

## The Second Virial Coefficient for Rubidium-87 ( $^{87}\text{Rb}$ ) Gas in the Temperature-Range 1000-40000 K and Beyond

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### Abstract

The classical second virial coefficient and the corresponding first quantum correction for  $^{87}\text{Rb}$  gas are calculated at high temperatures (1000-40000 K, and beyond). The Boyle and critical temperatures are determined. The main input is the Rb-Rb potential. Here, two potentials are considered: the extended-Hartree-Fock-approximate-correlation-energy (EHFACE) potential and Morse potential. The results are in good agreement with previous results.

### 1. Introduction

The aim of this work is to calculate the classical second virial coefficient  $B_{cl}$  and the corresponding quantum correction  $B_{qcl}$  in the temperature-range 1000-40000 K and beyond.  $B$  measures the deviation of a real gas from the classical ideal law. The knowledge of critical-point parameters makes it possible to predict the high-temperature properties of the system on the basis of the law of corresponding states (Dillon *et al.*, 1966). In recent years, the behavior of fluid alkali metals in the critical state has been intensively studied. Here, the critical temperature  $T_c$  is calculated from Boyle's temperature  $T_B$  (Balasubramanian, 2002).

The main input in calculating  $B_{cl}$  and  $B_{qcl}$  is the interaction potential. In this work, two potentials are considered. The first is the widely-used Morse potential (Morse, 1929). The second is the extended-Hartree-Fock-approximate-correlation-energy (EHFACE) potential. This consists of the sum of the (extended) Hartree-Fock energy and the (remaining) correlation energy (Varandas and Silva, 1986; Braga and Varandas, 1990).

### 2. Formalism

$B_{cl}(T)$  and  $B_{qcl}(T)$  [ $T$  being the absolute temperature] are given by (Feynman, 1992)

$$B_{cl}(T) = 2\pi \int_0^{\infty} [1 - e^{-\beta V(r)}] r^2 dr; \quad (1)$$

$$B_{qcl}(T) = \frac{\pi \hbar^2 \beta^3}{6m} \int_0^{\infty} [e^{-\beta V(r)}] V'(r) r^2 dr, \quad (2)$$

where  $V(r)$  is the binary interatomic potential,  $V'(r)$  is its first derivative with respect to the argument  $r$ , which is the magnitude of the interatomic separation, and  $\beta$  is the temperature parameter  $(k_B T)^{-1}$ ,  $k_B$  being Boltzmann's constant.

The critical temperature  $T_c$  is determined from Boyle's temperature  $T_B$  (Balasubramanian, 2002) according to

$$T_c = \frac{4n(n-1)}{(n+1)^3} T_B, \quad (3)$$

$n$  being the thermodynamic similarity parameter = 1.523 for Rb (Balasubramanian, 2008).

The EHFACE potential is written as (Braga and Varandas, 1990)

$$V_i(r) = V_{EHF,i}(r) + V_{CORR,i}(r), \quad (4)$$

Where  $i=0(1)$  denoting singlet (triplet) states;

$$V_{EHF,0}(r) = \frac{D}{r} \left( 1 + \sum_{i=1}^3 a_i (r - r_e)^i \right) \exp[-\gamma(r - r_e)], \quad (5)$$

$$V_{EHF,1}(r) = -\frac{E}{r} \exp\left(-\sum_{i=1}^4 b_i r^i\right); \quad (6)$$

$$V_{CORR,i}(r) = -\sum_{n=6,8,10} C_n \left[ 1 - \exp\left(-A(n)\frac{R}{\rho_i} - B(n)\frac{R^2}{\rho_i^2}\right) \right]^n R^{-n}; \quad (7)$$

$$A(n) = \alpha_0 n^{-\alpha_1}; \quad (8a)$$

$$B(n) = \beta_0 \exp(-\beta_1 n); \quad (8b)$$

$\alpha_0 = 25.953$ ,  $\alpha_1 = 1.1868$ ,  $\beta_0 = 15.738$ , and  $\beta_1 = 0.09729$ . The parameters for singlet and triplet states are given in Table 1, and those for the correlation energy in Table 2.

Table 1: The parameters of the extended Hartree-Fockenergy for singlet and triplet states. The values listed are all in atomic units.

