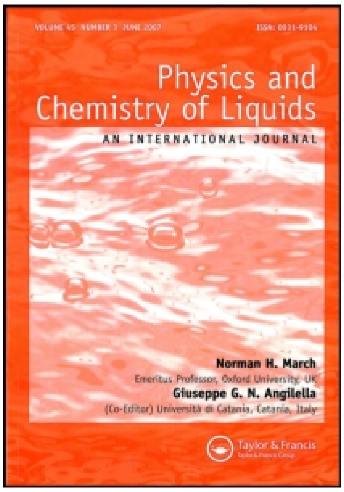

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Pressure Effect on the Concentration Fluctuations for Liquid Na–Ga and Na–Cd Mixtures with S-Shape Liquidus Curves

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Measurements of the electromotive force (EMF) for liquid Na–Ga and Na–Cd mixtures have been made up to 630°C and 700 bar by using β-alumina as a separator. The pressure variations of thermodynamic quantities, such as free energy, enthalpy and entropy, etc., are obtained. The concentration variation of the molar volume of mixing is deduced from the relative partial molar volume determined directly from the pressure derivative of the EMF. The concentration fluctuations for both mixtures are large in the Na-rich concentration range and diminish considerably by a slight application of pressure. The difference of the pressure effect on the concentration fluctuations between the liquid Na–Ga and Na–Cd mixtures is discussed.

1 INTRODUCTION

The studies of the pressure effect on the two-phase region in liquid binary mixtures[1–4] revealed that the two-phase region disappears under high pressure and there appears the S-shape liquidus curve. Some recent investigations[5–11] have directed attention towards the thermodynamic properties of liquid metal mixtures with the S-shape liquidus curves.

In previous paper[12] we reported the pressure effect on the electromotive force (EMF) of the liquid Na–Ga mixture, in which the S-shape liquidus curve appears[13] in the concentration range between Na and the stable stoichiometric compound Na_5Ga_8 (m.p. 556°C) at atmospheric pressure. It was found[12] that the concentration fluctuations, $S_{cc}(0)$ for the liquid mixture along the S-shape liquidus curve are much larger than that for ideal mixture as if a miscibility gap is submerged just below the liquidus curve and diminishes remarkably by a slight application of pressure.

In the liquid Na–Cd mixture the S-shape liquidus curve also appears in the Na-rich concentration range. This S-shape liquidus curve[14] ends in the vicinity of the concentration corresponding to the stable stoichiometric compound $NaCd_2$ (m.p. 384°C). The large concentration fluctuations along the S-shape liquidus curve are considered to be related to the immiscible nature between Na and the stable stoichiometric compound $NaCd_2$.

In this paper, we report the results of the EMF measurements under pressure for the liquid Na–Cd mixture together with the liquid Na–Ga mixture over the wide concentration range. The pressure variations of the thermodynamic quantities, such as free energy, enthalpy, entropy, etc., are studied. The concentration variation of the volume of mixing is deduced from the relative partial molar volume determined directly from the pessure derivative of EMF, $(\partial E/\partial P)_T$. From these results we discuss the difference of the pressure effect on the concentration fluctuations between the liquid Na–Cd and Na–Ga mixtures.

2 EXPERIMENTAL PROCEDURE

The electromotive force (EMF) of a concentration cell was measured by using as a separator the solid superionic conductor β-alumina, in which Na^+ ions diffuse rapidly. The cell used was:

$$\text{Mo-wire, Na}(L)/\beta\text{-alumina}/\text{Na}_xM_{1-x}(L)\text{, Mo-wire,}$$

where M is Cd or Ga, x the atomic fraction of sodium and L denotes liquid state. For the liquid Na–Cd mixture the stainless steel wire was also used. The cell assembly developed for the present high pressure measurement is described elsewhere.[12] A mixture of Ga (99.999% purity) and Na (99.9% purity) or a mixture of Cd (99.999% purity) and Na was contained in a closed end β-alumina tube (10 mm in outer diameter, 6.5 mm in inner diameter and 70 mm in length) and was connected to Mo-wire whose position was settled by fired pyrophyllite block. The β-alumina tube was dipped into a liquid Na in a stainless steel vessel. The β-alumina tube was fixed on the outer alumina tube by glass frit. The whole cell was set in an internally heated autoclave and heated up to 630°C. Pressures up to 700 bar were generated by using argon gas as pressure transmitting medium. The EMF was measured to ±2 μV with a digital voltmeter. The results obtained on heating and cooling agreed satisfactorily. The concentration of Na in the mixture was both established and measured by coulometric titration. The error of pressure was less than 3%. The error of temperature was less than 2°C. The error of concentration, x was within 0.003.

