Study of the reaction $CaSO_4 \cdot \frac{1}{2}H_2O$ *(β-hemihydrate)* = $CaSO_4$ *(β-soluble anhydrite)* + $\frac{1}{2}H_2O$ *in the temperature range 20–100° C*

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Summary. A thermogravimetric vacuum microbalance has been used to study the reaction between β-soluble anhydrite and water vapour in the temperature range 20–100° C. Equilibrium water-vapour pressures for the hydration reaction in this temperature range were determined directly and have been compared with available data obtained by Kelly, Southard, and Anderson (1941) in the temperature range 80–120° C. The kinetics of the hydration and dehydration reactions have also been studied in a series of isothermal experiments with varying water-vapour pressure. These experiments indicate that in a vapour-pressure range close to the equilibrium value very low rates for both hydration and dehydration are observed. Outside this range of vapour pressures both hydration and dehydration rates increase suddenly and show an approximately linear increase with imposed water-vapour pressure.

At low temperatures (25° C) the dehydration reaction has an associated activation energy of approximately 10 kcal $mole^{-1}$. In the same temperature range additional, physical adsorption of water vapour by the specimen was noted.

Introduction

The present paper contains an account of the first of a series of studies on low-temperature, reversible hydration reactions and involves a new thermogravimetric vacuum balance which has been designed specifically for this purpose. The present results were obtained during study of the water-sorption characteristics of β-soluble anhydrite prepared as previously described by Southard (1941).[1] In the present experiments the sample was maintained at controlled temperature and

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[1] It is important to note at this point that Southard has described two modifications of soluble anhydrite which are distinguished by their mode of preparation and heat of hydration. β-soluble anhydrite may be prepared, as in the present experiments, by heating gypsum in a vacuum at a temperature of 100° C. α-soluble anhydrite may be prepared by dehydrating well-crystallized hemihydrate under similar conditions. The observed heats of hydration for the two modifications of soluble anhydrite differ by approximately one kcal $mole^{-1}$ $CaSO_4$, the β-modification having the larger heat of hydration. β-soluble anhydrite is also distinguished by the fact that it retains some water under conditions of extended heating in high vacuum at 100° C.

vapour pressure and the mass of the sample was used to define the hydration state and the rate of approach to equilibrium.

The experiments fall into three groups. In the first instance a series of experiments were performed to determine the rate of equilibration for both hydration and dehydration in the temperature range 20–100° C. These experiments were followed by a series in which the onset of hydration under isobaric conditions and with slowly falling temperature was used to derive equilibrium vapour pressure–temperature data for the reaction. Finally the relationship between reaction rate and imposed water-vapour pressure was studied in a series of isothermal experiments at 86·25° C.

Experimental technique

A detailed account of the construction of the new thermogravimetric microbalance will appear elsewhere. In the present paper the relevant characteristics of the instrument will be summarized. The instrument can best be described in terms of (*a*) balance characteristics, (*b*) vacuum and vapour-pressure control and measurement, and (*c*) furnace characteristics.

(*a*) *Balance characteristics.* The balance used was of conventional design employing a light steel beam supported on agate knife edges but one arm was attached in suspension to a delicate glass spring (extension 0·5754 mm per milligram). The upper end of the spring was supported by a spring-loaded stainless-steel plunger actuated by a Shadlow micrometer which could be read to the nearest micron. The centre of gravity of the balance was adjusted to yield an oversensitive condition in the balance. In this condition deflexion of the balance arm was effectively controlled by the characteristics of the glass spring and the balance beam was returned to the horizontal position using the micrometer head. In order to define a reference position for the balance beam the latter carried centrally a small ferrite rod which moved within the field of a stationary three-coil transducer. The central coil of the transducer was supplied with a 10 kilocycle sine wave signal at one volt (r.m.s.). The outer coils of the transducer were connected in opposition and yielded an output voltage of phase 0° or 180° depending on the direction of deflexion of the balance arm.

In practice the out-of-balance signal from the transducer was brought to zero using the micrometer head and weight readings were made directly from the micrometer indication. In certain experiments involving rapid weight change the out-of-balance signal from the transducer was used as a direct weight indication. It was found that the spring provided very effective damping of the swing of the balance arm. The secondary voltage from the transducer was measured with a high impedance valve voltmeter using a single stage of amplification. Using this instrument the reference position of the balance arm could be set readily and reproducibly with an accuracy limited only by the positioning of the micrometer head (±2 microgm). The second arm of the balance carried a fine glass rod which supported the specimen pan well above the level of the balance arm.

The characteristics of the balance were studied in a short series of experiments. Changes in the zero point indication on arrest and release over a period of 24 hours were of the order of ±5 microgm.

(*b*) *Vacuum and humidity control.* The balance mechanism was contained in a vacuum chamber which was connected directly through a standard baffle valve to an oil diffusion pump. This vacuum chamber was supplied with two wide-bore (1 in.) tubes leading, via wide-bore taps (1 in.), to two reservoir flasks which could be evacuated independently of the main chamber. In use these reservoir flasks contained a desiccant, or a humidity liquid, appropriate to the experiment in hand. Water-vapour pressures were measured, in the absence of air, with an oil manometer which could be read to the nearest 20 microns Hg. The low-pressure limb of the manometer was continuously and independently backed. The main vapour-pressure chamber when outgassed showed a consistent and slow rate of pressure rise of 0·5 micron Hg per hour which permitted lengthy experiments without the introduction of any serious errors in the determination of water-vapour pressures.

