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A STUDY OF THE REACTION $Na_2SO_4 \cdot 10H_2O \rightarrow Na_2SO_4 + 10H_2O$ IN THE TEMPERATURE RANGE 0 TO 25°C

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ABSTRACT

Thermogravimetry was used to obtain data on the isothermal rate of dehydration and hydration of the reaction $Na_2SO_4 \cdot 10H_2O \rightarrow Na_2SO_4 + 10H_2O$ in the temperature range 10 to 25°C. The thermodynamic functions, ΔH, ΔG and ΔS were calculated and compared with data in the literature. The dissociation pressures of $Na_2SO_4 \cdot 10H_2O$ at temperatures in the range 0 to 25°C were measured in a volumetric dissociation apparatus. The results obtained were compared with those using thermogravimetry and the accuracy of the two techniques was assessed.

INTRODUCTION

The salt hydrate, known in natural deposits as Glauber's salt or mirabilite, $Na_2SO_4 \cdot 10H_2O$, is an efflorescent mineral which under conditions short of equilibrium transforms to the anhydrous phase thenardite, Na_2SO_4. Work of early investigators[1–6] was centred on the measurement of its dissociation pressure. Their attention was concentrated on refining different volumetric techniques.

In the present work dehydration–hydration studies on artificial $Na_2SO_4 \cdot 10H_2O$ were undertaken in order to revise the existing data. All the experiments were done in the absence of air and X-ray powder diffraction and/or optical microscopy were used as a means of identification. The rate of attainment of equilibrium for both the dehydration and hydration stages of the reaction in the temperature range 10 to 25°C was determined as a function of imposed water vapour pressure. From the data provided the equilibrium vapour pressures at various temperatures were determined and the enthalpy was calculated.

For the sake of comparison of results, a further series of experiments were performed in a volumetric dissociation apparatus where the dissociation pressure of the salt hydrate was measured at different temperatures in the range 0 to 25°C. The accuracy of the two techniques was assessed.

EXPERIMENTAL

Materials

B.D.H. Analar Grade sodium sulphate decahydrate was used in all the experiments undertaken. It contains not less than 99% $Na_2SO_4 \cdot 10H_2O$. On exposing a weighed portion of the crystalline sample to the dry atmosphere, 25°C, the loss in weight after 3 h was 55.25% which was equivalent to 9.95 H_2O moles per mole of $Na_2SO_4 \cdot 10H_2O$. Using Cu-K_α radiation an X-ray powder photograph of the residue showed that the values of the Bragg *d*-spacings were in reasonable agreement with those of orthorhombic thenardite, Na_2SO_4 (A.S.T.M. card No. 5-0631).

In view of the efflorescent character of the salt hydrate, great care was taken to avoid the loss of weight by the samples during the procedures prior to the start of the experiments. The samples were weighed in a cool room and they were introduced immediately into the specimen chamber of the apparatus.

Apparatus

A thermogravimetric balance[7] was used to obtain dehydration–hydration data on $Na_2SO_4 \cdot 10H_2O$. For the experiments performed at temperatures less than 25°C, the apparatus was modified so that low temperatures could be obtained inside the balance chamber. The furnace was replaced by a pyrex-glass condenser through which cold water was allowed to circulate. The condenser was connected via a rubber tube to a 5 mm copper tube designed in the shape of a spiral which was placed in a vessel containing water and ice. The other end of the spiral was connected to a water tap. This technique allowed cold water to circulate around the specimen chamber. The rate of flow of water was controlled with the water tap; constant rates of flowing water gave temperatures accurately to within ±0.5°C which were measured with the Pt/Pt–13% Rh thermocouple. In increasing or decreasing the temperature, the rate of flow of water was changed and approximately 10 min were allowed for each desired temperature to reach a constant value before the start of the experiment.

EXTENT OF DEHYDRATION AND HYDRATION ON $Na_2SO_4 \cdot 10H_2O$

To explore the extent of dehydration and hydration on $Na_2SO_4 \cdot 10H_2O$ a series of preliminary experiments were carried out on 200-mg portions of $Na_2SO_4 \cdot 10H_2O$. In one experiment the specimen was dehydrated under vacuum conditions and over P_2O_5 at a temperature of 16.3°C. The data are illustrated in Fig. 1, curve A. On another portion of $Na_2SO_4 \cdot 10H_2O$, an experiment was carried out at 22.0°C and as a function of imposed water vapour pressure. The vapour pressure in the dehydration process was 12.00 mm Hg and in the rehydration reaction it was 19.7 mm Hg. Plots of the percentage loss and gain in weight as a function of time are shown in Fig. 1, curves B and C.

