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INSTRUMENTATION OF THERMAL ANALYSIS AND CALORIMETRY

NEW METHOD FOR DETERMINATION OF THE EQUILIBRIUM STATE IN SYSTEMS INVOLVING REACTIONS OF THE TYPE
A(s) = B(s) + C(g)

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A static method is described for measurement of the equilibrium values of temperature, pressure and composition of the solid phase, and determination of the number of degrees of freedom in heterogeneous systems containing a gaseous phase, including water vapour. With this method, it has been found that in the system formed in the thermal dehydration of $CaC_2O_4 \cdot H_2O$ a solid solution of monohydrate and anhydride coexists in equilibrium with water vapour. The composition of the solid solution changes with the temperature and the pressure of water vapour. The dehydration enthalpy of the solid solution referred to 1 mol H_2O does not depend on its composition. It was found to be $\Delta H_{\text{deh}} = (69 \pm 3)\ \text{kJ} \cdot \text{mol}^{-1}$.

The method is based on investigation of the temperature-dependence of the composition of a solid phase which is in equilibrium with a gaseous phase, using an apparatus which allows simultaneously isothermal heating of solid samples at different temperatures and equal constant partial pressures of the gaseous component. The required functions are obtained by interpolation of the dissociation and association dependences of the losses of mass of samples on sufficiently long isothermal heating. From the shapes of these functions, the number of degrees of freedom can be determined.

When a monovariant equilibrium is achieved in a binary system containing three coexisting phases, the dependence of the equilibrium composition of the solid phase on temperature is similar to that shown in the upper part of Fig. 1. Then, only one equilibrium temperature T_1 corresponds to the chosen equilibrium pressure p_1 of the gaseous component C(g) (lower part of Fig. 1).

When components A(s) and B(s) form a solid solution, a bivariant equilibrium is established and two phases (a solid solution of components A(s) and B(s) and a gaseous phase C(g)) coexist in equilibrium. The shape of the temperature-dependence of the equilibrium composition of the solid phase at constant pressure of the gaseous component is similar to that shown in the

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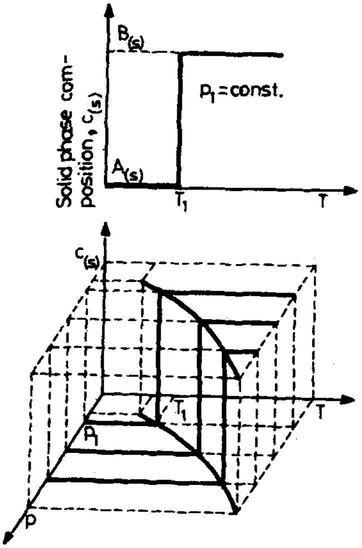

Fig. 1 Dependences of the solid phase composition on temperature and gaseous component pressure in a binary system containing three coexisting phases.

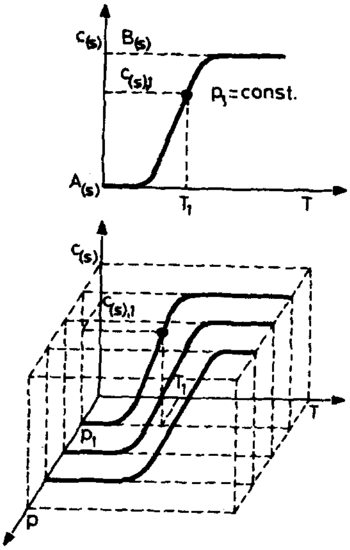

Fig. 2 Dependences of the solid phase composition on temperature and gaseous component pressure in a binary system containing two coexisting phases.

upper part of Fig. 2. The composition of the solid solution depends on the temperature and pressure of the gaseous phase, as shown in the lower part of Fig. 2.

Experimental

The main parts of the experimental equipment: a furnace with an adjustable (unchangeable during the experiment), nonlinear temperature gradient; either a closed cell with an adjustable water vapour pressure, or an open tube with a permanently flowing carrier gas with a defined partial water vapour pressure, is placed in the axis of the furnace; a tempered box which prevents the condensation of water vapour on the colder parts of the apparatus; a manostat of water vapour with adjustable absolute pressure or a through-flow saturator, where the carrier gas is saturated with water vapour at atmospheric pressure.

For a detailed description of the construction and functioning of the apparatus, see [1].

Results and discussion

The described method was used to investigate the equilibrium states in the system formed on thermal dehydration of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$, at 80–360° and water vapour partial pressures of 2.4–85.2 kPa. The duration of isothermal heating was 5, 24 or 71 h, and the mean temperature difference between neighbouring sample carriers was 3–5°. In Fig. 3, the diagrams of relative mass losses of samples of $CaC_2O_4 \cdot H_2O$ are shown as a function of temperature at a water vapour partial pressure of 22.9 kPa. Curve *a* corresponds to 5 h dehydration, curve *b* to 24 h dehydration and curve *c* to 71 h dehydration. Curves *d, e* and *f* were obtained by rehydration of previously dehydrated samples. Curve *d* corresponds to 71 h rehydration, curve *e* to 24 h rehydration and curve *f* to 5 h rehydration. Curves *c* and *d* are already close to equilibrium conditions. The dependences equilibrium pressure of water vapour *vs.* temperature for different solid solution compositions (composition is given in mass fraction of anhydride) are plotted in Fig. 4. Curve *a* in Fig. 4 corresponds to the part of the equilibrium dependence $p = f(T)$ obtained by Gerard *et al.* [2]. In conformity with [3], these authors assumed that the system in question consists of three phases.

