

IN THE NAME OF ALLAH

Second Virial Coefficients of Alkali Metals from Diatom
Fractions and Assessment of ISM EOS by Real Data

BY

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Dedicated to:

**My dear teacher Dr. M. H. Ghatge
Who has taught me how to live better.**

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Abstract

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In this work, the calculation of mean second virial coefficients $\langle B_2 \rangle$ of alkali metals by using data on diatom fractions at pressure 10^{-5} bar is reported. A corresponding states description of the alkalis is followed in terms of reduced second virial coefficients versus the new reduced temperature $T_{al}^* = T^*(T; \gamma_m, \rho_m, \Lambda)$ where, T is the absolute temperature, γ_m and ρ_m are the surface tension and liquid density at melting temperature, respectively. The de Boer constant Λ accounts for the quantum effects that are highly essential in physical properties especially of the lighter metals.

We use the calculated second virial coefficients to apply the Ihm-Song-Mason (ISM) equation of state (EOS) to molten alkali metals. Two other temperature dependent coefficients α and b of the EOS, are calculated by integration using the Rydberg potential function, to remade the lack of Boyle volume requested by the present procedure. The perturbation scheme of ISM EOS has considered a small perturbation and thus to bring the highly attractive polarizable alkali metals in the ISM regime a cofactor is applied by normalizing the potential well-depth of metals to the corresponding nobles.

Application of ISM EOS to molten alkali metals by our method is theoretically advantageous in that we have used the real data. It reproduces the liquid densities within <10% of the experimental values. The results suggest that ISM EOS is applicable to alkali metals within 250-300 K

around the boiling temperature, and is likely to report an internal conversion in liquid alkali metal close to their boiling temperature.

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Chapter One

Introduction

1-1. Theory of Second Virial Coefficient

An equation of state of a gas merely gives a mathematical relation among the pressure, volume, temperature, and number of moles (P, V, T, n) at equilibrium. Such a relation does not have to be expressed in the form of an equation, of course, and sets of graphs or tables of numerical values are often used, especially in practical work. The simplest and best known equation of state is that for perfect gas

$$Pv = RT \quad (1.1.1)$$

where $v = V/n$ is the molar volume and R is a universal gas constant. Real gases and liquids exhibit deviation from this equation, but, as far as is known, all gases approach perfect gas behavior in the limit of very low density. This important empirical fact is the basis for the precise measurement of the absolute temperature, T .

Many modifications of the perfect-gas equations of state have been proposed in order to secure better representations of the P - V - T properties of real gases. Indeed, new equations of state are proposed and currently equations of state for condense fluids are in progress. Empirical and semi-empirical equations of state are a general subject of equilibrium thermodynamics. Out of all the equations of state that have been proposed, the following equation expresses the deviations from the perfect-gas equation as an infinite series in the density ρ ,

$$\frac{Pv}{RT} = 1 + B_2\rho + C\rho^2 + D\rho^3 + \dots, \quad (1.1.2)$$

where $\rho=1/v$, and B_2, C, D, \dots , are called second, third, fourth, ..., virial coefficients, respectively. The virial coefficients depend on the temperature and on the nature of the gas under consideration, but are independent of density or pressure. The virial equation of state is sometimes written as a series in the pressure instead of density,

$$\frac{Pv}{RT} = 1 + B_2'P + C'P^2 + D'P^3 + \dots \quad (1.1.3)$$

this series is mathematically equivalent to the density series, and the coefficients of the series are uniquely related to each other. The first few relations are:

$$\left. \begin{aligned} B_2 &= RTB_2', \\ C &= (RT)^2(C' + B_2'^2), \\ D &= (RT)^3(D' + 3B_2'C' + B_2'^3), \\ E &= (RT)^4(E' + 4D'B_2' + 6C'B_2'^2 + 2C'^2 + B_2'^4). \end{aligned} \right\} \quad (1.1.4)$$

It may seem surprising that the virial equation of state should be singled out for such special attention. Considered solely as an empirical equation, it would not deserve so much attention, since it undoubtedly has important limitations, from this point of view. For instance, the convergence of the series is not very good except at moderately low densities, as seems reasonable from the form of the expansion, and indeed there is some experimental evidence that series diverges at high densities. Furthermore, at high densities many terms of the series must be included to obtain satisfactory accuracy, and this means that many parameters (the virial coefficients) have to be determined experimentally.