The results showed that the dehydration over P_2O_5 was very fast in spite of the fact that the experiment was conducted at a low temperature. On the other hand, in the presence of water vapour the reaction was much slower. Although the dehydration and the reversible hydration processes were performed at different vapour pressures, the rate of the two reactions was almost the same.

The total amount of water involved in this reversible reaction was equivalent to 9.30 moles of H_2O per mol of $Na_2SO_4 \cdot 10H_2O$. In view of the efflorescent character of the salt-hydrate, it is possible that at least a fraction of the difference of 0.70 moles

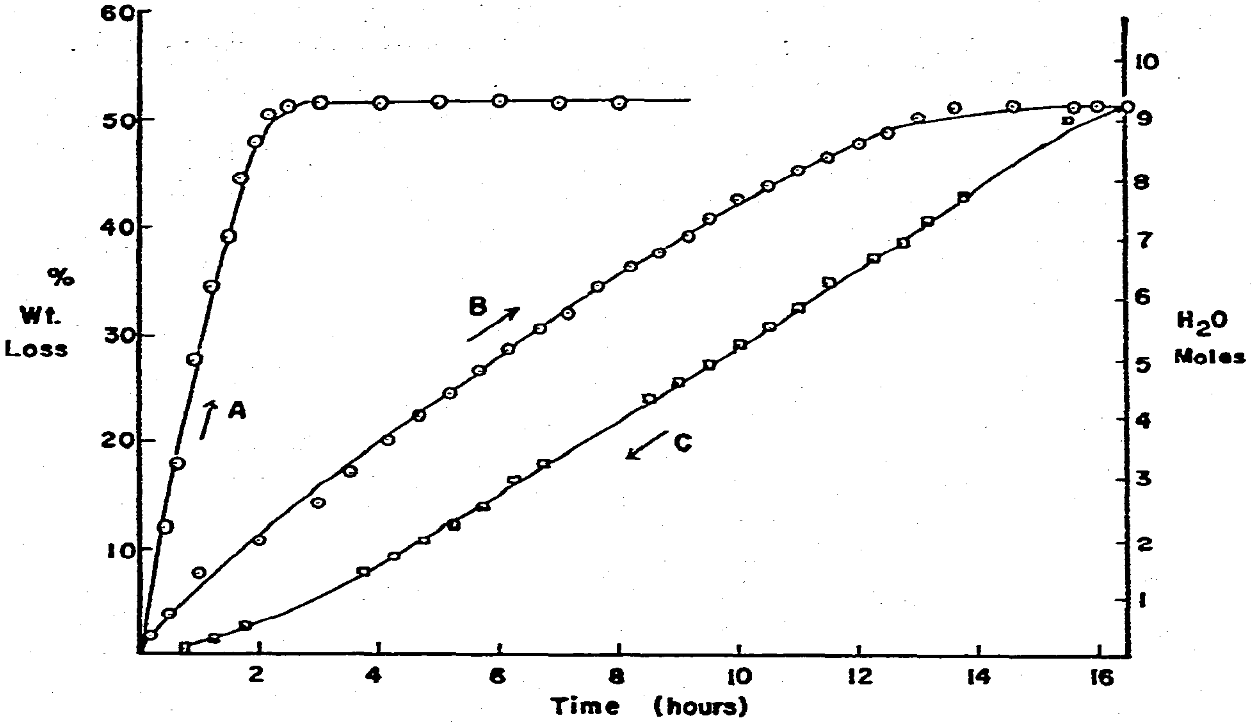

Fig. 1. Comparison of dehydration and hydration rates for $Na_2SO_4 \cdot 10H_2O$. A, dehydration under vacuum conditions at 16.3 °C; B, dehydration at 22 °C vapour pressure 12.00 mm Hg; C, hydration at 22 °C vapour pressure 19.7 mm Hg.

of H_2O had been lost from the specimen during the short time taken between its weighing in the analytical balance and its introduction into the apparatus.

