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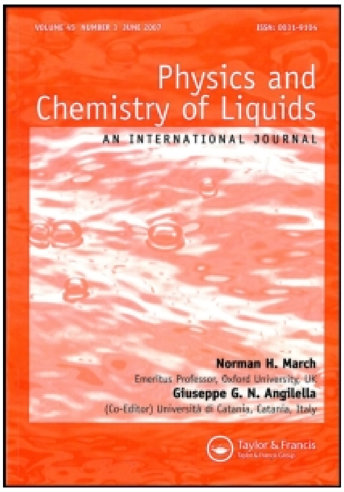

## Physics and Chemistry of Liquids

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# Empirical Relations Between the Critical Constants of Fluid Alkali Metals

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**To cite this Article** Chapman, R. G. and March, N. H.(1986) 'Empirical Relations Between the Critical Constants of Fluid Alkali Metals', Physics and Chemistry of Liquids, 16: 1, 77 — 81
**To link to this Article: DOI:** 10.1080/00319108608078502
**URL:** http://dx.doi.org/10.1080/00319108608078502

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*Phys. Chem. Liq.*, 1986, Vol. 16, pp. 77–82
0031-9104/86/1601-0077$18.50/0

Printed in the United Kingdom

# Letter

## Empirical Relations Between the Critical Constants of Fluid Alkali Metals

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(*Received February 20, 1986*)

It is demonstrated that $T_c V_c^n$ = constant for the critical constants of the alkali metals, where the exponent $n$ is about 0.3. This is in marked contrast to the noble gases, where $n$ is about $-2$. Further, the compressibility ratio $p_c V_c / R T_c$ for the alkalis ranges from 0.06 for Li to 0.20 for Cs, while for the noble gases the value is $0.29 \pm 0.01$. The importance of Coulomb forces in interpreting the results for the alkali metals is stressed.

The purpose of this note is twofold:

i) To draw attention to some regularities in the behaviour of the critical constants $p_c$, $V_c$ and $T_c$ of fluid Li, Na, K, Rb and Cs at the critical point and

ii) To compare these regularities with the predictions of the classical one-component plasma (OCP) model at its 'critical point', when a modification is introduced to include core size.

With regard to point (i) above, it can be seen from the ln–ln plot of $T_c$ vs. $V_c$ to the five alkali metals in Figure 1 that to useful accuracy one can write

$$T_c V_c^n = \text{constant} \qquad (1)$$

and from the slope of the straight line drawn there one finds $n = 0.28$. The data for Rb and Cs obtained recently seems appreciably better than for the other metals. We will return to a discussion of the interpretation of this exponent below, in terms of a model based on long-range Coulomb forces, but by way of motivation for this model we show in Figure 2 a similar ln–ln plot of $T_c$ vs. $V_c$ for the neutral noble gas fluids. In contrast to the exponent $n \sim 0.3$ for the alkalis, an exponent of $-2$ is obtained for the noble gases. In

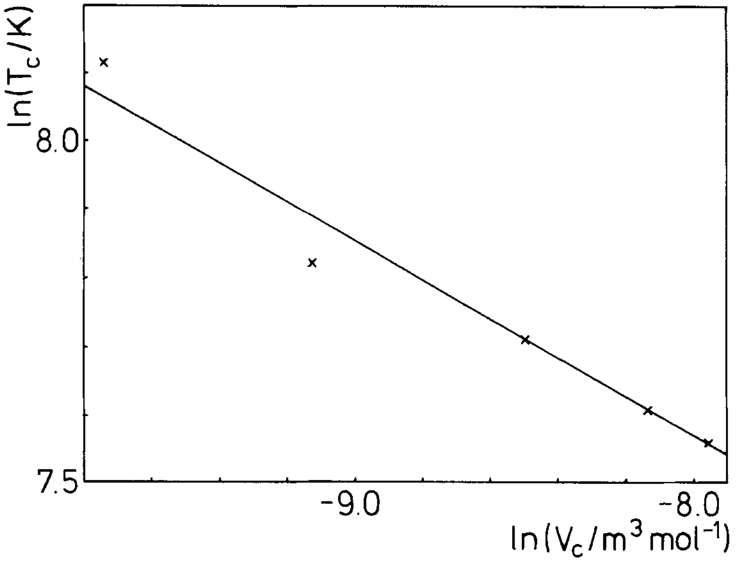

FIGURE 1 ln–ln plot of $T_c$ vs. $V_c$ for alkali metals. Straight line drawn is well represented by Eq. (1) with exponent $n = 0.28$.

