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SECOND VIRIAL COEFFICIENT FOR DIATOMIC MOLECULES OF LITHIUM

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In this note, using Konowalow's MCSCF potential, we calculated the temperature dependence of the second virial coefficient (SVC) of diatomic molecules of lithium. The numerical results for the ground state and triplet state contributions to SVC are given in tabular form. Our results are compared with other theoretical data.

The second virial coefficient $B(T)$ for a system of particles (atoms or molecules) interacting according to a central force law is given by [1]:

$$B(T) = B_{\mathrm{cl}}(T) + \frac{h^2}{m} B_{\mathrm{I}}(T), \tag{1}$$

where

$$B_{\mathrm{cl}}(T) = 2\pi N_{\mathrm{A}} \int_0^\infty \{1-\exp[-U(r)/kT]\} r^2 dr, \tag{2}$$

and

$$B_{\mathrm{I}}(T) = \frac{N_{\mathrm{A}}}{24\pi k^3 T^3} \int_0^\infty \left(\frac{dU}{dr}\right)^2 \exp[-U(r)/kT] r^2 dr. \tag{3}$$

$B_{\mathrm{cl}}(T)$ is the classical SVC and $B_{\mathrm{I}}(T)$ — the first quantum correction to it. Here N_{A} is Avogadro's number, k — Boltzmann's constant, h — Planck's constant, m — the mass of the particle and $U(r)$ is the interaction potential between pairs of particles separated at a distance r.

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While dealing with the binary interactions of an assembly of chemically reacting atoms, usually more than one diatomic electronic state need to be considered in the calculation of $B(T)$. Thus the total SVC, $B_{tot}(T) = \frac{1}{4}[B^{(1)}(T)+3B^{(3)}(T)]$ [2], should include the contributions $B^{(1)}(T)$ and $B^{(3)}(T)$ arising respectively from the $^1\Sigma$ and $^3\Sigma$ states of Li_2. A knowledge of the interaction potentials $U^{(1)}(r)$ and $U^{(3)}(r)$ is needed in this connection. Several semiempirical potentials are available for the $^1\Sigma$ state [3, 4]. Sannigrahi and Noor Mohammad, using calculated values [5] for the ground state potential parameters of alkali dimers in the Morse [6] and Rydberg [7] potential, have calculated second virial coefficients and added their contribution to some thermodynamic properties for the alkali vapours [8]. These calculations were, however, only made for two temperatures and did not take the contribution of the triplet state into account.

Recently Sannigrahi, Noor Mohammad and Mookherjee [9] calculated the SVC of alkali vapours over a wider range of temperatures using the Morse and Rydberg potentials for the ground state, and the anti-Morse potential [10] as well as the modified anti-Morse potential [11] for the triplet state of dimers [9, 10]. Nevertheless, the triplet state potential has been expressed in terms of ground state potential parameters.

In this note we have calculated the temperature dependence of SVC for Li_2 using an accurate potential curve obtained using the multiconfiguration selfconsistent field calculation (MCSCF) for the ground [12, 13] and triplet state [14] of the Li_2 dimer. Our results are compared with those of Sannigrahi. Eqs. (2) and (3) have been integrated numerically using the second-order Runge–Kutta method [15, 16]. The MCSCF potentials $U^{(1)}(r)$ and $U^{(3)}(r)$, given numerically [12–14], have been approximated analytically in the following way:

(*i*) For the ground state we have used the Morse function:

$$U(r) = D_e\{\exp[-2\beta(r-r_e)]-2\exp[-\beta(r-r_e)]\}, \quad 0 \leqslant r \leqslant r_1, \tag{4}$$

with $r_1 = 1.587516$ [nm]; and the long-range term of the form:

$$U(r) = -C_6 r^{-6}, \quad r_1 \leqslant r \leqslant \infty,$$

with $C_6 = 13.3054556 \times 10^{-23}$ [J(nm)^6].

(*ii*) The triplet state has been represented by the general formula:

$$U(r) = D_e\{\exp[-2\beta(r-r_e)]+2\exp[-\beta(r-r_e)]\}. \tag{5}$$

The parameters D_e, r_e and β appearing in Eqs. (4) and (5) mean: D_e — dissociation energy, r_e — internuclear distance at equilibrium, β — constant with dimension of reciprocal distance.

