

**SOLID-GAS EQUILIBRIA IN THE BINARY SYSTEMS
ALKALI HYDROGEN SULPHATE-WATER
AND AMMONIUM HYDROGEN SULPHATE-WATER***

J. HEJTMÁNKOVÁ and Č. ČERNÝ

*Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

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An investigation has been made of the equilibria of hydration of alkali hydrogen sulphates and of ammonium hydrogen sulphate in the temperature interval from 20 to 50°C by a direct measurement in a flow apparatus. From measured equilibrium decomposition pressures, the changes of the thermodynamic functions accompanying these reactions and the values of some of the thermodynamic functions of the hydrated salts at 298.15 K were determined.

In Part VI of this series¹, a report on the hydration of the sodium hydrogen sulphate was given; the reason for that study was the technologic importance of the hydration reaction in question. In connection with that problem, it was decided to investigate these hydration reactions also in the case of other alkali hydrogen sulphates and of ammonium hydrogen sulphate. Wherever the supplementary data were found in the literature, the thermodynamic functions for the respective reaction components were also calculated.

The results obtained in this investigation together with the outcomes of the previous one¹ give a complete picture of the hydration equilibria, *i.e.* the values of the equilibrium constants, of the decomposition pressures and of the changes of the free enthalpy, of the enthalpy and of the entropy in the temperature interval from 20 to 50°C for the reactions



where M^+ denotes the cation of the alkali metal or NH_4^+ .

In all these hydration reactions, the individual compounds were components of a binary three-phase systems. The method and experimental arrangement used for investigating these systems were the same as before¹. The apparatus and the dynamic method of measurement used for the reactions of the type (A) were discussed in the previous paper and they proved to be fully adequate to our needs.

* Part VII in the series Chemical Equilibria in Heterogeneous Systems; Part VI: This Journal 39, 1187 (1974).

EXPERIMENTAL

Substances used. The primary substances under investigation, the hydrogen sulphates, were not available in sufficient purity in all the cases. In preliminary experiments with the sodium salt it became evident that if the starting solid phase was not exactly defined, the reproducibility of the results obtained was much poorer than it could have been expected on the basis of our knowledge of the presence of minute amounts of impurities. It was found that the various procedures recommended for the preparation and/or for the purification of alkali hydrogen sulphates found in older and even in more recent papers²⁻⁴, were not quite reliable. For the preparation of the hydrogen sulphates, an individual procedure was therefore adopted for each substance with respect to the final use of the pure solid phase in the reactor. The primary criterion for the use of reagents of analytical purity without further purification was — first of all — a good reproducibility of the results obtained. The details are given below for each individual system. Nitrogen from a cylinder has been used as the carrier gas; it was the purest commercially available nitrogen, declared as "nitrogen for bulbs". The remaining reagents used for analysis were altogether of analytical purity and redistilled water was used throughout the experiments. As far as it is of any importance for the described procedure, the purity of substances used for the preparations is given in the text.

Apparatus and experimental procedure. The experimental method and the apparatus used were the same as in the previous paper¹ without any substantial changes. In individual cases, it was of course necessary to adjust the proper thickness of the bed in the reactor to ensure the saturation of the carrier gas with water vapour to the value corresponding to the equilibrium tension above the solid phase. It was further necessary to change the percentage of the inert admixture (*i.e.* of the glass balls) to the substance under investigation in the reactor bed in order to prevent caking.

The decomposition pressures were measured in nearly the same temperature interval as in the previous communication. In individual cases, however, it was necessary to modify this interval with respect to these two requirements: first, it was necessary to avoid condensation of the water vapour in the cooler absorption section of the apparatus behind the reactor which occurred at higher decomposition pressures. Secondly, the accuracy of the measured values of the decomposition pressures was dependent on their absolute values. In the case of relatively low temperatures and in connection with it of relatively low decomposition pressures (below approx. 1 Torr), the accuracy was considerably lower. In such cases, the error of weighing the absorbed water vapour in the absorber remained essentially the same only at the cost of increasing the duration of the experiment or of increasing the flow rate of the carrier gas but this invariably brought forth the growth of other random errors connected with the attainment of equilibrium and/or with the measurement of volume, temperature and pressure of the flowing gas. The accuracy of the data is given in each individual case.

