

THE SECOND AND THIRD VIRIAL COEFFICIENTS OF ALKALI METAL VAPORS

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ABSTRACT

The two-body and three-body interactions of atoms with one valence electron have been studied. The potentials for the $^1\Sigma$ and $^3\Sigma$ ground-state interactions of alkali metal atoms have been obtained by a semi-empirical scaling procedure from those of hydrogen atoms. The second virial coefficients of alkali metal vapors have been calculated by numerical integration using both the interaction potentials obtained by scaling and the analytical potentials (Rydberg and antibonding Morse potential functions) with the statistical weight factors of 1/4 and 3/4 for the $^1\Sigma$ and $^3\Sigma$ potentials, respectively. It has been shown that there is good agreement between the calculated and experimental values over the experimental range and also that the potentials obtained by scaling are better representative of the true potentials than the analytical potential functions. The additive third virial coefficients have also been calculated by numerical integration as a weighted combination of the two types of the three-body interactions, which are the singlet-singlet-triplet and triplet-triplet-triplet interactions, with the statistical weight factors of 7/16 and 9/16, respectively. It has been seen that the nonadditive(correction) terms of the third virial coefficients may be rather small for alkali metal vapors.

I. INTRODUCTION

Alkali metals are being considered as working fluids in nuclear power plants, magnetohydrodynamic power generators, thermionic power converters, and ion propulsion systems. Therefore, the equations of state of alkali metal vapors are of great importance not only for their possible practical applications but also for theoretical studies.

The present paper is concerned with calculations of the interaction potentials and the second and third virial coefficients. The interaction potentials will be obtained by scaling from the best data and estimates for those of hydrogen atoms currently available. The

second and additive third virial coefficients will be calculated by means of statistical mechanics in terms of the potentials over the temperature range of 500° to 5000° K under the assumption that the vapors consist entirely of ground-state atoms. The accuracy of the potentials used will be tested by comparing the calculated second virial coefficients with the experimental data.

The three-body interactions of atoms with one valence electron will be studied in connection with the calculation of the third virial coefficients of alkali metal vapors. Also, the nonadditive third virial coefficient for a gas of atoms with one valence electron will be qualitatively estimated.

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II. INTERACTION POTENTIAL ENERGY CURVES

Since alkali metal atoms like hydrogen atoms have one valence electron, two alkali metal atoms attract each other when their electron spins are antiparallel and repel each other when their spins are parallel. Therefore, the interaction of two ground-state alkali metal atoms leads to singlet($^1\Sigma$) states. The singlet states are bound, and their potential energies have been determined over limited ranges of internuclear separation. However, the triplet states are purely repulsive except at large separations where a long range van der Waals attraction predominates, and no experimental data are available. Thus, in the present study the potential energies for the singlet and triplet ground-state interactions of alkali metal atoms have been obtained from those of hydrogen atoms by a semi-empirical scaling procedure, which is based on the repulsive core theory suggested by Jenč and Pliva⁽¹⁾. Davies *et al.*⁽²⁾ have also carried out the same scaling procedure to obtain the interaction potential energies of alkali metal atoms. In the scaling procedure it is very important to use the best potential curves of hy-

drogen atoms currently available. The singlet ground state potential curve of hydrogen atoms has been constructed using the results of Vanderslice *et al.*⁽³⁾, obtained from spectroscopic vibrational-rotational data by the Rydberg-Klein-Rees method, and the quantum-mechanical calculations of Dalgarno and Lynn⁽⁴⁾, which are

TABLE. Molecular and Repulsive Core Constants

Molecule	D_e (eV)	V_e (Å)	σ (Å)	σ' (Å)
H ₂	4.726	0.7417	0.0172	0.0172
Li ₂	1.14	2.6725	1.0800	1.0645
Na ₂	0.74	3.0786	1.7056	1.708
K ₂	0.520	3.923	2.7580	2.787
Rb ₂	0.493	4.127	2.8522	2.860
Cs ₂	0.453	4.465	3.2421	3.237

D_e , V_e , and σ' taken from Davies *et al.*⁽²⁾

D_e =dissociation energy of diatomic molecule

V_e =equilibrium internuclear distance of diatomic molecule

σ =repulsive core constant calculated in the present study

σ' =repulsive core constants adjusted by Davies *et al.*⁽²⁾ to make the reduced potential curves fit exactly on the reduced hydrogen potential curve at their highest observed data

valid at large separations. The triplet ground-state potential energies of hydrogen atoms also have been