3 RESULTS AND DISCUSSION

Figures 1 and 2 show the pressure variations of EMF, $E(x, T, P)$ for the liquid Na–Ga mixture at 570°C and those for the liquid Na–Cd mixture at 400°C, respectively. For both mixtures E changes almost linearly with pressure. For the liquid Na–Ga mixture the values of E obtained by extrapolating the curves in Figure 1 to $P = 0$ are slightly large compared to the results at atmospheric pressure determined by Tamaki and Cusack[6] using the β-alumina as a separator. The values of E obtained at $P = 0$ for the liquid Na–Cd mixture are in fairly good agreement with those at atmospheric pressure in the Na concentration range $x \gtrsim 0.3$ by Bartlett *et al.*[15] using the borosilicate glass as a separator. In the concentration range $x < 0.3$ the agreement between our results and theirs is not satisfactory.

In Figure 3 the concentration variations of the pressure derivative of E, $(\partial E/\partial P)_{T,x}$ are shown for the liquid Na–Ga and Na–Cd mixtures at 570°C and 400°C, respectively. It is found that $(\partial E/\partial P)_{T,x}$ is positive over the whole concentration range and becomes small with increasing Na concentration. It should be noted that there appear discontinuities in the concentration dependence of $(\partial E/\partial P)_{T,x}$ around $x = 0.7$ for the liquid Na–Ga mixture and $x = 0.65$ for the liquid Na–Cd mixture.

Figure 4 shows some results of the temperature variation of E for the liquid Na–Ga and Na–Cd mixtures at $P = 1$ bar and 500 bar, respectively. For the liquid Na–Ga mixture with $x = 0.113$ at 1 bar E decreases with increasing temperature and the rate of decrease becomes small at high temperatures. At 500 bar E decreases almost linearly with temperature. For the mixtures with $x = 0.530$ and 0.730 the slope $(\partial E/\partial T)_{P,x}$ is positive and little pressure dependent in contrast to the mixture with $x = 0.113$. Similar behaviors are seen for the liquid Na–Cd mixtures with $x = 0.120$, 0.510 and 0.750.

Figure 5 shows the concentration variations of the temperature derivative of E, $(\partial E/\partial T)_{P,x}$ at 1 bar for the liquid Na–Ga and Na–Cd mixtures at 570°C and 400°C, respectively. For the liquid Na–Ga mixture $(\partial E/\partial T)_{P,x}$ in the Na-rich concentration range is positive and shows a maximum around $x = 0.53$. In the concentration range $x < 0.44$ $(\partial E/\partial T)_{P,x}$ becomes negative

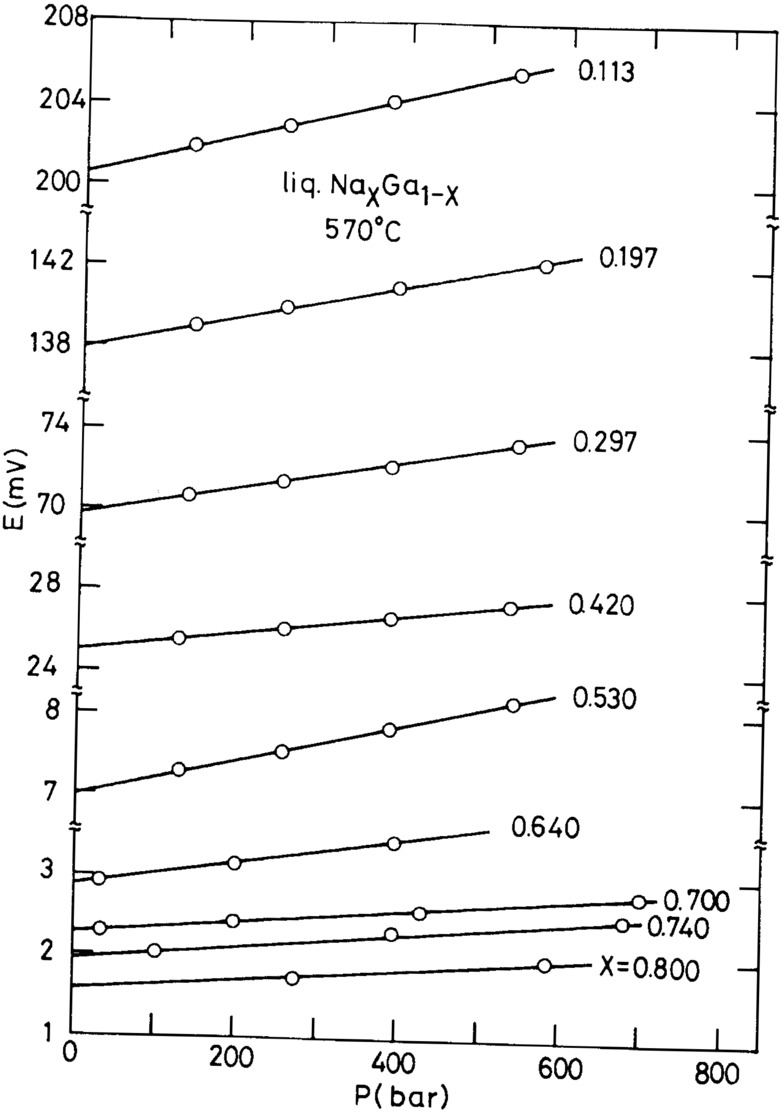

FIGURE 1 EMF vs. pressure for the liquid Na_xGa_{1-x} mixture at 570°C at different concentrations.

