Fig. 2(b). Exsolution dome and chemical spinodal of NaBr–NaI for zero pressure and for two pressures above the transition pressure.

Fig. 3. Exsolution dome and chemical spinodal of KBr–KI for three pressures.

NaCl–KCl the difference ΔT increases initially and decreases after passing through a maximum; however, the initial increase is not large enough to cause a decrease in the maximum temperature T_{coh}.

The different pressure dependence of the temperature difference ΔT arises from the competing effects of the pressure dependence of the different factors (equation (2.8)). The elastic modulus Y usually increases monotonically with pressure, except for KBr–KI and RbBr–RbI, where a maximum occurs near 15 and 2 kbar, respectively. These maxima are caused by the negative pressure coefficient of the shear modulus c_{44}, but since they are very broad they have no effect on the temperature difference ΔT which for these two systems decreases monotonically with pressure. The factor η decreases monotonically with pressure, except for NaBr–NaI, where a minimum occurs, which has, however, no ef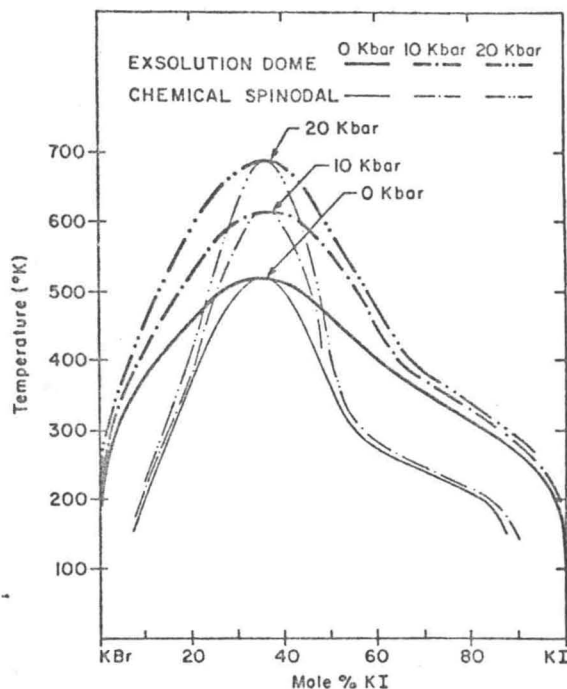fect on the monotonical increase of the temperature difference with pressure. The third factor $1/N_0$ is the volume per molecule and decreases monotonically with pressure.

The data of Table 3 indicate that for LiBr–LiI and for KBr–KI the maximum of the coherent spinodal should lie very close to 300°K, so that no spinodal decomposition is to be expected at room temperature. For NaBr–NaI, RbBr–RbI and NaCl–KCl, however, the maximum of the coherent spinodal lies from 50° to 100°C above room temperature, and spinodal decomposition should take place. This is contrary to the observations of Wolfson et al.[14], who did not observe spinodal decomposition in NaCl–KCl at room temperature. Probably this discrepancy reflects the large uncertainty of the theoretical estimates for the coherent spinodal.

In spite of the uncertainty in the absolute magnitude of T_{coh} one should expect the pressure dependence to be predicted correctly. Thus spinodal decomposition may be ex-

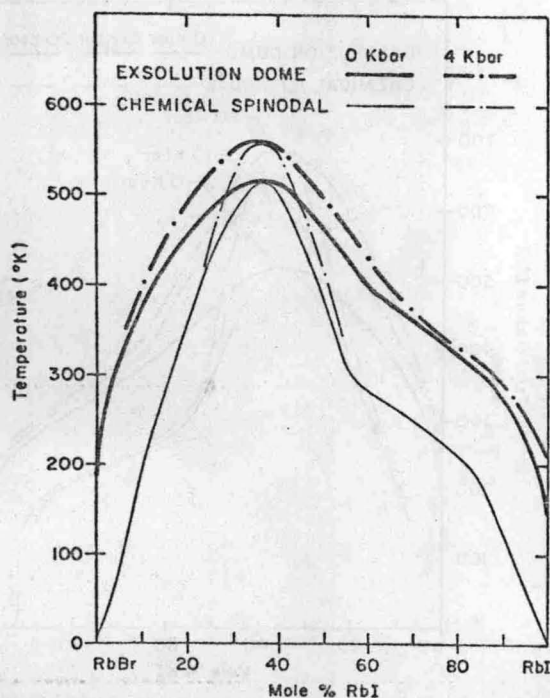Fig. 4. Exsolution dome and chemical spinodal of RbBr–RbI for two pressures.

