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Citation: *The Journal of Chemical Physics* **63**, 5500 (1975); doi: 10.1063/1.431290

View online: <http://dx.doi.org/10.1063/1.431290>

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# On the contribution of the triplet state to the second virial coefficients of alkali vapors

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(Received 31 May 1974)

The second virial coefficient  $B(T)$  for a system of particles (atoms or molecules) interacting according to a central force law is given by<sup>1</sup>

$$B(T) = 2\pi N \int_0^\infty \{1 - \exp[-U(r)/kT]\} r^2 dr, \quad (1)$$

where  $N$  is the Avogadro number,  $U(r)$  is the interaction potential between pairs of particles separated at a distance  $r$ , and  $k$  is the Boltzmann constant. While dealing with the binary interactions of an assembly of chemically reacting atoms, usually more than one diatomic electronic state needs to be considered in the calculation of  $B(T)$ . Thus, the total  $B(T)$  of alkali vapors should include the contributions,  $B^{(1)}(T)$  and  $B^{(3)}(T)$  arising, respectively, from the  $^1\Sigma$  and  $^3\Sigma$  states of alkali dimers. A knowledge of the interaction potentials,  $U^{(1)}(r)$  and  $U^{(3)}(r)$ , is needed in this connection. Although several semiempirical potentials are available<sup>2</sup> for the  $^1\Sigma$  state, we do not have sufficient information about the triplet state of alkali dimers. Sinanoglu and Pitzer<sup>3</sup> employed the Lennard-Jones (6-9) potential<sup>4</sup> in the calculation of  $B^{(3)}(T)$  of Na vapor. We have extended their method to all possible alkali-pair interactions. Calculated values of the interaction virial coefficients  $B_{ij}^{(3)}(T)$  are given in Table I for two arbitrary temperatures,  $T=1720$  and  $2320^\circ\text{K}$ . Use has been made of the  $^1\Sigma$  potential parameters of Sannigrahi and Noor Mohammad<sup>5</sup> in this calculation. As can be seen from Table I, both positive and negative values of  $B_{ij}^{(3)}(T)$  are obtained by this method. But  $B_{ij}^{(3)}(T)$  cannot be negative, since the triplet state of alkali dimers is repulsive over the entire potential surface. The present absurd results, therefore, stem from the very unrealistic potential assumed for the triplet state.

As an alternative to the Lennard-Jones (6-9) potential, one might use the anti-Morse potential of Sato<sup>6</sup> for the triplet state. This is given by

$$U^{(3)}(r) = 0.5 U_e^{(1)} [\exp(-2ax) + 2 \exp(-ax)], \quad (2)$$

where  $a = r_e^{(1)}(k_e/2U_e^{(1)})^{1/2}$  and  $x = (r/r_e^{(1)}) - 1$ . Using the calculated values<sup>5</sup> for  $U_e^{(1)}$ ,  $r_e^{(1)}$ , and  $k_e$ , the Sato potential for LiNa is constructed; the resulting curve is compared in Fig. 1 with the calculated triplet curve of Bertoncini *et al.*,<sup>7</sup> which has been claimed<sup>8</sup> to be sufficiently accurate for the calculation of  $B_{ij}^{(3)}(T)$ . The disagreement between these curves is rather drastic and indicates that the use of Eq. (2) is not justified in the present calculation. This has been further verified by comparing the corresponding  $F(r)$  vs  $r$  plot in the same figure, where  $F(r) = \{1 - \exp[-U(r)/kT]\} r^2$  and  $T=1720^\circ\text{K}$ .

It may be noted that the area under this curve is directly proportional to  $B_{ij}^{(3)}(T)$ .

Equation (2) is now modified so as to give an overall fit to the theoretical curve for LiNa.<sup>7</sup> This modified potential,

$$U^{(3)}(r) = 0.4427 U_e^{(1)} [\exp(-2ax) + 0.0920 \exp(-ax)], \quad (3)$$

TABLE I. Triplet state contribution [ $B_{ij}^{(3)}(T)$ ] to the second virial coefficients<sup>a</sup> of alkali vapors.

