Journal of Thermal Analysis, Vol. 20 (1981) 275—280

THE SYSTEM $K_2SO_4-K_2S$

A NEW EXPERIMENTAL TECHNIQUE

C. W. So and D. Barham

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, M5S 1A4

(Received April 22, 1979; in revised form March 24, 1980)

A new experimental technique has been developed to determine the phase equilibrium diagram for the system $K_2SO_4-K_2S$.

The technique involves isothermal thermogravimetry of potassium sulphate during reduction to potassium sulphide at elevated temperatures in a stream of dry oxygen-free hydrogen gas. Several abrupt changes in the rate of weight loss occur in each curve and these can be related to phase changes in the phase diagram for the system.

On the basis of such results the liquidus and solidus (solid solution) boundaries can be located.

Simple thermal analysis is used to confirm the eutectic temperature and various liquidus temperatures.

The diagram $K_2SO_4-K_2S$ is a simple eutectic system with the eutectic at 610° and 23 mole % K_2S. The limits of solid solubility of K_2S in K_2SO_4 and K_2SO_4 in K_2S at the eutectic temperature are 11% and 36 mole% respectively.

The odd shape of the liquidus curves on each side of the eutectic suggests the possibility of phase changes in both K_2SO_4 and K_2S solid solutions. No evidence for this was obtained from thermal analysis.

There are many conventional techniques used in the compilation of high temperature phase equilibrium diagrams. These include thermal analysis, which includes differential thermal analysis and thermogravimetry, equilibrium annealing and rapid quenching of various compositions followed by X-ray analysis, or microscopic analysis, or separation and chemical analysis, or electron microprobe analysis, and hot stage microscopy[1].

All of the above techniques can be described as either static composition-dynamic temperature or static composition-static temperature techniques.

A technique involving static temperature-dynamic composition measurements has been described for compiling various vanadium pentoxide containing systems [2—5]. This technique moves horizontally across the phase diagram instead of vertically in the diagram as do all of the other techniques mentioned above.

Not all of the above techniques are applicable to all systems, and in particular, difficulties are encountered when high viscosities occur or one of the elements in the system appears with more than one oxidation state. In the latter case it is necessary during the experimental measurements to maintain a constant oxygen partial pressure which is unique to each temperature/composition point. This makes conventional techniques, such as thermal analysis, difficult.

Because of such difficulties, phase equilibrium diagrams are unavailable for sulphide-sulphate bearing systems of interest to workers concerned in the production of wood pulp by the closed cycle kraft process [6].

The present work describes the first phase equilibrium diagram produced in such a sulphate-sulphide system by the new technique.

Experimental

A small known weight of anhydrous solid potassium sulphate (Analar grade) contained in a small platinum crucible was continuously weighed while suspended in a stream of dry oxygen-free hydrogen at an elevated temperature. Heating was provided by a platinum wound resistance furnace. The hydrogen atmosphere was contained in the furnace in a 316 stainless steel tube.

Weighing was performed using a two pan balance accurate to 1 mg. The weight versus time curve was built up by removing weights from one pan and timing the system to rebalance, which occurred by loss of weight of potassium sulphate in the crucible suspended from the other pan. The final weight of the reduced mixture was measured to check the thermogravimetric end result.

The same furnace/stainless steel tube system was adapted for thermal analysis by inserting a silica glass tube support containing a platinum/platinum 13% rhodium thermocouple into the stainless steel tube. A small platinum crucible, having a thermocouple well in the bottom which is fitted over the thermocouple on the support, held a known weight of potassium sulphate.

This was heated in dry oxygen-free hydrogen for a time, estimated from the previous thermogravimetry results as being sufficient to produce the required composition of sulphide-sulphate in the sample. The hydrogen was then replaced with dry oxygen-free nitrogen, the sample rapidly quenched by moving it to a cooler portion of the furnace, and the furnace cooled in readiness for a heating curve experiment. The sample weight was checked before and after the experiment and less than 0.1% weight change was observed. The thermal analysis was performed by heating the sample at approximately 15 to 30° degree/min and measuring the crucible temperature on a recorder. The recorder had a 1 mV full scale deflection and a backing off millivoltage source used to expand this scale up to 15 mV in 1 mV sections. Such temperature-time traces were examined for deviations from a continuous gentle curve.

Results

A typical thermogravimetry curve is shown in Fig. 1. A compilation of the composition of all points of rapid change in the rate of weight loss at various temperatures are given in Table 1. Many of these points are the average of duplicated or triplicated measurements.

Table 2 lists the temperatures of thermal events occurring during the heating curves for various compositions.

