Similarity Relations and Critical Constants of Heavy Fluid Alkali Metals

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LETTER

Similarity Relations and Critical Constants of Heavy Fluid Alkali Metals

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Chapman and March demonstrated from experimental data on critical constants for temperature and volume of the fluid alkali metals that $T_c V_c^n = $ constant, where n is about 0.3. It is pointed out here that the similarity relations given by Likalter, though restricted in their validity to the heavy fluid alkali metals, yield $n = 1/3$.

KEY WORDS: Compressibility ratio, critical volume and temperature.

In earlier work, Chapman and March[1] emphasized that, from experimental data for the critical constants of the fluid alkali metals,

$$T_c V_c^n = \text{constant} \tag{1}$$

where the exponent n was about 0.3. As these workers noted, this situation is in marked contrast to the noble gases, where n is about -2. Furthermore, the compressibility ratio Z_c, defined by

$$Z_c = p_c V_c / R T_c, \tag{2}$$

where R is the usual gas constant, ranges from 0.06 for Li to 0.20 for Cs, while for the noble gases the value is 0.29 ± 0.01. Because of these results, Chapman and March[1] stressed the essential role of Coulomb forces in interpreting the above results for the fluid alkali metals.

The recent work of Likalter[2] has been concerned with the theory of the electronic structure of metals near their liquid-gas critical points, via arguments based on the metal-insulator transition. While Likalter's results appear to be most appropriate to noble and to d transition metals, he also invokes them for the heaviest fluid alkali metals Rb and Cs. Of particular interest in the present context is his claim[2,3] that

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the critical parameters obey the similarity relations

$$T_c = \alpha_1 z \Delta, \quad p_c = \alpha_2 z \Delta^4, \quad Z_c = 0.1(z + 1). \tag{3}$$

In Eq. (3), we have written Δ for a characteristic energy; Likalter identifies this with the atomic ionization potential I, but for reasons to be summarized below we prefer to keep the more general form (3). With $\Delta = I$, Likalter proposes the values $\alpha_1 = 0.0425$ and $\alpha_2 = 0.405$, but again we prefer, as with Δ, to leave these constants general for present purposes. Finally, in Eq. (3), z denotes the valence.

Though the similarity prediction for Z_c in particular breaks down severely for Li, it is correct for Rb and Cs and still reasonable for K(experimental $Z_c = 0.175$). Therefore, for the heavier fluid alkalis, it is appropriate to bring the similarity relations (3) into direct contact with Eq. (1) which is obeyed empirically by the alkalis. Writing therefore, from Eq. (3),

$$Z_c = \frac{p_c V_c}{R T_c} = \frac{\alpha_2}{\alpha_1 R} \Delta^3 V_c = \left(\frac{\alpha_2}{\alpha_1 R}\right) \frac{T_c^3 V_c}{(\alpha_1 z)^3}, \tag{4}$$

one is led to the result

$$T_c V_c^{1/3} = \alpha_1 z \left(\frac{Z_c \alpha_1 R}{\alpha_2}\right)^{1/3} = \text{constant}. \tag{5}$$

This Eq. (5) is now precisely of the form of Eq. (1) deduced from experiment by Chapman and March for the fluid alkalis and confirms that $n = 1/3$ of the heavy members of this series.

This argument supports the view that the critical point and the metal-insulator transition can be taken as one and the same for the heavy alkalis Rb and Cs. Plainly, however, there is different physics and chemistry associated with the critical point in the case of Li (and probably Na also). In particular, the similarity prediction $Z_c = 0.2$ from Eq. (3) is badly violated for Li ($Z_c = 0.06$). It is relevant to note here that the experimental structure factor measurements of Hensel and coworkers[4,5] have demonstrated the approximate constancy of the near-neighbour distance in Rb and Cs along the liquid-vapour coexistence curve, the lowering of the density on approaching the critical point coming dominantly from a reduction in coordination number. This leads one to expect that properties of alkali dimers should enter formulae such as those in Eq. (3). In particular, we note that for Na, admittedly in the solid state, Malrieu et al.[6] following the lead of Poshusta and Klein[7] on hydrogen, have constructed an effective Heisenberg Hamiltonian from diatom potential curves. In particular, for Na this Hamiltonian was characterized by the $1\Sigma_g^+$ and $3\Sigma_u^+$ potential curves of the free-space diatom Na_2.

It will not be surprising to us therefore if, in a final theory, the characteristic energy Δ in Eq. (3) reflects in some direct manner the separation between these potential energy curves, rather than the atomic ionization potential with which Δ is identified in the treatment of Likalter.

In summary, though the similarity relations (3) are only quantitatively successful for the heavier alkali metals, and best for just Rb and Cs, they lead to the theoretical prediction (5) which is in accord with the empirical relation (1) exposed in the work of Chapman and March[1] for the fluid alkali metal series.

References

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