

bands, LO (Γ), LA (M), and TA (M), is weak. The TA (M) and LA (M) bands are due to residual disorder. The libration ν_6 is forbidden by symmetry but the second harmonic $2\nu_6$ is allowed. In the phase diagram for NH_4I derived from these measurements the triple point is found at higher pressure than in the diagrams of Zlunitsyn (1938, 1939) and of Stevenson (1961) (figure 2).

Special attention was given to the possible occurrence of a fifth phase in NH_4Br as reported by Garland and Young (1968) and more recently by Ebisuzaki (1973)

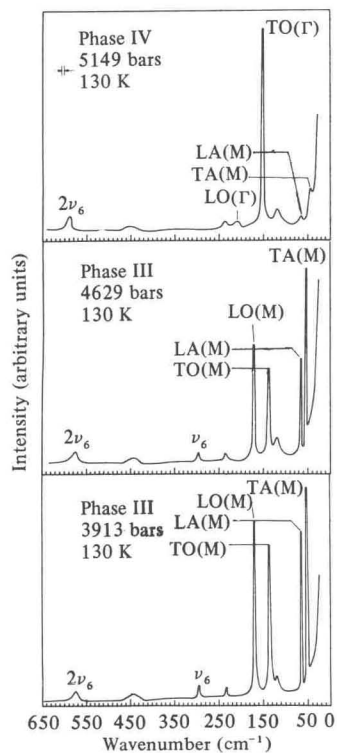


Figure 1. Raman spectra of NH_4I at three different pressures.

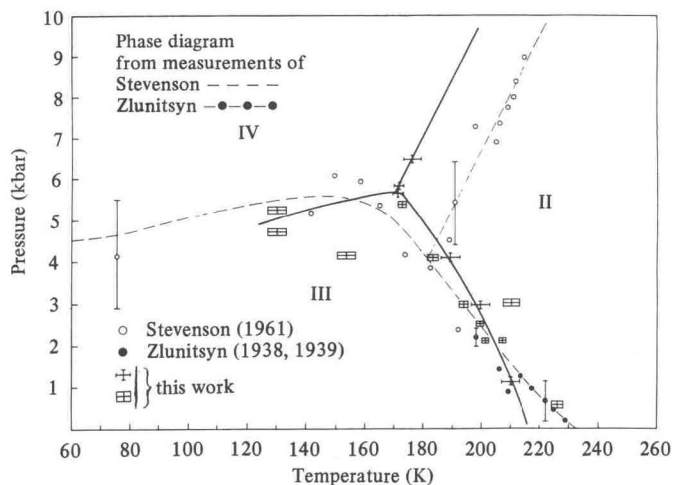


Figure 2. Phase diagram of NH_4I . The crosses mark the uncertainty of the phase line. The crossed rectangles give the range of measurement with unique phase determination.

Results for binary fluid mixtures of carbon dioxide with large molecular size hydrocarbons [e.g. 2,6,10,15,19,23-hexamethyltetracosane (perhydrosqualene), squalane), squalene] and some alcohols (e.g. 2-hexanol, 2-octanol, 2,5-hexanediol) in the temperature range -20 to $+200^{\circ}\text{C}$ at up to 1 kbar are presented and compared to earlier data on CO_2 binaries with alkanes up to hexadecane [*Chem.-Ing.Tech.*, **39**, 649 (1967)]. Whereas CO_2 -2-hexanol and CO_2 -2-octanol resemble CO_2 -octane and exhibit critical liquid-liquid and liquid-gas phenomena that do not intersect in the three-dimensional pressure-temperature-composition space, for CO_2 -squalane and CO_2 -squalene the liquid-liquid and liquid-gas critical curves are superimposed, as found earlier for the CO_2 -hexadecane system. For CO_2 -squalane the critical curve runs through a temperature minimum at $(55 \pm 0.5)^{\circ}\text{C}$ and (705 ± 20) bars and then rises steeply to higher pressures with increasing temperatures; thus its phase behaviour resembles that of systems that exhibit gas-gas equilibria of the second type [*J. Chem. Thermodyn.*, **7**, 805 (1975)]. Additional results on binary mixtures of ethane with methanol, 2,5-hexanediol, and nitromethane show that all these systems resemble the CO_2 -squalane type. Practical applications for industrial extractions and separation methods, e.g. supercritical fluid chromatography are briefly discussed.

Earlier measurements of phase equilibria and critical phenomena in fluid mixtures of water with hydrocarbons [see *Ber. Bunsenges. Phys. Chem.*, **71**, 633 (1967); **73**, 294 (1969); **74**, 682 (1970)] were extended to aqueous solutions of fluorocarbons. Results are presented for the system water-fluorobenzene in the temperature range 300 to 360°C at up to 3.5 kbar; from the measurements parts of the critical curves were determined. The results show that the critical curve of this system has a similar shape to that for the CO_2 -squalane system. It is quite astonishing that the critical $p(T)$ curve of this system nearly coincides with that of the water-benzene system measured earlier.

All results are discussed in relation to data on related systems reported in the literature. They show that a whole pattern of transition types between liquid-gas, liquid-liquid and gas-gas equilibria exists, confirming thus earlier attempts to explain the phase separation effects in fluid mixtures at high pressures on the basis of phase-theoretical arguments [for a review see G. M. Schneider, *Pure Appl. Chem.*, **47**, 277 (1976); G. M. Schneider in *Chemical Thermodynamics* (Chemical Society Specialist Periodical Report), volume 2, in the press].

Phase diagrams of NH_4I and NH_4Br from Raman measurements at high pressure

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We report on the Raman spectra of the three CsCl-type phases of NH_4Br and NH_4I which differ in the orientations of the NH_4 tetrahedra. The two possible orientations are randomly occupied in phase II (O_h symmetry). The tetrahedra are all equally oriented in phase IV (T_d symmetry). In the tetragonal phase III neighbouring tetrahedra are equally oriented along the tetragonal axis and alternately along the other Cartesian axes (D_{4h} symmetry). The Raman spectra of the three phases differ sharply. Owing to disorder in phase II all phonons may contribute more or less to the Raman spectra. The D_{4h} symmetry of phase III bisects the Brillouin zone of the CsCl-type lattice. Only M point modes of this Brillouin zone and the libration ν_6 can be observed in this phase (figure 1). In the T_d symmetry of phase IV strong scattering from the TO (Γ) mode is observed, whereas the intensity of the other