the so-called "double plaitpoint". The separation into two phases at pressures above this point is clearly marked. The coordinates of the double plaitpoint are 1240 (± 25) atm. and -108.43 (± 0.02) °C. The critical mixture contains 37.5% Kr. In fig. 2 is shown the p - T projection of the critical locus with its temperature minimum. This confirms that the gas-gas equilibrium in the system Ne-Kr is of type II. To the best of our knowledge this is the first occurrence of gas-gas equilibrium in a mixture containing neither helium nor a polar component.

A detailed discussion of these results as well as the complete phase diagram will be given in a subsequent publication.

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MOBILITY MAXIMA IN THE RARE-GAS LIQUIDS

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It is proposed that at a certain density in liquid argon, krypton and xenon the average scattering length for electron-atom scattering is zero. The mobility then has a maximum, determined by fluctuations in the effective potential.

We wish to give an explanation of certain anomalies observed by Schnyders et al. [1] in the mobilities of electrons injected into liquid argon and krypton. They found a sharp maximum in the mobility in krypton at about 180°K, and a steep rise in the mobility in argon in the range 140 - 150°K. In a calculation of the scattering of electrons moving in the conduction band of liquid argon [2], I found the scattering length to be positive near the triple point. In the gas it is negative. Now the effective potential scattering the electrons in the liquid is the atomic potential modified by screening and overlap [2]. Since both screening and overlap vary continuously with density, it follows that somewhere in the phase diagrams of argon, krypton and xenon (all of which have negative scattering lengths in the gas) lies a locus at which the scattering length passes through zero. This locus should be approximately a line of constant density.

The effective atomic potential scattering an electron depends on the environment of each given atom. This environment fluctuates about the ensemble average. Thus even when the average scattering length $\langle a\rangle$ is zero, $\langle a^2\rangle$ is non-zero and the electron mobility remains finite. We can give an order of magnitude estimate for the maximum mobility as follows. Consider an atom at the origin. The probability of finding another atom in $\mathrm{d}\boldsymbol{R}$ at $\boldsymbol{R}$ is $ng(R)\mathrm{d}\boldsymbol{R}$, where n is the atomic density and $g(R)$ is the pair correlation function. If this second atom is given a displacement $\Delta\boldsymbol{R}$ the change in the potential at the origin is $\Delta U = (\mathrm{d}U/\mathrm{d}R)\cos(\Delta\boldsymbol{R},\boldsymbol{R})|\Delta\boldsymbol{R}|$. We take the displacement $\Delta\boldsymbol{R}$ to be uncorrelated with $\boldsymbol{R}$, so that averaging over the directions of displacement, we get

$$\langle\Delta U^2\rangle = \tfrac{1}{3}\langle\Delta R^2\rangle\, 4\pi n\int_0^\infty \mathrm{d}R\,R^2 g(R)(\mathrm{d}U/\mathrm{d}R)^2 . \qquad (1)$$

The mean square displacement $\langle\Delta R^2\rangle$ can be estimated on the Einstein-model of atomic motions. Assume each atom to be vibrating in a spherical box formed by its neighbours, oscillating near the bottom of a potential well $\epsilon(R)$. Assume further that its mean kinetic energy $\frac{3}{2}kT$ is equal to its mean potential energy $\frac{1}{2}\langle\Delta R^2\rangle(d^2\epsilon/dR^2)_0$. The force constant $d^2\epsilon/dR^2$ can be related to the compressibility χ by [3, p.16] $\frac{1}{9}R_s^2(d^2\epsilon/dR^2)_0 = (n\chi)^{-1}$ where R_s is the Wigner-Seitz radius, defined by $\frac{4}{3}\pi R_s^3 = 1/n$. We find therefore

$$\langle\Delta R^2\rangle \approx \tfrac{1}{3}R_s^2\, nkT\chi \approx \tfrac{1}{3}R_s^2 kT/Mc^2, \tag{2}$$

where c is the speed of sound. Now consider the variation in the scattering length away from its verage zero value. In the Born approximation this is

$$\Delta a = \frac{2m}{\hbar^2}\int_0^\infty dR\, R^2 \Delta U. \tag{3}$$

To calculate the mobility we need the average cross-section, $4\pi\langle a^2\rangle$. Since $\langle a\rangle = 0$, $\langle a^2\rangle = \langle\Delta a^2\rangle$, which we will calculate from eq. (3) by assuming that ΔU can be replaced by a constant, equal to its value at the origin, up to $R = R_s$, the Wigner-Seitz radius. Then (3) becomes

$$\Delta a = \left(\frac{2m}{\hbar^2}\right)\tfrac{1}{3}R_s^3\,\Delta U = \left(\frac{m}{2\pi n\hbar^2}\right)\Delta U\ , \tag{4}$$

and the average cross-section is

$$\langle\sigma\rangle = 4\pi\langle\Delta a^2\rangle = 4\pi\left(\frac{m}{2\pi n\hbar^2}\right)^2\langle\Delta U^2\rangle. \tag{5}$$

Using eqs. (1), (2) and (5) we may estimate the mobility from the Lorentz formula [2]:

$$\mu = \tfrac{2}{3}\left(\frac{2}{\pi mkT}\right)\frac{e}{n\langle\sigma\rangle}. \tag{6}$$

Before comparing this numerically with experiment, we note that if μ is measured along a locus (of approximately constant density) where the maximum occurs, this maximum will vary with the thermodynamic varibles as $\mu \sim c^2T^{-\frac{3}{2}}$.

Schnyders et al. found a maximum in the electron mobility in liquid krypton at 180°K. Their results are shown in their table 3 and fig. 11. There are three values of μ clustered around 2300 cm^2/Vsec, measured at a field strength of 100 V/cm; there is also another value of 3610 cm^2/Vsec, measured at 50 V/cm (not shown in fig. 11). This discrepancy indicates that the drift velocity is already non-linear in the field at these low field strengths, since the scattering is so weak. We shall obtain an order of magnitude estimate of μ by replacing $g(R)(dU/dR)^2$ in eq. (1) by its approximate asymptotic value $(2\alpha e^2 f_L/R^5)^2$ for R greater than the hard sphere diameter δ and zero for $R < \delta$. Here α is the atomic polarizability and $f_L = (1 + \frac{8}{3}\pi n\alpha)^{-1}$ is the Lorentz local field factor [2].
Then $\langle\Delta a^2\rangle$ reduces to

$$\frac{4}{63}\,\frac{kT}{Mc^2}\,\frac{1}{\pi n\delta^3}\left(\frac{R_s}{\delta}\right)^2\left(\frac{\alpha f_L}{a_0\delta}\right)^2. \tag{7}$$

For krypton at 180°K and 30 atmospheres [4], $n = 0.013$ Å^{-3}, $R_s = 2.64$ Å, $\delta \approx 3.7$ Å. The mobility at maximum then comes out to be 4300 cm^2/Vsec. In view of the number of approximations made, the agreement with the probable experimental value of about 4000 cm^2/Vsec is just a happy coincidence. But the order of magnitude agreement is encouraging.

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