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EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF GASES AT HIGH TEMPERATURES I. DIATOMIC MOLECULES

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I. DIATOMIC MOLECULES

O. Sinanoğlu and K. S. Pitzer

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EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF
GASES AT HIGH TEMPERATURES
I. DIATOMIC MOLECULES

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ABSTRACT

Methods for evaluating the thermodynamic properties of assemblies of chemically reacting unionized atoms are discussed. The desirability of using the virial coefficients at high temperatures instead of the customary use of the molecular partition functions with anharmonicity corrections is pointed out. The most realistic three parameter diatomic potential energy function that is available at present, i.e. the Rydberg potential: $U/U_e = -(1 + b'\xi) \exp(-b'\xi)$ with $\xi = (\frac{r}{r_e} - 1)$ is selected for the evaluation of the classical second virial coefficient. $B(T)$, $T \frac{dB}{dT}$ and $T^2 \frac{d^2B}{dT^2}$ are obtained as linear combinations involving the five functions: $A_k(\theta) = \sum_{n=1}^{\infty} \frac{(\theta e)^n}{n+k}$, ($k = -1, 0, 1, 2, 3$ and $\theta = \frac{U_e}{kT}$) with only the coefficients that multiply A_k depending on b' . A_k is tabulated for $0.05 \leq \theta \leq 10$. A simple expression for estimating the quantum correction

to $\underline{B}(\underline{T})$ is given. The inclusion of the contribution of the higher diatomic electronic states to $\underline{B}(\underline{T})$ is considered. The treatment is applied to sodium (including the 3σ repulsive state), and $\underline{B}(\underline{T})$ and thermodynamic properties calculated at two temperatures by several methods are compared.

EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF
GASES AT HIGH TEMPERATURES

I. DIATOMIC MOLECULES

INTRODUCTION

The thermodynamic properties and equation of state of a dissociating but unionized gas could in principle be obtained by the use of two different formalisms. In the first of these the gas is treated as a mixture of certain significant molecular species, e.g. diatomic, triatomic, etc. molecules, i.e. it is assumed that only those portions of the phase space that are in the vicinity of some highly probable configurations are important and the equilibrium composition of the gas in terms of these species and the contribution of each to the thermodynamic properties are calculated from the ordinary partition functions of the "molecules". It is apparent that this method is most appropriate for an assembly of chemically reacting atoms and at such temperatures that certain molecular species are unambiguously definable. In the second method the entire gas is treated as a monatomic assembly with imperfections given by

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

or $PV = RT + B(T)P + C(T)P^2 + \dots$ (1b)

and then all the thermodynamic properties are obtainable¹

¹See, for example, Hirschfelder, Curtiss, Bird, "Molecular Theory of Gases and Liquids", John Wiley and Sons, Inc., New York (1954), p. 230.

as corrections to those of the monatomic gas in terms of the virial coefficients $B(T)$, $C(T)$. . . and their first and second temperature derivatives.

Of course the two formalisms are in principle quite equivalent as can best be seen from the most general derivation of the virial coefficients by the use of the quantum grand canonical partition function which is not restricted to a classical gas with pairwise additive interactions². For instance, the second virial coefficient for a

²J. E. Kilpatrick, J. Chem. Phys., 21, 274 (1953).

general gas is given by

$$B(T) = - \frac{N_0}{2V} \left(\frac{V}{Q_1} \right)^2 (2Q_2 - Q_1^2) \quad (2)$$

where N_0 is Avogadro's number and Q_1 and Q_2 are the partition functions for monomer and dimer in the volume V .

The equivalence between the two formalisms has been discussed in great detail by Hill³ and Kilpatrick⁴. Differences

³T. L. Hill, "Statistical Mechanics", McGraw-Hill Book Co., Inc., New York (1956), p. 146 ff.

⁴J. E. Kilpatrick, J. Chem. Phys., 21, 1366 (1953).

arise for the most part from the ambiguity of defining "physical clusters" and in the manner the two methods are conventionally applied; for instance the chemical equilibrium method will not give the correct pressure unless interactions between unbound molecules are introduced amounting to the use of activities rather than concentrations in the equilibrium quotient^{3,5}.

⁵H. W. Woolley, J. Res. N. B. S., 61, 469 (1958).