As far as the characterization of the solid phase was concerned, it was even with one of the samples investigated impossible to supplement the equilibrium experiments with a reliable X-ray analysis of the solid in the reactor. Using the powder X-ray method (FeK α radiation), all the samples on the cobalt anode deliquesced to such an extent that the corresponding diffractogram was distorted and that it was possible to assign only some of the strongest lines; the comparison of these lines with the published values in the case of KHSO₄ and NH₄HSO₄ (ref.⁵) could serve only for the identification of the anhydrous salt.

RESULTS AND DISCUSSION

Lithium Hydrogen Sulphate

The preparation of the solid phase suitable for equilibrium measurements met with the greatest difficulties of all the solids investigated in this study. According to the older sources², the existence of a well-defined compound LiHSO_4 is rather doubtful; the more recent authors are not so sceptical, however^{6,7}. This nevertheless proves that this substance cannot easily be characterized. The flow method used by us for investigating the hydration equilibrium allows to start either with the anhydrous salt or with the hydrate. When preparing this substance, it was therefore not necessary to dry carefully the products prepared. Because of the extremely high hygroscopicity of this substance, however, it was very difficult to obtain products in a loose state, suitable for filling the reactor. The preparation of lithium hydrogen sulphate from lithium hydroxide and sulphuric acid or from sulphuric acid and the aqueous solution of hydrate of lithium sulphate by procedures described in the literature^{2-4,8} did not yield desirable products, although in some instances the analyses indicated that these products corresponded to lithium hydrogen sulphate with a bigger or a smaller amount of water. The most reproducible results in the equilibrium measurements were obtained when using lithium hydrogen sulphate prepared from the anhydrous lithium sulphate (analytical grade purity), carefully desiccated by a procedure described in the literature⁹, and from concentrated sulphuric acid of the same purity grade. The relative amounts of both starting materials and the temperature at which the lithium hydrogen sulphate was prepared were chosen with respect to the phase diagram of the condensed system $\text{Li}_2\text{SO}_4\text{-H}_2\text{SO}_4$ (ref.¹⁰). According to the paper cited, the compounds Li_2SO_4 and H_2SO_4 form addition compounds of the type $\text{Li}_2\text{SO}_4 \cdot (\text{H}_2\text{SO}_4)_x$ with the range of existence of these compounds indicated in the diagram. The final product of anhydrous lithium hydrogen sulphate was obtained by crystallization from the melt containing 70 mol % of H_2SO_4 and 30 mol % of Li_2SO_4 by cooling it to 76°C. The crystals were quickly filtered from the hot mother liquor and then cooled in a desiccator without any further draining. The chemical analysis of this product led to the following results (in per cent by weight): the average content of water: 5.7; the deviation in the content of the sulphate ion from the theoretical value for LiHSO_4 : 1.39; in the case of the hydrogen ion, this deviation amounted to 0.087%. (These last two results are given with respect to the dry substance). The final measurements were therefore made using a product containing less than 50% of water corresponding to the monohydrate of this salt (theoretical content of water is 14.76 per cent by weight).

Except at the highest temperature, it was possible to approach the equilibrium composition of the system under investigation from both sides, depending on the water content in the carrier gas before the reactor. Nitrogen from a cylinder has been

used as a carrier gas either dried (the content of water vapour corresponded to about 0.1 Torr), or without any drying (1.0 to 1.1 Torr).

The vapour pressures above this system 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. 1 (line 1). The vapour pressures above this system were altogether very low; this caused a relatively great scattering of the data obtained and at the same time a greater uncertainty in individual values when compared with other systems.

The dependence of $\log P$ on $1/T$ for this system is linear (see line 1 in Fig. 1). From this fact, it can be inferred that under given conditions, only reaction (A) takes place in this system, and that in the temperature range investigated, the standard change of the enthalpy of this reaction is substantially independent of temperature. No data

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

$t, ^\circ\text{C}$	P, Torr
20	0.49, 0.45, 0.36, 0.29, 0.29, 0.37, 0.32, 0.33, 0.40, 0.27, 0.37, 0.33, 0.37, 0.37, 0.28
30	0.54, 0.52, 0.55, 0.49, 0.75, 0.59, 0.56, 0.46
40	0.86, 1.02, 0.94, 1.09, 1.07, 1.06, 1.10, 1.00, 0.95, 0.96, 1.11, 0.97, 1.14, 1.06, 1.04, 1.04, 1.03, 0.93
50	1.52, 1.67, 1.56, 1.49, 1.39, 1.61, 1.58, 1.49, 1.36, 1.11, 1.85, 1.33, 1.03, 1.46, 1.28, 1.09