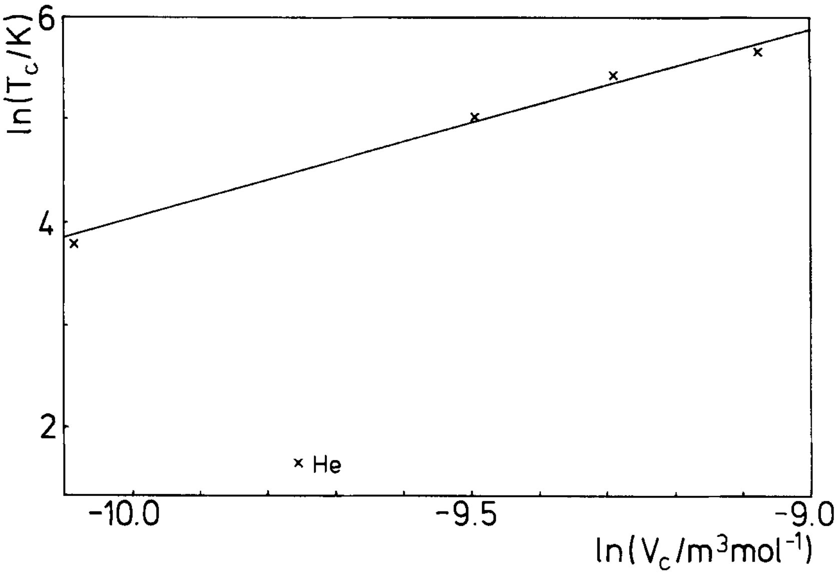

FIGURE 2 Similar to Figure 1 but for noble gases. The exponent $n$ in Eq. (1) required to fit the data is now negative and of magnitude 2. The quantal fluid He obviously behaves quite differently.

TABLE I

Observed critical constants of alkali metals

| Element | $p_c$ in MPa | $10^4$ $V_c$ in $m^3$ $mol^{-1}$ | $T_c$ in K | $Z_c$ | Reference |
|---|---|---|---|---|---|
| Li | 30.4 | 0.588 | 3344 | 0.064 | 1 |
| Na | 25.22 | 1.09 | 2497 | 0.132 | 1 |
| K | 15.95 | 2.04 | 2239 | 0.175 | 1 |
| Rb | 12.45 | 2.93 | 2017 | 0.217 | 2 |
| Cs | 9.25 | 3.51 | 1924 | 0.203 | 2 |

addition, the compressibility ratio $Z_c = p_c V_c/RT_c$ is recorded along with the critical constants for the alkalis in Table I, while Table II records similar data for the noble gases. These Tables show that $Z_c$ varies significantly through the five alkali metals, but in all cases the compressibility ratio is substantially lower than the almost constant value of 0.29 obtained for the noble gases. We may note again here that data for the lighter alkali metals involves some extrapolation from experiment[1] and that only for Rb and Cs were all three critical quantities obtained simultaneously by direct measurement.[2]

We shall comment next on the relation of the empirical regularities discussed above for the alkalis to the predictions of the OCP model. The thermodynamic properties of this system are well established from the simulation work of Hansen *et al.*[4] and may be written in terms of the OCP coupling parameter Γ given by

$$\Gamma = e^2/ak_B T \tag{2}$$

TABLE II

Critical data for noble gases[3]

| Element | $p_c$ in MPa | $10^5$ $V_c$ in $m^3$ $mol^{-1}$ | $T_c$ in K | $Z_c$ |
|---|---|---|---|---|
| He | 0.2285 | 5.80 | 51.25 | 0.304 |
| Ne | 2.7262 | 4.17 | 44.45 | 0.308 |
| Ar | 4.8641 | 7.52 | 150.75 | 0.292 |
| Kr | 5.4917 | 9.22 | 209.35 | 0.291 |
| Xe | 5.8938 | 11.42 | 289.75 | 0.279 |

where $\frac{4}{3}\pi a^3 = \rho^{-1}$ if $\rho$ is the particle density.[5] From these expressions we find that the isothermal compressibility vanishes at $\Gamma = 3.1$ and that the pressure is nearly linear in $\Gamma$ over a substantial range. We therefore write for the pressure $p$ in an OCP model modified to account for core size the expression

$$\frac{p}{k_B T} = \frac{p_{HS}}{k_B T} - \alpha\Gamma \tag{3}$$

where $\alpha$ is found to be 0.24 in the linear approximation from the fact that in the OCP the value of $\Gamma$ corresponding to $p = 0$ is 4.1.

Using the expression of Carnahan and Starling for the hard sphere pressure $p_{HS}$ one readily obtains the form of Eq. (1), with the exponent $n = \frac{1}{3}$. This is encouragingly close to the exponent of 0.28 derived from the slope of the line in Figure 1, but it must be added that the above model predicts only the order of magnitude of the empirically determined constant in Eq. (1), the theoretical value of the constant being a factor of 4 greater than the experimentally determined value. It is also of interest that the above Coulomb force model predicts the compressibility ratio to be 0.14, which is considerably smaller than would be obtained from classical equations of state such as those of van der Waals or of Dieterici.

Clearly then, the merits of the simple model based on Eq. (3) are that it offers a simple explanation of the reaction (1) with exponent $n$ near to 0.3 and yields a low compressibility ratio as required. We must caution, however, that in addition to the failure to predict the constant in Eq. (1) to better than a factor of 4, the model based on Eq. (3) fails to predict the coexistence curve at all correctly on the high density side of $\rho_c$ except very near to $T_c$. These points indicate, of course, that important physical processes have been omitted in writing Eq. (3), and two points that immediately come to mind are the existence of dimers in the fluid phases and the existence of a metal-insulator transition along the high density side of the coexistence curve. Nevertheless, the results of the present work can leave no doubt that the long-range Coulomb interaction $e^2/r_{ij}$ between ions is playing an essential role in interpreting the empirical regularities for the fluid alkali critical constants. Quantitative calculations relating to the coexistence curve of Cs are currently in progress, in order to investigate further questions arising from these preliminary observations.

## Acknowledgement

One of us (R.G.C.) wishes to acknowledge the award of an SERC postgraduate studentship during the course of this work.

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