In practice, for atoms with strong chemical interactions and at ordinary temperatures i.e. when appreciable fractions of molecules are present, the chemical equilibrium treatment is the convenient one, since even with a gas composed of only diatomic molecules and atoms, in the virial treatment not only $B(T)$ but also higher coefficients would be important. On the other hand the virial coefficients formalism is most useful when interatomic potential energies are comparable to kT . At these temperatures the virial coefficients can usually be taken in their classical limit; for instance $B(T)$ for atoms interacting on only one potential curve reduces to

$$B_{cl}(T) = -2\pi N_0 \int_0^{\infty} \left[\exp \left(- \frac{U(r)}{kT} \right) - 1 \right] r^2 dr \quad (3)$$

and has been extensively used in this form for chemically inert atoms¹. It is clear that a gas containing a large fraction of molecules and treated by the use of quantum partition functions that are good approximations near the most stable configurations approaches more and more a classical assembly of atoms at higher temperatures and the virial coefficient formalism becomes more and more appropriate since it avoids some of the difficulties encountered in the use of partition functions near dissociation. It is this approach that will form the basis for our treatment of the thermodynamic properties of a gas composed of chemically reacting atoms at high temperatures. In this article we shall be concerned with a gas that contains only unionized atoms and "diatomic molecules" but at such temperatures that only a relatively small fraction of "dimers" are involved so that the second virial coefficient, taking care of all the binary interactions of the atoms including "chemical association", is the most important term in contributing to the thermodynamic properties. We expect to extend this treatment in the near future to the third virial coefficient of an assembly of chemically reacting atoms which have strongly non-pairwise additive interatomic potentials.

DIATOMIC MOLECULES

At quite low temperatures the partition function (p.f.) of a diatomic molecule, Q_2 , is approximated by the harmonic

oscillator-rigid rotator p.f. At higher temperatures the population of levels corresponding to the non-parabolic regions of the potential energy curve $U(r)$ is no longer negligible and it becomes necessary to modify the simple p.f. by the introduction of "anharmonicity corrections", into the energy levels of the molecule in the form

$$\frac{E_{v,j}}{hc} = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})\omega_e x_e + j(j+1)B_e - j^2(j+1)^2 D_e - (v + \frac{1}{2})j(j+1)a_e \dots \quad (4)$$

where ω_e , $\omega_e x_e$, B_e , D_e , a_e are the usual spectroscopic constants. The p.f. should be calculated from

$$Q_{2,int.}^{(1)} = \sum_{v,j} \exp \left(- \frac{E_{v,j}^{(1)}}{kT} \right) \quad (5a)$$

and

$$Q_{2,int.} = \sum_i Q_{2,int.}^{(1)} \omega_i \exp \left(- \frac{E_i}{kT} \right) \quad (5b)$$

where ω_i is the degeneracy and E_i energy to the minimum of the i th electronic state of the molecule. Equation (4) for $E_{v,j}^{(1)}$ is an approximation valid not too near dissociation and due to the $(v + \frac{1}{2})^2$ term the sum (5a) will diverge if carried to infinity. Mayer and Mayer⁶ have

⁶J. E. Mayer, M. G. Mayer, "Statistical Mechanics", John Wiley and Sons, Inc., New York (1940), p. 160 ff.

obtained expressions for thermodynamic functions from (4) and (5a) however, by expanding some of the exponentials

arising from (4) and taking only the first two terms. At not too high temperatures the Boltzmann factor for the main part of $E_{v,j}$ overtakes the higher terms in this expansion and the sum converges. At higher temperatures, however, errors from several sources are introduced and are difficult to estimate. Firstly at high enough temperatures, the range of validity of (4) will no longer be sufficient, and it must be emphasized that the range important in the p.f. is not determined solely by the magnitude of the Boltzmann factor for different energies but also by the density of states (the entropy effect). Thus even though the dissociation energy of Na_2 is $k \times 8600^\circ\text{K}$, at 1600°K and 1 atm the gas will contain almost all monomers. Secondly, even in the range where (4) is still quite valid, the errors⁷ introduced in the approximate summation procedure

⁷For a discussion of these errors see also G. Baumann, Z. Physik. Chemie (Frankfurt), 14, 113 (1958).

itself might become appreciable, especially if $\frac{\omega_e x_e}{U_e}$ is large, since each term in the sum (5a) will have some error due to the neglected terms of the exponential series, and at higher energies there will be more and more terms near the same energy. With strongly bound atoms, i.e. when binding energies (U_e) are greater than several ev's, errors might become appreciable above $3-4000^\circ\text{K}$; on the other hand with weakly bound ($U_e < 1$ ev, e.g. alkali vapors, Hg, etc.) atoms even at ordinary temperatures all of the potential energy

curve ($\underline{U}(r)$) contributes to $\underline{Q}_2$, and since energy levels near dissociation generally are not known, it becomes necessary to revert to the virial coefficient treatment. Under the conditions of concern here, the use of the classical second virial coefficient (3) (quantum corrections will be considered later) provides a good approximation. Thus it becomes necessary to choose suitable semi-empirical potentials to represent the interaction of atoms. One hopes to select a potential which is applicable to a large number of systems and adequate in the region of repulsive as well as attractive forces. For chemically non-reacting systems (e.g. inert gases) and for repulsive electronic states (e.g. the $^3\Sigma$ state of $\underline{\text{Na}}_2$) two parameter functions that are simply sums of an exponential or inverse power repulsion and inverse sixth power London attraction are quite adequate. Among these the Lennard-Jones (6-12) potential has been most widely used to obtain the virial coefficients and transport properties. Tables of $B^*(T^*)$ have been extended by Epstein⁶ to the low reduced temperatures [$T^* = (kT/U_e) < 0.3$] necessary for application to atoms interacting much more strongly than the inert gases. (He has also treated the Lennard-Jones (6-9) potential⁹).