<i>i</i>	<i>j</i>	$B_{ij}^{(3)}(T)$ (cc/mole)	
		Lennard-Jones (6-9)	Modified Sato [Eq. (3)]
Li	Li	-177.0	71.0
		-297.0	83.3
Na	Na	-31.2	81.2
		-94.4	93.8
K	K	134.2	130.5
		93.0	149.7
Rb	Rb	193.3	155.4
		169.2	178.7
Cs	Cs	249.5	182.6
		230.0	209.5
Li	Na	-172.6	83.9
		-290.9	97.7
Li	K	-24.4	117.5
		-115.3	136.2
Li	Rb	137.1	124.1
		109.8	140.4
Li	Cs	187.7	166.1
		164.7	187.9
Na	K	92.3	110.0
		54.8	125.6
Na	Rb	183.2	124.4
		170.7	139.6
Na	Cs	231.8	150.0
		238.1	166.7
K	Rb	216.2	139.1
		213.3	156.4
K	Cs	240.8	155.1
		240.6	173.7
Rb	Cs	263.5	176.8
		256.2	199.1

<sup>a</sup>The upper and lower value in each row corresponds to  $T=2320$  and  $1720^\circ\text{K}$ , respectively.

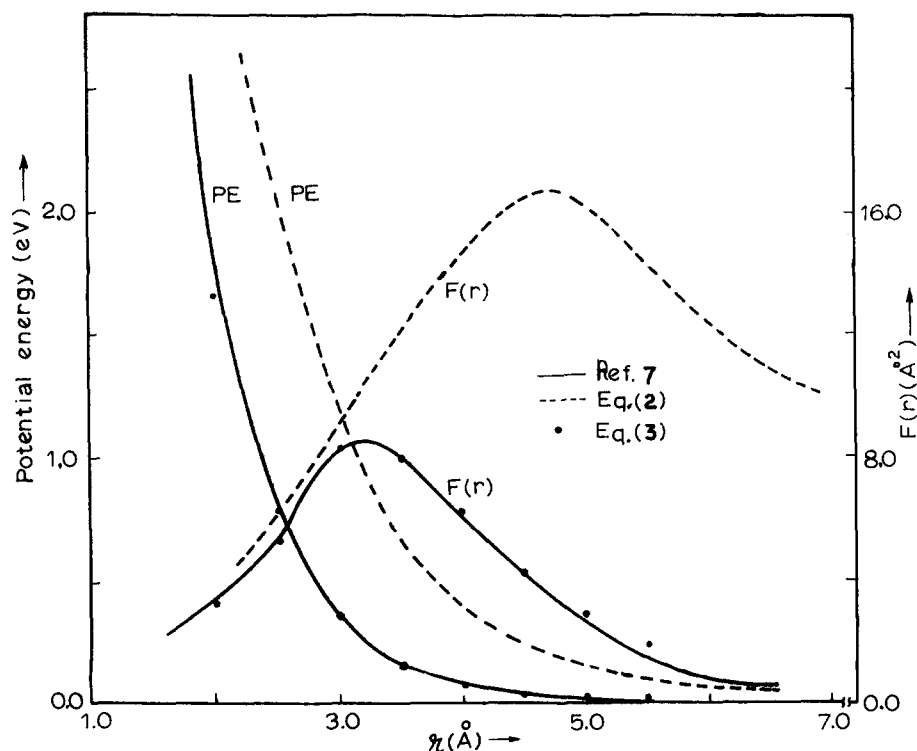


FIG. 1. Comparison of the triplet state potential curves for LiNa and the corresponding  $F(r)$  vs  $r$  plots, where  $F(r) = 1 - \exp[-U(r)/kT] r^2$  and  $T = 1720^\circ\text{K}$ .

as well as its  $F(r)$  vs  $r$  plot, is found (Fig. 1) to compare favorably with the corresponding *ab initio* curves. Using the  $^1\Sigma$  potential parameters of Ref. 5,  $B_{ij}^{(3)}(T)$  values are now evaluated for the modified Sato potential by the numerical integration of Eq. (1). These are compared in Table I with the Lennard-Jones values. It is observed that only for heavier vapors, the two sets of values are somewhat comparable; otherwise, widely different values are obtained for the Lennard-Jones and modified Sato potentials.

Although further information on the triplet state of alkali dimers is needed to test the validity of the proposed potential, we believe that it has nevertheless proved useful in making a reasonable estimate of the triplet state contribution to the second virial coefficients of alkali vapors. This potential, though obtained for the specific case of LiNa, has recently<sup>9</sup> been employed in the valence bond calculations of the symmetrical alkali trimers. The excellent agreement of the results obtained therein with some previous work<sup>10</sup> lends further

support to the usefulness of the proposed potential in the present study.

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