(*c*) *Temperature control and measurement.* The sample, as already noted, was supported above the balance arm. It moved vertically within a heavy, cylindrical block of copper which was surrounded in turn by a non-inductively wound furnace element carried on a ceramic support. Temperature control to ±0·1° C or better was achieved using a Transitrol controller. The temperature of the specimen was measured with a chromel-alumel thermocouple which was positioned to within several millimetres of the sample. The couple used was calibrated against a suitable mercury in glass thermometer. The e.m.f. of the couple was measured with a Tinsley vernier potentiometer with reference to a cold junction at 0° C.

The influence of change in both water-vapour pressure and temperature on the balance indication was studied in a short series of experiments, using an inactive tare weight in the specimen pan. The results of these experiments were found to be very reproducible. The main change in indication occurred in going from atmospheric pressure to high vacuum conditions and was thought to be associated with distortion of the vacuum chamber. The direct effects of temperature change were small but appreciable change occurred in going from high vacuum conditions to conditions of high humidity. The latter effect was explained as being due to adsorption of water vapour on the balance mechanism. The results of a test cycle have been presented in table I and indicate that the overall change in quite a complicated and lengthy sequence is of the order of 30 microgm.

TABLE I. Data from a test cycle on the vacuum microbalance using an inactive tare weight

		Balance indication (microgm)	
Atmospheric pressure	20° C	+230	0
High vacuum	20° C		+230
9 mm water vapour	20° C	−98	+140
9 mm water vapour	100° C		+132
High vacuum	100° C	+92	+255
High vacuum	20° C		+224
Atmospheric pressure	20° C	−198	+26

Preparation of the sample of β-soluble anhydrite

The sample of β-soluble anhydrite used in the present experiments was prepared in the vacuum balance by dehydrating a single crystal of gypsum (69·11 milligm). The dehydration was effected at high vacuum in the presence of fresh P_2O_5 at a temperature just below 100° C. Prior to this experiment no appreciable change in the weight of the gypsum sample was observed at high vacuum (2×10^{-4} mm Hg) at 20° C and 34° C. The observed dehydration curve for gypsum heated at 100° C was a smooth curve and a total water loss of 20·14 % was observed,[1] the theoretical water loss corresponding to complete dehydration being 20·91 %.[2]

Preliminary investigation of the water-sorption characteristics of β-soluble anhydrite

A series of preliminary experiments on the water-sorption characteristics of β-soluble anhydrite showed that both hydration and

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[1] As already noted complete dehydration of β-soluble anhydrite cannot be effected at 100° C.

[2] Throughout the present paper weight changes recorded represent percentages of the original weight of the gypsum sample.

dehydration were reversible at temperatures above 15° C, and that the total water uptake by the sample corresponded approximately to that required for the formation of the hemihydrate. Additional physical adsorption of water vapour by the sample was clearly evidenced at high water-vapour pressures at room temperature (10 mm). It was noted that, at low temperatures, physically adsorbed water vapour was readily lost and regained by the sample. Loss of the main water fraction at low temperatures was, by comparison, extremely slow. Dehydration at 26·25° C under high vacuum conditions, in the presence of P_2O_5, has been illustrated in fig. 1. The total weight change in this experiment, which followed hydration at 2 mm water-vapour pressure, corresponded to 4·89 % of the original weight of the gypsum sample. (The calculated value for the formation of the hemihydrate is 5·23 %.) A dehydration curve obtained at 47° C under similar conditions is also shown in fig. 1.

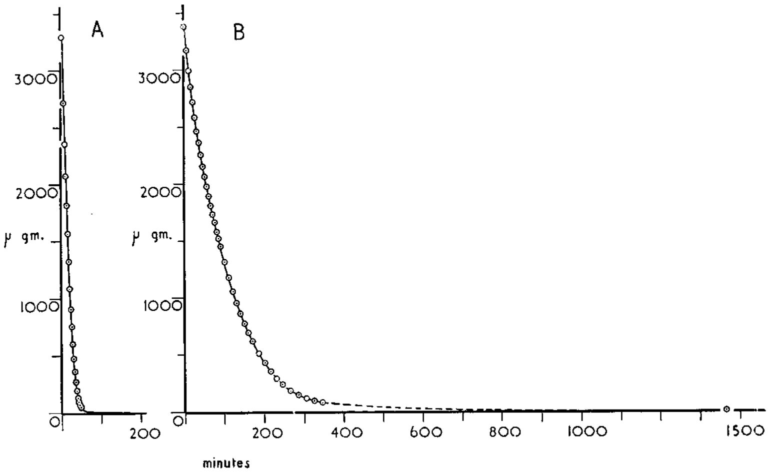

FIG. 1. Comparison of the dehydration rates for β-hemihydrate under high vacuum conditions at (*A*) 47° C and (*B*) 26·25° C.

Hydration experiments at room temperature (vapour pressure 3·2 mm, 19° C) and at 65° C (7·6 mm) indicated that hydration was extremely rapid in the absence of air and effectively complete in ten minutes in both cases. By contrast hydration of the sample at 23° C in the presence of a normal laboratory atmosphere was approximately fifty times slower. This effect was provisionally associated with the effects of air blockage in the fine pore structure of the compact specimen.

In the hydration experiment at 19° C a total uptake of 5·80 % was observed. This is considerably in excess of the uptake at higher temperatures and includes physically adsorbed water vapour which, as already noted, is readily lost and regained at high water-vapour pressures at low temperature.

The preliminary experiments indicated that water sorption by the β-soluble anhydrite sample was likely to be rapid at all temperatures. From the low-temperature dehydration experiments an activation energy of 10 kcal mole^{-1} was derived. This value was provisionally associated with the heat of vaporization of the water present.