⁶L. F. Epstein, G. M. Roe, J. Chem. Phys., 19, 1320 (1951).

⁹L. F. Epstein, J. Chem. Phys., 20, 1665 (1952); L. F. Epstein, C. J. Hibbert, J. Chem. Phys., 20, 752 (1952).

However with chemical interactions a two parameter potential

is no longer satisfactory since the exchange attraction depends strongly on the nature of the atoms involved. A very large number of semi-empirical potentials have been proposed by various investigators for such systems, i.e. "diatomic molecules". An excellent critical review of these has recently been given by Varshni¹⁰. A good potential

¹⁰Y. P. Varshni, Rev. Mod. Phys., 29, 664 (1957).

must have a minimum number of parameters yet predict the remaining spectroscopic constants in Eq. (4) with sufficient accuracy as well as being adequately close to the dispersion forces at large distances. The most widely known three parameter potential is that of Morse

$$U^* = \frac{U}{U_e} = e^{-2a\xi} - 2e^{-a\xi} \quad (6)$$

where $a = r_e(k_e/2U_e)^{1/2}$; $\xi = \frac{r}{r_e} - 1$

This potential (which "has been overworked in many branches of investigation" as Partington¹¹ remarks) gives too much

¹¹J. R. Partington, "An Advanced Treatise on Physical Chemistry", Vol. 1, Longmans Green and Co., New York (1943), p. 327.

attraction at long distances and predicts $\omega_e x_2$ on the average within $\pm 31.2\%$ and α_e within $\pm 33.1\%$ for the twenty-seven diatomic molecules studied¹⁰. Hulburt and Hirschfelder¹²

¹²H. M. Hulburt and J. O. Hirschfelder, J. Chem. Phys., 9, 61 (1941).

have tried to compensate for this excess attraction by adding a term to the Morse function with two additional parameters.

$$U_{H.H.} = U_{\text{Morse}} + U_e c x^3 e^{-2x} (1 + b x) \quad (7)$$

$$x = a \xi$$

This potential has a total of five parameters and makes use of all the available spectroscopic constants given in (4); it is probably the most accurate known potential over a wide range of r . The second term in (7) introduces unnecessarily large "corrections" for $x < 0$, but this defect is eliminated if we replace x in e^{-2x} by its absolute value $|x|$. Equation (7) is impractical for our use in the calculation of $B(T)$ because of the large number of its parameters, some of which moreover, may not be available for some systems. Of all the three parameter potentials examined by Varshni¹⁰, the one proposed by Rydberg¹³ in 1931

¹³R. Rydberg, Z. Physik., 73, 376 (1931).

gives on the average the best prediction for both $\omega_e x_e$ (within $\pm 23.1\%$) and α_e ($\pm 28\%$). (Lippincott potential gives a better value for $\omega_e x_e$ although not for α_e at all; however, it gives $U = U_e$ at $r = 0$, and when corrected for this important defect it loses the advantage of its simple analytic form. The Rydberg function is not infinite either at $r = 0$, but is sufficiently large.) The Rydberg function

in general will give considerably less excess attraction at large r than the Morse function and has the simple analytical form

$$U = -U_e(1 + b'\xi)e^{-b'\xi} \quad (8)$$

$$b' = r_e \left(\frac{k_e}{U_e} \right)^{1/2} \text{ and } \xi = r^* - 1 = \frac{r}{r_e} - 1$$

In Fig. 1 the Rydberg and Morse functions for the $^3\Sigma_u^-$ excited electronic state of O_2 are shown as well as a curve (shown as "experimental") that Rydberg has constructed by a graphical method from the vibrational levels which for this state are available up to quite near dissociation. (The curves are from Ref. 13.) The $B(T)$ that we are about to give is necessary for the thermodynamic properties of alkali vapors at ordinary temperatures because of the weakness of interactions, therefore in Fig. 2 we examine and compare various functions for sodium ($^1\Sigma$). It is observed that the Lennard-Jones (6-12) and (6-9) potentials give too narrow a bowl. The Hulburt-Hirschfelder function may be considered as the "true" potential. The attraction for distances where overlap is negligible (i.e. ca. $r^* > 2$) can be estimated¹⁴

¹⁴H. Margenau, Rev. Mod. Phys., 11, 1 (1939)

using second order perturbation theory and is given in the form

$$\frac{c_1}{r^6} + \frac{c_2}{r^8} + \frac{c_3}{r^{10}} + \dots \quad (9)$$

where $\underline{c}_1, \underline{c}_2, \underline{c}_3 \dots$ can be calculated from the atomic energy levels and their oscillator strengths. Because of their large polarizability, alkali atoms exhibit dispersion forces that are particularly large and even at $\underline{r}^* = 2$, the multipole interaction terms $\underline{r}^{-6}, \underline{r}^{-10}$, contribute as much as the $\underline{r}^{-6}$ term¹⁴. A lower limit to the dispersion attraction calculated from the $\underline{c}_1, \underline{c}_2, \underline{c}_3$ given by Margenau¹⁴ for Na is also shown in Fig. 2. Both figures indicate the considerable improvement resulting from the use of Rydberg function over a wide range of $\underline{r}$. Hence in the following, this potential will be used in Eq. (3) for the evaluation of $\underline{B}(\underline{T})$ and might be expected to be a good approximation except for ionically binding systems and for states that show some anomaly such as a maximum in the potential curve.

