

sponding minimum values of the coefficient Y are [18]

$$Y = \begin{cases} (C_{11} + 2c_{12})(c_{11} - c_{12})/c_{11} & (\alpha < 0) \\ 6(c_{11} + 2c_{12})c_{44}/(c_{11} + 2c_{12} + 4c_{44}) & (\alpha > 0). \end{cases} \quad (2.6)$$

The temperature difference $\Delta T = T_s - T_{s'}$ between the chemical and coherent spinodals (T_s and $T_{s'}$, respectively) may be according to Hilliard[19] approximately written as

$$\Delta T = T_s - T_{s'} = -2\eta^2 Y / \left(\frac{\partial^2 \Delta S}{\partial x^2} \right). \quad (2.7)$$

If ΔS is assumed to consist of the entropy of ideal mixing only [20, 2] equation (2.7) becomes

$$\Delta T = \frac{2\eta^2 Y}{kN_0} x(1-x) \quad (2.8)$$

where k is Boltzmann's constant and N_0 is the number of molecules per unit volume.

The composition dependence of the heat of formation and of the solid solubility were calculated for several pressures in the same manner as in I and II, but with (2.1) as free energy function, and with Q_F , ΔS , V_{ss} and V_M occurring in (2.1) dependent on pressure. As in I and II, the heat of formation has been assumed to be independent of temperature. The pressure dependence of Q_F results from the pressure dependence of the nearest neighbor distance and of the electronic polarizabilities. The pressure dependence of the nearest neighbor distance was calculated from the isothermal bulk modulus and its isothermal pressure derivative obtained from the data presented in Table 1 by using Murnaghan's equation of state[21]. The pressure dependence of the polarizabilities was calculated from the available experimental data of the pressure dependence of the refractive index[30-32] by assuming that the electronic polarizabilities of cations and anions are additive.

Table 1. Isothermal elastic constants (in 10^{11} dynes/cm²) and their isothermal pressure derivatives for several alkali halides

	c^T	c_{12}^T	c_{44}	$(\partial c_{11}^T / \partial p)_T$	$(\partial c_{12}^T / \partial p)_T$	$(\partial c_{44}^T / \partial p)_T$
LiBr	3.74[a]	1.67	1.93	8.02[h]	2.20	0.19
LiI	2.64[b]	0.78	1.35	9.60[h]	2.07	0.09
NaBr	3.82[c]	0.958	1.015	11.04[i]	1.80	0.423
NaI	2.93[d]	0.807	0.742	11.85[d]	2.36	0.584
KBr	3.35[e]	0.450	0.508	13.03[j]	1.66	-0.328
KI	2.62[e]	0.344	0.369	13.93[j]	2.36	-0.241
RbBr	3.10[f]	0.404	0.383	13.43[f]	1.38	-0.54
RbI	2.52[f]	0.322	0.279	13.64[f]	1.45	-0.50
NaCl	4.77[g]	1.13	1.27	11.74[g]	2.16	0.37
KCl	3.97[g]	0.615	0.630	12.89[g]	1.67	-0.385

[a] Calculated from adiabatic data of Haussühl[22].

[b] Calculated from adiabatic data of Haussühl[23].

[c] Koliwad *et al.*[24].

[d] Barsch and Shull[25].

[e] Reddy and Ruoff[26].

[f] Chang and Barsch[27].

[g] Bartels and Schuele[28].

[h] Theoretical data by Ghate[29] (Table 4, repulsive parameter $b = 0.333$).

[i] Calculated from the isothermal derivatives of the adiabatic elastic constants of Koliwad *et al.*[24].

[j] Calculated from the isothermal derivatives of the adiabatic elastic constants of Reddy and Ruoff[26].

The volume of the solid solution, V_{ss} , is calculated by assuming Vegard's law for the nearest neighbor distance of the solid solution, i.e. a linear variation with composition. Even though the individual volumes, V_{ss} and V_M , are temperature-dependent, the difference ($V_{ss} - V_M$) is assumed to be independent of temperature*, but dependent on pressure according to Murnaghan's equation of state. Below 100 kbar, the work term, $p(V_{ss} - V_M)$, in (2.1) amounts only to less than about 10 per cent of the heat of formation, so that neglecting the temperature dependence of this term is not critical.

The total entropy of solution consists of two parts, the entropy of ideal mixing, ΔS^{id} , and the vibrational contribution, ΔS^{vib} , as explained in II. The term, ΔS^{vib} , is assumed to be independent of temperature. Calculations were made to test this assumption about ΔS^{vib} and it was found that ΔS^{vib} was essentially independent of temperature. The pressure dependence of the vibrational contribution to the entropy was, however, taken into account through the pressure dependence of the constant A occurring in the formula for the composition dependence of the elastic constant c_{11} II:

$$\Delta c_{11} = Ax(1-x) \quad (2.9)$$

Δc_{11} is the difference between the elastic constant of the solid solution and that of the

solid mixture, and A depends on the molar volumes and the bulk moduli of the two end members of the solid solution series (equations (2.8) and (2.13) of II), which are here considered as pressure-dependent according to Murnaghan's equation of state, and according to the linear pressure dependence of the elastic constants, respectively. For the alkali halide systems contained in Table 1 the constant A and the relative deviation $\Delta c_{11}/c_{11}^{Mix}$ of the elastic constant c_{11} in the solid solution from the value in the solid mixture are for a composition $x = 0.5$ presented in Table 2 for several pressures.

3. RESULTS AND DISCUSSION

Solid solubility curves and chemical spinodals were calculated for five alkali halide systems for several pressures from

Table 2. The quantity A (in 10^{11} dynes/cm²) defined in equation (2.9) and the predicted relative deviation (in per cent) of the elastic constant c_{11} for the solid solution from the value for the solid mixture at $T = 300^\circ\text{K}$ and at the composition $x = 0.5$ for several pressures p (in kbar)

System	p	A	$\frac{\Delta c_{11}(0.5)}{c_{11}^{Mix}(0.5)}$
LiBr-LiI	0	-2.514	-19.7
	50	-0.887	-2.9
	100	-0.439	-0.91
NaBr-NaI	0	-0.587	-4.3
	5	-0.476	-3.01
	10	-0.390	-2.16
	50	-0.055	-0.15
KBr-KI	100	+0.139	+0.23
	0	-0.444	-3.7
	10	-0.233	-1.3
RbBr-RbI	20	-0.124	-0.55
	0	-0.314	-2.8
	2	-0.293	-2.4
NaCl-KCl	4	-0.275	-2.1
	0	-1.225	-7.0
	10	-1.048	-4.7
	20	-0.935	-3.4

*As the reviewer has kindly suggested it would have been easy to take into account the temperature dependence of the term $\Delta V = V_{ss} - V_M$ in an approximate manner by assuming, e.g. the ratio $\Delta V/\bar{V}$ to be temperature independent, so that ΔV has the same thermal expansion as $\bar{V} = (V_{ss} + V_M)/2$. This improvement would have increased the work term $p\Delta V$ by about 5 to 10 per cent, and the total Gibbs free energy by about 0.5 to 1 per cent, at the highest pressures considered, and at temperatures corresponding to the maximum of the exsolution dome. At lower pressures and/or temperatures the change would be proportionally smaller. It is therefore safe to assume that the resulting changes would be barely noticeable in Figs. 1-5. It would be desirable, however, to have this effect included in any future calculations.