CRITICAL VAPOUR PRESSURES OF THE REACTION $Na_2SO_4 \cdot 10H_2 \rightleftharpoons Na_2SO_4 + 10H_2O$

Method

A series of experiments on sodium sulphate decahydrate were carried out in absence of air in order to determine the critical vapour pressures of the reaction, $Na_2SO_4 \cdot 10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$ at temperatures in the region (10–25)°C. A sample weighing 200 mg was dehydrated in vacuum and over P_2O_5 until the weight loss was equivalent to a state of approximately half dehydration. The tap connecting the vacuum pump with the P_2O_5 trap was then closed, and while the system was still under vacuum the desired temperature was brought to a constant value inside the specimen chamber. Vapour pressure was imposed and four readings of weight loss were recorded every 5 min. From these measurements the average loss of weight per minute was obtained. The vapour pressure was then increased, and in a similar way, the rate of weight loss at this vapour pressure was obtained. Measurement of the rate of weight change as a function of increased vapour pressure was maintained in the same manner until equilibrium had been reached and the specimen began to hydrate.

Results

Data expressed in microgram per minute at half dehydration–hydration and as functions of imposed water vapour are plotted in Fig. 2.

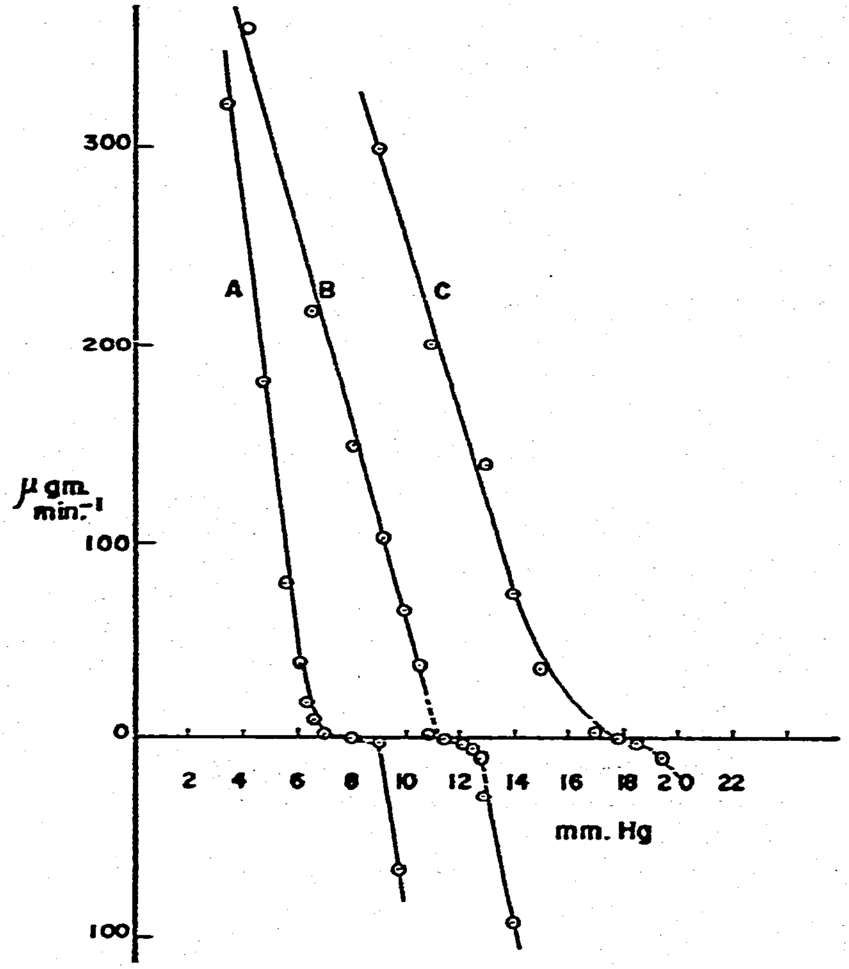

Fig. 2. Reaction rates of dehydration and hydration for $Na_2SO_4 \cdot 10H_2O$ at a state of half dehydration and as functions of imposed water vapour pressure. A, At 13.0°C; B, at 17.2°C; C, at 23.1°C.

It is clear from these results that the rates of dehydration and hydration outside the regions of the equilibrium vapour pressures showed linear relationship with vapour pressure. However, in the regions close to the critical vapour pressures, the rates had decreased to considerable low values. The equilibrium vapour pressures of the reactions were taken as those vapour pressures corresponding to zero rates:

Temp. (°C)	*Critical vapour pressure (mm Hg)*
13.0	8.20
17.2	11.45
23.1	17.70

Using the integrated form of Van't Hoff's equation

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

values of ln P (mm) were plotted against $T(\mathrm{K})^{-1}$ as shown in Fig. 3. From the slope of the straight line the heat of hydration was calculated.