THE SECOND VIRIAL COEFFICIENT

At high temperatures usually more than one atomic and diatomic electronic state need to be considered when dealing with the binary interactions of an assembly of chemically reacting (i.e. spinwise unsaturated) atoms. For such systems $\underline{B}(\underline{T})$ must include contributions from various potential energy curves. An examination of Eqs. (2) and (5b) shows that the complete $\underline{B}(\underline{T})$ is given by

$$\underline{B}(\underline{T}) = \frac{\sum \omega_i \exp(-E_i/kT) B^{(1)}(T)}{[\sum_j \Omega_j \exp(-E_j/kT)]^2} \quad (10)$$

where $\underline{\omega}_1$ and $\underline{\omega}_j$ are the electronic multiplicities of the diatomic and atomic states respectively. $\underline{E}_j$ is the excitation energy of one atom; $\underline{E}_1$ is zero if the $\underline{1}$ th diatomic potential dissociates into ground state atoms, otherwise it is the energy difference between the dissociation products and the ground state atoms of the $\underline{1}$ th diatomic electronic state and $\underline{B}^{(1)}$ is the virial coefficient for the $\underline{1}$ th potential energy curve (taken to become zero at its dissociation) and will be given by Eq. (3) when quantum effects are negligible. If $\underline{1}$ is a state for which the Rydberg potential (6) is applicable, $B_{cl}^{(1)}(T)$ in reduced form is given by

$$B_{cl}^{(1)}(T) = \frac{2\pi N_o}{b_1^3} \int_{-b_1'}^{\infty} (1 - \exp[\theta_1(1+x)e^{-x}])(x + b_1')^2 dx \quad (11)$$

where we have substituted

$$b_1 = \frac{b_1'}{r_e^{(1)}} = \left(\frac{k_e^{(1)}}{U_e^{(1)}} \right)^{1/2}$$

$$\theta_1 = \frac{1}{T_1^*} = \frac{U_e^{(1)}}{kT}$$

$$x = b_1' (r_{(1)}^* - 1) = b_1' \left(\frac{r}{r_e^{(1)}} - 1 \right)$$

For each of the contributing electronic state potentials there will be a different $\underline{b}'$, and a different reduced temperature.

Eq. (11) can be exactly integrated term by term after expanding the exponential and denoting $(\underline{x} + \underline{b}')$ by $\underline{y}$; the result is

$$\frac{b^3 B_{2,0}(T)}{2\pi N_0} = I(\theta, b') = - \sum_{n=1}^{\infty} \frac{\theta^n}{n!} \int_0^{\infty} e^{-ny} (y - b' + 1)^n y^2 dy \quad (12)$$

or

$$I(\theta, b') = - \sum_{n=1}^{\infty} \theta^n \sum_{r=0}^n \frac{(1 - b')^r (n - r + 2)(n - r + 1)}{r! n(n - r + 3)}$$

where $\theta' = \theta e^{b'}$.

However, this series is not desirable for the computation of $\underline{I}$, because for the $\underline{\theta}$ range of interest here, it is very slowly convergent and depends on $\underline{b}'$ in each term so that it would be necessary to prepare tables of $\underline{I}$ versus $\underline{\theta}$ and $\underline{b}'$. Instead $\underline{I}(\underline{\theta}, \underline{b}')$ can be conveniently evaluated in the following manner.

Let us break the integral in Eq. (11) into two parts

$$\begin{aligned} \underline{I} &\equiv \underline{I}_0 + \underline{I}_1 = \int_{-b'}^{-1} (1 - \exp[\theta(1+x)e^{-x}]) (x + b')^2 dx \\ &\quad + \int_{-1}^{\infty} (1 - \exp[\theta(1+x)e^{-x}]) (x + b')^2 dx \end{aligned} \quad (13)$$

Notice that $\underline{I}_0$ corresponds to the contribution of the positive portion of $\underline{U}(\underline{r})$ and $\underline{I}_1$ of the negative portion and that for $\underline{\theta} > 1$, $\underline{I}_0$ is usually a small fraction of $\underline{I}_1$. Now $\underline{I}_1$ can be integrated exactly by substituting $\underline{z}$ for $(\underline{x} + 1)$, then expanding the exponential in (13) and we obtain after

manipulation

$$-I_1(\theta, b') = 2A_3 + (2b' + 1)A_2 + b'^2 A_1 \quad (14a)$$

$$\text{where } A_k(\theta) = \sum_{n=1}^{\infty} \frac{(\theta e)^n}{n^{n+k}} \quad (14b)$$

