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P-T-X PHASE DIAGRAM AND NON-STOICHIOMETRY OF Zn_3As_2

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ABSTRACT

DTA, X-ray diffraction and total vapour pressure measurements were used to investigate P-T-X phase equilibria in the system Zn--As at temperatures and pressures up to 1200 K and 101 kPa. Deviation from stoichiometry in Zn_3As_2 was estimated. Congruent sublimation of β-Zn_3As_2 was studied and standard enthalpy of formation calculated.

Experimental investigations are summerized in P-T and T-X projections of the space model of the phase equilibria in the system Zn-As shown in the figure. The vapourus line is drawn schematically. Two compounds, Zn_3As_2 and $ZnAs_2$, were identified wich are denoted S_1 and S_2. The range of co-existence of Zn_3As_2 and the saturated vapour is within the following three-phase lines: VLS_1 (DKB), S_1S_2V (CME_1) and S_1LV (E_1QB). The minimum vapour pressure AOB in this field is due to congruent sublimation of Zn_3As_2. This univariant process has been examined in the temperature range 947 to 1181 K and the following temperature dependence of the total vapour pressure was deduced:

$$\mathrm{Lg}(\ P,\mathrm{Pa}\ ) = -(8160 \pm 50)/T + (11.130 \pm 0.045) \qquad (1)$$

It has been found that the sublimation of Zn_3As_2 is accompanied by dissociation to the elements according to

$$Zn_3As_2(s) = 3Zn(g) + 1/2As_4(g) \qquad (2)$$

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

For the reaction (2) equilibrium constants were calculated to be

$$\mathrm{Lg}(\ K,\mathrm{Pa}^{7/2}) = -(28320 \pm 170)/T + (38.02 \pm 0.16) \qquad (4)$$

In the equations (1) and (4) the standard least-squares deviations are given. The second- and third-law molar enthalpies of formation of β-Zn_3As_2 were calculated. The recommended value is

$$\Delta_f H^\circ_m(\beta\text{-}Zn_3As_2,s,\ 298.15\ K) = -(103 \pm 8)\ kJ\cdot mol^{-1}.$$

P-T space within the three-phase curves CME_1 (for the S_1S_2V equi-

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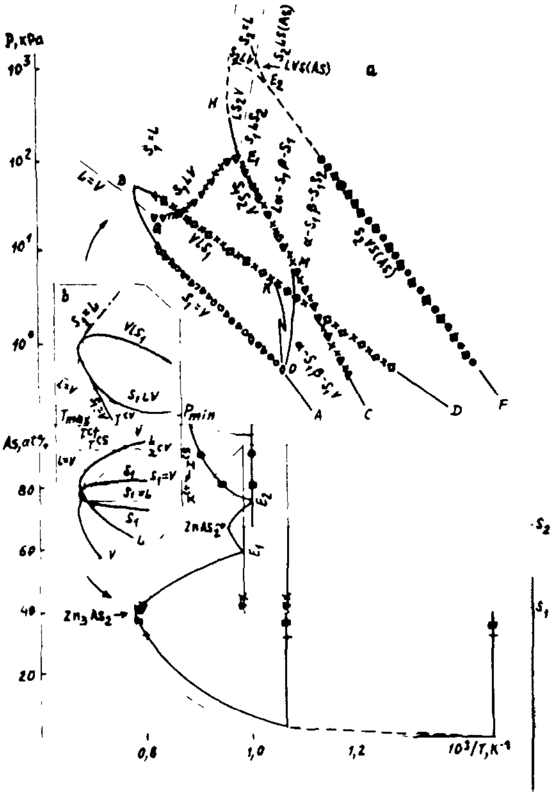
librium), E_1H (for LS_2V), HE_2 (for S_2LV), and FE_2 (for $S_2VS(As)$) corresponds to the incongruent sublimation of the $ZnAs_2$ crustalline phase. E_1 is the invariant point of the four-phase equilibrium (Zn_3As_2 + $ZnAs_2$ + eutectic liquid + vapour) with the co-ordinates P=100,5 kPa, T=1026 K. The characteristic features of the phase diagram Zn-As are the negative P(T) slopes of the congruent melting curves S_1=L and S_2=L, a vapour pressure minimum in the three-phase equilibrium S_1LV (P_{min}=33.07 kPa, T~1200 K), and the azeotropic vaporization point Q with the temperature T^{cv} (see the P-T projection of the figure).



An enlargement of the pre-melting range of Zn_3As_2 is also shown in the figure. Since the congruent fusion temperature decreases with the rising pressure, the point of tangency of the lines $S_1=L$ and VLS_1 is lower in temperature than the maximum melting point ($T^{cf} < T_{max}$), and the composition of the solid X^{cf} at this point is $Zn_3As_{2-\delta}$, i.e. $X^{cf} < X_{L,S}(T_{max})$, X being given in at.%As. Similar consideration of the relative positions of the congruent sublimation and the S_1LV curves leads to the following inequalities: $T^{cs} < T_{max}$, $X^{cs} > X_{S,V}(T_{max})$, and $X_V(T_{max}) < X_S(T_{max})$. Thus, the vapour pressure results show that at maximum melting point the compositions of the equilibrium phases do not coindcide: $X_V(T_{max}) < X_S(T_{max}) < X_L(T_{max})$.

Non-stoichiometry of β-Zn_3As_2 was examined by the vapour pressure measurements. The maximum solubility of Zn (about 0.01 at.%) was found in the solid state phase-transition region at 947 K and was shown to drop sharply with the increasing temperature. On the contrary, the solubility of As in β-Zn_3As_2 increases with the temperature rising from 937 K up to eutectic. The corresponding estimates are given in the table:

T/K	P/kPa	X_s/at.%As	T/K	P/kPa	X_s/at.%As
960.0	19.95	40.019	1012.0	75.66	40.086
985.5	38.60	40.032	1012.5	76.80	40.060
992.0	46.13	40.020	1014.8	81.46	40.042
994.0	49.26	40.049	1070.8	86.39	40.049
1002.5	59.92	40.044	1089.0	78.20	40.045
1010.0	71.66	40.036	1107.5	68.53	40.050

From the vapour pressure experiments the composition of the vapours for the two-phase (β-Zn_3As_2 + vapour) equilibrium was calculated by means of the "intersections" method described earlier [1] . Isoplethal sections for the β-Zn_3As_2 range of existence were made and the partial thermodynamic functions of Zn and As were estimated.

REFERENCES

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