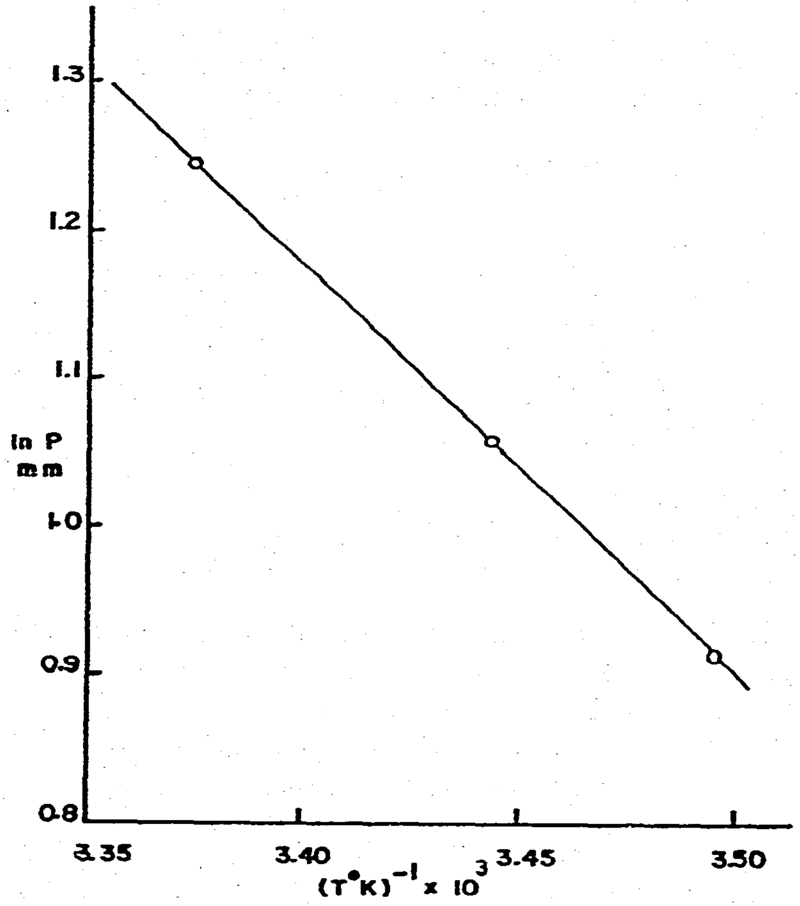

Fig. 3. Temperature dependence of the vapour pressure for the reaction $Na_2SO_4 \cdot 10H_2O = Na_2SO_4 + 10H_2O$.

slope = 2.716×10^3

∴ In the temperature range studied the heat of hydration

= $-2.716 \times 10^3 \times 2.3026 \times 1.986$

= -12.470 kcal mol^{-1} H_2O

Applying this value to all the water held by Na_2SO_4 when it is fully hydrated to $Na_2SO_4 \cdot 10H_2O$, the heat of the reaction

$Na_2SO_4 + 10H_2O \rightarrow Na_2SO_4 \cdot 10H_2O$ will be $\Delta H = -124.700$ kcal

The free energy changes ΔG for a reaction such as $MX+nH_2O \rightarrow MX\cdot nH_2O$ is given by the expression

$$\Delta G=\Delta G^{\circ}\ RT\ln K$$

Where ΔG° is the standard free energy of hydration and K is the equilibrium constant of the reaction. At equilibrium,

$$\Delta G=0 \qquad \therefore\ \Delta G^{\circ}=-RT\ln K$$

Assuming that at standard state the solid phases are pure substances and the water vapour behaves as an ideal gas, then the equilibrium constant will be proportional to the partial pressure P_{H_2O}.

For the equilibrium $Na_2SO_4(s)+10H_2O(g)\rightleftharpoons Na_2SO_4\cdot 10H_2(S)$

$$\Delta G^{\circ} = -RT\ln\frac{1}{P^{10}} = RT\ln P^{10}$$

In this equation P is the critical vapour pressure of the reaction in atmospheres, $T=298.16°K$ and $R=1.986$ cal deg^{-1} mol^{-1}.