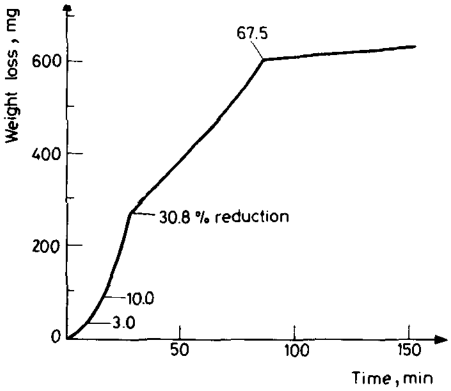

Fig. 1. Typical TG curve in H_2 at 750 °C

Table 1

Thermogravimetric data

Temp., °C	mole % K_2S at points of rate change in TG curves			
630	10	22.5	24	38
640	—	20	25	40.1
662	—	18	27	45
695	6.5	15	29	53
725	4.6	12.5	30.5	61.
750	3	10.5	31.5	67
775	2	8	33	73
831	1	6	37.5	82.5
872	—	—	45	90
912	—	—	60	97.5

Table 2

Thermal analysis data (heating curves only)

mole % K_2S	Thermal event temperatures, °C		
4.6	600	731	880
7.1	600	685	780
19.2	600	—	638
27.5	600	—	660
34.8	600	—	807
60.5	600	(690 740)	898
82.5	600	832	901

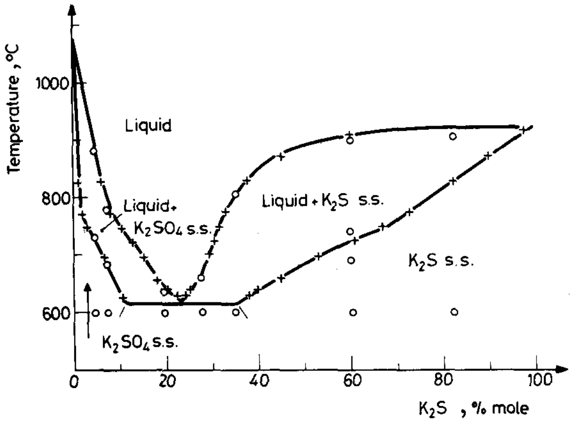

Fig. 2. Proposed phase equilibrium diagram for the system K_2SO_4—K_2S +TG, O heating curve data

Figure 2 shows the proposed phase diagram for the system K_2SO_4—K_2S. Temperatures are accurate to ±10° and compositions to ±2 mole %.

Discussion

The excellent agreement between the eutectic temperature predicted from the extrapolation of liquidus curves produced by thermogravimetry and that produced by thermal analysis (heating curves) is all that is required to confirm the new technique. The presence of eutectic temperature events in the thermal analysis results inside the areas indicated as being solid solid-solutions by the thermogravimetry is readily explained by non-equilibrium composition solids in the specimens used for thermal analysis caused by "coring" of precipitated phases during the rapid quench used in producing these specimens.

Again, the excellent agreement between the liquidus curves produced by both techniques gives credence to the new technique and indicates that the explanation of the shape of the thermogravimetric analysis curves is correct. It is proposed that the initial slow weight loss is indicative of a solid-gas reaction to produce K_2S (in solid solution). The first rate increase represents a change to a gas-liquid-solid reaction and therefore defines a point on the liquidus between K_2SO_4 solid solution and liquid. Such a reaction involving both a gas-liquid and liquid-solid reaction would be more rapid than a simple gas-solid reaction. The next change, a rate increase, indicates a change to a simple liquid-gas reaction and defines a point on the liquidus. The first rate decrease indicates a change back to a gas-liquid-solid reaction with the precipitation of K_2S solid solution. The composition of this solid solution is constant throughout the cross section of the precipitated material due to the constant temperature conditions. This rate decrease defines a point on the other liquidus, while the final rate decrease defines a point on the other solidus, K_2S solid solution, and indicates a return to a slow solid-gas reaction.

Conclusion

A new technique for studying phase equilibrium diagrams in systems containing one element which has two simultaneous oxidation states has been proven using the system $K_2SO_4-K_2S$. The new technique is rapid and convenient and does not require control of the ambient oxygen partial pressure during the experimental procedure. The technique also defines the limits of solid-solubility above the eutectic temperature.

*

The authors would like to thank the National Research Council of Canada for their financial support.

