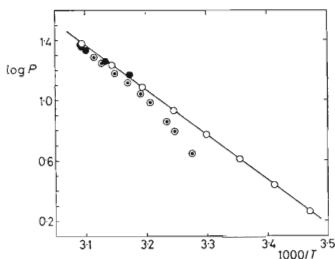


FIG. 2

Logarithm of Equilibrium Vapour Pressure of Water (Torr) vs the Reciprocal Absolute Temperature (K) for the Decomposition of Sodium Hydrogen Sulphate Monohydrate

○ This paper (the diameter of these circles is 2.5 times the average per cent error of the experimental data), ● ref.<sup>8</sup>, ⊙ ref.<sup>3</sup>.

the saturation was very nearly complete. At temperatures above 25°C, the saturation was decreasing very quickly. At 35°C, the carrier gas was saturated to about 50 per cent and at 45°C, to about 30 per cent of the theoretical vapour pressure of water. In all these cases, however, the actual vapour pressure of water in the carrier gas after saturation was higher than the measured equilibrium value in the reactor at the same temperature. Only at 50°C, it was impossible to make the experiment with the "wet" gas, *i.e.* to approach the equilibrium under investigation from the reversed side. The relation between the flow rate of the carrier gas and the resulting vapour pressure of water was also studied. In the range from 0.3 to 2.0 l/h, no dependence of the vapour pressure on the flow rate was found; it was possible, therefore, to give up to the extrapolation of

TABLE I  
Equilibrium Vapour Pressure of the System  $\text{NaHSO}_4\text{-NaHSO}_4\cdot\text{H}_2\text{O}$

Temperature °C	P, Torr											
15	1.85, 2.06,	1.92, 1.88	1.90,	1.74,	1.79,	1.86,	1.91,	1.97,	1.72,	1.86,	1.81,	2.07,
20	2.72,	2.70,	2.77,	2.75,	2.69,	2.68,	2.79,	2.73,	2.68,	2.80,	2.85,	2.73
25	4.09, 4.04,	3.93, 4.05,	4.16, 4.14,	3.87, 4.15,	3.91, 4.08,	3.93, 4.00	3.88,	3.85,	3.85,	3.95,	4.00,	3.90
30	6.10,	5.88,	6.06,	5.81,	5.91,	5.85,	5.98,	5.83,	5.94,	6.09		
35	8.80, 8.76,	8.42, 8.78,	8.62, 8.39,	8.24, 8.61,	8.48, 8.59,	8.76, 8.38,	8.52, 8.39,	8.71, 8.69,	8.73, 8.58,	8.27, 8.69,	8.77,	8.79, 8.42
40	12.35, 12.29	12.46,	12.64,	12.12,	12.52,	12.50,	12.07,	12.48,	12.49,	12.24,	12.44,	12.29,
45	17.31, 17.61,	17.46, 17.39,	17.31, 17.68,	17.21, 17.17,	17.34, 17.06,	17.10, 17.72,	17.38, 17.17,	17.96, 17.52,	17.51, 17.22,	17.14, 17.66,	17.48, 17.22,	17.18, 17.20
50	24.36, 24.01, 24.22, 24.47, 24.71, 24.10, 24.14, 24.30											

the measured values to zero flow rate of the carrier gas. The correctness of the determination of the total amount of water in the gas was checked by measurements of the vapour pressure of water above the aqueous solution of sulphuric acid for which this value was exactly known. For this purpose, a solution of sulphuric acid having a density  $d_4^{20} = 1.5112 \text{ g/cm}^3$  (61.2 per cent by weight of  $\text{H}_2\text{SO}_4$ ) was used. At 25°C, the vapour pressure of water in the carrier gas passing through this solution at different flow rates and for different times of duration of this experiment was determined. The value found at 25°C in this way was 3.50 Torr which was in accord with the published<sup>7</sup> value of 3.48 Torr. The calculations have been based on the assumption that both nitrogen and water vapour behave as ideal gases.