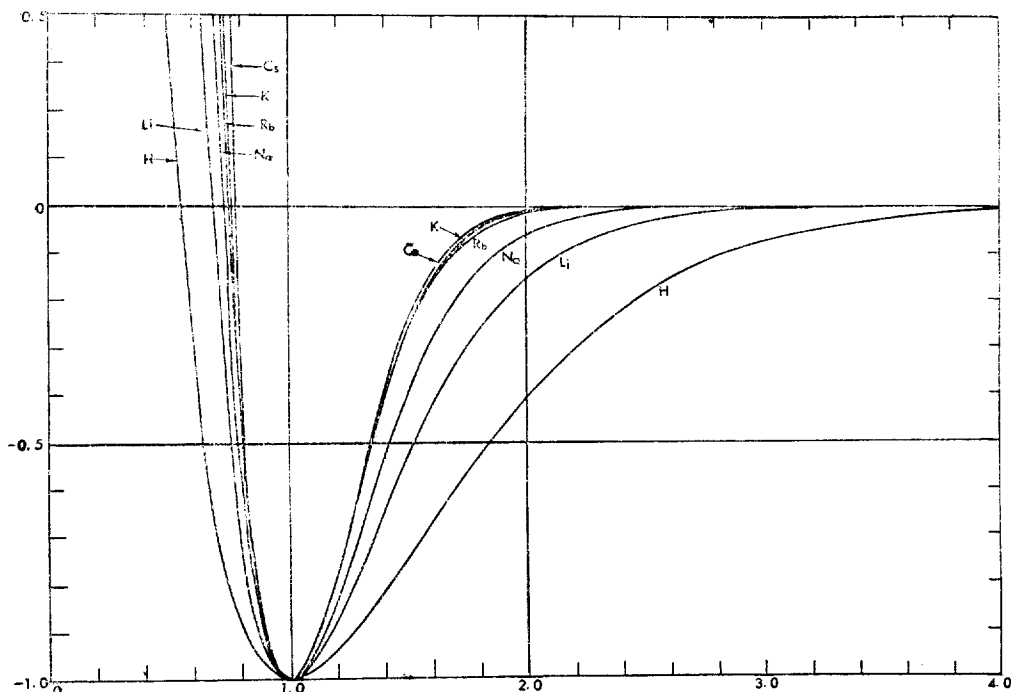


Fig. 1

obtained from the quantum-mechanical calculations of James *et al.*⁽⁵⁾ at small separations and those of Dalgarno and Lynn⁽⁴⁾ at large separations, reported by Buckingham⁽⁶⁾ and Coulson and Haigh⁽⁷⁾.

The molecular and repulsive core constants of hydrogen and alkali metal diatomic molecules used in the present scaling procedure are given in Table 1. The interaction potential energies of hydrogen atoms and those of alkali metal atoms obtained by scaling are shown in a reduced form in Figures 1 and 2.

III. THE EQUATIONS OF STATE

The equations of state of alkali metal vapors can be expressed in terms of the virial coefficients for the volume expansion form.

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots \quad (1)$$

If the virial coefficients, $B(T)$, $C(T)$ etc. are taken in their classical limit, they can be calculated only from the knowledge of the interaction potentials for alkali metal atoms in the vapor. The second virial coefficient $B(T)$ takes care of all of the two-body interactions and the third virial coefficients $C(T)$ takes care of all of the three body interactions including those between atoms and diatomic molecules. Over the range of our interest in temperature and pressure, the equations of state of alkali metal vapors can be sufficiently represented in terms of the second and third virial coefficients.

1. The Second Virial Coefficients

The second virial coefficient of a gas may be expressed

$$B(T) = -2\pi N_A \int_0^\infty \left[\exp\left(-\frac{V(r)}{kT}\right) - 1 \right] r^2 dr \quad (2)$$

by where $V(r)$ is the binary interaction potential. The theory of the second virial coefficient for a gas of atoms which interact along more than one potential energy curve has been given by Sinanoglu and Pitzer⁽⁸⁾. Since alkali metal atom interact along two potential curves for the singlet and triplet ground-states, the second virial coefficients $B(T)$ of alkali metal atoms in the vapor can be obtained by averaging the contributions from both the interactions according to a priori stat-

istical probability: where $B_s(T)$ and $B_T(T)$ are the

$$B(T) = 1/4 B_s(T) + 3/4 B_T(T) \quad (3)$$

second virial coefficients calculated for the singlet and triplet potentials, respectively.