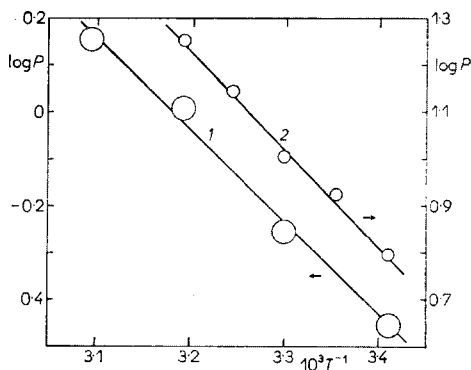


FIG. 1
Logarithm of Equilibrium Vapour Pressure of Water P (Torr) vs the Reciprocal Absolute Temperature (K)
Decomposition of 1 $\text{LiHSO}_4\cdot\text{H}_2\text{O}$,
2 $\text{NH}_4\text{HSO}_4\cdot\text{H}_2\text{O}$.

on this equilibrium have been found in the literature; it is therefore impossible to compare our results with values obtained by some other method.

The dependence of pressure P (Torr) on temperature, reproduced in Fig. 1, can be represented by the relation

$$\log P = -(1971 \pm 70)/T + (6.62 \pm 0.23). \quad (1)$$

From this relation it follows for the dependence of the equilibrium constant of the reaction (A) (where $M = \text{Li}$) on temperature (standard state for water vapour: ideal gas at the pressure of 1 atm):

$$\log K = (1971 \pm 70)/T - (3.38 \pm 0.23). \quad (2)$$

For the changes of thermodynamic functions accompanying this reaction in the temperature interval from 20 to 50°C, we obtain from the last equation

$$\Delta G^0 = -(9018 \pm 322) + (28.6 \pm 1.0) T (\text{cal});$$

$$\Delta H^0 = -9018 \pm 322 (\text{cal});$$

$$\Delta S^0 = -28.6 \pm 1.0 (\text{cal K}^{-1}).$$

The errors given in these equations follow from the standard deviations of the slope and of the constant term in equation (1).

Potassium Hydrogen Sulphate

According to the literature, the existence of a hydrate of this salt is not quite clear. There is no mention made of any hydrate in more recent literature. According to some older sources¹², the monohydrate crystallizes from water solution; there even exist reports on the existence of some higher hydrate which easily deliquesces.

We therefore proceeded directly to orientation experiments using a commercially available potassium hydrogen sulphate of analytical purity without any further purification. The declared contents of individual impurities in the sample used (the ions of heavy metals, Al, Ca, phosphates, nitrates and others) were in all the cases in the range of thousandths of a per cent by weight.

The water content in this potassium hydrogen sulphate was determined both just before the filling of the reactor and for control purposes after the end of the experiment in a sample of the reactor bed. The average water content in the original sample was 1.1 per cent by weight; in the sample of the reactor bed, the percentage of water was practically unchanged, ranging from 1.0 to 1.3.

During all the measurements of vapour pressure above this sample of potassium hydrogen sulphate, we did not reach such a state when the content of water vapour above the solid phase would be constant, *i.e.* a state in which the vapour pressure would be an unambiguous function of temperature alone. The water content in the carrier gas leaving the reactor always changed continuously toward its value in the carrier gas before entering the reactor, irrespectively whether "dry" or "wet" carrier gas was used. Because it was impossible that the minute amounts of impurities in the solid would influence the measured vapour pressure to any considerable extent and because the velocity of the carrier gas did not affect the measured vapour pressures at all, it was evident that these vapour pressures were the equilibrium ones. When attaining the equilibrium "from above", the saturation of the carrier gas with water vapour was secured — especially at the lower temperatures — practically to the value of the saturated vapour pressure at the given temperature.

The fact that even under these conditions and even in prolonged experiments, no constant value of the equilibrium vapour pressure has been attained, can be considered as a convincing evidence for non-attainment of any equilibrium hydration in the system under investigation; this also confirms the previous findings that the potassium hydrogen sulphate does not form any stable hydrate under the conditions given.

Rubidium Hydrogen Sulphate and Caesium Hydrogen Sulphate

Both in the old^{13,14} and in the more recent literature, there is no mention made of the existence of a hydrated rubidium or caesium salt in the solid state.

It was impossible to get these two sulphates as commercial products and the method of their preparation described in the current literature¹⁴ did not promise — by analogy with other alkali hydrogen sulphates — to get chemical individua having well-defined properties.