From the plot of ln P vs. $T(K)^{-1}$ of Fig. 3, the equilibrium vapour pressure at 25°C was obtained.

$$P=19.72\ \text{mm Hg}=0.02622\ \text{atm.}$$
$$\therefore\ \Delta G^{\circ} = 1.986\times 2.3026\times 298.16\times 10\log 0.02622 = 21.660\ \text{kcal,}$$
$$\text{i.e.,} \quad = 2.166\ \text{kcal mol}^{-1}\ H_2O$$

According to Kirchoff's equation, $\Delta H_T=\Delta H^{\circ}_{298}+\int^{T}_{298}\Delta C_p dT$, the heat evolved or absorbed in a reaction is slightly dependent on temperature but for a short range of temperatures, ΔC_p is very small, hence ΔH is approximately constant.

Using the defining equation $\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$ and the values of ΔG° and ΔH obtained above, the entropy of hydration ΔS° was calculated.

$$\Delta S^{\circ}=\frac{\Delta H-\Delta G^{\circ}}{T}=\frac{-124700+21660}{298.16}$$
$$=-345.30\ \text{cal deg}^{-1}\ \text{mol}^{-1}.$$

Since for the reaction $Na_2SO_4(s)+10H_2O(g)=Na_2SO_4\cdot 10H_2O(S)$

$$\Delta S^{\circ}_{298} = S^{\circ}_{Na_2SO_4\cdot 10H_2O}-(S^{\circ}_{Na_2SO_4}+10S^{\circ}_{H_2O})$$
$$S^{\circ}_{Na_2SO_4(S)} = 35.73\ \text{cal deg}^{-1}\ \text{mol}^{-1}\ \text{(Latimer, 1952)}$$
$$S^{\circ}_{H_2O(g)} = 45.106\ \text{cal deg}^{-1}\ \text{mol}^{-1}\ \text{(Latimer, 1952)}$$

$\therefore$ The entropy of $Na_2SO_4\cdot 10H_2O(S)$ at 298.16 K

$$= -345.3+35.73+451.06 = 141.50\ \text{cal deg}^{-1}\ \text{mol}^{-1}.$$

It is of interest to compare the results of the present investigation with similar results obtained by other research workers who calculated the entropy of the sodium sulphate decahydrate using the known entropy of water vapour together with the dissociation pressure of the decahydrate and the entropy and heat of solution of Na_2SO_4. These authors determined also the entropy of $Na_2SO_4 \cdot 10H_2O$ from low temperature heat capacities using the expression $S^\circ_{298} = S^\circ_0 + \int_0^{298} C_p \, d \ln T$.

The results are summarised below:

ΔS° (*cal deg*$^{-1}$ *mol*$^{-1}$)		$S^\circ_{Na_2SO_4 \cdot 10H_2O(S)}$ (*cal deg*$^{-1}$ *mol*$^{-1}$)	$\int_0^{298} C_p \, d \ln T$ (*cal deg*$^{-1}$ *mol*$^{-1}$)	*Residual entropy* (*e.u.*)
Present investigation	−345.30	141.50	—	—
Pitzer and Coulter[8]	−344.30	142.20	140.50	1.70
Brodale and Giauque[9]	−345.31	141.46	139.95	1.51

Brodale and Giauque claimed that there was an error in the $\int_0^T C_p \, d \ln T$ value obtained by Pitzer and Coulter. After correcting the data, the results showed a residual entropy of 1.54 e.u. instead of 1.70 e.u. The entropy of $Na_2SO_4 \cdot 10H_2O$ obtained in the current investigation is 1.55 e.u. higher than the value calculated by Brodale and Giauque[9] from the integral of $\int_0^T C_p \, d \ln T$. This discrepancy is in close agreement with the values obtained by the various investigators. It is also close to the entropy of $R \ln 2$ cal mol^{-1} which Ruben et al.[10] believed to be due to the disorder in $Na_2SO_4 \cdot 10H_2O$.

THE DISSOCIATION PRESSURE OF $Na_2SO_4 \cdot 10H_2O$

Method

An experiment was performed in absence of air and in the temperature range (0–25) °C to measure directly the decomposition pressure of the crystalline $Na_2SO_4 \cdot 10H_2O$ and the vapour pressure of the saturated water solution of $Na_2SO_4 \cdot 10H_2O$. The usual static technique of measuring the vapour pressure was used. The apparatus, a schematic diagram of which is shown in Fig. 4. consisted of a sample tube, a manometer and a P_2O_5 trap connected to a high vacuum oil pump. The sample tube containing approximately 100 g of $Na_2SO_4 \cdot 10H_2O$ was placed in a thermostatically controlled waterbath. The temperature of the stirred water was measured with a mercury-in-glass thermometer which gave readings to within ±0.1 °C. To obtain 0°C the waterbath was filled with ice, and 30 min were allowed to enable the sample to reach this temperature before the equilibrium vapour pressure was measured. The ice was then removed from the waterbath and the desired temperatures above 0°C were obtained by switching on the heating element and adjusting the thermostat control.