The second virial coefficients of lithium, sodium, potassium, rubidium, and cesium vapors have been calculated as a function of temperature by numerical

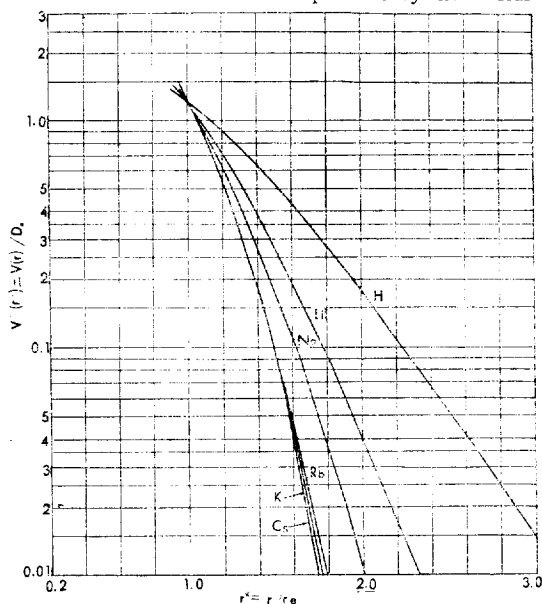


Fig. 2

integration using Eqs. (2) and (3), and the interaction potential energies obtained by scaling.

They have also been calculated using the Rydberg and antibonding Morse potential functions⁽⁹⁾ for the singlet and triplet potentials, respectively.

The calculated values of the second virial coefficients of cesium vapor are shown in Fig. 3 and compared with the experimental data of Ewing *et al.*⁽¹⁰⁾, and Dillon⁽¹¹⁾. The calculated values of potassium vapor are given in Fig. 4 and compared with the experimental data of Ewing *et al.*⁽¹²⁾. The calculated second virial coefficients of rubidium, sodium and lithium vapors are shown in Fig. 5 and those of sodium vapor are compared with the experimental data of Stone *et al.*⁽¹³⁾

2. The Third Virial Coefficients

The third virial coefficient of a gas may be written as a sum of the additive and nonadditive (correction)

terms: ^(14, 15)

$$C(T) = C^{add}(T) + \Delta C(T) \quad (4)$$

$$C^{add}(T) = -\frac{8\pi^2 N_A^2}{3} \int_0^\infty \int_0^\infty \int_0^\infty f_{12} f_{13} f_{23} r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23} \quad (5)$$

$$\Delta C(T) = -\frac{8\pi^2 N_A^2}{3} \int_0^\infty \int_0^\infty \int_0^\infty \exp\left(-\frac{\sum V_{ij}}{kT}\right) \left[\exp\left(-\frac{\Delta V}{kT}\right) - 1\right] r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23} \quad (6)$$

where $f_{ij} = \exp\left(-\frac{V_{ij}}{kT}\right) - 1$

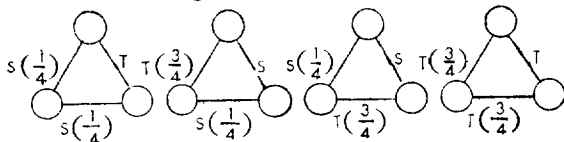
$$\sum V_{ij} = V_{12} + V_{13} + V_{23}$$

V_{ij} is the two-body interaction potential, V_{ij} is the distance between atoms i and j , and ΔV is the three-body interaction energy.

Graben and Present⁽¹⁴⁾ have shown that three-body dispersion forces exist in the three-body interactions and made a significant contribution to the third virial coefficients. Sherwood and Prausnitz⁽¹⁵⁾ have obtained the third virial coefficients for the Kihara, exp-6, and square-well potentials by taking into account the additive and nonadditive (correction) terms.

Now let us consider the three-body interactions of alkali metal atoms in the vapor.