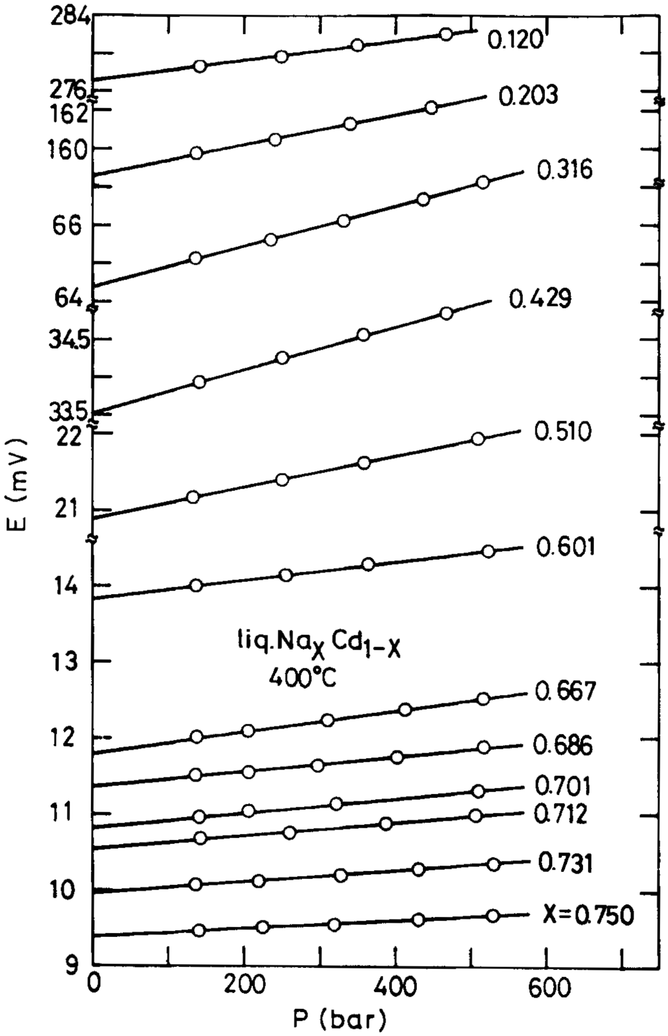

FIGURE 2 EMF vs. pressure for the liquid Na_xCd_{1-x} mixture at 400°C at different concentrations.

and shows a minimum with a large negative value around $x = 0.17$. Interestingly, there appears a slight discontinuity in the concentration dependence of $(\partial E/\partial T)_{P,x}$ around $x = 0.7$ where the anomaly is observed for the concentration dependence of $(\partial E/\partial P)_{T,x}$.

For the liquid Na-Cd mixture $(\partial E/\partial T)_{P,x}$ changes sign around $x = 0.24$ and there appears a slight discontinuity in the concentration dependence of

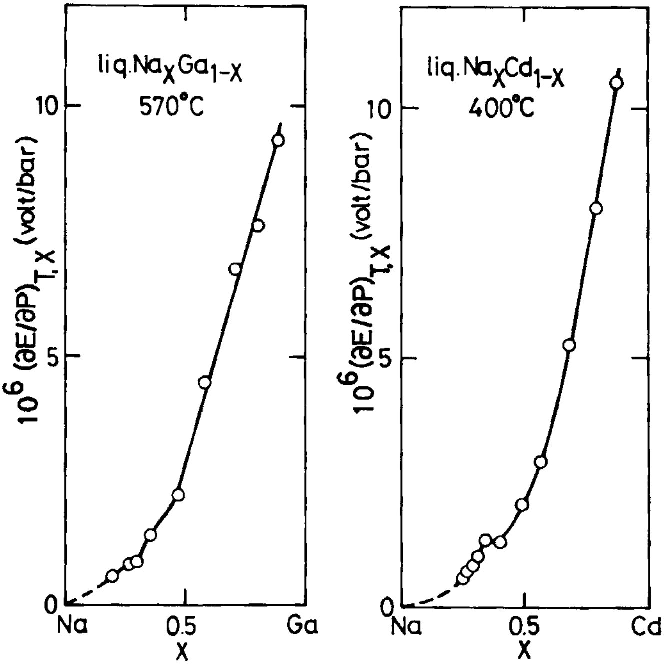

FIGURE 3 Pressure derivative of EMF, $(\partial E/\partial P)_{T,x}$ vs. atomic fraction of Na for liquid Na_xGa_{1-x} mixture at 570°C and for the liquid Na_xCd_{1-x} mixture at 400°C.