Direct determination of equilibrium vapour pressures for the onset of hydration for β-soluble anhydrite

On the basis of the results of the preliminary experiments it was considered possible to derive equilibrium water-vapour pressures for the hydration of β-soluble anhydrite by observing, in terms of weight change, the onset of hydration in isobaric experiments in which the temperature was allowed to fall very slowly. It was hoped that such experiments would yield data which could be compared with prior results obtained by Southard by a quite different technique in the temperature range 80–120° C (Kelly, Southard, and Anderson, 1941).

The interpretation of the results of experiments of the type envisaged necessarily involves consideration of the actual form of the equilibrium adsorption isobar (a plot of equilibrium weight as a function of temperature under isobaric conditions). In an ideal case where complete hydration occurs rapidly and reversibly in a narrow temperature range the onset of hydration can be considered as defining equilibrium conditions for the total water fraction. In practice the adsorption isobar is likely to be smeared as illustrated in fig. 3 in which case hydration commences, with falling temperature, at a point *A* somewhat above the temperature appropriate to the main water fraction.[1]

In determining the critical temperatures for the onset of hydration under isobaric conditions the temperature of the sample was allowed to fall very slowly (at a rate of several °C per hour), the water-vapour pressure was maintained constant or nearly so and recorded and time–

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[1] In the present series of experiments the adsorption isobar for β-soluble anhydrite was not investigated in detail but in the final suite of experiments under isothermal conditions the limits of adsorption and desorption were studied over a wide vapour-pressure range. The results of these experiments suggest that, at least at high temperatures, the form of the adsorption isotherm approximates closely to that for the ideal case.

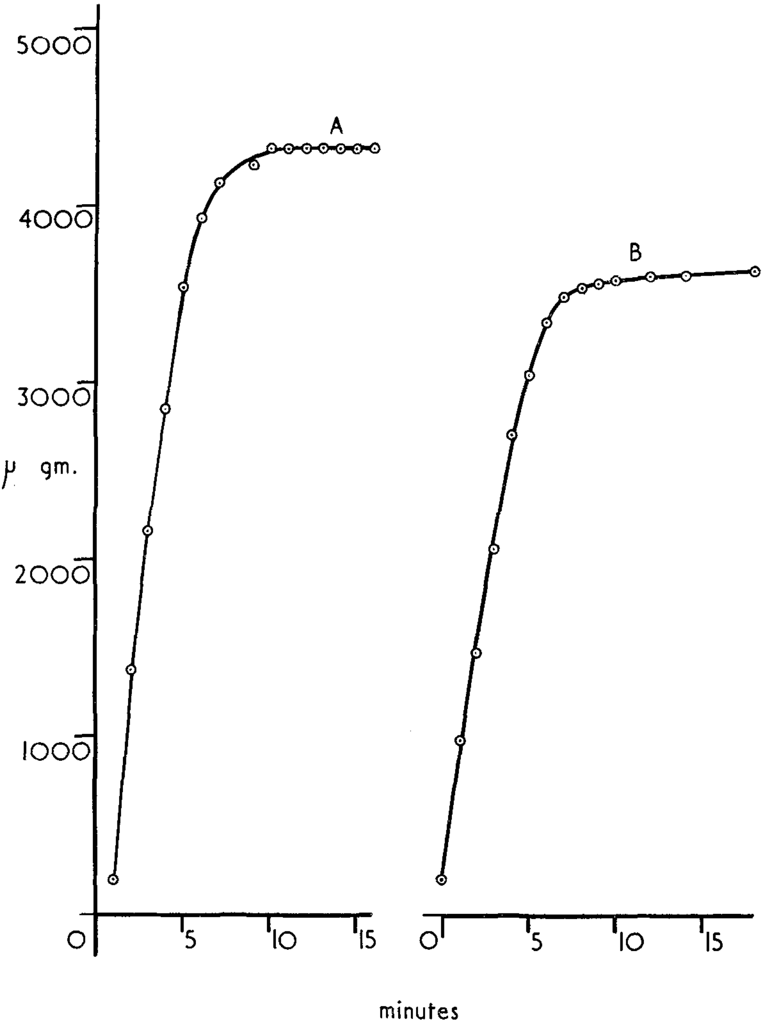

FIG. 2. Comparison of the hydration curves for β-soluble anhydrite at (*A*) 19° C and 3·2 mm and (*B*) 65° C and 7·6 mm. The higher water-vapour uptake at 19° C is considered to be due to physical adsorption by the specimen.

weight change curves were plotted from the balance indication. In fig. 4 the record of a typical experiment of this type has been reproduced. In this diagram the point at which a marked discontinuity of slope in the weight change curve occurs was taken as defining the critical conditions for water sorption. In experiments of this type it was possible to reverse the hydration tendency by allowing the temperature to rise after rapid hydration had commenced. In all cases where such reversal effects were studied the temperature for reversal under isobaric conditions was somewhat lower than that observed for the initial onset of hydration. This observation implies that the adsorption–desorption process is quite reversible but that slight smearing of the adsorption isobar is detectable. Data for reversal of the hydration tendency at approximately 80° C