On the other hand for $\underline{I}_0$ we write

$$\underline{I}_0 = \frac{b''^3}{3} - b''^2 R_0 + 2b'' R_1 - R_2 \quad (14c)$$

where $b'' = b' - 1$

$$\text{and } R_k = \int_0^{b''} z^k \exp [-\theta z e^{(z+1)}] dz \quad (k = 0, 1, 2)$$

For θ greater than about 1.0 which covers most of the temperature range of interest as it is apparent from the $\underline{U}_e/k$'s shown in Table I, the exponential part in $\underline{I}_0$ is negligible and we get

$$I(\theta, b') \approx \frac{(b' - 1)^3}{3} - 2A_3 - (2b' + 1)A_2 - b'^2 A_1 \quad (15)$$

This provides a very good approximation to $\underline{I}$ at $\theta > \text{ca. } 1.0$ since not only the $\underline{R}_k$ terms in (14c) become small with increasing θ , but also $\underline{I}_0$ itself becomes a small fraction of $\underline{I}$. For instance at $\theta = 5$ and $b' = 4$, $\underline{I}_1$ equals -3531 and $\underline{I}_0 \approx 9$. On the other hand to obtain $\underline{I}_0$ for $1 > \theta > 0.1$ the finite limits of the integrals in (14c) can be replaced by infinity, thus reducing $\underline{R}_k$ to functions of θ only. The functions $\underline{R}_k(\theta)$ obtained by numerical

TABLE I

Molecular Constants^a for the Ground Electronic States
of Some Diatomic Molecules

	$r_e (\text{\AA})$	$\omega_e (\text{cm}^{-1})$	$U_e/k (^\circ\text{K})$	b'
H ₂	0.7417	4395.2	55,100	2.04
Li ₂	2.672	351.43	12,100	3.28
Na ₂	3.078	159.23	8,600	3.71
K ₂	3.923	92.64	6,020	4.26
Hg ₂ ^b	3.2	36.	755	8.66
I ₂	2.667	214.6	18,000	7.02
O ₂	1.207	1580.4	60,500	4.51

^aAll values are taken from Ref. 10 unless otherwise indicated.

^bT. B. Douglas, A. F. Ball, D. C. Ginnings, J. Res. Natl. Bur. Standards, 46, 334 (1951)

integration are shown in Fig. 3 and can be used to obtain the corrections to (15) at small θ 's.

We have already remarked that all the thermodynamic functions as corrections to those of the monatomic gas could be obtained if, in addition to B , its first and second temperature derivatives were known. We differentiate (15) and note from (14a) that

$$\begin{aligned}\theta \frac{dA_k}{d\theta} &= A_{k-1} \\ \theta^2 \frac{d^2 A_k}{d\theta^2} &= A_{k-2} - A_{k-1}\end{aligned}\tag{16}$$

obtaining (for $\theta > 1$, $I \cong I_1 + b''^3/3$)

$$-\theta \frac{dI}{d\theta} = T \frac{dI}{dT} \cong T \frac{dI_1}{dT} = 2A_2 + (2b' + 1)A_1 + b'^2 A_0\tag{17}$$

and

$$\begin{aligned}-\theta^2 \frac{d^2 I}{d\theta^2} &= -T^2 \frac{d^2 I}{dT^2} \cong -T^2 \frac{d^2 I_1}{dT^2} = b'^2 A_{-1} - (b'^2 - 2b' - 1)A_0 \\ &\quad - (2b' - 1)A_1 - 2A_2\end{aligned}\tag{18}$$

where again A_k 's are defined by (14b). The functions $A_k(\theta)$ with $k = -1, 0, 1, 2, 3$ were computed on an IBM 701 computer for $0.05 < \theta < 10$ and are given in Table II. They might be useful also in other applications.

TABLE II

The Functions $A_k(\theta) = \sum_{n=1}^{\infty} (\theta e)^n / n^{n+k}$ for the Evaluation of

I_1 and Its Derivatives

θ	A_{-1}	A_0	A_1	A_2	A_3
.05	.1454294	.1406253	.1582542	.1370790	.1364948
.10	.3110905	.2910661	.2613176	.2765304	.2741652
.15	.4988512	.4519280	.4293886	.4184190	.4130325
.20	.7107323	.6238547	.5826738	.5626122	.5531186
.25	.9489262	.8075297	.7413899	.7097795	.6944461
.30	1.2157737	1.0036731	.9057626	.8593925	.8370381
.35	1.5138080	1.2130494	1.0760279	1.0117255	.9809183
.40	1.8457663	1.4364687	1.2524322	1.1668549	1.1261106
.45	2.2145644	1.6747851	1.4352327	1.3248602	1.2726402
.50	2.6233614	1.9289047	1.6246982	1.4858234	1.4205326
.55	3.0755561	2.1997876	1.8211096	1.6498287	1.5698139
.60	3.5747837	2.4884453	2.0247594	1.8169837	1.7205105
.65	4.1249600	2.7959528	2.2359550	1.9873194	1.8726506
.70	4.7302899	3.1234435	2.4650151	2.1609686	2.0262614
.75	5.3953028	3.4721212	2.6822751	2.3360685	2.1813728
.80	6.1248254	3.8432533	2.9180836	2.5186591	2.3380140
.85	6.9240646	4.2381846	3.1628058	2.7028639	2.4962153
.90	7.7985988	4.6583360	3.4168234	2.8907901	2.6560083
.95	8.7544226	5.1052126	3.6805351	3.0825489	2.8174254
1.00	9.7979280	5.5804003	3.9543564	3.2782541	2.9604985