To ensure the absence of air, the apparatus was pumped briefly at certain intervals, and the vapour pressures at the appropriate temperatures were then allowed to reach equilibrium before they were recorded. All the measurements were made at temperatures lower than that of the surrounding atmosphere. This was to

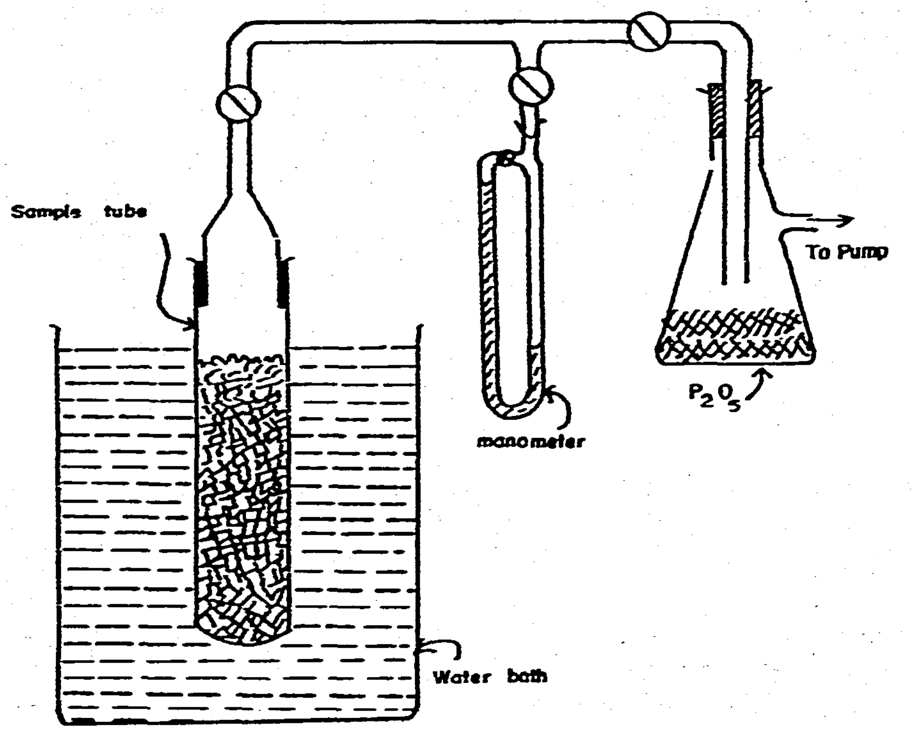

Fig. 4. Schematic diagram of apparatus for measuring the dissociation pressure in the system $Na_2SO_4 \cdot 10H_2O = Na_2SO_4 + 10H_2O$.

avoid the danger of condensation. At the same time part of the tube connecting the specimen with the manometer and P_2O_5 trap was made as short as possible from a tubing of narrow diameter.

The values of the vapour pressure up to 13.00 mm Hg were measured with an oil manometer, but for measurements of higher vapour pressures, it was replaced by a mercury manometer which could be read to the nearest 250 microns.

Results

The results of the dissociation pressure measurements for the reactions, $Na_2SO_4 \cdot 10H_2O = Na_2SO_4 + 10H_2O(V)$ and for saturated solution of $Na_2SO_4 \cdot 10H_2O$ = vapour, obtained in a similar manner using the same apparatus, are plotted in Fig. 5. It is evident that the plots lie on two smooth curves A and B. Using the integrated form of Van't Hoff's equation,

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right],$$

values of $\ln P$ were plotted against $T(\mathrm{K})^{-1}$, Fig. 6.

From the slopes of the two graphs A and B of Fig. 6 the value of ΔH was calculated for each reaction.