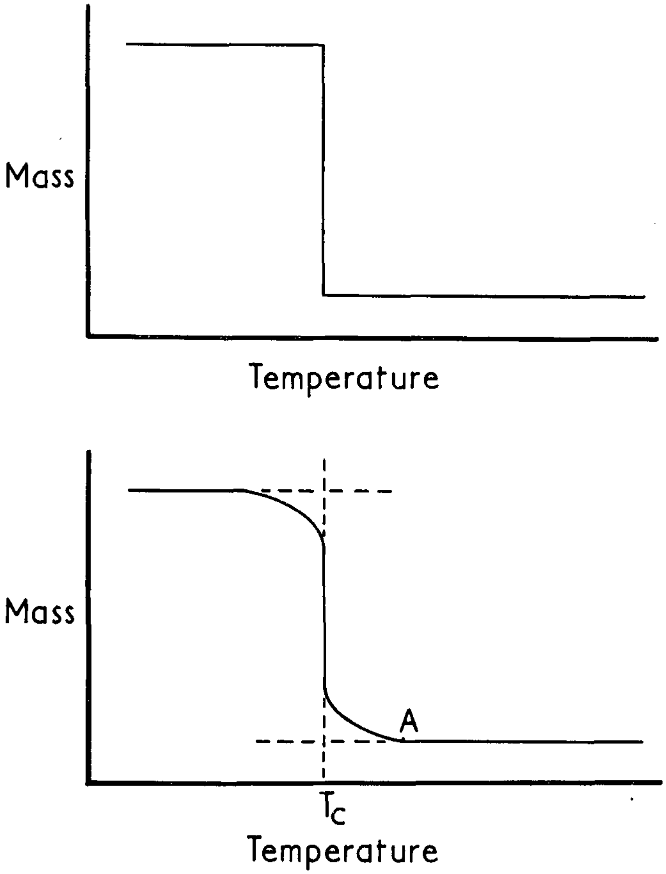

Fig. 3. Comparison of an idealized and a smeared adsorption isobar. In the latter case adsorption commences at point *A* with falling temperature in advance of the main water fraction.

are shown in fig. 5. The extreme facility with which the β-soluble anhydrite sample responds to minor changes in experimental conditions is illustrated in fig. 6 which provides data on the onset of hydration and reversal at approximately 95° C.

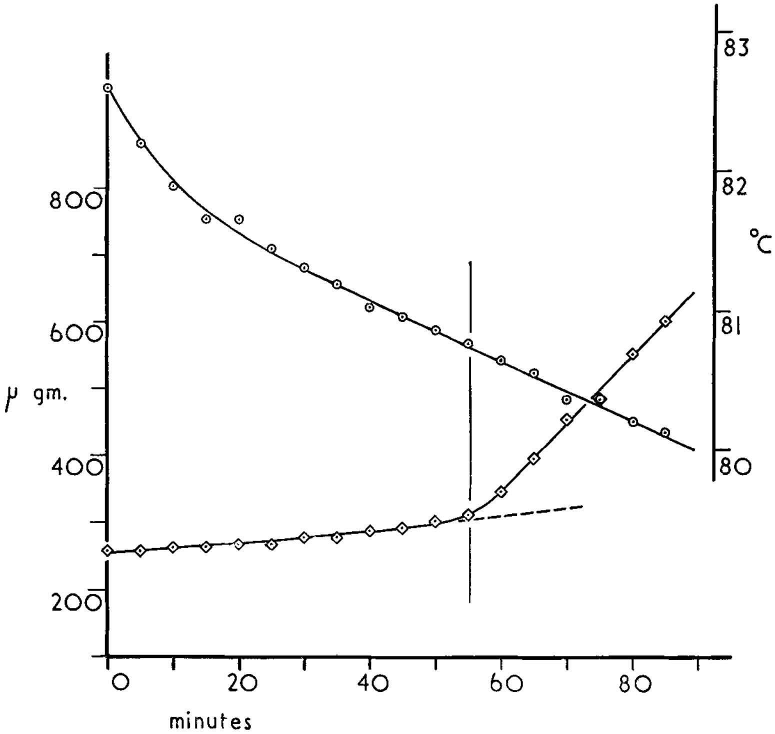

FIG. 4. Plot of the relative mass change of the sample of β-soluble anhydrite as a function of time with slowly falling temperature at approximately 81° C under isobaric conditions. Note the abrupt onset of hydration at a temperature just below 81° C.

In this and similar diagrams which follow the mass change of the sample is represented by diamonds (microgm), circles indicate the temperature (°C), and the vapour pressure, where it has been necessary to record variation, is shown by triangles (mm Hg).

Data on the critical temperatures associated with the onset of hydration and reversal in the temperature range 40–95° C have been set out in table II. A plot of ln critical water-vapour pressure against T (°K)$^{-1}$ is given in fig. 7. Using temperature values for the onset of hydration (the full circles of fig. 7) a value of 14·955 kcal mole^{-1} of water vapour adsorbed was derived using the integrated form of the van't Hoff equation:

$$\ln\frac{p_2}{p_1} = -\frac{\Delta H}{R}\left\{\frac{1}{T_2}-\frac{1}{T_1}\right\}.$$