$(\partial E/\partial T)_{P,x}$ around $x = 0.65$ at which the anomaly is found for the concentration dependence of $(\partial E/\partial P)_{T,x}$. The behaviors at 500 bar for both mixtures are nearly the same as those shown in Figure 5.

The relevant thermodynamics is straightforward.[16] The relative partial molar thermodynamic properties of Na can be calculated from E using the following relations:

$$\Delta \bar{G}_{Na} = -FE \tag{1}$$

$$\Delta \bar{S}_{Na} = F\left(\frac{\partial E}{\partial T}\right)_{P,x} \tag{2}$$

$$\Delta \bar{H}_{Na} = F\left[T\left(\frac{\partial E}{\partial T}\right)_{P,x} - E\right] \tag{3}$$

$$\Delta \bar{V}_{Na} = -F\left(\frac{\partial E}{\partial P}\right)_{T,x}, \tag{4}$$

where $\Delta \bar{G}_{Na}$, $\Delta \bar{S}_{Na}$, $\Delta \bar{H}_{Na}$ and $\Delta \bar{V}_{Na}$ are the relative partial molar Gibbs free energy, entropy, enthalpy and volume of Na, respectively; F is the Faraday

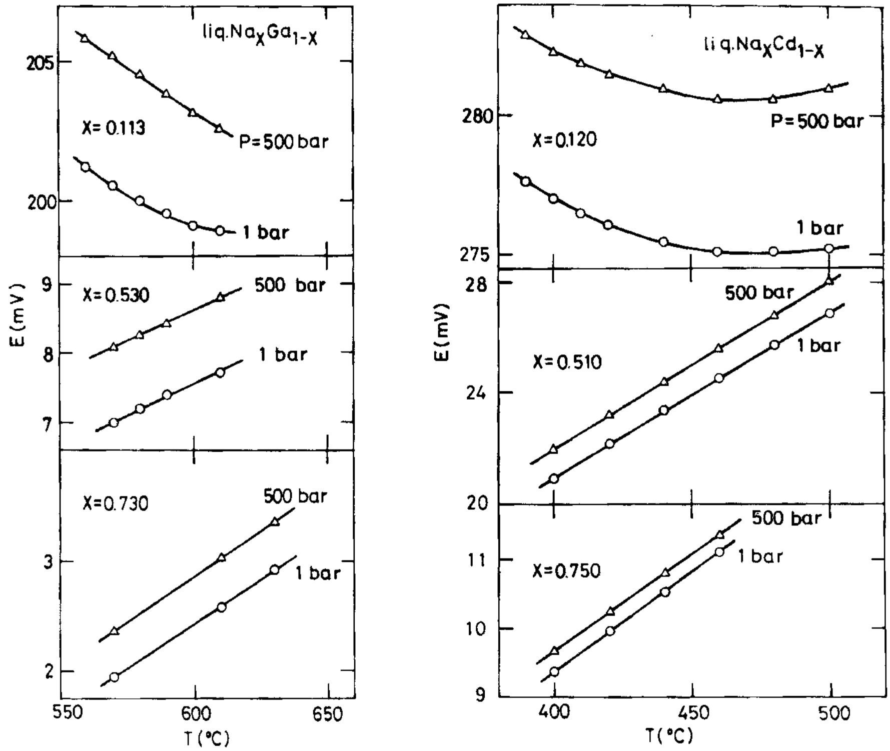

FIGURE 4 EMF vs. temperature for the liquid Na_xGa_{1-x} mixture and for the liquid Na_xCd_{1-x} mixture at different pressures.

constant and the valency of sodium ion is taken to be one. The activity of Na, $\mathscr{A}_{Na}(x, T, P)$ in the liquid mixtures is given by

$$-FE = RT \ln \mathscr{A}_{Na}, \tag{5}$$

where R is the gas constant.

The corresponding functions for Ga or Cd are obtained from the expression like

$$\Delta\bar{G}_{Cd} = -\frac{\Delta\bar{G}_{Na}x}{(1-x)} + \int_0^x \left[\frac{\Delta\bar{G}_{Na}}{(1-x)^2}\right] dx, \tag{6}$$

where the integral is evaluated graphically. From the relative partial thermodynamic functions the integral values are calculated with expressions as follows:

