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P-T-X PHASE DIAGRAM AND HOMOGENEITY RANGE OF $CdAs_2$

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ABSTRACT

DTA, X-ray diffraction and total vapour pressure measurements were used to investigate P-T-X phase equilibria for the system Cd-As at T=770-950 K and P=10^2-10^5 Pa. The co-ordinates of two eutectic points were determined as well as the maximum melting temperatures of Cd_3As_2 and $CdAs_2$. By geometrical analysis of the vapour pressure results both arsenides were shown to melt congruently. Sublimation of Cd_3As_2 was shown to be a congruent process while $CdAs_2$ sublimes incongruently. Non-stoichiometry of $CdAs_2$ was estimated.

P-T and T-X projections for Cd-As are presented in the figure. S_1 stands for Cd_3As_2, and S_2 for $CdAs_2$. Solid lines in the figure represent experimental results for the P-T projections of the univariant equilibria for this system in which the vapour phase participate. Three-phase curves on the P-T projection separate the adjoining bivariant fields of two-phase equilibria between the corresponding condensed phases and the saturated vapours: the sublimation area of the $Cd_3As_{2\pm\delta}$ crystalline phase is within CNF(A)E_1B, the sublimation of $CdAs_{2\pm\delta}$ is within BE_1MHE_2D, and the vaporization of the liquid (liquid-vapour equilibrium) is outside these curves. It can be seen from the figure that all these P-T fields are partially juxtaposed. This is a characteristic feature of the Cd-As system.

By means of the vapour pressure measurements maximum temperatures and vapour pressures were determined for the three-phase equilibria in which both cadmium arsenides participate: for Cd_3As_2, T_m^{max}=988 K(point F), P^{max}=26.6 kPa(point N); for $CdAs_2$, T_m^{max}=901 K (point M), P^{max}=106.4 kPa(point H). These are in reasonable agreement with our DTA results. Since the T_m^{max} values for both compounds exceed the temperatures in the adjoining invariant equilibria, the melting behaviour of Cd_3As_2 and $CdAs_2$ is congruent.

From the intersection of the experimental P(T) curves for the S_1LV, LS_2V, and S_1S_2V equilibria the eutectic E_1 temperature and pressure were determined for the four-phase invariant equilibrium

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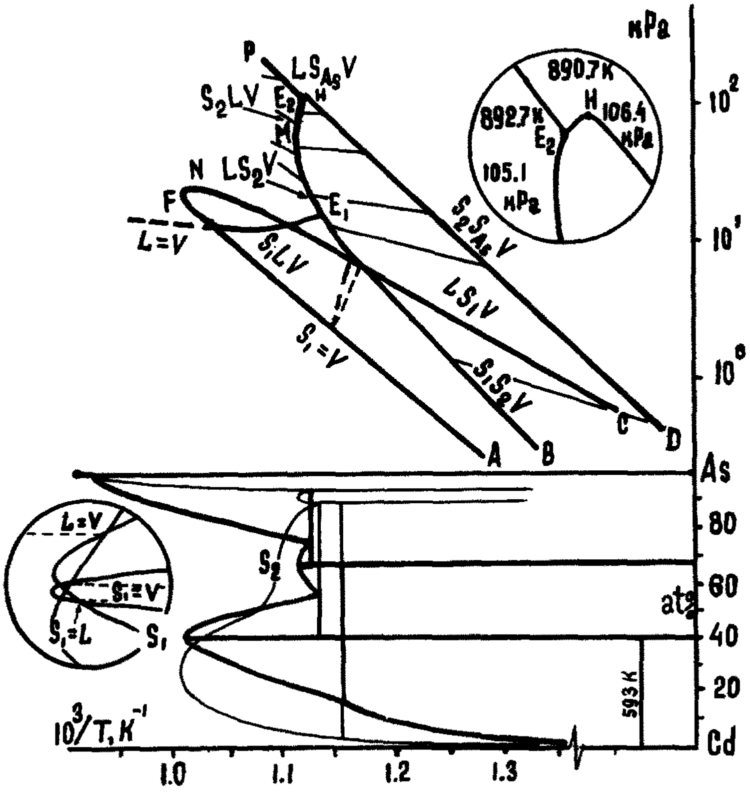
$S(Cd_3As_2)LS(CdAs_2)V$: $T(E_1)=883$ K, $P(E_1)=14.7$ kPa. Similarly for the other invariant, $S(CdAs_2)LS(As)V$, co-ordinates $T(E_2)=892.7$ K, $P(E_2)=105.1$ kPa were obtained. Of special applied interest is the composition of all four equilibrium phases in E_2.