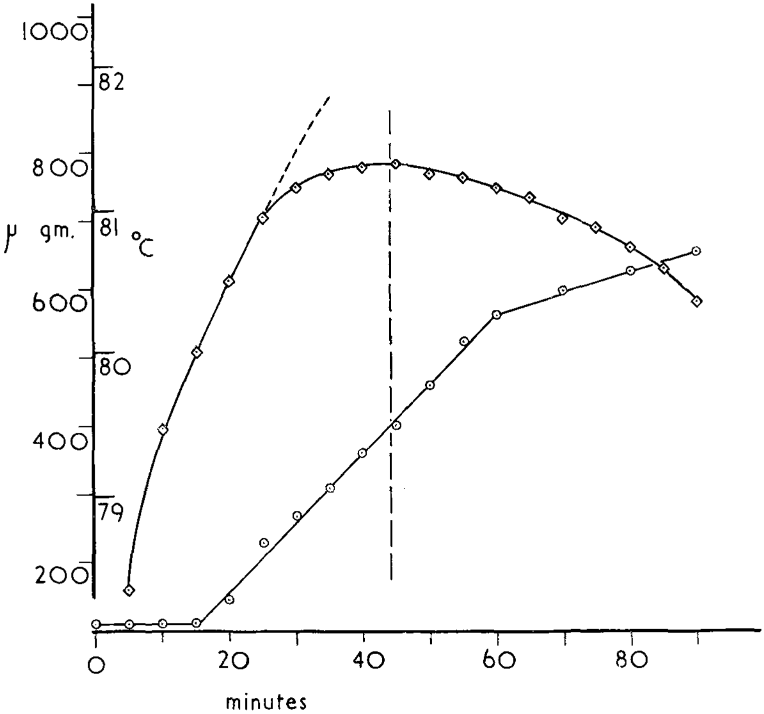

FIG. 5. This diagram illustrates reversal of the hydration process with rising temperature at approximately 79·5° C.

An additional experiment was carried out under isobaric conditions. In this case the temperature was allowed to rise rapidly and the onset of rapid dehydration was observed. The experiment, which is completely illustrated in fig. 8, indicates that a reasonable estimate of the critical conditions for desorption can be obtained in fast experiments at high temperature. Data from this fast experiment have been plotted in fig. 7 and the resulting point lies close to the straight line derived from the previous experiments.

A more detailed discussion of the results of the isobaric experiments will be presented at the end of the present paper where they have been compared with existing experimental data.

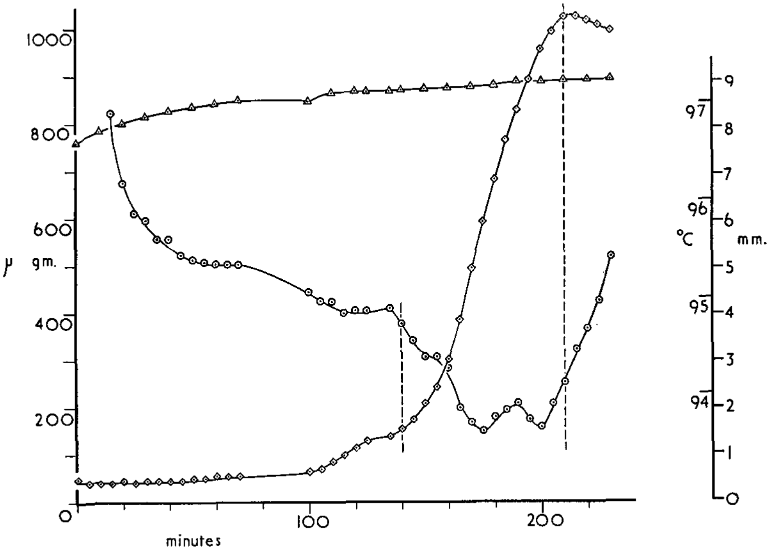

FIG. 6. This diagram shows a complete record of data on the onset of hydration and subsequent reversal at approximately 95° C. Examination of the record shows that minor changes in both the vapour pressure and the temperature are reflected in the recorded mass change of the sample.

TABLE II. Critical water-vapour pressure–temperature data for water sorption by β-soluble anhydrite

Temperature °C	Vapour pressure mm Hg
40·0 onset of hydration	0·25
39·5 reversal	0·26
58·0 onset of hydration	0·92
59·0 reversal	1·00
80·7 onset of hydration	3·90
79·5 reversal	3·81
94·7 onset of hydration	8·98
93·8 reversal	9·18

Isothermal experiments

A further series of experiments were carried out under isothermal conditions in order to determine the limits of adsorption over a wide vapour-pressure range, and to study the relationship between the rates of hydration and dehydration, and imposed water-vapour pressure. Two temperatures were chosen (63° C and 86·25° C) and yielded closely