In both these cases, the intention to start even some preliminary experiments in the flow apparatus was therefore given up. The existence of hydrates of the salts of these two heavy alkali metals in the solid state can after all be excluded upon closer inspection of the literature, without resorting to an experimental proof based on the measurement of the respective equilibria.

Ammonium Hydrogen Sulphate

As in the case of potassium hydrogen sulphate, it was impossible to make an unequivocal decision on the existence of a stable hydrate from the inspection of the literature alone. Although there are some indications of the hydration of this salt¹⁵, no concrete proof of the existence of a hydrate on the solid state has been found.

It was therefore decided to start directly the equilibrium measurements with a commercially available specimen of this salt; its purity has been checked with respect

to the content of the hydrogen sulphate ion, ammonium ion and of water by usual methods¹⁶. The water content in different samples of this salt was about 5 per cent by weight (the theoretical value for the monohydrate is 13.53 per cent by weight). The percentage by weight of the ions was as follows: HSO_4^- : 83.54 (theoretical : 84.33); NH_4^+ : 15.52 (theoretical : 15.67). The consistence of this sample was adequate for filling the reactor and the results of the equilibrium measurements obtained with it were sufficiently reproducible.

In this case, the equilibrium was approached from both sides of the final, equilibrium value of the vapour pressure as far as the gradient of temperature and of concentration is concerned. The results obtained when gradually increasing or decreasing the temperature or the water content in the carrier gas entering the reactor were mutually consistent.

It was found that the reattainment of the equilibrium vapour pressure after the temperature of the reactor had been changed was slower in this case when compared with other systems. We suppose that this has been caused by the coarser crystallinity of this salt. The slower attainment of equilibrium required approximately a twofold number of experiments with respect to the number utilizable for calculating the equilibrium vapour pressure.

The decomposition pressures of water vapour above this system at various temperatures are given in Table II. The final values derived from the data in Table II by the method of the least squares are plotted in Fig. 1 (line 2). This dependence of $\log P$ on $1/T$ for this system being linear as in the case of lithium hydrogen sulphate, it can be stated that even here only reaction (A) takes place and that the standard change of enthalpy accompanying the hydration of ammonium hydrogen sulphate is substantially independent of temperature.

For this system, no published data on the equilibrium under investigation have been found even at one temperature; it is therefore impossible to compare both our

TABLE II
Equilibrium Vapour Pressure of the System $\text{NH}_4\text{HSO}_4\text{-NH}_4\text{HSO}_4\cdot\text{H}_2\text{O}$

$t, ^\circ\text{C}$	P, Torr
20	6.43, 6.14, 6.06, 6.13, 6.19, 6.21, 6.38, 6.36
25	8.94, 8.27, 8.37, 8.71, 8.02, 8.58, 8.32, 8.27, 8.38, 8.71, 8.42, 8.00
30	9.39, 9.14, 9.32, 9.72, 9.92, 9.85, 9.60, 9.88, 10.07, 10.06, 10.13, 10.52, 11.24, 10.16, 10.20, 10.89, 10.51, 10.59, 10.85, 10.32
35	13.80, 14.20, 14.24, 14.40, 14.31, 14.03, 14.05, 13.31, 13.17, 14.16, 13.38, 14.81
40	17.62, 18.40, 17.84, 18.59, 17.06, 18.06, 17.28, 18.74

measured equilibrium decomposition pressures and the calculated changes of the thermodynamic functions accompanying the reaction (A) with some independent values.

The dependence of pressure (Torr) on temperature for ammonium hydrogen sulphate, plotted in Fig. 1 (line 2), can be represented by the relation

$$\log P = -(2080.5 \pm 45.6)/T + (7.89 \pm 0.15). \quad (3)$$

From this relation, it follows for the dependence of the equilibrium constant of hydration [reaction (A); $M = \text{NH}_4$] on temperature (standard state for water vapour: ideal gas at the pressure of 1 atm):

$$\log K = (2080.5 \pm 45.6)/T - (5.01 \pm 0.15). \quad (4)$$

For the changes of thermodynamic functions accompanying this reaction in the temperature interval from 20 to 40°C, we obtain from equation (4)

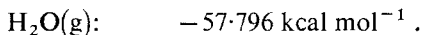
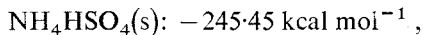
$$\Delta G^0 = -(9520 \pm 208) + (22.92 \pm 0.43) T \text{ (cal)};$$

$$\Delta H^0 = -9520 \pm 208 \text{ (cal)};$$

$$\Delta S^0 = -22.92 \pm 0.43 \text{ (cal K}^{-1}\text{)}.$$

The errors given in these equations follow from the standard deviations of the slope and of the constant term in equation (3).