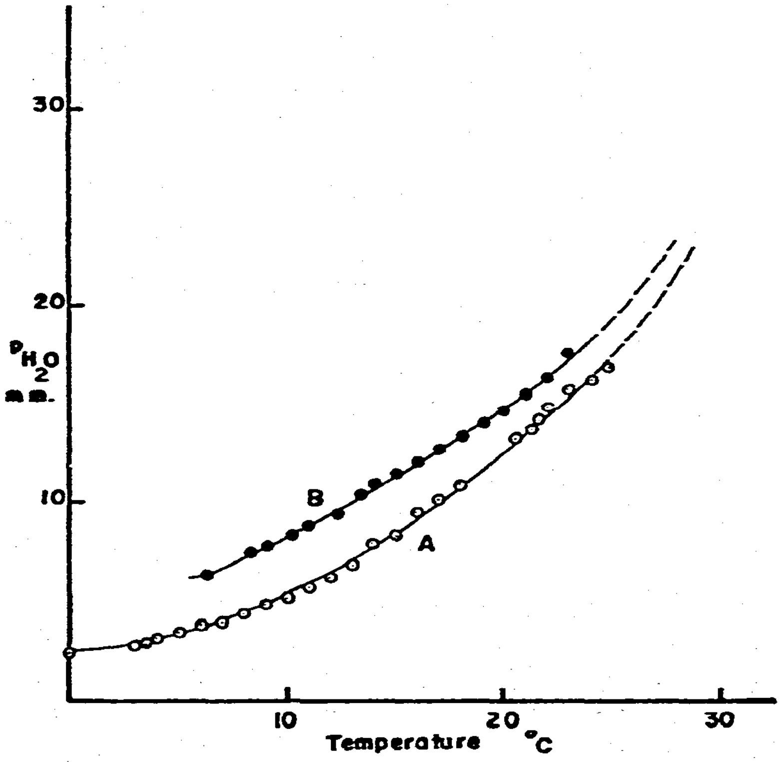

Fig. 5. Dissociation curve of the salt hydrate $Na_2SO_4 \cdot 10H_2O$ in absence of air. A, Equilibrium $Na_2SO_4 \cdot {}_{(s)}10H_2O$–$Na_2SO_{4(s)}$–water vapour; B, equilibrium $Na_2SO_{4(s)} \cdot 10H_2O$–saturated solution–water vapour.

(A) The heat of dissociation of $Na_2SO_4 \cdot 10H_2O = Na_2SO_4 + 10H_2O$

$$\begin{aligned}\Delta H &= 3.00 \times 10^3 \times 1.986 \times 2.3026 \\ &= 13.620 \text{ kcal mol}^{-1}\ H_2O\end{aligned}$$

(B) The heat of vaporisation of water solution saturated with $Na_2SO_4 \cdot 10H_2O$

$$\begin{aligned}\Delta H &= 2.786 \times 10^3 \times 1.986 \times 2.3026 \\ &= 10.410 \text{ kcal mol}^{-1}\ H_2O\end{aligned}$$

The point of intersection of the two straight lines Fig. 6, representing the temperature dependence of the vapour pressure for the reactions $Na_2SO_4 \cdot 10H_2O(S) = Na_2SO_4(S) + 10H_2O(V)$ and $Na_2SO_4 \cdot 10H_2O$—saturated solution—vapour, lies at 32.25°C and at a vapour pressure of 30.55 mm Hg. These figures are in close agreement with the established values of 32.28°C and 30.80 mm Hg obtained for the quadruple point where $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4, saturated solution and water vapour are in equilibrium[11].