TABLE II (con't)

θ	A_{-1}	A_0	A_1	A_2	A_3
1.1	12.175992	6.622532	4.534090	3.6819835	3.3117505
1.2	14.993891	7.799371	5.159749	4.1029784	3.6500460
1.3	18.521669	9.127274	5.835402	4.5423110	3.9956818
1.4	22.239609	10.624526	6.565494	5.0011293	4.3489705
1.5	26.839591	12.311552	7.354884	5.4806639	4.7102418
1.6	32.226717	14.211168	8.208885	5.9822363	5.0798450
1.7	38.521113	16.348859	9.133303	6.5072637	5.4581475
1.8	45.859932	18.753076	10.134492	7.0572675	5.8455386
1.9	54.399717	21.455584	11.219400	7.6336828	6.2424293
2.0	64.318921	24.491840	12.395624	8.2388638	6.6492541
2.2	89.1374	31.72841	15.056071	9.541610	7.494573
2.4	122.3041	40.83745	18.192229	10.962364	8.385507
2.6	166.3919	52.28507	21.895636	12.580635	9.326555
2.8	224.7213	66.65079	26.276051	14.359025	10.322775
3.0	301.5696	84.65469	31.465135	16.343759	11.379855
3.2	402.4360	107.19106	37.620921	18.565307	12.504211
3.4	534.3777	135.36992	44.933172	21.059094	13.703080
3.6	706.4373	170.56848	53.629894	23.866378	14.984650
3.8	930.1832	214.49466	63.985139	27.035254	16.358184
4.0	1220.3932	269.26541	76.326449	30.621836	17.834192

TABLE II (con't)

θ	A_{-1}	A_0	A_1	A_2	A_3
4.2	1595.921	337.5038	91.05626	34.69168	19.424602
4.4	2080.788	422.4589	108.64570	39.32145	21.142980
4.6	2705.567	528.1532	129.67120	44.60088	23.004769
4.8	3509.119	659.5655	154.82451	50.63507	25.027578
5.0	4540.793	822.8558	184.93914	57.54734	27.231512
5.2	5863.191	1025.6435	221.01958	65.48237	29.639545
5.4	7555.657	1277.3509	264.27694	74.61016	32.277985
5.6	9718.646	1589.6233	316.17137	85.13055	35.176964
5.8	12479.257	1976.8546	378.46469	97.27870	38.371069
6.0	15996.152	2456.8284	453.28256	111.33155	41.900019
6.2	20478.25	3051.508	543.1904	127.61541	45.80948
6.4	26175.67	3788.019	651.2856	146.51516	50.15206
6.6	33413.45	4699.849	781.3080	168.46491	54.98834
6.8	42598.70	5828.332	937.7753	194.06105	60.38827
7.0	54244.27	7224.480	1126.1454	223.87739	66.43259
7.2	68995.64	8951.228	1353.0128	258.68336	73.21468
7.4	87664.89	11086.218	1626.3492	299.36567	80.84258
7.6	111272.97	13725.200	1955.7903	346.97411	89.44145
7.8	141102.81	16986.248	2352.9877	402.75227	99.15639
8.0	178765.58	21014.936	2832.0308	468.17383	110.15578

TABLE II (con't)

θ	A_{-1}	A_0	A_1	A_2	A_3
8.2	226284.0	25990.72	3409.966	544.9870	122.63524
8.4	286195.5	32134.76	4107.411	635.2651	136.82211
8.6	361682.1	39719.59	4949.316	741.4701	152.98092
8.8	456732.9	49081.02	5965.877	866.5258	171.41971
9.0	576344.9	60632.71	7193.639	1013.9060	192.49742
9.2	726777.3	74884.25	8676.849	1187.7411	216.63269
9.4	915864.5	92463.12	10469.072	1392.9423	244.31403
9.6	1153410.6	114142.09	12635.178	1635.3537	276.11202
9.8	1451679.8	140872.68	15253.735	1921.9324	312.69370
10.0	1826005.8	173826.14	18419.900	2260.9618	354.83900

