

CONDENSED SOLUTIONS OF THE RARE GASES

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The condensed rare gases have a number of properties which make them suitable substances for an experimental test of solution theories. Their molecules have spherical symmetry and have no internal motions and their "radii" may differ by as little as 7 per cent. With the exception of helium, the rare gases crystallize in the same form—face-centred cubic.

Measurements of the total vapour pressure of solid solutions of the two systems A-Kr and Kr-Xe have been reported¹⁻⁴. These measurements have been compared with theory and in particular with the average potential model theory developed by Prigogine and his associates. This theory leads to an expression for the excess molar free energy (G_E) of the form:

$$G_E = \sigma x_1 x_2 \quad (1)$$

where x_1 and x_2 are mole fractions of the components and σ is a function of temperature (but not of composition) which may be calculated from a number of properties of one component. When σ is positive, as it is for the two systems considered here, there exists a critical temperature T_c , below which the components are insoluble for some values of the composition. The value of the critical temperature, T_c , is given by $T = (1/2R)\sigma$. From the measured vapour pressure, P , at several temperatures, T , σ may be determined as a function of T . The temperature T_c at which $\sigma = 2RT$ may thus be estimated. The values of T_c so calculated^{1, 2} are shown in *Table 1*. No direct experimental evidence of the existence of two solid phases has been obtained for either the A-Kr or the Kr-Xe system. Some recent experiments with the latter system in which *indications* of a phase separation have been observed, are described below.

In the investigations of A-Kr solutions by Walling and Halsey² and Kr-Xe solutions by Freeman and Halsey¹ an amount of the heavier gas was condensed into a thermostated vessel at a temperature T_1 . Subsequently, amounts of the other component were condensed into the same vessel. The solid mixtures were allowed twenty-four hours to attain equilibrium before the vapour pressure was measured. From these measurements a mean value of σ , $\bar{\sigma}$ for solutions of different compositions was calculated for each value of T_1 . These values of $\bar{\sigma}$ are compared with the prediction of the average potential theory in *Table 1*. Considering the nature of the theory, the agreement is good.

In the author's experiments the two gases were mixed in the gaseous state and condensed into a calorimeter which was subsequently heated. Vapour pressure measurements were made at intervals during the heating

period (6–10 h). The measurements were extended through the heterogeneous region until the mixtures were liquid. By this means the solidus and liquidus curves were determined. In the case of A–Kr mixtures the measurements were found to be inconsistent with equation (1), *i.e.* σ as calculated by this equation was a function of composition. Nevertheless, the actual magnitude of the vapour pressure predicted by the average potential theory is in very good agreement with the observed vapour pressure^{3, 4}.

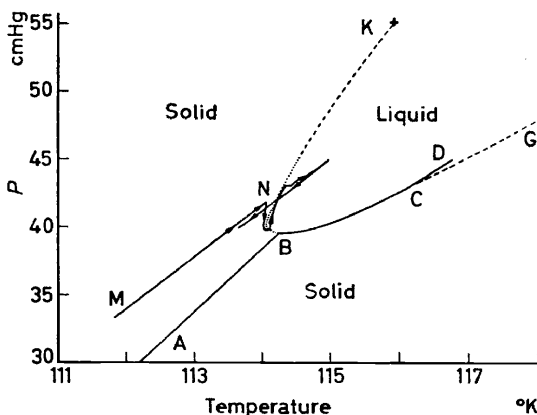


Figure 1. The P - T diagram for Kr–Xe mixtures: K, triple point of xenon, KBCG three-phase curve, ABCD and MN, curves for mixtures for which $x = 0.28$ and $x = 0.11$ respectively

The Kr–Xe system has been examined by the same method in the range $x = 0$ to $x = 0.44$ where x is the mole fraction of xenon. In Figure 1, the P - T graph ABCD of a mixture of composition $x = 0.28$ is shown (P = the total vapour pressure at the temperature T). The phases present in the mixture are: along AB solid and vapour, along BC solid, liquid and vapour and along CD liquid and vapour. The three-phase portions (BC, in this case), for all mixtures lie on the continuous curve KBCG. The liquid–solid phase transition points from which the phase equilibrium diagram, Figure 2, is drawn may be discovered from the intersection of the curves AB and DC with the three-phase curve.

Within the ranges $0 < x < 0.04$ and $0.27 < x < 0.44$ the P - T graphs were of the form ABCD, *i.e.* the phase transition points and the three-phase curve were well defined. In the intermediate range $0.04 < x < 0.27$ irregularities in the P - T curves make the exact form of the solidus and liquidus and three-phase curve (shown dotted in this region in Figure 1) uncertain. It is quite possible that a eutectic point exists, in which case the three-phase curve would have a cusp at $P \approx 40$ cm Hg and $T \approx 114^\circ\text{K}$.

The uncertainty in both Figures 1 and 2 arises from irregularities in the results obtained for all mixtures in this range, as exemplified by the curve MN for a mixture $x = 0.11$. As this mixture was heated a sudden fall in P , accompanied by an absorption of heat, was observed. After the mixture had melted completely the calorimeter was cooled and the subsequent behaviour of the mixture may be seen from Figure 1. (The behaviour of

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these mixtures on cooling is not properly understood and is now the subject of further investigation.) Many mixtures within this intermediate range have been examined and all the P - T curves take the same form as MN on Figure 1. The maximum absorption of heat recorded is approximately 90 J/mole. It may be seen from Figure 2 that the measurements of Freeman and Halsey do not cover this region of the phase equilibrium diagram.

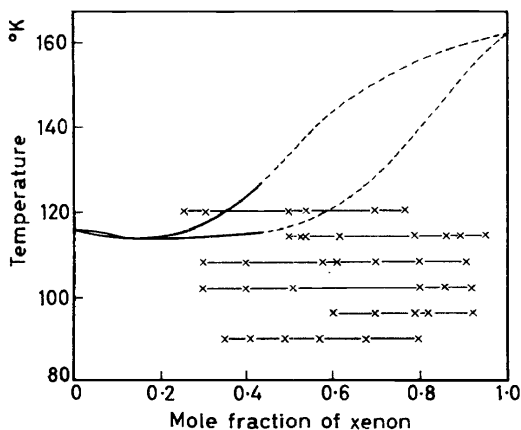


Figure 2. The solid-liquid phase equilibrium diagram of the Kr-Xe system. Measurements of vapour pressure were made at points marked by crosses by Freeman and Halsey¹

The behaviour of the mixtures within this limited range of composition is consistent with the assumption that the gases, on condensation, form a two-phase solid mixture, the pressure fall and absorption of heat being associated with a transition to one single solid phase. To test whether an inhomogeneous mixture was created solely by the method of condensation used, the condensation temperature was varied between 65°K and 110°K. In all cases the measured P - T curves took the same form. Since, however, the solid mixtures are clearly not in a state of thermodynamic equilibrium, it is not possible to assert that the existence of a stable two-phase region in the phase equilibrium diagram of the Kr-Xe system has been demonstrated.

Table 1. Solid solution data compared with theory

System	$\bar{\sigma}$ (J/mole)		Temp. (°K)	Ref.	T_c estim. (°K)
	Exp.	Calc.			
Argon-krypton	750	685	83	2	56 ± 8
Krypton-xenon	1350	2320	105	1	91 ± 2

References

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