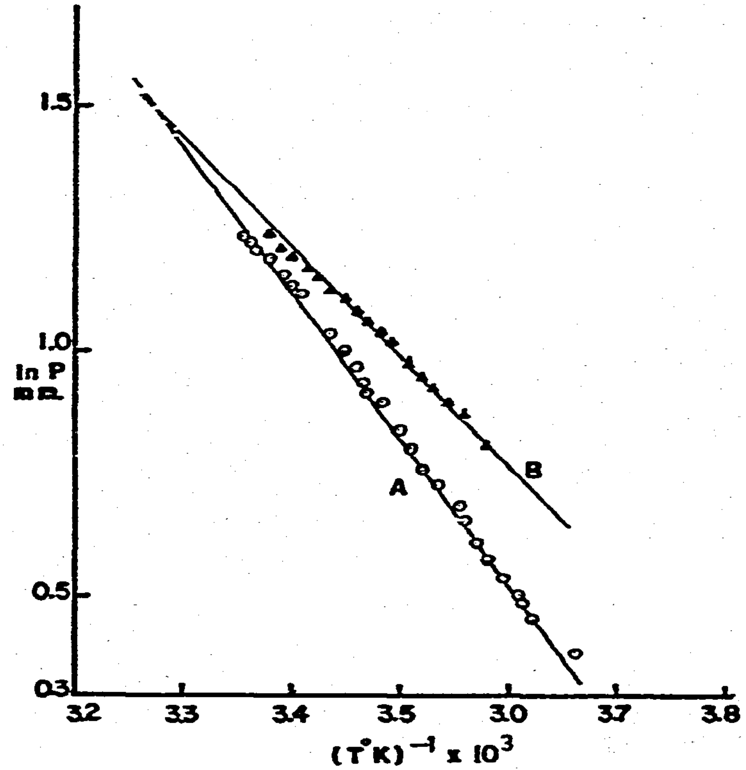

Fig. 6. Plots in *P* (mm) against *T*(K)$^{-1}$. A, equilibrium $Na_2SO_{4(s)}\cdot 10H_2O$–$Na_2SO_4$–water vapour; B, equilibrium $Na_2SO_{4(s)}\cdot 10H_2O$–saturated solution–water vapour.

CONCLUSIONS

The results obtained using the technique of thermogravimetry showed that the highly efflorescent salt hydrate $Na_2SO_4\cdot 10H_2O$ loses and regains approximately all its water content in a single stage. In a series of isothermal experiments at temperatures in the range 10 to 25°C the equilibrium vapour pressures were determined for the reaction $Na_2SO_4\cdot 10H_2O = Na_2SO_4 + 10H_2O$. These data gave the heat of hydration = 12.470 kcal mol^{-1} H_2O. Other thermodynamic functions calculated were in accord with those of other investigators. The amount of heat of hydration indicates that the water molecules are weakly bound in the crystal structure of $Na_2SO_4\cdot 10H_2O$.

It is of interest to compare the data obtained in the present investigations with those reported in the literature. The dissociation pressure of $Na_2SO_4\cdot 10H_2O$ at 25°C obtained from Fig. 6 after extrapolation, is 18.62 mm Hg compared with the equilibrium vapour pressure of 19.72 mm Hg derived for the equilibrium reaction $Na_2SO_4\cdot 10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$ which was performed in the thermogravimetric balance.

The table below contains some of the results obtained in comparison with those of other workers, viz, the equilibrium vapour pressures in mm Hg at different temperature:

	Equilibrium vapour pressure (mm Hg)			
	25°C	*23°C*	*17°C*	*13°C*
Present investigation (thermobalance)	19.72	17.70 (23.1°C)	11.45 (17.2°C)	8.20
Present investigation (dissociation apparatus)	18.62	15.65 (23.1°C)	10.20 (17.2°C)	6.87
Foote and Scholes[1]	18.20	—	—	—
Baxter and Lansing[2]	19.20	—	—	—
Norton and Johnstone[3]	18.55	—	—	—
Wilson[4]	19.22	—	—	—
Perman and Urry[5]	19.17	16.0 (22.5°C)	11.56 (17.5°C)	—
Schumb[6]	19.16	—	—	—

It is clear from the above table that the results obtained in the current investigation using the static method of measuring dissociation pressures are consistent with the data of other investigators who used similar techniques. But most of these values are slightly lower than those obtained in the present study in the thermogravimetric balance. These slight discrepancies may be due to certain factors and limitations in the dissociation apparatus:

(a) In this apparatus equilibrium for the reaction is approached from one side only and it is difficult to visualise how closely equilibrium is reached. On the contrary this difficulty is non-existent in the technique of the thermobalance where equilibrium can be approached from both sides with very low rates of reaction.

(b) As indicated by Wilson[4] salt hydrates approach equilibrium with extreme slowness if they are left undisturbed. In the present study the values of the dissociation pressures of $Na_2SO_4 \cdot 10H_2O$ were recorded 20 min after the desired temperatures were brought to constant values. Since no changes were observed in the position of the oil in the manometer after this period, the readings recorded were taken as the true equilibrium pressures.

In the light of the results obtained in the present study one may conclude that the technique of thermogravimetry had yielded results of considerable accuracy. In comparison with the data obtained using the volumetric dissociation apparatus, one may add, that in spite of the agreement of there data with those reported elsewhere, the difficulties and limitations of this technique should always be borne in mind when experiments of this nature are contemplated.

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