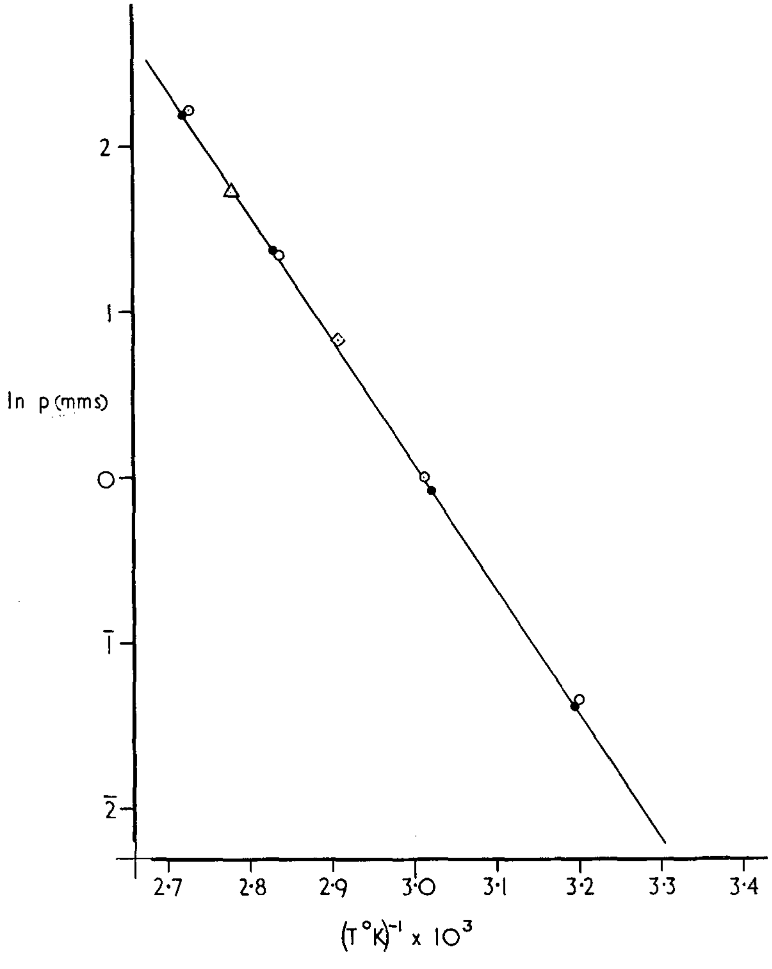

FIG. 7. Plot of ln p (mm Hg) as a function of T (°K)$^{-1}$. The full circles represent results obtained from the onset of hydration in the isobaric experiments. Open circles represent data for reversal. The single diamond-shaped point was obtained on dehydration with rapidly rising temperature. The triangular point represents the equilibrium vapour pressure for the hydration reaction as determined in the isothermal experiments at 86·25° C.

comparable results. Data for the experiments at 86·25° C were more complete and are given below.

In these experiments the temperature was carefully controlled while the vapour pressure was changed either by removing water vapour with the P_2O_5 trap or by introducing water vapour from a suitable source. The experiments were performed in the absence of air (permanent gas pressure less than 20 microns Hg).

A relatively complete set of hydration and dehydration rate curves at different water-vapour pressures at 86·25° C have been set out in figs. 9 and 10. Both hydration and dehydration proceeded very rapidly when the vapour pressure differed appreciably from the equilibrium value at this temperature (5·6 mm). In such experiments the reaction was followed directly using the millivoltmeter indication but the limits of the individual experiments were determined, in the usual way, by returning the balance arm to its horizontal position at the end of each experiment, using the micrometer head. In this way it was possible to follow successfully experiments in which the reaction was complete in times of the order of five minutes.

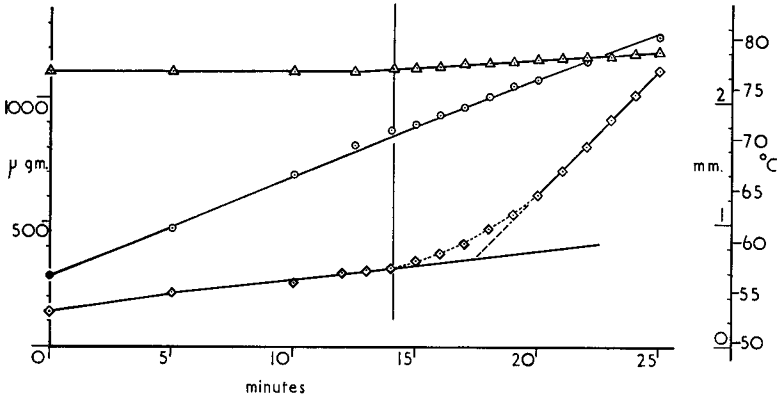

FIG. 8. This diagram illustrates the onset of dehydration in an experiment involving relatively rapid heating.

The experiments indicate that the limits of weight change are sensibly constant over a wide vapour-pressure range. The total weight change corresponds to 4·35 % of the weight of the original gypsum sample and is considerably lower than the theoretical value of 5·23 % equivalent to the adsorption of half a mole of water vapour. This discrepancy has already been explained by Southard in terms of the existence of a small and more tightly bound water fraction in β-soluble anhydrite.

Comparison of the hydration and dehydration curves of figs. 9 and 10 shows that they are closely comparable in form. An attempt to derive a simple rate law for the reaction was unsuccessful however.

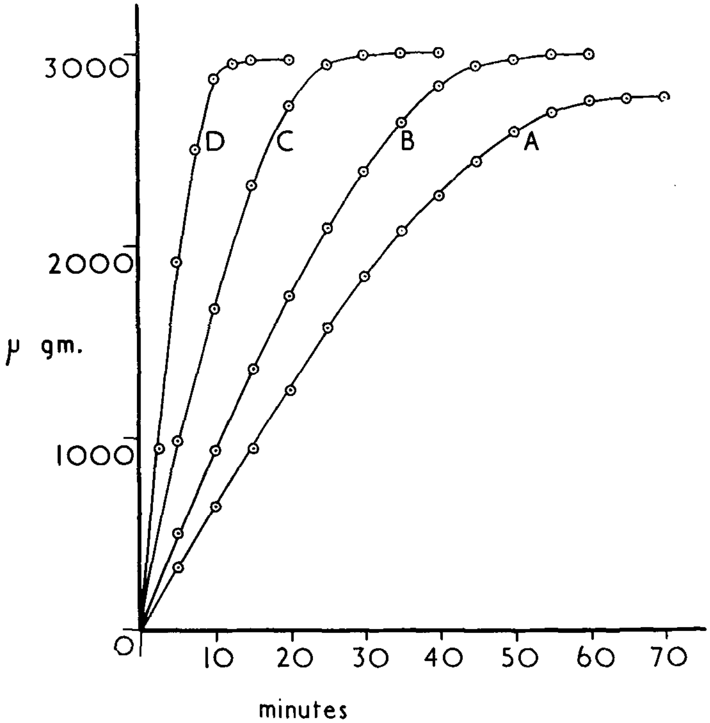

FIG. 9. Comparison of hydration rates as a function of imposed water-vapour pressure in experiments at 86·25° C. (*A*) 6·57 mm, (*B*) 7·20 mm, (*C*) 8·06 mm, and (*D*) 10·60 mm.