QUANTUM CORRECTION

When the energy of a vibrational quantum of the diatomic molecule in the particular electronic state considered is small compared to the thermal energy, i.e. if

$$1.44 \frac{\omega_e(\text{cm}^{-1})}{T(^{\circ}\text{K})} < 1 \quad (19)$$

Eq. (3) might be expected to be a good approximation to (2). This condition is satisfied for most systems of interest here, nevertheless, it is possible to obtain an estimate of the quantum effects on $\underline{B}(\underline{T})$. The usual quantum correction on $\underline{B}(\underline{T})$ is ordinarily obtained from a WKB approximation (or solution of the Bloch differential equation)¹ and the first two terms are

$$B(T) = B_{cl}(T) + \frac{h^2}{m} B_I(T) + \dots$$

where

$$B_I(T) = \frac{N_0}{24\pi k^3 T^3} \int_0^{\infty} (\exp [-U(r)/kT]) \left(\frac{\partial U}{\partial r} \right)^2 r^2 dr \quad (20)$$

$\underline{B}_I(\underline{T})$ can be evaluated by substituting the Rydberg potential in (20) and expanding the exponential; however, the resulting series is inconvenient for computation. Instead, the first quantum correction can be estimated by noticing that at the lower temperatures at which the quantum effect should be examined, the greatest contribution to the integral in (20) comes from the parabolic region of $\underline{U}(\underline{r})$. For instance for Li at 1720°K ($\theta = 7.1$), a graph

of the integral in (20) shows that there is a very tall and narrow peak at $r^* = 0.85$. Since the quantum effect (only the diffraction effect is important and the symmetry effect need not be considered) comes largely from the vibrational motions, we write in the usual fashion

$$Q_2 = Q_{tr} Q_{rot} Q_{c.l-vib} Q_{correction} \exp (|U_e|/kT) \quad (21)$$

for Q_2 in (2), then

$$Q_{correction} = \frac{x e^{-x/2}}{1 - e^{-x}} = \left(1 - \frac{x^2}{24} + \frac{5x^3}{48} \dots \right)$$

where $x = (h\nu/kT)$, and substituting in (2) we get

$$\underline{B}(T) = B_{c.l} + \left(\frac{h^2}{m} \right) \frac{r_e^2 k_e^{1/2} \exp |U_e|/kT}{12(2\pi)^{1/2} (kT)^{3/2}} + \dots \quad (22)$$

or

$$\underline{B}(T) = B_{c.l} + \frac{\pi^{1/2} h^2 r_e^2 \omega_e \exp |U_e|/kT}{12 m^{1/2} (kT)^{3/2}} + \dots \quad (23)$$

Notice that the same expression is obtained if one substitutes

$$U(r) = -U_e + \frac{1}{2} k_e (r - r_e)^2 + \dots$$

in Eq. (20). Equation (23) gives the first quantum correction term as 89.3 cc/mole for $\underline{Li}_2$ at 1720°K, or roughly half a per cent of $\underline{B}$. Thus for heavier elements and smaller $\underline{Q}$, the quantum correction ordinarily will be negligible.

APPLICATION

We shall now demonstrate the use of the equations developed above, with an application to sodium vapor. As we have already remarked, because of the relative weakness of their interactions, alkali vapors constitute a case where the above treatment is applicable at relatively low temperatures and for instance would be useful in the analysis of their vapor pressure data.

With alkali atoms it is necessary to consider the two diatomic electronic states that arise, namely $^1\Sigma$ and $^3\Sigma$. The potential curve for the $^1\Sigma$ state of Na was already discussed and the Rydberg potential will be used for this. On the other hand the $^3\Sigma$ state is repulsive and its potential energy curve arises from exchange repulsion and only Van der Waal's attraction (Eq. 8) at distances greater than about $r^* = 2$.

Using the constants given in Table I for the $^1\Sigma$ state of Na, in connection with Eqs. (11), (15), (17), and (18) and obtaining the functions $A_k(\theta)$ from Table II, we have calculated $B^{(1)}(T)$ and its derivatives at two temperatures, 1720°K and 2390°K. The results are shown in Table III. For comparison the values of $B^{(1)}(T)$ obtained for Lennard-Jones (12-6) and (9-6) potentials from the tables in Refs. (8) and (9) are also given; the differences are of the order of a factor of two as would have been expected from a comparison of the areas under the bowls of the potential energy curves in Fig. 2.

