

lattice of type A-III, and thallium a close-packed hexagonal lattice of type A6. With increase of pressure, all these elements undergo phase transformations. It is interesting that, with increase of pressure to 12 kbar, gallium assumes a face-centred tetragonal lattice of type A-III, i.e. the same as that of indium. The axial ratio is $c/a = 1.104$ for gallium and $c/a = 1.075$ for indium, i.e. the indium lattice is distorted less. On further increase of pressure to 70 kbar, the gallium A-III lattice is converted into a face-centred cubic lattice⁵. It would be logical to postulate the occurrence of the same transition in indium at lower pressures, since its lattice is distorted less.

The following indirect facts may be adduced as proof. It has been shown⁶ by X-ray diffraction analysis that, with increase of pressure, indium becomes less tetragonal. Indium exhibits equivalent behaviour also on addition of impurity atoms. Thus, following the addition of 19.6% of thallium, the face-centred tetragonal indium is converted into a face-centred cubic form⁷. Using these data, we shall perform certain thermodynamic calculations.

The Gibbs free energy difference between two phases is given by the expression

$$\Delta G_{(T,P)}^{\alpha \rightarrow \beta} = \Delta H^{\alpha \rightarrow \beta} - \Delta S^{\alpha \rightarrow \beta} T + 24 \int_{P_0}^P \Delta V^{\alpha \rightarrow \beta} dP, \quad (2)$$

where ΔG , ΔH , ΔS , and ΔV are respectively the Gibbs free energy, enthalpy, and entropy of transition and the corresponding volume change, T and P are the temperature and pressure, and α and β denote various modifications of the substance; the superscripts can also be replaced by $\alpha \rightarrow L$ and $\beta \rightarrow L$, i.e. denoting the transition to the liquid phase. From tabulated data for indium⁸

we find $\Delta H^{\alpha \rightarrow L} = 782.2 \text{ cal mole}^{-1}$, $\Delta S^{\alpha \rightarrow L} = 0.324 \text{ cal mole}^{-1} \text{ deg}^{-1}$, $\Delta V^{\alpha \rightarrow L} = 0.324 \text{ cm}^3 \text{ mole}^{-1}$, and

$$\Delta G^{\alpha \rightarrow L} = 782.2 - 1.82 T + 24 (0.324) P. \quad (3)$$

In order to estimate $\Delta G^{\alpha \rightarrow L}$, we shall employ an empirical rule for close-packed metals⁹: $V\Delta S/\Delta V \approx 60 \text{ cal mole}^{-1} \text{ deg}^{-1}$. For indium, we have $\Delta V/V = 0.020$ and therefore one can postulate that $\Delta S^{\beta \rightarrow L} = 1.213$, whence it follows that $\Delta S^{\alpha \rightarrow \beta} = \Delta S^{\alpha \rightarrow L} + \Delta S^{L \rightarrow \beta} = 0.607 \text{ cal mole}^{-1} \text{ deg}^{-1}$. $\Delta S^{\alpha \rightarrow \beta}$ can also be determined using data for the transition of indium to the face-centred cubic structure following the addition of impurities:

$$\Delta S = -Nk [N \ln N - (1-N) \ln (1-N)]. \quad (4)$$

We substitute $N = 19.6\%$ and obtain $\Delta S^{\alpha \rightarrow \beta} = 0.968 \text{ cal mole}^{-1} \text{ deg}^{-1}$. Thus one can assume that $\Delta S^{\alpha \rightarrow \beta} \approx 0.8 \text{ cal mole}^{-1} \text{ deg}^{-1}$. $\Delta H^{\alpha \rightarrow \beta}$ may be estimated from the data of Graham et al.⁶ Extrapolation shows that this transition might occur at 686°K. Then $\Delta H^{\alpha \rightarrow \beta} = 548.8 \text{ cal mole}^{-1}$. According to Moore et al.⁷, the change in the lattice parameters of indium in the transition from the face-centred tetragonal to the face-centred cubic lattice is from $c = 4.800 \text{ \AA}$ and $a = 4.737 \text{ \AA}$ to $a = 4.758 \text{ \AA}$, i.e. $\Delta V^{\alpha \rightarrow \beta} = 0.003 \text{ cm}^3 \text{ mole}^{-1}$. We obtain

$$\Delta G^{\alpha \rightarrow \beta} = 548.8 - 0.8 T - 24 (0.003) P. \quad (5)$$

For the estimation of $\Delta G^{\beta \rightarrow L}$, it is easy to find $\Delta S^{\beta \rightarrow L} = 1.02 \text{ cal mole}^{-1} \text{ deg}^{-1}$ and $\Delta V^{\beta \rightarrow L} = 0.327 \text{ cm}^3 \text{ mole}^{-1}$. Using the above equations, we found that the

transition pressure and temperature (triple point) are $P \approx 2950 \text{ kgs cm}^{-2}$, and $T \approx 441^\circ \text{K}$. The experimental coordinates of the triple point are $P = 3240 \text{ kgf cm}^{-2}$ and $T = 444.9^\circ \text{K}$. If these coordinates are assigned to the triple point, the fusion lines for α -indium and β -indium can be described by Simon's equations:

$$P = 20578[(T/429.42)^{4.133} - 1] \text{ and } P = 28004[(T/444.90)^{2.975} - 1]$$

with a discrepancy of $+4.86 \text{ kgf cm}^{-2}$ with experimental points.

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Variation of the Equivalent Conductance of Electrolyte Solutions with Ion Hydration Energy†

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An empirical relation has been found between the equivalent conductance of an aqueous electrolyte solution and the sum of the reciprocals of the ion hydration energies divided by the electrovalences of the ions. The accuracy of the calculation of the equivalent conductances of solutions of electrolytes of different valence types in their concentration range 0.5-1 N is $\pm 10-20\%$ at 18-20°C.

Analysis of the experimental conductivity data for binary aqueous strong electrolyte solutions reveals an approximate relation between the equivalent conductance Λ and the sum of the reciprocals of the hydration energies of the ions divided by their electrovalences:

$$\Lambda \propto [1 / (\Delta\Phi_c / z_c) + 1 / (\Delta\Phi_a / z_a)]^2, \quad (1)$$

where $\Delta\Phi_c$ and $\Delta\Phi_a$ are the hydration energies of the cation and anion at infinite dilution and 25°C^{1,2} in

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