$$\Delta G_m = x\Delta\bar{G}_{Na} + (1-x)\Delta\bar{G}_{Cd}. \tag{7}$$

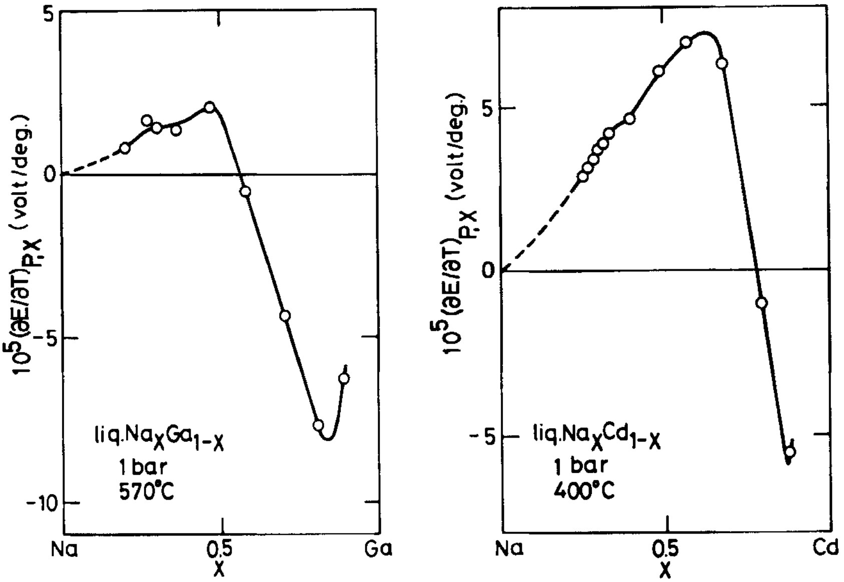

FIGURE 5 Temperature derivative of EMF, $(\partial E/\partial T)_{P,x}$ vs. atomic fraction of Na for the liquid Na_xGa_{1-x} mixture at 570°C and for the liquid Na_xCd_{1-x} mixture at 400°C at atmospheric pressure.

The calculated values of ΔG_m, ΔH_m, ΔS_m and the heat capacity of mixing, ΔC_p^{17} at $P = 1$ bar and 500 bar are presented in Table I for the liquid Na–Ga mixture at 570°C and in Table II for the liquid Na–Cd mixture at 400°C. The values of ΔG_m and ΔH_m for both mixtures are negative over the whole concentration range and become small with increasing pressure. The values of ΔS_m for both mixtures show maxima with positive values in the Na-rich concentration range and minima with negative values in the Na-poor concentration range. For both mixtures ΔS_m decreases with increasing pressure.

The long wavelength limit of the concentration-concentration correlation $S_{cc}(0)$ of liquid binary mixtures gives the concentration fluctuations and is defined as follows:[18]

$$\begin{aligned} S_{cc}(0; x, T, P) &= N\langle(\Delta x)^2\rangle = RT(\partial^2 \Delta G_m/\partial x^2)^{-1}_{T,P} \\ &= (1-x)\left(\frac{1}{\mathscr{A}_{\mathrm{Na}}}\cdot\frac{\partial \mathscr{A}_{\mathrm{Na}}}{\partial x}\right)^{-1}_{T,P}. \qquad (8) \end{aligned}$$

The values of $S_{cc}(0)$ are deduced graphically from the results of $\mathscr{A}_{\mathrm{Na}}$ using Eq. (8). In Figure 6 the concentration variations of $S_{cc}(0)$ at different pressures are shown for the liquid Na–Ga mixture at 570°C and in Figure 7 for the liquid Na–Cd mixture at 400°C. The values of $S_{cc}(0)$ for both mixtures in the

TABLE I

The values of ΔG_m, ΔH_m, ΔS_m and ΔC_p for the liquid Na_xGa_{1-x} mixture at 570°C at different pressures, together with molar volume of mixing and volume fraction of Na

	ΔG_m(cal/mol)		ΔH_m(cal/mol)		ΔS_m(cal/K · mol)		ΔC_p(cal/K · mol)			
x	1 bar	500 bar	1 bar	500 bar	1 bar	500 bar	1 bar	500 bar	V_m (cm^3/mol)	ϕ_{Na}
0.0	0	0	0	0	0	0	0	0	12.1	0
0.1	−599	−614	−677	−693	−0.093	−0.094	2.1	0.5	12.7	0.15
0.2	−972	−994	−1184	−1244	−0.251	−0.296	3.6	1.4	13.5	0.31
0.3	−1134	−1162	−1470	−1572	−0.398	−0.486	4.3	2.6	14.4	0.45
0.4	−1126	−1160	−1467	−1582	−0.404	−0.501	4.6	3.1	15.6	0.60
0.5	−1012	−1046	−1261	−1366	−0.295	−0.380	4.2	2.9	17.1	0.74
0.6	−842	−873	−992	−1087	−0.178	−0.254	3.3	2.4	18.9	0.84
0.7	−649	−675	−661	−732	−0.014	−0.068	2.5	1.8	20.9	0.91
0.8	−447	−467	−385	−429	0.073	0.046	1.7	1.2	23.1	0.96
0.9	−235	−247	−144	−160	0.107	0.102	0.8	0.6	25.4	0.99
1.0	0	0	0	0	0	0	0	0	28.2	1.00

TABLE II

The values of ΔG_m, ΔH_m, ΔS_m and ΔC_p for the liquid Na_xCd_{1-x} mixture at 400°C at different pressures, together with molar volume of mixing and volume fraction of Na