Since the interaction of two ground-state alkali metal atoms depends on whether their electron spins are parallel or antiparallel, as mentioned earlier, the pair-wise interactions in a three-body interaction also depend on the electron spins of two atoms involved in each pair-wise interaction and any two pair-wise interactions decide the third one. Thus, the following combinations of three pair-wise interactions can be considered in forming three-body interactions:



where S and T represent the singlet and triplet potentials, respectively, and the fractions in the parentheses are the statistical weight factors. From the above three-body interactions, it can be found that there are only two types of the three-body interactions, which are the singlet-singlet-triplet and triplet-triplet-triplet interactions with statistical weight factors of 7/16 and 9/16,

respectively. Thus, the third virial coefficients of alkali metal atoms in the vapor can be expressed as a weighted combination of the third virial coefficients for the S-S-T and T-T-T interactions:

$$C = \frac{7}{16} C_{SS\bar{T}} + \frac{9}{16} C_{TTT} \quad (7)$$

$$C = \frac{7}{16} (C_{SS\bar{T}}^{add} + \Delta C_{SS\bar{T}}) + \frac{9}{16} (C_{TTT}^{add} + \Delta C_{TTT}) \\ = \left(\frac{7}{16} C_{SS\bar{T}}^{add} + \frac{9}{16} C_{TTT}^{add}\right) + \left(\frac{7}{16} \Delta C_{SS\bar{T}} + \frac{9}{16} \Delta C_{TTT}\right) = C^{add} + \Delta C \quad (8)$$

$$C^{add} = \frac{7}{16} C_{SS\bar{T}}^{add} + \frac{9}{16} C_{TTT}^{add} \quad (9)$$

$$\Delta C = \frac{7}{16} \Delta C_{SS\bar{T}} + \frac{9}{16} \Delta C_{TTT} \quad (10)$$

The integrals for the additive third virial coefficients of S-S-T and T-T-T interactions can be expressed, using geometric considerations⁽¹⁶⁾, as follows:

$$C_{SS\bar{T}}/b_0^3 = C^*_{S\bar{T}T}(T^*) \\ = -6(L_S^3 L_T - (M_{S,ST} + M_{S,TS} + M_{T,SS})) \\ = -6(L_S^3 L_T - (2M_{S,ST} + M_{T,SS})) \quad (11)$$

$$C_{TTT}/b_0^3 = C^*_{TTT}(T^*) \\ = -6(L_T^3 - 3M_{T,TT}) \quad (12)$$

where $b_0 = \frac{2}{3}\pi N r_0^3$, $T^* = \frac{kT}{D_e}$,

$$L_S = \int_0^\infty g_S(T^*, R^*) dr^*$$

$$L_T = \int_0^\infty g_T(T^*, R^*) dr^*$$

$$M_{S,ST} = \int_0^\infty \int_0^\infty g_S(T^*, r_1^*) g_T(T^*, r_2^*) Q_S(T^*, (r_1^* + r_2^*)) dr_1^* dr_2^*$$

$$M_{S,TS} = M_{S,ST}$$

$$M_{T,TT} = \int_0^\infty \int_0^\infty g_T(T^*, r_1^*) g_T(T^*, r_2^*) Q_T(T^*, (r_1^* + r_2^*)) [dr_1^* dr_2^*]$$

$$Q_S(T^*, w) = \int_w^\infty g_S(T^*, r^*) dr^*$$

$$g_S = r^* [\exp(-V_S(r^*)/kT) - 1]$$

$$g_T = r^* [\exp(-V_T(r^*)/kT) - 1]$$

$$r^* = r/r_0$$

$V_S(r^*)$ and $V_T(r^*)$ are the two-body interaction potentials singlet and triplet states in terms of the reduced distance, r^*

The additive third virial coefficients of lithium,

sodium, potassium, rubidium, and cesium vapors have been calculated by numerical integration using the above relations and the interaction potentials obtained by scaling. The present computer programs have been satisfactorily checked by comparing their results for the Lennard-Jones(6-12) potential with those of Bird and Spatz,⁽¹⁶⁾ and Sherwood and Prausnitz⁽¹⁵⁾.