The reason for the special importance of the virial equation of state is that it is the only equation of state known which has a thoroughly sound

theoretical foundation. There is a definite interpretation for each virial coefficient in terms of molecular properties. The second virial coefficient represents deviation from perfection corresponding to interactions between two molecules, the third represents the deviation corresponding to interactions among three molecules, and so on.

Thus the virial equation of state forms the connection between experimental results and knowledge of molecular interactions. If it was not for the fact that the virial coefficients form a link between the macroscopic and microscopic points of view, work on the P-V-T properties of gases would have little interest aside from some rather obvious practical applications. Moreover, statistical mechanical theories of dense fluids and of phase transitions are usually expected to be also applicable in the dense region where the virial equation of state is valid, and virial equation of state thus furnishes an important check on many proposed theories.

Other equations of state have a more or less empirical basis, and their adjustable parameters therefore yield little or no molecular information. Furthermore, they are valid only in the regions for which empirical data have been fitted, and extrapolation outside of such regions is very risky. When extrapolation is necessary, it is better to use an equation with a sound theoretical foundation.

The major importance of the virial equation of state lies not in any small advantage it may have for extrapolation, however, but rather in its theoretical connection with molecular interactions, in particular with the forces between molecules. There are many macroscopic properties of matter which depend strongly on inter-molecular forces. For some of these, such as the virial coefficients of dilute gases, and some of properties of simple crystals, the dependence on inter-molecular forces is sufficiently well understood for us to proceed with some confidence in either direction from experimental measurement of properties to the calculation of inter-molecular forces, or from knowledge of inter-molecular forces to the

calculation of the macroscopic properties. For other properties, such as the equation of state and transport properties of dense gases, or the properties of liquid and complicated solids, theoretical progress may depend to a considerable extent on independent knowledge of inter-molecular forces, for which we must turn to experimental measurement on the well understood properties.

To summarize, the importance of the virial equation of state lies in its theoretical connection with the forces between molecules. These forces can be considered the basic unifying element connecting a host of widely different properties.

It thus becomes unnecessary to measure all of these properties extensively. Making only enough measurement would be needed to determine the force law with reasonable precision, and then the rest of properties can be calculated.

1-1-2. Theoretical Background

Attempts to devise equation of state which would be important over the perfect-gas equation is continuing at the present. The form of the virial equation of state is certainly consisting as it does of an expansion in powers of the density, and there are plenty of precedents in mathematics and theoretical physics for the expansion of an unknown function as a power series. Thus it is not surprising that equation of state of the virial form were suggested empirically before rigorous theoretical derivations were developed. Thiesen, who calculated values of B_2 and C from Regnault's P-V-T measurements [1], proposed an infinite series expansion of the form of (1.2) as early as 1885. The major development, however, came in 1901 from Kamerlingh Onnes [2], who wrote the equation in the polynomial form

$$Pv = A + \frac{B''}{v} + \frac{C''}{v^2} + \frac{D''}{v^4} + \frac{E''}{v^6} + \frac{F''}{v^8} \quad (1.1.5)$$

and suggested the name virial coefficients. If v in (1.1.5) is in some form of molar units, then A must be the same for all gases and be proportional to T .

Kamerlingh Onnes changed the equation (1.1.5) into reduced form, using critical constants, and gave an extensive discussion of the virial coefficients from the standpoint of the principle of corresponding states. (A modern discussion of virial coefficient along similar lines has been given by Guggenheim [3].)

Note that the odd powers of $(1/v)$, other than the first, have been omitted from (1.1.5). This omission was simply an empirical curvefitting device. A number of variations in the form of the equation tried by Kamerlingh Onnes. Theory indicates that all powers should be included.

An important point by Kamerlingh Onnes emphasized that the coefficients determined by fitting a polynomial like (1.1.5) to experimental measurements would not be the same as the infinite series.

To emphasize this point, he wrote the infinite series as

$$Pv = A + \frac{B(\infty)}{v} + \frac{C(\infty)}{v^2} + \dots + \frac{N(\infty)}{v^n} \quad (1.1.6)$$

and suggested that the name "virial coefficients" be reserved for $B(\infty)$, $C(\infty)$, etc. The values of B'' , C'' , of (1.1.5) might be good approximation to $B(\infty)$ and $C(\infty)$ but the coefficients D'' , E'' , F'' would be entirely different from the corresponding coefficients in (1.1.6), and he suggested that the name virial coefficients would be more appropriate for the linear coefficient of the polynomial.

The quantity A is the same in both Eqs (1.1.5) and (1.1.6), and is obviously equal to RT when v is expressed in units of volume per mole. If (1.1.6) is written as