References

1. Phase Diagrams for Ceramists, Ed. Levin, E. M., Robbins, C. R., McMurdie, H. F., American Ceramic Society Inc., pp. 29—31, 1964.
2. D. BARHAM, Trans. Brit. Ceram. Soc., 64, 371, 1965.
3. N. C. GRAVETTE, D. BARHAM and L. R. BARRETT, Trans. Brit. Ceram. Soc., 65, 1966, 199.
4. J. SHIMOTAKAHARA and D. BARHAM, J. Can. Ceram. Soc., 38, 1969, 109.
5. E. C. COPLESTON, M. Y. C. SIMONS and D. BARHAM, Trans. Brit. Ceram. Soc., 76, 1977, 68.
6. D. W. REEVE and W. H. RAPSON, Pulp & Paper Mag. of Canada, 71, T274, 1970.

RÉSUMÉ — Une nouvelle technique expérimentale a été développée afin de déterminer le diagramme d'équilibre des phases dans le système $K_2SO_4-K_2S$.

La technique fait appel à la thermogravimétrie isotherme du sulfate de potassium lors de sa réduction en sulfure de potassium à températures élevées dans un courant de gaz hydrogène sec exempt d'oxygène. Plusieurs changements abrupts de vitesse de perte de poids ont lieu sur chaque courbe et ces changements peuvent être rapportés aux changements de phases dans le diagramme de phases du système.

A partir de tels résultats on peut déterminer les limites du liquidus et du solidus (solution solide).

L'analyse thermique simple a été utilisée pour confirmer la température eutectique et diverses températures du liquidus.

Le diagramme $K_2SO_4-K_2S$ forme un système eutectique simple à 610° et 23 p.c. molaires de K_2S. Les limites de la solubilité en phase solide de K_2S dans K_2SO_4 et de K_2SO_4 dans K_2S sont, à la température eutectique, respectivement de 11 et 36 mol %.

La forme particulière des courbes du liquidus de chaque côté de l'eutectique fait penser à la possibilité de changements de phases dans les solutions solides tant de K_2SO_4 que de K_2S, mais l'analyse thermique n'en a pas donné de preuve.

ZUSAMMENFASSUNG — Eine neue experimentelle Technik wurde zur Bestimmung des Phasengleichgewichtsdiagramms des Systems $K_2SO_4-K_2S$ entwickelt.

Die Technik umfasst die isotherme Gravimetrie von Kaliumsulfat während der Reduktion zu Kaliumsulfid bei erhöhten Temperaturen in strömenden trockenen und Sauerstoff-freien

Wasserstoff. Verschiedene plötzliche Änderungen der Geschwindigkeit des Gewichtsverlustes treten bei jeder Kurve auf und können mit den Phasenänderungen im Phasendiagramm des Systems in Zusammenhang gebracht werden.

Durch diese Ergebnisse können die Grenzflächen der flüssigen und der Festphasenlösung festgestellt werden.

Die einfache Thermoanalyse wird zur Bestätigung der eutektischen Temperatur und verschiedener Liquidus-Temperaturen herangezogen.

Das Diagramm K_2SO_4—K_2S ist ein einfaches eutektisches System mit dem Eutektikum bei 610° und 23 Mol % K_2S. Die Grenzwerte einer festen Lösung von K_2S in K_2SO_4 und K_2SO_4 in K_2S betragen bei der eutektischen Temperatur 11% bzw. 36 Mol %.

Die aussergewöhnliche Form der Liquidus-Kurven zu beiden Seiten des Eutektikums lässt auf die Möglichkeit von Phasenänderungen in den Festlösungen von sowohl K_2SO_4 wie auch von K_2S schliessen Hierzu ergab jedoch die Thermoanalyse keine Bestätigung.

Резюме — Для определения диаграммы фазового разновесия в системе K_2SO_4—K_2S разработан новый экспериментальный метод. Метод включает в себя изотермическую термогравимметрию сульфата калия во время его восстановления до сульфида при повышенных температурах и в струе сухого водорода, не содержащего кислорода. На каждой кривой наблюдается несколько резких изменений скорости потери веса, что может быть связано с фазовым изменением на фазовой диаграмме системы. На основании этих результатов могут быть установлены границы ликвидуса и солидуса (твердый раствор). Для подтверждения температуры эвтектики и различных температур ликвидуса использован простой термический анализ. Диаграмма K_2SO_4—K_2S представляет собой простую эвтектическую систему с эвтектикой при 610° и при 23 мольных% K_2S. Пределы твердой растворимости K_2S в K_2SO_4 и K_2SO_4 в K_2S при температуре эвтектики составляли, соответственно, 11 и 36 мольных процента. Необычайный вид кривых ликвидуса на каждой стороне эвтектики указывает на возможность фазового изменения в обоих K_2SO_4 и K_2S твердых растворах. Однако, доказательств этому не было получено из термического а нализа.