TABLE III

Calculations for Na Vapor

Second Virial Coefficient			
T	1720°K	2390°K	Ref.
$^1\Sigma$ state: θ_1	5.0	3.6	
$B^{(1)}$ in cc/mole	$\left\{ \begin{array}{l} \text{Ryd.} \\ \text{L-J, 6-9} \\ \text{L-J, 6-12} \end{array} \right.$	$\left\{ \begin{array}{l} -6662.7 \\ -1061 \\ -904 \end{array} \right.$	$\left\{ \begin{array}{l} \\ 9 \\ 8 \end{array} \right.$
$^3\Sigma$ state: θ_3	0.195	0.140	
$B^{(3)}$ cc/mole (L-J, 6-9)	+12.29	+37.99	9
$B = (B_{\text{Ryd}}^{(1)} + 3B^{(3)})/4$ cc/mole	-1656	-492.3	
Thermal Properties at 1 atm (neglecting $^3\Sigma$ state)			
T	1720°K	2390°K	Ref.
$(H - H^0)$ in cal/mole	$\left\{ \begin{array}{l} \text{Ryd.} \\ \text{Anh.} \end{array} \right.$	$\left\{ \begin{array}{l} -50.5 \\ -41 \end{array} \right.$	15
$(S - S^0)$ in cal/mole deg	$\left\{ \begin{array}{l} \text{Ryd.} \\ \text{Anh.} \end{array} \right.$	$\left\{ \begin{array}{l} -0.0157 \\ -0.013 \end{array} \right.$	15
$(C_p - C_p^0)$ cal/deg mole, Ryd.	0.45	0.047	

The contribution of the second virial coefficient to the thermodynamic functions of Na vapor at 1 atm have been calculated from the relations¹

$$\begin{aligned} H - H^0 &= \frac{RT}{V} \left[B - T \frac{dB}{dT} \right] \\ S - S^0 &= -R \left\{ \ln p + \frac{T}{V} \frac{dB}{dT} + \dots \right\} \\ C_p - C_p^0 &= -R \left\{ \frac{T^2}{V} \frac{d^2B}{dT^2} + \dots \right\} \end{aligned} \quad (22)$$

where H^0 , S^0 , C_p^0 refer to one mole of ideal monatomic gas, using the Rydberg potential for the $^1\Sigma$ state. These and the values obtained by Benton and Inatomi¹⁵ from the

¹⁵A. Benton, T. H. Inatomi, J. Chem. Phys., 20, 1946 (1952); see also W. H. Evans, R. Jacobson, T. R. Munson, D. D. Wagman, J. Res. N.B.S., 55, 83 (1955).

usual anharmonicity treatment⁶ are also compared in Table III.

To get the total $B(T)$ the contribution of the $^3\Sigma$ state must also be taken into account using Eq. (10). Since we do not have sufficient information on the potential energy curve of this state, we shall only give an order of magnitude estimate.

The repulsive portion of the curve can be estimated using the semi-empirical method¹⁶; i.e. we write the energy

¹⁶Glasstone, Laidler, Eyring, "The Theory of Rate Processes", McGraw-Hall Book Co., Inc., New York (1941), p. 76.

of the singlet state simply as $\underline{Q} + \underline{a}$ where $\underline{Q}$ is the Coulombic and $\underline{a}$ the exchange integral, then the energy of the repulsive state ($^3\Sigma$) is $\underline{Q} - \underline{a}$, and we can assume that $\rho = \underline{Q}/(\underline{Q} + \underline{a})$ is reasonably constant and for Na is about 0.30. Thus away from the dispersion region, the repulsion is roughly $-0.4\underline{U}^{(1)}(\underline{r})$ where $\underline{U}^{(1)}(\underline{r})$ is the Rydberg curve for $^1\Sigma$. On the other hand at larger distances (say beyond $r = 6 \text{ \AA}$) the energy is given by Eq. (9). To get a rough estimate of $B^{(3)}(T)$, we fit a Lennard-Jones (6-9) potential to this information since there is no exchange attraction for $^3\Sigma$. Making Lennard-Jones (6-9) equal $-0.4\underline{U}^{(1)}(\underline{r})$ at $r = 5.08 \text{ \AA}$ and Eq. (8) at $r = 6.94 \text{ \AA}$ (see Fig. 2) we obtain $\underline{r}_e^{(3)} = 5.7 \text{ \AA}$ and $\underline{U}_e^{(3)} = 0.0289 \text{ ev.}$ With these parameters $\underline{B}^{(3)}(\underline{T})$ is obtained from the tables in Ref. (9). (See Table III).

The total $\underline{B}(\underline{T})$ is given by

$$\underline{B}(\underline{T}) = \frac{\underline{B}^{(1)}(\underline{T}) + 3\underline{B}^{(3)}(\underline{T})}{4}$$

according to Eq. (10). Examination of results summarized in Table III shows that the contribution of the triplet state to $\underline{B}(\underline{T})$ is about 0.54% at 1720°K and about 5.8% at 2390°K. The thermodynamic functions calculated from the Rydberg potential are somewhat larger than those from the anharmonicity treatment as would be expected. We should also remark that the functions at pressures other than 1 atm would be very easily obtained from Eq. (22),

whereas with the chemical equilibrium treatment one has to evaluate the equilibrium composition at each pressure first, before obtaining the functions; we note that the B(T) treatment will give also the equation of state easily and more correctly.

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CAPTIONS FOR FIGURES

Fig. 1 - Comparison of potential energy curves for the excited ${}^3\Sigma_u^-$ state of O_2 (ref. 13).

Fig. 2 - Comparison of potential energy curves for the ground state of Na_2 .

Fig. 3 - The functions $R_k(\theta)$ for the evaluation of I_0 .

FIG 1
55236-1

Fig 2
55221-1