The nonadditive third virial coefficients of alkali metal vapors can not be accurately evaluated in the present study because the three-body energies of the S-S-T and T-T-T interactions are not known. However, Rosen⁽¹⁷⁾ has calculated $\Delta V(\text{overlap})/\sum V_{ij}$ for three helium atoms in equilateral and linear configurations using the first-order perturbation theory, where $\Delta V(\text{overlap})$ is the repulsive part of the three-body energy. Sherwood and Prausnitz⁽¹⁵⁾ have used his approximate expression for the equilateral orientation in evaluating the effect of $\Delta V(\text{overlap})$ on the nonadditive third virial coefficients in the equilateral case of helium and found that the inclusion of the three-body overlap energy reduces the nonadditive term of the three-body dispersion energy by about 20%. In effect, they have shown that the attractive and repulsive parts of the three-body energy lead to the positive and negative nonadditive third virial coefficients, respectively, and their absolute values are approximately five to one ratio.

Now we can at least qualitatively evaluate the nonadditive third virial coefficients of the S-S-T and T-T-T interactions. Since the S-S-T interaction has two attractive and one repulsive pair-wise interactions, the attractive part of its three-body energy can be estimated to be about one-third of the three-body dispersion energy and the repulsive part to be a little greater than the three-body overlap energy. Therefore, its contribution to the nonadditive term may be positive and very small. On the other hand, the three-body energy of the T-T-T interaction is purely repulsive and hence, contributes a negative correction to the third virial coefficients. Its nonadditive term is expected to be small, since the additive third virial coefficients of the T-T-T interactions are much smaller than those of the S-S-T interactions as shown in Table 2. Therefore,

the overall nonadditive third virial coefficient of alkali metal atoms in the vapor may be estimated to be very small, and furthermore, decreases with increasing temperature.

TABLE 2. The Additive Third Virial Coefficients of the S-S-T and T-T-T Interactions

T, °K	$C_{SST}, (\text{cm}^3/\text{g-mole})^2$	$C_{TTT}, (\text{cm}^3/\text{g-mole})^2$
500	4.105×10^{12}	1.058×10^5
1000	2.185×10^8	7.257×10^4
1500	8.687×10^6	5.604×10^4
2000	1.607×10^6	4.559×10^4
2500	5.364×10^5	3.826×10^4
3000	2.400×10^5	3.279×10^4
4000	7.559×10^4	2.519×10^4
5000	3.290×10^4	2.017×10^4

The calculated values of the additive third virial coefficients of cesium vapor are plotted against reciprocal temperature and compared with the experimental data of Ewing *et al.*⁽¹⁰⁾, and Dillen⁽¹¹⁾, in Fig. 6. Those of potassium vapor are shown and compared with the experimental data of Ewing *et al.*⁽¹²⁾, in Fig. 7. The calculated values of rubidium, sodium, and lithium vapors are also shown in Fig. 8, and those of sodium vapor are compared with the experimental data of Stone *et al.*⁽¹³⁾.

IV. RESULTS AND DISCUSSIONS

The reliability of a semi-empirical scaling procedure between hydrogen and alkali metals has been examined by comparing the calculated values with the available experimental data on the singlet ground-state potentials of alkali metal diatomic molecules. It has been found that there is good agreement between them, even though no adjustment has been made for the repulsive core constants. However, the repulsive core constants σ have been slightly adjusted to make the reduced alkali metal potential curves fit exactly on the reduced hydrogen curve at their highest observed data, and the adjusted constants $\sigma'^{(2)}$ have been used in obtaining the potentials for $^1\Sigma$ and $^3\Sigma$ ground-state interactions of alkali metal atoms. Therefore, the accuracy of the potentials for $^1\Sigma$ groundstate interactions of

alkali metal atoms extrapolated beyond the experimental ranges and the entire potential curves for their $^3\Sigma$ ground-state interactions depends on that of the respective potential curves of hydrogen atoms.

Some analytical potential functions such as the Lennard-Jones (6-12), the Rydberg, the Morse, the Lippincott, or the Hulburt-Hirschfelder potential functions⁽¹⁷⁾ have been tested by comparing them with the available data over the limited experimental ranges, and the Rydberg potential function has been found to be the best approximation among them. For the $^3\Sigma$ ground-state interactions the antibonding Morse potential function⁽⁹⁾ has been used and found to be much different from the potential curves obtained by scaling.

