Laboratori Nazionali di Frascati

LNF-71/74

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Estratto da : Phys. Letters 36A, 261 (1971)

DIFFUSION OF Kr IN CO_2

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Received 23 July 1971

New measurement of the diffusion of ^{85}Kr in CO_2 for $\rho \leq 0.3$ g/cm^3 and $T = 31.5^{\circ}$C and $T = 40.2^{\circ}$C are reported. Some behaviour, previously reported, of diffusion at the liquid gas critical point is discussed.

Considering the few measurements of the diffusion at the liquid-gas critical point, one of the most astonishing results is the one reported by Krichevskii et al. [1], about the impurity (I_2) diffusion in CO_2 near the CO_2 liquid gas critical point. They reported that approaching the critical point the diffusion coefficient seems to become zero. In this note we report some new measurements of impurity diffusion in CO_2. These measurements show that the results of Krichevskii appear to be incorrect and therefore any of their conclusion concerning the behaviour of the binary diffusion at the critical point must be disregarded. The quantitative measurement of the anomaly of any physical property at the critical point, means obviously to measure the difference from the "normal" behaviour. In the case of diffusion in dense fluids we do not have, at the moment, any exact theoretical formula useful for quantitative predictions, therefore it is necessary to infer such a "normal" behaviour from a phenomenoligical analysis. It has been suggested [2] that a proper way to analyse the experimental data it is to look at the behaviour of $D\rho$, where D is the diffusion coefficient and ρ is the fluid density. Such a quantity seems to depend slightly on the absolute temperature and, up to the critical density, it is quite independent of ρ. Moreover the value of $\lim_{\rho \to 0} D\rho$ must satisfy the Chapman-Enskog prediction [3]. In fig. 1 the Krichevskii's results are reported in the form of $D\rho$ as a function of ρ. If the straight line is assumed to represent the "normal" behaviour, the decrease of D near the critical density it is clearly very big. However the suggested "normal" behaviour contains two strange features: 1) the $\lim_{\rho \to 0} D = 9 \times 10^{-7}$ g/cm-s whereas the Chapman-Enskog theory, with $\sigma_{12} = 4.5$ Å and $\epsilon_{12}/k = 336^{\circ}$K, would indicate a value of $D\rho = 9 \times 10^{-5}$ g/cm-s which is 100 times bigger than the Krichevskii data; 2) At constant temperature $D\rho$ increase tremendously fast with ρ. In fact $D\rho = 9 \times 10^{-7} \times \exp(5.2\rho)$ cm^{-1} sec^{-1}. To check these two points we measured the diffusion of an impurity (^{85}Kr) in CO_2 at the same temperatures as the Krichevskii data and for $\rho \leq 0.3$ g/cm^3 i.e. just outside the critical region. Our experimental method [4] was the capillary one arranged in an horizontal position so to avoid any influence of gravitational effect. The temperature regulation of the diffusion

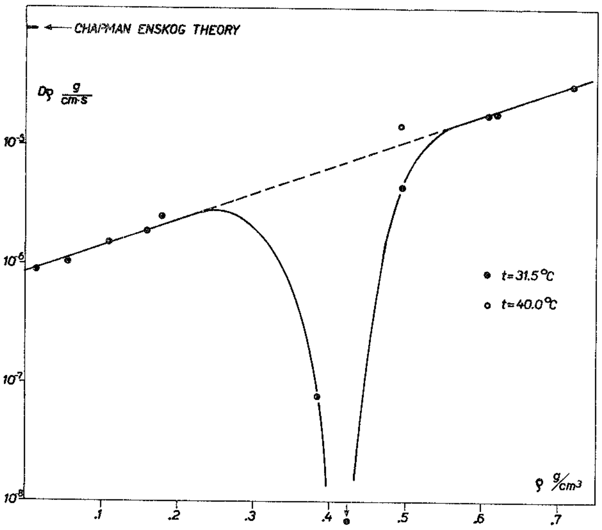

Fig. 1. $D\rho$ as a function of ρ for diffusion of I_2 in CO_2 (ref. 1). The dashed line represent the "normal behaviour".

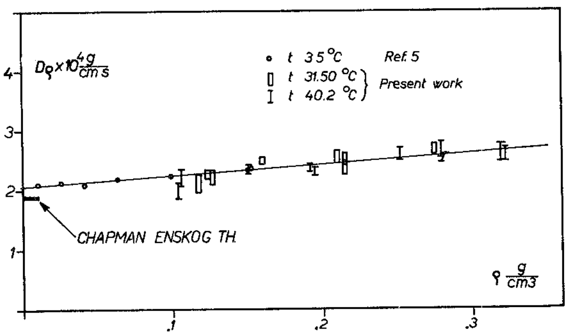

Fig. 2. $D\rho$ as a function of ρ for diffusion of Kr in CO_2.

cell was maintained constant better than 0.02°C. During the diffusion, the cell was closed to avoid external disturbances and the density inside the cell was continously measured through a capacitor connected to the cell and it was in very good agreement with *PVT* measurements. Our experimental results at 31.50°C and 40.2°C are shown in fig. 2 together with some previous measurements [5] at very low densities and $T = 35^{\circ}C$. We can see that our data show: 1) $\lim_{\rho\to 0} D\rho = 2 \times 10^{-4}$ g/cm-s in perfect agreement with the Chapman-Enskog value, which, is 1.9×10^{-4} g/cm-s [we have taken $\sigma_{12} = 3.8$ Å and $(\epsilon_{12}/k = 185^{\circ}K]$; 2) At constant temperature $D\rho$ increases only linearly with like $D\rho = (2+2\rho) \times 10^{-4}$ g/cm-s showing therefore a very small density dependence in very good agreement with the phonomenological relationship found in many other cases. Since the qualitative behaviour of the diffusion coefficient as a function of ρ should be independent of the kind of impurity [6] we can conclude that the Krichevskii data are wrong in the thermodynamic region just outside the critical one. Since such data are necessary to infer about the "normal" behaviour, we must conclude that also the Krichevskii suggestion about the behaviour of the diffusion at the critical point should be disregarded.

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