To determine these vapour pressures and composition of the vapour were examined for two-phase equilibria /$S(CdAs_2)$+vapour/ and (liquid+vapour) in the P-T-X space adjoining point E_2. The composition of the vapour was investigated by means of the "intersection" method described in our earlier publication /1/. This method is based on the phase rule. The compositions of both equilibrium phases (solid + vapour, liquid + vapour) are calculated at the intersection point of two vapour pressure curves, obtained with two separate initial samples of different compositions. For the Cd-As system the composition of the condensed phase (either solid or liquid) is calculated according to

$$\frac{n(Cd)}{n(As)} = \frac{n_1(Cd)V_2 - n_2(Cd)V_1}{n_1(As)V_2 - n_2(As)V_1} \qquad (1)$$

where $n_i(Cd)$ and $n_i(As)$ are the numbers of Cd and As gram-atoms in the initial samples used for the two experiments ($i=1,2$); V_i are the reaction volumes in these experiments; n(Cd) and n(As) refer to the intersection points. From the calculated ratio (1) and the measured P and T the partial pressure $P(As_2)$ can be calculated:

$$X_s(\text{at.\% As}) = \frac{n_1(Cd)RT - [P-P(As_2)-K_pP^2(As_2)]V_1}{[n_1(Cd)+n_1(As)]RT - [P+P(As_2)+3P^2(As_2)]V_1} \qquad (2)$$

where K_p is the equilibrium constant of the reaction

$$2As_2(g) = As_4(g) \qquad (3)$$

at the intersection point temperature. The composition of the vapour X_v(at.% As) at this point is calculated from the partial pressures:

$$X_v = \frac{2P(As_2) + 4P(As_4)}{P(Cd) + 2P(As_2) + 4P(As_4)} \qquad (4)$$

11 vapour pressure curves for the / $S(CdAs_2)$+vapour/ equilibrium and 10 liquid-vapour curves have been analysed. The composition of the vapours was calculated in the two-phase fields adjoining points M and E_2 and was shown to be about 100 at.% As.

The compositions of the condensed phases in the three-phase equilibria around the E_2 eutectic were determined from the vapour pressure experiments at the phase transition points as described previously /2/. The composition of the liquid was determined from S_2LV - LV transitions while that of the solid $CdAs_2$ was calculated from S_2V - S_2LV phase transition. It has been shown that at the eutectic temperature $T(E_2)$ the solubility of As in the $CdAs_2$ phase is about 0.1 at.% and the eutectic composition of the liquid is 73.5 at.% As. Solubility of Cd in the solid As at $T(E_2)$ was proved to be outside the experimental limits. For geometrical analysis of the compositional sequence of phases and the arrangement of the univariant curves around the E_2 eutectic the Schreinemakers' rule was applied. An enlargement of the R-T-X phase space around the E_2 eutectic is shown on the P-T projection of the figure while on the T-X projection the relative arrangement of the congruent processes near the mahimum melting point of Cd_3As_2 is detailed.

Vapour pressure analysis of the S_2V - S_1S_2V phase transition made it possible to estimate maximum solubility of Cd in the $CdAs_2$ phase which was shown to be under 0.03 at.% Cd at temperatures 810 to 880 K.

REFERENCES

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