## RESULTS AND DISCUSSION

The results obtained with the purified sample of the monohydrate were mutually consistent when the equilibrium in the system was attained from both sides (increasing or decreasing temperature of the reactor bed, the vapour pressure of water in the carrier gas entering the reactor higher or lower than the equilibrium value). The vapour pressures at various temperatures found experimentally are given in Table I. The data obtained from these experimental vapour pressures by the method of the least squares are plotted in Fig. 2 together with the data found by Ingraham and coworkers<sup>3</sup> and by Watelle and coworkers<sup>8</sup>. From the strictly linear dependence in Fig. 2 it can be inferred that in the temperature range under investigation, only reaction (A) takes place and that its heat of reaction is substantially independent of temperature. It is obvious that our data are in very good accord with the results of the thermogravimetric measurements made by Watelle and coworkers<sup>8</sup>. The agreement with the data of Ingraham and coworkers<sup>3</sup>, who have measured the decomposition pressures above this system, is satisfactory at higher temperatures. In the range from 32 to 40°C, the above-mentioned authors<sup>3</sup> observed a curvature in the dependence of  $\log P$  vs  $1/T$  but they were unable to elucidate the cause of this phenomenon. We did not observe any such curvature. The X-ray powder diffraction method (radiation Fe  $K_{\alpha}$ ) in the range of angles from 2 to 50° did not prove any changes of the solid phase in the reactor bed when experimenting at lower temperatures. The above-mentioned curvature in the paper of Ingraham and coworkers<sup>3</sup> could perhaps be explained by an underestimation of the time factor in the attainment of equilibrium in static experiments. At lower temperatures, the attainment of the hydration equilibrium is much slower than at higher temperatures. We have proved this phenomenon qualitatively even in our dynamic experiments.

The dependence in Fig. 2 can be reproduced by the relation

$$\log P (\text{Torr}) = -(2978.0 \pm 8.3)/T + (10.599 \pm 0.027). \quad (2)$$

From this relation, it follows for the dependence of the equilibrium constant of the reaction (A) on temperature

$$\log K = (2978.0 \pm 8.3)/T + (7.718 \pm 0.027). \quad (3)$$

For the changes of thermodynamic functions accompanying the reaction (A) in the temperature interval from 15 to 50°C, we obtain from the last equation

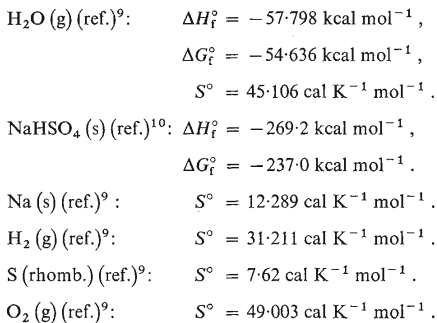
$$\Delta G^{\circ} = -(13627 \pm 38) \pm (35.31 \pm 0.12) T \quad (\text{cal});$$

$$\Delta H^{\circ} = -13627 \pm 38 \quad (\text{cal});$$

$$\Delta S^{\circ} = -35.31 \pm 0.12 \quad (\text{cal K}^{-1}).$$

The errors given in these equations follow from the standard deviations of the slope and of the constant term in equation (2).

Combining the values of thermodynamic functions accompanying the reaction (A) with the known thermodynamic properties of solid sodium hydrogen sulphate and of water vapour, we obtain the thermodynamic properties of sodium hydrogen sulphate monohydrate. For this calculation, the following values of the thermodynamic properties, all at 298.15 K, have been used:



From these data, the enthalpy of formation, the free enthalpy of formation and the absolute entropy of solid sodium hydrogen sulphate monohydrate have been calculated at 298.15 K:

$$\begin{aligned} \Delta H_f^\circ &= -340.6 \text{ kcal mol}^{-1} \\ \Delta G_f^\circ &= -294.7 \text{ kcal mol}^{-1} \\ S^\circ &= 35.32 \text{ cal K}^{-1} \text{ mol}^{-1} \end{aligned}$$

For the enthalpy of formation of the monohydrate, two values have been found in the literature, *i.e.*:  $-339.2 \text{ kcal mol}^{-1}$  (see<sup>10</sup>), and  $-340.4 \text{ kcal mol}^{-1}$  (see<sup>11</sup>), which are in a very good agreement with the value found by us. The second of the above-mentioned values found in the literature was determined by a direct calorimetric measurement in aqueous solutions, *i.e.* by a method quite differing from our own. The difference between the absolute entropies of sodium hydrogen sulphate monohydrate and of the corresponding anhydrous salt, *i.e.*  $35.32 - 25.52 = 9.8 \text{ cal K}^{-1} \text{ mol}^{-1}$  is also in a very good accord with the value of  $9.4 \text{ cal K}^{-1} \text{ mol}^{-1}$  given by Latimer<sup>12</sup> for the common contribution of one mole of the hydrate water to the value of the absolute entropy of a solid substance. The mutual consistency of

the data found by us and a very satisfactory agreement of these data with the values given by other authors prove the adequacy of the experimental method used and its ability to yield reliable results even in such instances, where the static measurements would probably be subjected to a very large error.

*We are indebted to Mr L. Jettmar for technical assistance.*

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Translated by the author (Č. Č.).