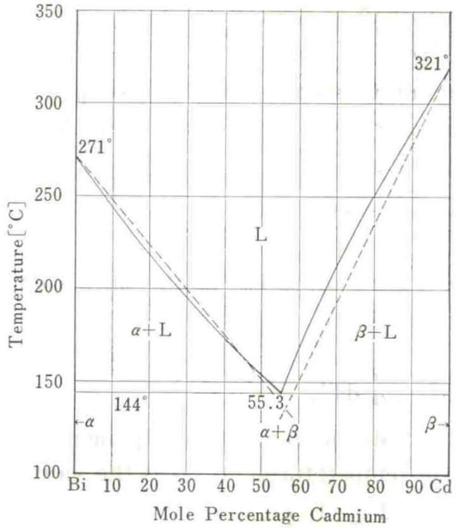

Fig. 3. The phase diagram for Bi-Cd system at atmospheric pressure. The solid curve shows the observed result and[2)] the dashed curve shows the calculated result.

were ambiguous or not appeared. But, nevertheless, the curves obtained in 11 runs had the same figure, that is, the figure shows the effect of pressure on the eutectic point.

In fact, we could not obtain correct solidification curves at high pressure. But ambiguous signals on a solidification curves were appeared sometimes, and we can say that the composition at the eutectic point may be nearly independent of pressure.

Now, we shall consider thermodynamically the Bi-Cd system. The solid curve in Fig. 3 shows the phase diagram for Bi-Cd system at atmospheric pressure[2)]. In two components (say α and β) system such as bismuth and cadmium the chemical potentials for component α and component β in liquid phase are generally given by

$$\mu_\alpha^1 = \mu_\alpha^{\circ 1} + \mathrm{RT}\ln \mathrm{x}\alpha\,\gamma\alpha, \tag{1}$$

and

$$\mu_\beta^1 = \mu_\beta^{\circ 1} + \mathrm{RT}\ln \mathrm{x}\beta\,\gamma\beta, \tag{2}$$

where a, 1, γ's, and x's mean a pure component, liquid phase, activity coefficients and mole fractions. On the solidification curves, the following relations must be satisfied,

$$\mu_\alpha^{\circ\mathrm{S}} = \mu_\alpha^1 = \mu_\alpha^{\circ 1} + \mathrm{RT}\ln \mathrm{x}\alpha\,\gamma\alpha \tag{3}$$

and

$$\mu_\beta^{\circ\mathrm{S}} = \mu_\beta^1 = \mu_\beta^{\circ 1} + \mathrm{RT}\ln \mathrm{x}\beta\,\gamma\beta, \tag{4}$$

where s means solid phase. Eq. (3) becomes

$$\ln x\alpha\,\gamma\alpha = -\frac{\mu_\alpha^{\circ 1} - \mu_\alpha^{\circ S}}{RT} = -\frac{\Delta\mu_\alpha^0}{RT}. \tag{5}$$

$\Delta\mu_\alpha'$ is the function of only temperature, because pressure is keeped constant at Po. So $\Delta\mu_\alpha^\circ$ is derived from the latent heat of fusion of the pure component α by the equation

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta\mu_\alpha^\circ}{T}\right)\right]_{P_0} = -\frac{\Delta h_\alpha^\circ}{T^2}, \tag{6}$$

where Δh_α° is the latent heat of fusion of the pure component α. Integrating eq. (6), we have

$$\Delta\mu_\alpha^\circ = -T\int_{T_\alpha^\circ}^{T} \frac{\Delta h_\alpha^\circ}{T'^2}\,dT', \tag{7}$$

where T_α° is the melting point of the pure component α at pressure Po. If Δh_α° is nearly independent of temperature and takes the value at T_α°, eq. (7) becomes

$$\Delta\mu_\alpha^\circ = -T\Delta h_\alpha^\circ\left(-\frac{1}{T} + \frac{1}{T_\alpha^\circ}\right)$$

and eq. (5) becomes

$$\ln x_\alpha\,\gamma_\alpha = \frac{\Delta h_\alpha^\circ}{R}\left(-\frac{1}{T} + \frac{1}{T_\alpha^\circ}\right), \tag{8}$$

similarly, we have

$$\ln x_\beta\,\gamma_\beta = \frac{\Delta h_\beta^\circ}{R}\left(-\frac{1}{T} + \frac{1}{T_\beta^\circ}\right). \tag{9}$$

For Bi-Cd system, α, β correspond to bismuth and cadmium. Δh_α°, Δh_β°, T_α° and T_β° are 2.60 kcal/col, 1.53 kcal/mol, 271°C and 321°C[3]. We assume the liquid phase as the ideal solution in the first place. Eq.'s (8) and (9) become

$$\ln(1-x) = 1.30\left(-\frac{1}{T} + \frac{1}{544}\right)\cdot 10^3$$

and

$$\ln x = 0.765\left(-\frac{1}{T} + \frac{1}{594}\right)\cdot 10^3. \tag{11}$$

Eq's (10) and (11) determine the solidification curves and the eutectic point. The calculated results are given by the dashed curves in Fig. 3, which agree well with the experimental result as a whole. Therefore, the liquid phase may be considered as a nearly ideal solution.

Next, we shall consider the effect of pressure on the eutectic point. The differencial of eq. (5) becomes

$$d\ln x_\alpha = -d\left(\frac{\Delta\mu_\alpha^\circ}{RT}\right). \tag{12}$$

Here, we make the approximation of $\gamma_\alpha = 1$. This is equivalent to

$$-\Delta S_\alpha^\circ\,dT + \Delta V_\alpha^\circ\,dp + \frac{RT}{x_\alpha}dx_\alpha = 0 \tag{13}$$