Calculated values of the ground and triplet state contributions to the classical second virial coefficients of Li_2 are given in Table I. The first quantum corrections to the classical SVC are listed in Table II. Table III shows the temperature dependence of $B_{tot}(T)$ for Li_2. In the tables we have compared our results with those obtained by Sannigrahi [5, 8, 9].

Although experimental information on the SVC of Li_2 is needed to test the validity of the proposed potential, we believe that it has nevertheless proved useful in making

TABLE I

Ground and triplet state contributions to the classical second virial coefficient of lithium

T [K]	$-B_{\mathrm{cl}}(T)$ [cm^3/mole]			
	Our results		Sannigrahi results	
	$^1\Sigma$	$^3\Sigma$	$^1\Sigma$	$^3\Sigma$
1720	28857.665290	115.929101	32278.9 [a]	83.3 [b]
1820	20373.021510	111.062729		
1920	14952.262790	106.613788		
2020	11361.748560	102.529906		
2120	8869.666620	98.766854		
2220	7079.809551	95.287856		
2320	5768.627277	92.061268	6558.1	71.0

[a] A. B. Sannigrahi, S. Noor Mohammad, Preprint. [b] Reference [9].

TABLE II

First quantum correction to the classical second virial coefficient

T [K]	$B_{\mathrm{I}}(T)$ [cm^3/mole]		
	this paper		Ref. [a]
	$^1\Sigma$	$^3\Sigma$	$^1\Sigma$
1720	83.156437	0.000470	131.41
1820	51.542506	0.000303	
1920	33.300637	0.000256	
2020	22.504662	0.000179	
2120	15.668190	0.000127	
2220	11.226842	0.000091	
2320	8.249424	0.000054	13.19

[a] A. B. Sannigrahi, S. Noor Mohammad, Preprint.

TABLE III

Temperature dependence of the total second virial coefficient for lithium

T [K]	$-B_{\mathrm{tot}}(T)$ [cm^3/mole]	
	Our calculations	Sannigrahi results [a]
1720	7106.680036	7974.39
1820	4997.072476	
1920	3649.780005	
2020	2757.913409	
2120	2139.424372	
2220	1695.6799918	
2320	1371.048472	1582.97

[a] Results obtained on the basis of Table I, II (without I quantum correction for $^3\Sigma$ state).

a reasonable estimate of the ground and triplet state contributions to the SVC of diatomic molecules of lithium. The good agreement of our results with those of previous works lend further support to the usefulness of the potential proposed in this study.

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REFERENCES

[1] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, J. Willey and Sons, New York 1954.
[2] O. Sinanoğlu, R. S. Pitzer, *J. Chem. Phys.* **31**, 960 (1959).
[3] Y. P. Varshni, *Rev. Mod. Phys.* **29**, 664 (1957).
[4] Y. P. Varshni, R. C. Shukla, *Trans. Faraday Soc.* **57**, 537 (1961).
[5] A. B. Sannigrahi, S. Noor Mohammad, *Mol. Phys.* **26**, 985 (1973); **27**, 269 (1974).
[6] P. M. Morse, *Phys. Rev.* **34**, 57 (1929).
[7] R. Rydberg, *Z. Phys.* **73**, 376 (1931).
[8] A. B. Sannigrahi, S. Noor Mohammad, *Ind. J. Pure Appl. Phys.* **13**, 35 (1975).
[9] A. B. Sannigrahi, S. Noor Mohammad, D. C. Mookherjee, *Mol. Phys.* **31**, 963 (1976).
[10] A. B. Sannigrahi, S. Noor Mohammad, D. C. Mookherjee, *J. Chem. Phys.* **63**, 5500 (1975).
[11] J. C. Whitehead, *Mol. Phys.* **29**, 177 (1975).
[12] D. D. Konowalow, M. L. Olson, Abstracts of the 31st Symposium on Molecular Spectroscopy, Ohio State University, papers MN-5 and MN-6, 1976.
[13] M. L. Olson, Ph. D. thesis, State University of New York at Binghamton, Binghamton, New York 1976.
[14] D. D. Konowalow, M. E. Rosenkrantz, Preprint.
[15] F. Ceschino, J. Kuntzman, *Numerical Solution of Initial Value Problems.* Chap. 1, Prentice-Hall Englewood Cliffs, New York 1963.
[16] G. E. Lance, *Numerical Method for High Speed Computers*, Iliffe & Sons, London 1960.