	ΔG_m(cal/mol)		ΔH_m(cal/mol)		ΔS_m(cal/$K\cdot$mol)		ΔC_p(cal/K $\cdot$ mol)			
x	1 bar	500 bar	1 bar	500 bar	1 bar	500 bar	1 bar	500 bar	V_m (cm^3/mol)	ϕ_{Na}
0.0	0	0	0	0	0	0	0	0	14.1	0
0.1	−842	−909	−900	−965	−0.086	−0.085	1.0	1.0	14.1	0.11
0.2	−1306	−1428	−1422	−1546	−0.172	−0.176	2.2	2.2	14.5	0.27
0.3	−1460	−1593	−1515	−1657	−0.082	−0.097	2.6	2.6	15.2	0.42
0.4	−1425	−1554	−1330	−1473	0.140	0.120	2.4	2.4	16.3	0.58
0.5	−1300	−1413	−1050	−1173	0.372	0.356	2.0	2.0	17.6	0.70
0.6	−1120	−1214	−748	−846	0.553	0.547	1.6	1.6	19.1	0.80
0.7	−912	−983	−468	−540	0.661	0.659	1.2	1.2	20.7	0.87
0.8	−682	−730	−237	−287	0.662	0.658	0.8	0.8	22.5	0.93
0.9	−414	−437	−70	−94	0.511	0.508	0.4	0.4	24.5	0.98
1.0	0	0	0	0	0	0	0	0	26.8	1.00

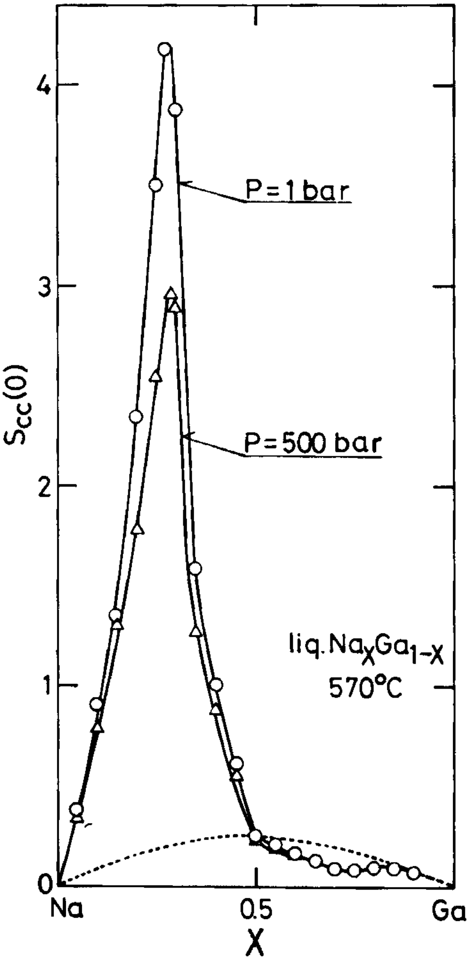

FIGURE 6 Zero wavenumber component, $S_{cc}(0)$ of concentration-concentration correlation in the liquid Na_xGa_{1-x} mixture vs. atomic fraction of Na at 570°C at 1 bar and 500 bar. The dotted curve denotes the value for ideal mixing.

Na concentration range $x > 0.5$ show positive deviations from the value of $S^0_{cc} = x(1 - x)$ for ideal mixing. In the range $x < 0.5$ $S_{cc}(0)$ for both mixtures show negative deviations from S^0_{cc}.

For the liquid Na–Ga mixture $S_{cc}(0)$ at atmospheric pressure shows a prominent peak around $x = 0.72$ with its height nearly 4. This indicates a tendency for Na and Ga atoms to cluster separately from one another. The values of $S_{cc}(0)$ in the Na-rich concentration range decrease considerably with increasing pressure, but there is little change in $S_{cc}(0)$ with pressure in the

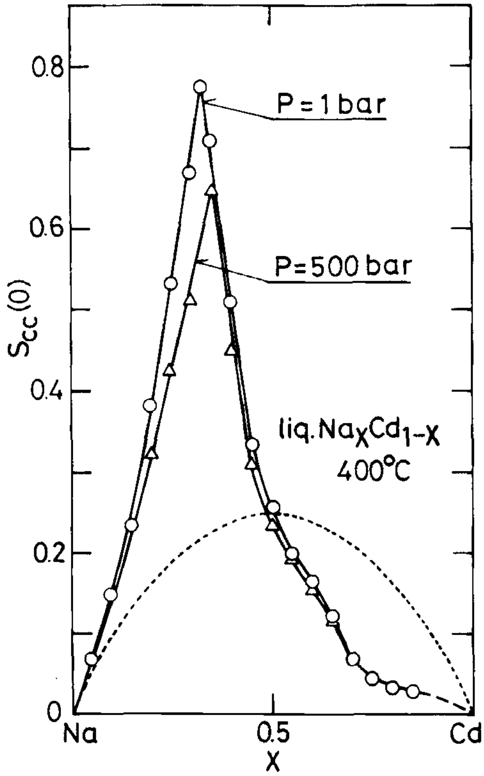

FIGURE 7 Zero wavenumber component, $S_{cc}(0)$ of concentration-concentration correlation in the liquid Na_xCd_{1-x} mixture vs. atomic fraction of Na at 400°C at 1 bar and 500 bar. The dotted curve denotes the value for ideal mixing.