From Figs. 3, 4, and 5 it can be seen that there is reasonably good agreement between calculated and experimental results for each alkali metal vapor, considering that no adjustable constants have been used. It can also be seen that the extrapolation of the experimental data at high temperatures deviates considerably from the calculated values. This fact suggests that the extrapolation may be incorrect. As far as the calculation of the virial coefficients by means of statistical mechanics is concerned, its accuracy is better at higher temperatures. Therefore, it can be concluded that the true second virial coefficients at high temperatures can be better represented by the calculated values than by the extrapolation of the experimental data.

Since alkali metal atoms interact along two potential curves, it is not easy to obtain information on the potential functions directly from the experimental values of the second virial coefficients. However, it is possible to test the accuracy of the proposed potentials by comparing the experimental values with the calculation from the proposed potentials. As can be seen in Figs. 3, 4, and 5, the calculated values from the potential energies obtained by scaling are in better agreement with the experimental data than those from the analytical potential functions, except in the case of potassium vapor. Therefore, it can be concluded that the interaction potentials obtained by scaling are better

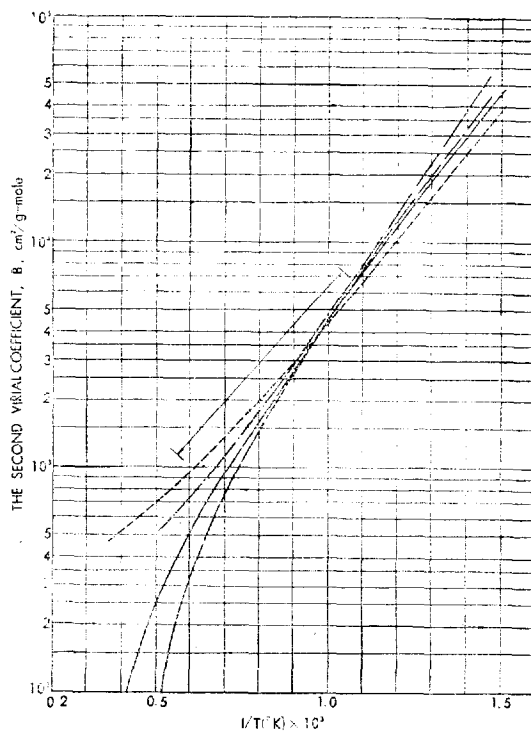


Fig. 3.

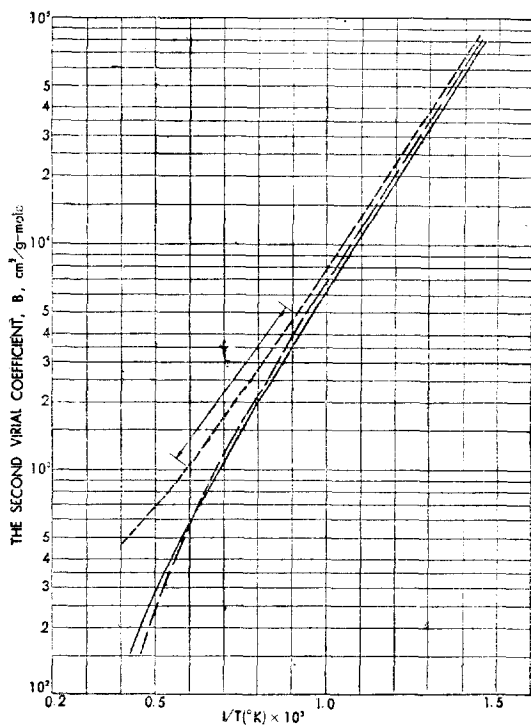


Fig. 4.