Combining the value of the standard change of enthalpy ΔH^0 accompanying the reaction (A) with the known value of the standard enthalpy of formation of the solid ammonium hydrogen sulphate and of the water vapour, we obtain the value of the standard enthalpy of formation of solid ammonium hydrogen sulphate monohydrate under the same conditions. For this calculation, the following values of the standard enthalpy of formation (ΔH_f^0), all at 298.15 K, have been used¹⁷:



From these data $\Delta H_f^0(\text{NH}_4\text{HSO}_4 \cdot \text{H}_2\text{O}, \text{s}, 298.15 \text{ K}) = -312.77 \text{ kcal mol}^{-1}$. Because other thermodynamic functions for the anhydrous salt were missing, it was impossible to calculate the corresponding values for the monohydrate.

Of all the alkali and ammonium hydrogen sulphates investigated, only the lithium, sodium, and ammonium salt showed stable values of the decomposition pressure of water vapour and consequently the existence of a hydration equilibrium. With

the potassium salt, no such equilibrium was observed although it could have been expected. However, this fact is in agreement with the values of the equilibrium constants for the individual salts at room temperature. These values fall in the sequence $(\text{Li}^+) > (\text{Na}^+) > (\text{NH}_4^+)$. Because of this limited number of existing equilibria, it is impossible to draw any quantitative conclusions on the correlation of thermodynamic and other characteristics for the reactions given with the nature of substances in the group of alkali metals, as has been originally intended.

The scantiness of tabulated thermodynamic functions of anhydrous alkali hydrogen sulphates restricted also the calculations of otherwise interesting thermodynamic properties of solid hydrates to only one case in this paper. When the necessary data on the thermodynamic properties of solid substances become available, it will be possible to use the equilibrium data from this paper also for this purpose, as has been shown in the preceding communication¹.

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REFERENCES

1. Hejtmánková J., Černý Č.: This Journal 39, 1187 (1974).
2. *Gmelins Handbuch der Anorganischen Chemie*, 8. Auflage, Syst.-Nr. 20. Verlag Chemie, Weinheim 1927.
3. Spitsyn V. J., Meerov M. A.: Zh. Obshch. Khim. 22, 901 (1952).
4. Thilo E., Lampe F.v.: Z. Anorg. Allg. Chem. 319, 387 (1963).
5. Kitaygorodskiy A. Y.: *Rentgenostrukturnyi Analiz Melkokristalicheskikh i Amorfných Tel*. Gos. Izd. Technikoteoret. Lit., Moscow 1952.
6. Turner D. J.: J. Chem. Soc., Faraday Trans. 2, 68 (4), 643 (1972).
7. Flowers R. H., Gillespie R. J., Robinson E. A.: J. Chem. Soc. 1960, 845.
8. *Gmelins Handbuch der Anorganischen Chemie*, 8. Auflage, Syst.-Nr. 20. Verlag Chemie, Weinheim 1960.
9. Akerlöf G.: J. Amer. Chem. Soc. 48, 1160 (1926).
10. Kendall J., Landon M. L.: J. Amer. Chem. Soc. 42, 2131 (1920).
11. Hillebrand W. F., Lundell G. E. F., Bright H. A., Hoffman J. I.: *Applied Inorganic Analysis*. Wiley, New York 1953.
12. *Gmelins Handbuch der Anorganischen Chemie*, Lieferung 3, Syst.-Nr. 22. Verlag Chemie, Weinheim 1937.
13. *Gmelins Handbuch der Anorganischen Chemie*, Nachdruck, Syst.-Nr. 24. Verlag Chemie, Weinheim 1955.
14. *Gmelins Handbuch der Anorganischen Chemie*, Nachdruck, Syst.-Nr. 25. Verlag Chemie, Weinheim 1955.
15. *Gmelins Handbuch der Anorganischen Chemie*, 8. Auflage, Lieferung 2, Syst.Nr. 23. Verlag Chemie, Weinheim 1936.
16. Čůta F.: *Analytická chemie odměrná*. Published by Nakladatelství ČSAV, Prague 1956.
17. Wagman D. D., Evans W. H., Parker V. B., Halow I., Bailey S. M., Schumm R. H.: *Selected Values of Chemical Thermodynamic Properties*. NBS Technical Note 270-3, Natl. Bur. Standards, Washington 1968.

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