Ga-rich concentration range including the compound Na_5Ga_8. It is noted that the peak position of $S_{cc}(0)$ is shifted slightly to lower Na concentration by applying pressure. For the liquid Na–Cd mixture $S_{cc}(0)$ at atmospheric pressure shows a peak around $x = 0.68$ with its height nearly 0.8. In the Na-rich concentration range $S_{cc}(0)$ decreases with increasing pressure and its peak position is shifted appreciably to higher Cd concentration by applying pressure. In the Cd-rich concentration range including the compound $NaCd_2$ the pressure variation of $S_{cc}(0)$ is small.

The excess molar Gibbs free energy, ΔG_m^{ex} is evaluated by the following expression[16]

$$\Delta G_m^{ex} = \Delta G_m - RT[x \ln x + (1 - x) \ln(1 - x)]. \tag{9}$$

Figure 8 shows the concentration variations of ΔG_m^{ex} for the liquid Na–Ga mixture at 570°C and Na–Cd mixture at 400°C at different pressures. The

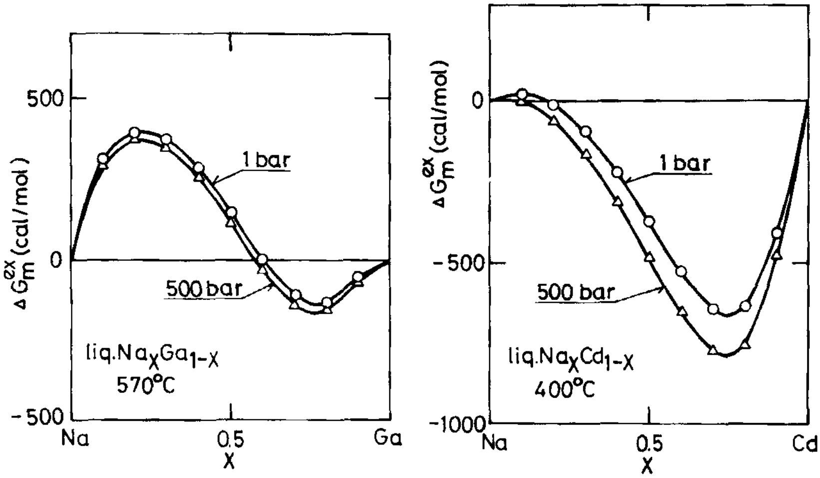

FIGURE 8 Excess molar Gibbs free energy, ΔG_m^{ex} vs. atomic fraction of Na for the liquid Na_xGa_{1-x} mixture at 570°C and for the liquid Na_xCd_{1-x} mixture at 400°C at different pressures.

positive deviation from the ideal Gibbs free energy in the Na-rich concentration range for the liquid Na–Ga mixture is much larger compared to that for the liquid Na–Cd mixture. This may suggest that an immiscible tendency between Na and Na_5Ga_8 in the liquid state is larger than that between Na and $NaCd_2$. The values of ΔG_m^{ex} for both mixtures decrease with increasing pressure. Therefore, $S_{cc}(0)$ for both mixtures diminish by application of pressure. The pressure derivative of ΔG_m^{ex} for the liquid Na–Cd mixtures around the concentration where the stable stoichiometric compound $NaCd_2$ is formed is about 4 times larger than that for the liquid Na–Ga mixture around the concentration where the stable stoichiometric compound Na_5Ga_8 is formed. It is considered that the large pressure shift in the peak position of $S_{cc}(0)$ for the liquid Na–Cd mixture is associated with the large pressure change in ΔG_m^{ex} around the concentration corresponding to $NaCd_2$.

From the data for the pressure variations of EMF, the relative partial molar volume of Na, $\Delta \bar{V}_{Na}$ for both mixtures can be calculated by using Eq. (4). The values of $\Delta \bar{V}_{Na}$ are negative over the whole concentration range and almost pressure independent. They become small with decreasing Na concentration for both mixtures. Following equations (6) and (7) the excess molar volume of the mixture

$$\Delta V_m^{ex} = V_m - V_{id} \tag{10}$$

can be deduced,[16] where V_m is the molar volume of the mixture and V_{id} the volume for ideal mixing. In order to determine V_m at atmospheric pressure the density data for Na[19], Cd[19] and Ga[20] are used. Figures 9 and 10 show the