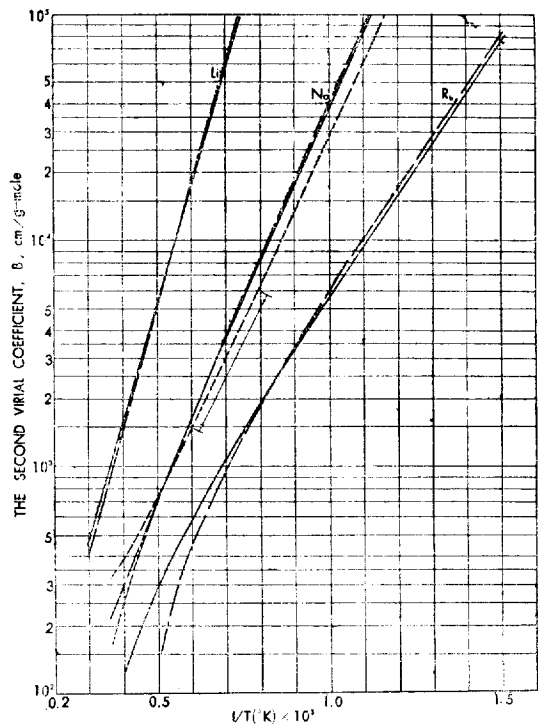


Fig. 5.

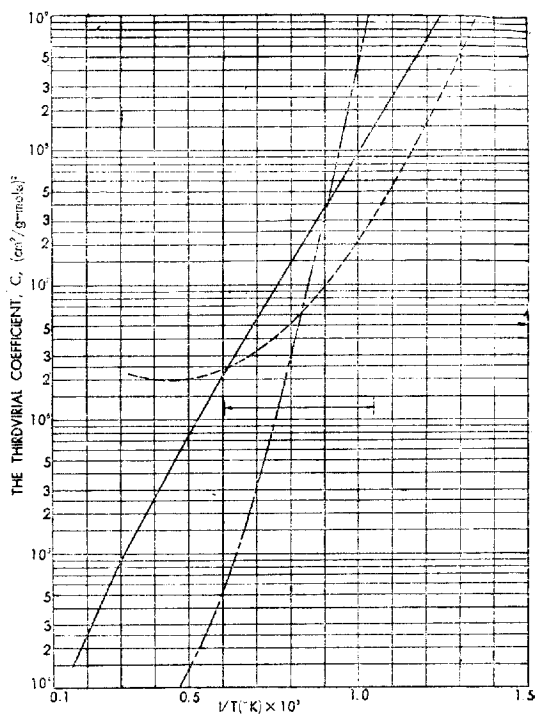


Fig. 6.

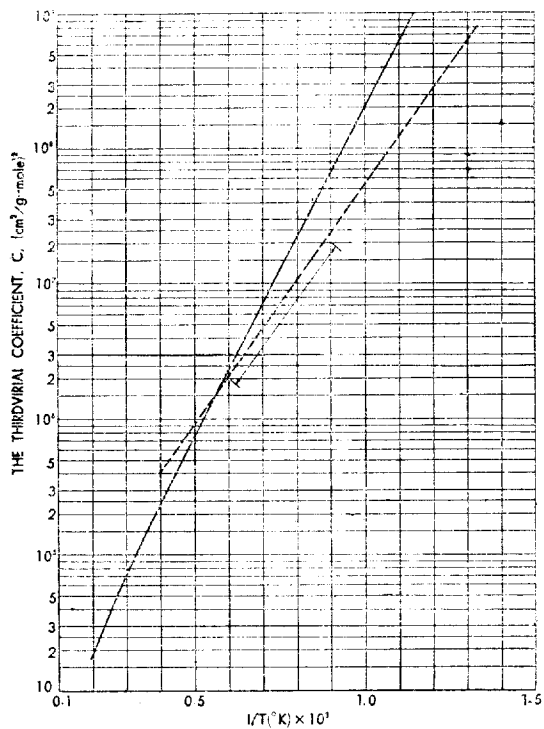


Fig. 7

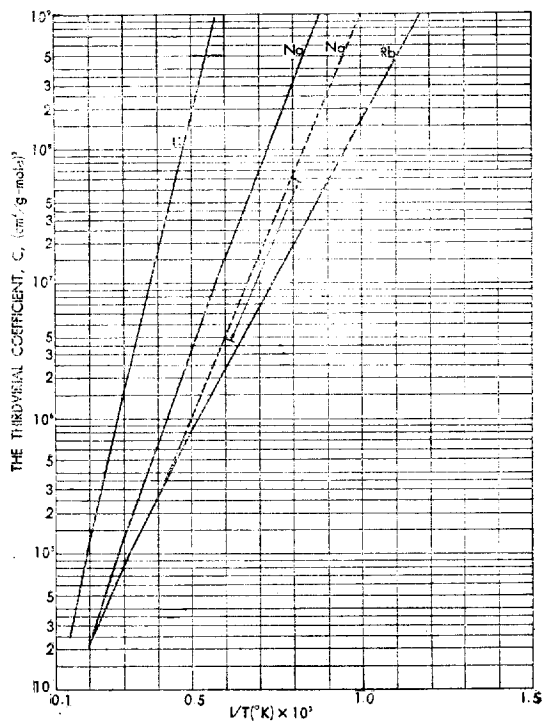


Fig. 8

representative of the true potentials of alkali metal atoms than the analytical potential functions.