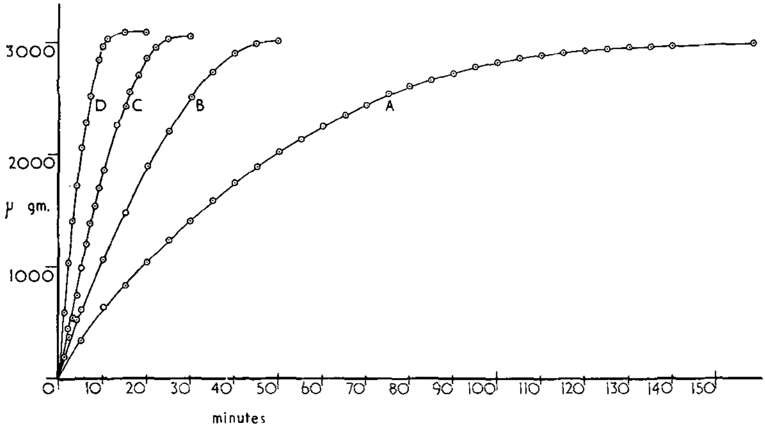

FIG. 10. Comparison of dehydration rates as a function of imposed water-vapour pressure at 86·25° C. (*A*) 4·54 mm, (*B*) 4·24 mm, (*C*) 3·20 mm, and (*D*) 0·50 mm.

In order to determine the dependence on vapour pressure of the reaction rates close to the equilibrium water-vapour pressure a further series of experiments were carried out. In these experiments the specimen was put into a state corresponding to half hydration and the rates were followed directly by using the millivoltmeter in its most sensitive range. Each experiment of this kind lasted approximately half an hour.

Table III. Isothermal rates of hydration and dehydration of β-soluble anhydrite in the middle of the hydration range. Temperature 86·25° C

Vapour pressure mm Hg	Weight change microgm min^{-1}
1·10	360
3·20	176
4·24	84
4·54	40
5·00	26
5·20	11
5·40	3·4
5·50	1·5
5·60	—
5·70	1·0
5·80	5·7
6·00	17
6·57	66
7·20	78
8·06	140
10·60	350

The sensitivity of the balance made it possible in this way to follow extremely low reaction rates in the immediate vicinity of the critical vapour pressure.

Data on the rates of hydration and dehydration in all experiments at 86·25° C have been set out in table III. They have been recorded in terms of the weight change (in microgm) per minute in the middle of the hydration–dehydration range. The data have also been plotted in fig. 11.

The most obvious feature of this plot of reaction rates as a function of water-vapour pressure is the existence of a zone of very low rates in the immediate vicinity of the equilibrium water-vapour pressure. Outside this zone of low rates the reaction rates increase approximately linearly with imposed vapour pressure. Extrapolation of the rate data for the regions of fast reaction indicates that the 'dead' zone has a width of approximately 0·4 mm at 86·25° C. The character of this 'dead' zone was checked in one experiment by proceeding directly from a vapour pressure of 5·7 mm to a vapour pressure of 5·5 mm. In this experiment small but definite rates of hydration and dehydration respectively were observed in consecutive half-hour periods. In attempting to derive rate data for vapour pressures at the edges of the 'dead' zone it was found that very minor fluctuations in the experimental conditions had a grossly exaggerated effect on the reaction rate.

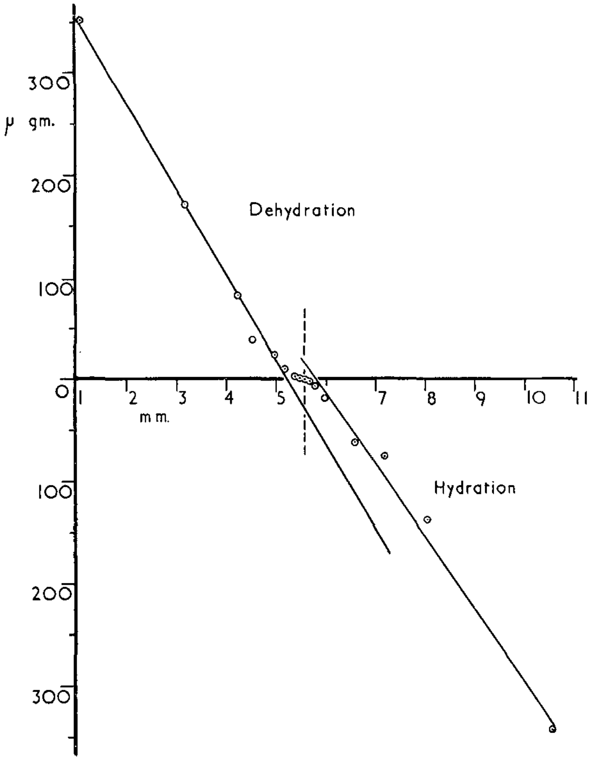

FIG. 11. Plot of reaction rate at half-hydration for all the experiments at 86·25° C as a function of imposed water-vapour pressure. Note the zone of very low rates in the immediate vicinity of the equilibrium vapour pressure.

The value of 5·60 mm corresponding to zero rate at half-hydration at 86·25° C has been plotted in fig. 7. It falls close to the plot of ln p against T^{-1} obtained from the isobaric experiments and endorses the technique used in these experiments.

