where, $\varDelta S^\circ_\alpha$ and $\varDelta V^\circ_\alpha$ are the entropy change and the volume change of component α during melting. Similarly, for component β we have

$$-\varDelta S^\circ_\beta \, dT + \varDelta V^\circ_\beta \, dp + \frac{RT}{x_\beta} dx_\beta = 0. \tag{14}$$

Eq's (13) and (14) must be satistied simultaneously at the eutectic point, so we have

$$\left(\frac{dT}{dp}\right)_e = T \frac{x_\alpha \varDelta V^\circ_\alpha + x_\beta \varDelta V^\circ_\beta}{x_\alpha \varDelta h^\circ_\alpha + x_\beta \varDelta h^\circ_\beta}. \tag{15}$$

We can calculate the initial slope of the eutectic temperature for Bi-Cd system using eq. (15). Substituting the experimental values[3) 4)], we have

$$\left(\frac{dT}{dp}\right)_e = 1.02 \times 10^{-1} \quad [\text{deg} \cdot \text{kb}^{-1}].$$

The calculated initial slope has a very small negative value. However, in fact, it has a positive value (see Fig. 2). Therefore, we cannot conclude the character of liquid phase as an ideal solution by considering only the phase diagram at atmospheric pressure.

A general form of eq. (15)[5)] is

$$\left(\frac{dT}{dp}\right)_e = T \frac{x_\alpha \varDelta^l_s V_\alpha + x_\beta \varDelta^l_s V_\beta}{x_\alpha \varDelta^l_s h_\alpha + x_\beta \varDelta^l_s h_\beta} \tag{16}$$

where, $\varDelta^l_S h_\alpha$ is $h^l_\alpha - h^{\circ S}_\alpha$ and h^l_α is a partial moler enthalpy of component α in liquid phase, the other notations are defined similarly. We shall explain Fig. 2 using eq. (16). Here, α and β correspond to bismuth and cadmium. At atmospheric pressure $\varDelta^l_S V_\alpha$ has a small negative or small positive value, as pressure increases it becomes largely negative, after the transition pressure of bismuth I-II it has a positive or small negative value again, and after the transition pressure of bismuth II-III it has a rather large positive value. This behavior of $\varDelta^l_S V_\alpha$ must have some relations with the solid phases of bismuth, but the explanation is difficult even qualitatively.

References

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