From Fig. 6 it can be seen that the calculated additive third virial coefficients of cesium vapor fall in between the two sets of the experimental data of Ewing *et al.* ⁽¹⁰⁾, and Dillon⁽¹¹⁾. In view of the fact that there is big discrepancy between the two sets of the experimental data, agreement between calculated and experimental values is fairly satisfactory even without a nonadditive correction. Fig. 7 shows very satisfactory agreement between the calculated additive third virial coefficients and the experimental data of Ewing *et al.*⁽¹²⁾ at high temperatures in particular in the case of potassium vapor.

However, the calculated additive third-virial coefficients of sodium vapor differ considerably from the experimental results of Stone *et al.* ⁽¹³⁾, as shown in Fig. 8. This difference may be due to a significant contribution of the nonadditive term to the third virial coefficient of sodium vapor. Since the lower the reduced temperature, the greater the nonadditive term, it can be expected that the contribution of the nonadditive term increases in order of cesium, rubidium, potassium, sodium, and lithium vapors at a given temperature. Therefore, we can conclude that the third virial coefficient of cesium, rubidium, and potassium vapors can be given by the calculated additive third virial coefficients alone without nonadditive corrections beyond the experimental ranges. However, those of sodium and lithium vapors can not be represented by the calculated additive third virial coefficient alone even at high temperatures, and the nonadditive correction terms must be considered for them. It is interesting to note that the nonadditive terms are negative.

It is known that alkali metal vapors contain not only atoms, but also diatomic molecules. Consequently, in order to calculate the virial coefficients the potential energy curves for the interactions between the various species in the vapor must be known. However, the amount of diatomic molecules is fairly small and decreases with decreasing pressure, and furthermore, the third virial coefficient can take care of the inte-

ractions between atoms and diatomic molecules. Thus, errors due to neglect of diatomic molecules in the vapor may be small, unless vapor pressures are extremely high.

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NOTATION

Fig. 1 The Reduced Potential Curves for the $^1\Sigma$ Ground-State Interactions of Hydrogen and Alkali Metal Atoms

Fig. 2 The Reduced Potential Curves for the $^3\Sigma$ Ground-State Interactions of Hydrogen and Alkali Metal Atoms

Fig. 3 The Second Virial Coefficients of Cesium Vapor
 ———; calculated from the potentials obtained by scaling
 ———; calculated from the analytical potential functions
; Ewing *et al.* ⁽¹⁰⁾
 ———; Dillon⁽¹¹⁾
 ←——→; experimental range

Fig. 4 The Second Virial Coefficients of Potassium Vapor
 ———; calculated from the potentials obtained by scaling
 ———; calculated from the analytical potential functions
; Ewing *et al.* ⁽¹²⁾
 ←——→; experimental range

Fig. 5 The Second Virial Coefficients
 ———; calculated from the potentials obtained by scaling
 ———; calculated from the analytical potential functions
; Stone *et al.* ⁽¹³⁾
 ←——→; experimental range

Fig. 6 The Third Virial Coefficients of Cesium Vapor
 ———; the additive third virial coefficients calculated from the potentials obtained by scaling
; Ewing *et al.* ⁽¹⁰⁾
 ———; Dillon⁽¹¹⁾

←—→; experimental range

Fig. 7 The Third Virial Coefficients of Potassium Vapor

———; the additive third virial coefficients
 ———; calculated from the potentials obtained
 by scaling
; Ewing *et al.* ⁽¹²⁾

←—→; experimental range

Fig. 8 The Third Virial Coefficients of Rubidium, Sodium,
 and Lithium Vapors

———; the additive third virial coefficients
 ———; calculated from the potentials obtained
 by scaling

.....; Stone *et al.* ⁽¹³⁾

←—→; experimental range

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