Conclusions

The present experiments indicate that β-soluble anhydrite readily loses and regains a discrete water content corresponding to 0·416 mole of water vapour per mole $CaSO_4$ in the temperature range 40–100° C. The whole of this water fraction is adsorbed and desorbed within a restricted temperature range in isobaric experiments (and within a restricted vapour-pressure range in isothermal experiments). β-soluble anhydrite retains an additional water fraction under high vacuum conditions at 100° C.

Values for the critical water-vapour pressure for adsorption as a function of temperature yield a value of 14·955 kcal $mole^{-1}$ H_2O for the mean heat of adsorption in the temperature range studied. Assuming that this value can be applied to all the water held by the sample of β-soluble anhydrite when fully hydrated a mean value for ΔH for the reaction β-$CaSO_4.\frac{1}{2}H_2O = \beta$-$CaSO_4+\frac{1}{2}H_2O$ may be defined as 7·477 kcal. The value of $\Delta H_{298\cdot 1}$ cited by Southard for the same reaction on the basis of thermochemical data is 7·860 kcal. For the corresponding reaction involving α-soluble anhydrite $\Delta H_{298\cdot 1}$ is given as 7·300 kcal (Kelly, Southard, and Anderson, 1941).[1]

It is of interest at this point to compare the present experimental results on the sorption of water vapour by β-soluble anhydrite with those obtained by Southard in the temperature range 80–120° C. In the latter case equilibrium vapour pressures were determined in a dissociation pressure apparatus in which the equilibrium water-vapour pressure, at defined temperature, was determined directly using a mercury manometer. In view of the fact that the two series of experiments overlap only in the temperature range 80–100° C they may be compared most easily by using a plot of the Σ function against T^{-1}. The Σ function as derived from the thermochemical data by Southard may be written $\Sigma = -R \ln p^{\frac{1}{2}}_{H_2O}+6\cdot 34 \ln T-0\cdot 0135T$ $(= \Delta H_0/T+I)$. The resulting plot of the combined results is shown in fig. 12 where the straight line has been drawn in the position defined originally by Southard.

The concordance of the present results, obtained with the vacuum microbalance, is striking. On the basis of this direct comparison with

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[1] Comparison of the present experimental data on the heat of adsorption of β-soluble anhydrite with available thermochemical data is complicated by the fact that β-soluble anhydrite retains some water at 100° C. This complication does not exist in the case of α-soluble anhydrite which can be obtained in a completely anhydrous state at the same temperature.

the thermochemical data it may be concluded that the present technique yields results of considerable accuracy.

A complete interpretation of the rate data obtained in the isothermal experiments at 86·25° C cannot be made at present. In isothermal experiments of this type where both hydration and dehydration reactions proceed with facility a simple relationship between the resultant reaction rate and the overall free energy change in the reaction might be anticipated. It may readily be shown that this is not the case by computing the free energy change from the relationship $\Delta G = -RT \ln (p/p_c)$, where p is the vapour pressure imposed and p_c is the critical vapour pressure for the reaction at the temperature concerned. The observed relationship between the rates of reaction and imposed water-vapour pressures indicates that a threshold value for the free energy change must be exceeded. In the experiments at 86·25° C this threshold has a value of 26 cal mole^{-1} H_2O. The existence of this threshold must lead, inevitably, to the appearance of hysteresis phenomena in short term experiments. The effect also constitutes the ultimate limitation in

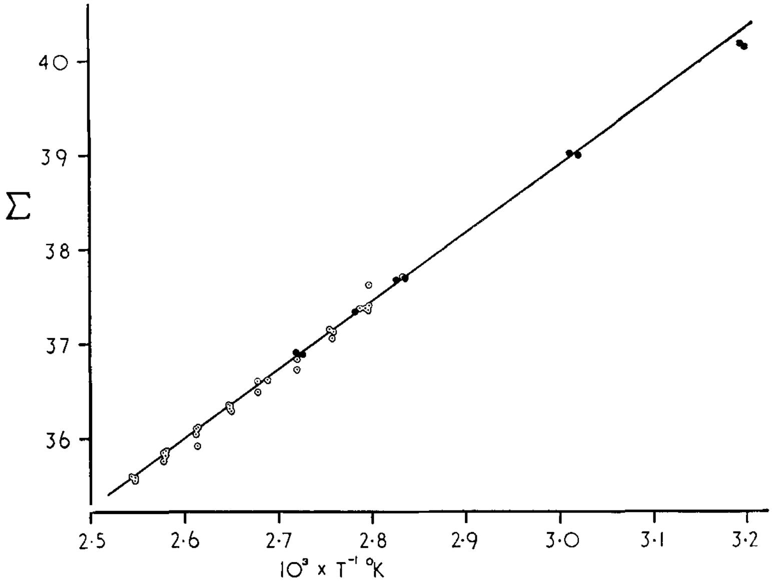

FIG. 12. Plot of the Σ function ($\Sigma = -R \ln p^{\frac{1}{2}}_{H_2O} + 6{\cdot}34 \ln T - 0{\cdot}0135\, T$) against T (°K)$^{-1}$ using the combined results of the present experiments (full circles) and those due to Southard (in Kelly *et al.*, 1941) (open circles).

deriving thermochemical data for the reaction by using the present technique involving observation of the onset of hydration under isobaric conditions.

Acknowledgements. The present series of experiments were made possible through financial assistance provided by the Director of the Building Research Station, which assistance is here gratefully acknowledged.

Reference

Kelly (K. K.), Southard (J. C.), and Anderson (C. F.), 1941. U.S. Bur. Mines Tech. Paper 625.