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THERMODYNAMICS AND PHASE DIAGRAMS

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ABSTRACT

This report is concerned with the construction of phase diagrams by means of DTA, special attention being given to erroneous results originating from metastable states.

INTRODUCTION

Phase diagrams of binary systems at constant pressure are representations of one- and two-phase regions with their phase boundaries as a function of the temperature and concentration. Assuming chemical equilibrium, the phase regions are zones of minimum Gibbs energy and the coexistence of phases is governed by the Gibbs phase rule. To generate a phase diagram means to detect all phase boundaries. In general, this is not done by measuring the dependence of ΔG on T (or c), but by measuring heating and cooling curves by DTA. Thus, the enthalpy of phase reactions is utilized, which is related to the free enthalpy ΔG by the heat capacity.

Unfortunately, the enthalpy ΔH tells us nothing about the kind of reaction by which it is generated. Therefore, today it is usual to support the use of DTA by additional methods. The most effective is X-ray crystallography. Generally, one compares the powder patterns of quenched or normally cooled samples with those of pure compounds. New, additional reflections indicate new compounds. However, a better procedure is to try to solve the structure of the new compound by indexing each single reflection. This is not possible in all cases. A further development is the application of high-temperature X-ray techniques. Other methods occasionally applied are high temperature microscopy, the measurement of electrical properties or of the micro-hardness and metallographic methods in the case of alloys.

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THE POSTER CONTRIBUTIONS

(a) The occurrence of metastable states

The main mistakes made in DTA work originate in the formation of metastable states. Two groups of such phenomena can be distinguished: undercooling in cooling, superheating in heating experiments, leading to incorrect temperatures; secondly, incomplete reactions of metallic and solidified materials in the case of peritectics or mixed-crystals-ranges which may lead to wrong stoichiometries for compounds.

The poster of A. Lendvai, Budapest [1] (phase diagram of the Al–Fe system up to 45 mass% iron), dealt with two non-equilibrium phenomena: (1) the appearance of a "wrong eutectic" in a quenched sample with a metastable two-phase state, which disappears after annealing, and (2) the considerable undercooling of liquidus curves in cooling experiments.

In the poster of M. Nevriva and J. Šesták, Prague [2], studies of solid–liquid stable–metastable phase equilibria were described. In the system $PbO–Ga_2O_3$ a compound $PbGa_2O_4$ exists which melts incongruently. By DTA a higher peritectic was found than by X-ray measurement of quenched samples. Reference was made to the calculation of metastable diagrams by superposing simple diagrams of the eutectic type, here those of $PbO–Ga_2O_3$ and $PbO–PbGa_2O_4$.

(b) Polycomponent systems

With ternary or polycomponent systems, the measurements and evaluations become much more complicated. Thus, the tendency is to calculate such diagrams, utilizing measured energy values for the mixing of the liquid phase. A widespread mistake in such investigations arises by not recognizing that an alleged pseudobinary slice is in reality a part of the multicomponent range.

In two contributions from A.S. Trunin and co-workers [3,4]. (Kuibyshev, U.S.S.R.) a method was described for a better evaluation of DTA data from polycomponent salt systems. This method employs a new concept, called "phase unit block", which was explained with the aid of the system $KF–KBr–K_2CO_3$.

Results of the investigation of ternary systems were presented in two other posters. J. Walczak, M. Kurzawa and L. Trześniowska (Szczecin, Poland) [5] investigated the diagonal slice $Fe_2V_4O_{13}–MoO_3$ in the three-component system $Fe_2O_3–MoO_3–V_2O_5$ by means of DTA heating curves and X-ray crystallography and found two main results: (1) $Fe_2V_4O_{13}$ reacts with MoO_3 up to ~ 40 mol%, forming mixed crystals by replacing V_2O_5 with MoO_3; (2) the investigated slice is not a pseudobinary slice but belongs to a ternary region.

J. Ziółkowski and K. Mocała (Krakow, Poland) [6] investigated the reaction of MeV_2O_6 (Me = Mn, Cu, Zn) metavanadates with MoO_3 by means of DTA heating experiments and X-ray crystallography. The measurements revealed that only the subsolidus regions of the Mn systems are natural subsystems of either the ternary system $MnO–V_2O_5–MoO_3$ or the quaternary system formed by addition of Li_2O.

(c) Corrections in pseudobinary systems

Another kind of error was discussed in a poster of M. Touboul, B. Costes and M. Vilatte-Zambetti (Paris) [7]. For the binary systems $TlVO_3–MVO_3$ (M = Li, Na), it was demonstrated that $TlVO_3$ does not have a phase transformation; older contrary results might be due to the volatility of thallium salts, a phenomenon which yields phases richer in V_2O_5.

D. Schultze and R. Uecker (Berlin, G.D.R.) [8] demonstrated by DTA and simultaneous high-temperature microscopy and by drawing single crystals with the Czochralski technique that a congruently melting compound at the Bi_2O_3-rich side of the systems $Bi_2O_3–P_2O_5$ and $Bi_2O_3–Nd_2O_3–P_2O_5$ has the composition $Bi_{5.8}PO_{11.2}$ (with a small phase range) and not Bi_5PO_{10}. The yellow crystals can be doped with Nd_2O_3.

(d) Industrial applications

Two posters concerning industrial problems were presented. K. Papp and J. Kürthy-Komlósi (Budapest) [9] investigated the system $Na_3AlF_6–Al_2O_3$ by DTA at the cryolite-rich side in open crucibles. For cryolite the transition and melting enthalpy were redetermined. Additionally, the enthalpies of solution for Al_2O_3 in cryolite melts under conditions similar to those used for the electrolytic production of the metal were measured.

L.A. Dobrzański and J. Kwarciak (Katowice, Poland) [10] employed DTA for determination of the equilibrium diagram for 9–0–2 + Si high-speed steel. Heating and cooling curves were measured to find out the influence of up to 4% Si on the phase transitions below the melting point of a high-speed steel with W–V–Cr. These investigations are of great practical interest, for Si is used to replace molybdenum in such steels.

CONCLUSION

Comparing the contents of the contributions with those submitted ten years ago (4th ICTA in Budapest), one can state two satisfactory improvements:

(1) It has become quite common to generate phase diagrams not only by DTA but to confirm the DTA results by additional methods. Thus, the

posters described results from X-ray structure analysis, calorimetry, high-temperature microscopy, etc.

(2) The problems with metastable states are well known. Thus, great emphasis is given to the approach to equilibrium by annealing the samples and by controlling this process.

Last but not least, the great importance of DTA in technical applications is appreciated, as was previously the case with TA.

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