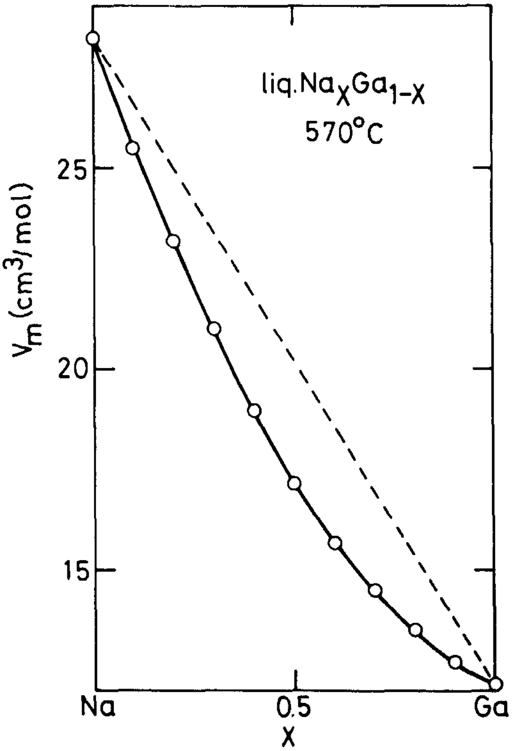

FIGURE 9 Molar volume of mixing, V_m vs. atomic fraction of Na for the liquid Na_xGa_{1-x} mixture at 570°C at atmospheric pressure. The dashed curve denotes the volume for ideal mixing.

concentration variations of V_m at atmospheric pressure for the liquid Na-Ga mixture at 570°C and for the liquid Na-Cd mixture at 400°C, respectively. The values of V_m are compiled in Tables I and II, together with the values of the volume fraction of Na, ϕ_{Na} which is defined[21] as $x\bar{V}_{Na}/V_m$. Here, $\bar{V}_{Na}$ is the partial molar volume of Na.

The values of V_m show negative deviation from the ideal behavior; that is, the volume contracts by mixing the component atoms. The volume contraction $\Delta V_m^{ex}/V_{id}$ is estimated to be as a minimum value about -15% at 400°C around the concentration corresponding to $NaCd_2$ and about -16% at 570°C around the concentration corresponding to Na_5Ga_8.

From Eq. (8) the pressure derivative of $S_{cc}(0)$ is given as follows:

$$\left(\frac{\partial S_{cc}(0)}{\partial P}\right)_T = -\left[\frac{(S_{cc}(0))^2}{RT}\right]\left(\frac{\partial^2 V_m}{\partial x^2}\right)_T. \qquad (11)$$

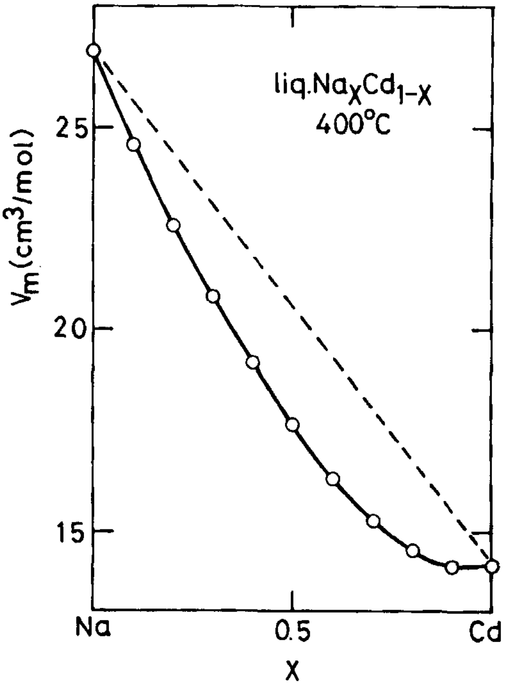

FIGURE 10 Molar volume of mixing, V_m vs. atomic fraction of Na for the liquid Na_xCd_{1-x} mixture at 400°C at atmospheric pressure. The dashed curve denotes the volume for ideal mixing.

Since the signs of $(\partial^2 V_m/\partial x^2)_T$ are positive over the whole concentration range from Figures 9 and 10, the signs of the pressure derivative of $S_{cc}(0)$ for both mixtures are negative from Eq. (11). This is consistent with the observed pressure variations of $S_{cc}(0)$.

It is interesting that the discontinuities of $(\partial E/\partial P)_{T,x}$ in Figure 3 and $(\partial E/\partial T)_{P,x}$ in Figure 5 are observed around the concentrations at which there appear peaks in $S_{cc}(0)$. This evidence means that the large concentration fluctuations give considerable effects on the concentration dependences of $\Delta\bar{S}_{Na}$ and $\Delta\bar{V}_{Na}$, since the concentration derivatives of $\Delta\bar{S}_{Na}$ and $\Delta\bar{V}_{Na}$ are related to $(\partial^2 \Delta G_m/\partial x^2)_{T,P}$.

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