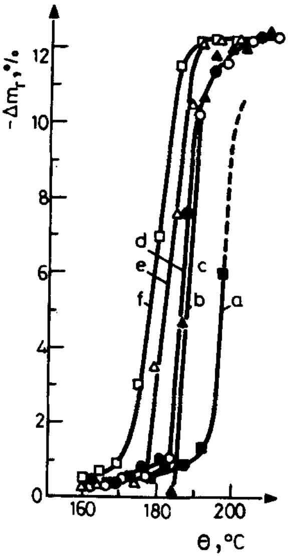

Fig. 3 Diagrams of relative mass loss *vs.* temperature after 5 h dehydration (*a*), 24 h dehydration (*b*), and 71 h dehydration (*c*) of $CaC_2O_4 \cdot H_2O$ and 71 h rehydration (*d*), 24 h rehydration (*e*), and 5 h rehydration of previously dehydrated $CaC_2O_4 \cdot H_2O$ at a water vapour partial pressure of 22.9 kPa.

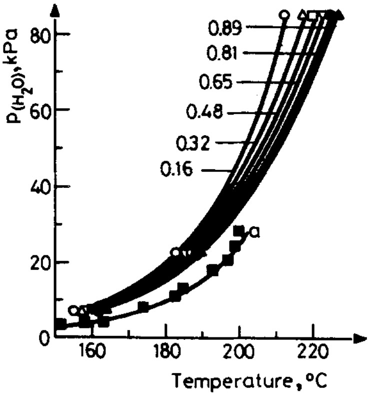

Fig. 4 Equilibrium water vapour pressure *vs.* temperature for different compositions of solid solutions, given as functions of mass of anhydride. Curve *a* represents the part of the equilibrium dependence obtained by Gerard *et al.* [2].

The dehydration enthalpy of solid solutions of monohydrate and anhydride referred to 1 mol of H_2O is practically independent of their composition. Its value was found to be $\Delta H_{\text{deh}} = (69.8 \pm 3)\ \text{kJ} \cdot \text{mol}^{-1}$.

Conclusions

On the thermal dehydration of $CaC_2O_4 \cdot H_2O$ a solid solution of monohydrate and anhydride coexists in equilibrium with water vapour. The composition of the solid solution changes with temperature. The equilibrium coexistence of two pure solid phases with water vapour proposed in literature has not been observed.

Comparison of the equilibrium temperatures at given pressures of water vapour determined by the described static method shows that the temperature values are clearly lower than those obtained with dynamic methods.

References

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2 N. Gerard, G. Watelle-Marion and A. Thrier-Sorel, Bul. Soc. Chim., France 11 (1968) 4367.
3 S. Shimizu and M. Taniguchi, Nippon Kagaku Kaishi, 7 (1977) 953.

Zusammenfassung – Eine isotherme Methode zur Messung von Temperatur, Druck und Zusammensetzung der festen Phase im Gleichgewicht und zur Bestimmung der Anzahl der Freiheitsgrade in heterogen Systemen mit einer Gasphase (z.B. Wasserdampf) wird beschrieben. Mit dieser Methode wurde nachgewiesen, dass bei der thermischen Entwässerung von $CaC_2O_4 \cdot H_2O$ eine feste Lösung von Monohydrat und Anhydrid im Gleichgewicht mit Wasserdampf existiert. Die Zusammensetzung dieser festen Lösung ändert sich mit der Temperatur und dem Wasserdampfdruck, ihre Dehydratationsenthalpie (pro 1 mol Wasser) hängt nicht von der Zusammensetzung ab und wurde zu $\Delta H_{\mathrm{deh}} = (69 \pm 3)$ kJ mol^{-1} bestimmt.

РЕЗЮМЕ — Описан статический метод измерения равновесных значений температуры, давления, состава твердой фазы и определения числа степеней свободы в гетерогенных системах, содержащих гозовую фазу, включая пары воды. Используя этот метод, было найдено, что образующийся при термическом разложении $CaC_2O_4 \cdot H_2O$ твердый раствор моногидрата и безводной соли существует в равновесии с парами воды. Состав этого твердого раствора изменяется с изменением температуры и давления паров воды. Энтальпия дегидратации твердого раствора, отнесенная к 1 молю воды, не зависит от его состава и составляет $\Delta H_{\text{дег.}} = 69 \pm 3$ кдж.моль$^{-1}$.