Fig. 5. Solid solubility curves for NaCl–KCl at two different pressures.

pected to occur at high pressure for LiBr–LiI, KBr–KI, and KCl–NaCl, whereas in NaBr–NaI very high pressure (above 50 kbar) should suppress spinodal decomposition if it were ever favored at intermediate pressures. For RbBr–RbI spinodal decomposition may take place at pressures close to the phase transition at 4 kbar, but the rise of T_{coh} is not large enough to predict this effect with certainty.

It is interesting to note that for LiBr–LiI, NaBr–NaI and NaCl–KCl the elastic anisotropy factor α changes sign at pressures of the order of 45, 35 and 8 kbar, respectively. One may therefore conclude that for these systems the direction of spinodal decomposition should change from ⟨100⟩ at low pressures to ⟨111⟩ at high pressures, whereas for the remaining systems KBr–KI and RbBr–RbI decomposition should occur in ⟨111⟩ at all pressures.

For the system NaCl–KCl the spinodal curves have not been included in Fig. 5 since

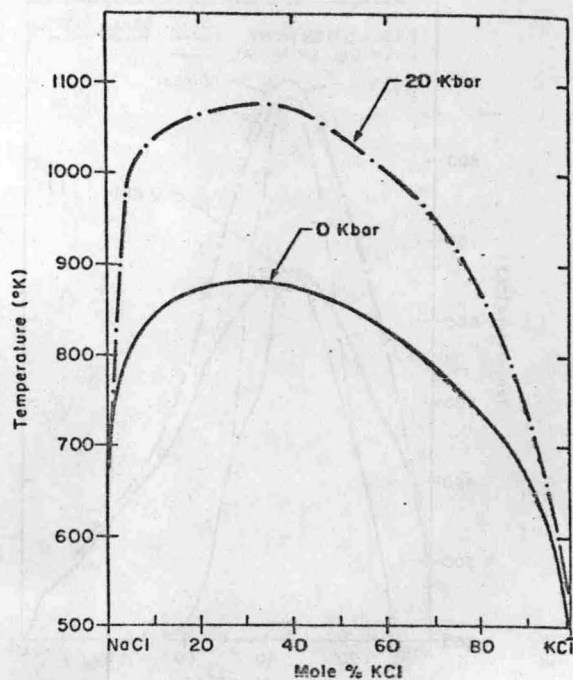for this system the free energy-vs. composition curve shows three minima, instead of the usual two. The exsolution dome shown in Fig. 5 was obtained from the common tangent to the two minima corresponding to the lowest and highest compositions, respectively.

The occurrence of three minima in the free energy curve would be indicative of an ordered phase resulting in two exsolution domes and two spinodal curves. No such effect has been observed, however, in alkali halides. In two papers, which only recently came to our attention, Hovi[41, 42] reports theoretical results for KBr–KI and RbBr–RbI solid solutions which show the same effect. These results are based on the theory of Wasastjerna [43, 44] which includes the entropy contribution from local order but does not include the vibrational entropy contribution. Since for the theoretical model used in the present work only one solubility gap is obtained for KBr–KI and RbBr–RbI it is suggested that the occurrence of two solubility gaps arises from the entropy term, and not from the heat of formation. The results obtained for these two systems and, on the basis of the present model, for NaCl–KCl seem to indicate that both the entropy contribution from local order and the vibrational entropy can cause two solubility gaps. Since experimental verification of two solubility gaps would be a rather difficult task the question must remain undecided whether the theoretical entropy contributions due to local order