SOVIET PHYSICS JETP VOLUME 30, NUMBER 6 JUNE, 1970

MELTING DIAGRAM OF THE pH_2–oD_2, pH_2–HD, *AND* oD–HD *SYSTEMS*

N. G. BEREZNYAK, I. V. BOGOYAVLENSKIĬ, L. V. KARNATSEVICH, and V. S. LOGAN

Physico-technical Institute, Ukrainian Academy of Sciences

Submitted April 28, 1969

Zh. Eksp. Teor. Fiz. 57, 1937–1939 (December, 1969)

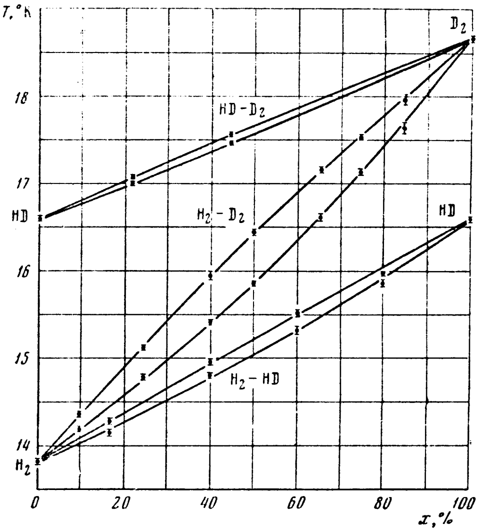
The melting diagrams of the H_2–D_2, H_2–HD, and D_2–HD systems are investigated. The diagrams of all these systems have a cigar shape. The excess Gibbs potential G_e in the solid phase is calculated from the data for the H_2–D_2 system. From the form of the dependence of G_e on the solution concentration it follows that in the solid phase near the melting diagrams the solutions are regular. The critical separation temperature calculated for H_2–D_2 solutions in the solid phase is 2.25°K.

THE solid-liquid phase diagram was investigated earlier for the system H_2–D_2[1-3]. However, the information concerning its character is contradictory: in[1], a peritectic diagram was observed at 16.4°K, whereas from[2,3], it follows that the diagram is a cigar. In addition, an estimate of the critical lamination temperature T_c in the solid phase, which is based on the constructed diagrams, leads to great uncertainty. The values of T_c lie between 2 and 6°K. As noted by the authors themselves[3], this is connected with the appreciable errors in the measurement of the solidus line, due to the slow establishment of equilibrium in the bulky sample.

The present investigation was undertaken in order to construct the melting diagrams of all binary systems made up of the hydrogen isotopes H_2, D_2, and HD, including a more exact determination of the topology of the H_2–D_2 diagram. The obtained experimental data on the melting diagrams together with the published data concerning the excess thermodynamic quantities of the liquid solution[4-6] were used to calculate these quantities in solid solutions, and also to estimate the critical lamination temperature of these solutions T_c in the solid phase.

The liquid-crystal equilibrium diagrams were investigated by the thermal-analysis method, i.e., by plotting thermograms (the dependences of the temperature of the solution sample on the time during the course of heating or cooling). To eliminate the errors connected with the lack of equilibrium, which is customary in the case of bulky samples, the cavity of the vessel, in which the investigated solution was condensed, was filled with a porous block pressed of copper powder and then sintered. By the same token, the region of crystallization of the solution was limited to pores with an average duration of approximately 10 μ. This ensured rapid establishment of thermal and concentration equilibrium in the process of plotting the thermograms, and consequently made it possible to measure with greater accuracy the true position of the liquidus and solidus lines on the diagrams.

For most mixtures, the thermograms were plotted in the temperature interval from 10 to 20°K. The mixture pH_2–oD_2 with concentration 50% was investigated in a still wider temperature interval, from 4.2 to 20°K. No irregularities were observed on the thermograms, with the exception of the points corresponding to the start and end of the melting of the solutions.



Melting diagrams of hydrogen isotope systems.

The figure shows the obtained diagrams. As seen, they represent smooth cigars without peritectic or any other singularities, corresponding to the existence of a continuous series of solid solutions of the hydrogen isotope, at least near the melting diagrams. The calculation of the excess Gibbs potential G_e for the solid phase of pH_2–oD_2 solutions gives the following dependence of G_e along the phase diagram of the fusion:

$$G_e = a x_{H_2}(1 - x_{H_2}),$$

where a = 9.1 ± 0.1 cal/mole and does not depend on the temperature, and x_{H_2} is the hydrogen concentration. This means that the solid solutions are regular, at any rate near the melting diagram. If we assume that the regularity of the solution is retained also for lower temperatures, then we can estimate the T_c of the lamination, which for the pH_2–oD_2 system turns out to be

$$T_c = a / 2R = 2.25^\circ \mathrm{K},$$

where R is the gas constant.

A complete calculation of all the diagrams and a

---

[1] We investigated modifications in equilibrium with respect to the ortho and para compositions at 20°K, and designated here pH_2 and oD_2.

comparison of the data obtained from it with the prediction of the theoretical paper[7,8] will be performed in the future.

We take the opportunity to thank Academician of the Ukrainian Academy of Sciences B. G. Lazarev for a useful discussion of the results. The authors are also indebted to engineer I. A. Shapoval for help with the measurements.

---

[1] V. S. Kogan, B. G. Lazarev, and R. F. Bulatova, Zh. Eksp. Teor. Fiz. 34, 238 (1958) [Sov. Phys.-JETP 7, 165 (1968)].

[2] M. Simon, Phys. Lett. 9, 122 (1964).

[3] D. White and J. R. Gaines, J. Chem. Phys. 42, 4152 (1965).

[4] R. B. Newman and L. C. Jackson, Trans. Faraday Soc. 54, 1481 (1958).

[5] A. Bellemans, Bull. Soc. Chim. Belg. 68, 270 (1959).

[6] H. F. P. Knaap, R. J. J. van Heijningen, J. Korving, and J. J. Beenakker, Physica 28, 343 (1962).

[7] J. Prigogine, R. Brinden, and A. Bellemans, Physica 20, 633 (1954).

[8] I. M. Lifshitz and G. I. Stepanova, Zh. Eksp. Teor. Fiz. 33, 485 (1957) [Sov. Phys.-JETP 6, 379 (1958)].

Translated by J. G. Adashko
222