Parameter	Value
D	$-9.7736 \times 10^{-2}$
a <sub>1</sub>	1.1247
a <sub>2</sub>	0.3991
a <sub>3</sub>	0.0524
γ	0.8936
r <sub>e</sub>	7.7989
E	$0.215\ 00 \times 10^2$
b <sub>1</sub>	0.712 53
b <sub>2</sub>	0.0
b <sub>3</sub>	0.0
b <sub>4</sub>	0.0

Table 2: The parameters of the correlation energy for singlet and triplet states. The values listed are all in atomic units.

Parameter	Value
C <sub>6</sub>	$4.870 \times 10^3$
C <sub>8</sub>	$6.100 \times 10^5$
C <sub>10</sub>	$8.010 \times 10^7$
ρ <sub>0</sub>	30.1957
ρ <sub>1</sub>	31.8912

TheMorse potential (Morse, 1929) is given by

$$V(r) = De(\text{Exp}[-2c(\frac{r}{r_e} - 1)] - 2\text{Exp}[-c(\frac{r}{r_e} - 1)]), \quad (9)$$

where De is the electronic dissociation energy, r<sub>e</sub> is the equilibrium intern clear separation of the interacting pair, and c is a dimensionless constant. Their values for both singlet and triplet states are given in Table 3.

Table 3: The parameters of the Morse potential for singlet and triplet states.  $D_e$  is in K, and  $r_e$  in Å;  $c$  is a dimensionless constant.

Singlet State		Triplet State	
Parameter	Value	Parameter	Value
$D_e$	5721.06K	$D_e$	351.491511K
$C$	2.98187	$c$	0.6963
$r_e$	4.14 Å	$r_e$	6.094 Å

### 3. Results and Discussion

Our results for  $B_{cl}$ , in the temperature-range 1000-40000 K and beyond, are displayed in Table 4 for the Morse potential, and in Fig. 1 for the EHFACE potential. The corresponding results for  $B_{qcl}$  (the Morse potential) are shown in Table 4.  $B_{cl}$  is large and negative in the low T-limit. It increases as T increases, becoming less negative. At a certain temperature, Boyle's temperature  $T_B$ ,  $B_{cl}$  has zero value.  $T_B$  is 12250 K for the Morse potential and 11240 K for EHFACE. Thereafter,  $B_{cl}$  becomes positive, increasing with increasing T, until it attains a maximum value, after which it decreases. The maximum value of  $B_{cl}$  for both potentials occurs at  $\approx 40000$  K.

On the other hand,  $B_{qcl}(T)$  decreases with increasing T, as shown in Table 4. The ratio  $|B_{qcl}|/|B_{cl}|$  indicates that  $|B_{qcl}|$  is less than  $|B_{cl}|$ ;  $B_{cl}$  dominates increasingly with increasing T, as expected on physical grounds.  $B_{cl}$  is also given in Table 4 over the whole T-range. This means that quantum effects become insignificant in this range. Finally,  $T_c$  is determined from  $T_B$  using Eq.(3), and is given in Table 5, together with three sets of previous results. Our results are in good agreement with those.

Table 4: The classical second virial coefficient  $B_{cl}[\text{cm}^3/\text{mole}]$ , together with the corresponding quantum correction  $B_{qcl}[\text{cm}^3/\text{mole}]$ , at different temperatures  $T$  [K], for the Morse potential.

T[K]	$B_{cl}(T)$	$B_{qcl}(T)$
1000	-6691.52	1.340002
2000	-613.727	0.027296
3000	-246.68	0.006223
4000	-136.487	0.002756
5000	-85.4622	0.001609
6000	-56.6644	0.001083
7000	-38.4693	0.000793
8000	-26.1055	0.000614
9000	-17.267	0.000493
10000	-10.7087	0.000408
11000	-5.70201	0.000345
12000	-1.79354	0.000297
12250	-0.00038	0.000275
13000	1.312678	0.000259
14000	3.817506	0.000228
16000	7.5467	0.000182
18000	10.11894	0.00015
20000	11.939	0.000126
30000	15.76125	$6.5 \times 10^{-5}$
40000	16.36235	$4.06 \times 10^{-5}$
42000	16.34576	$3.74 \times 10^{-5}$
44000	16.30388	$3.47 \times 10^{-5}$
46000	16.24182	$3.22 \times 10^{-5}$
48000	16.16367	$3.0 \times 10^{-5}$

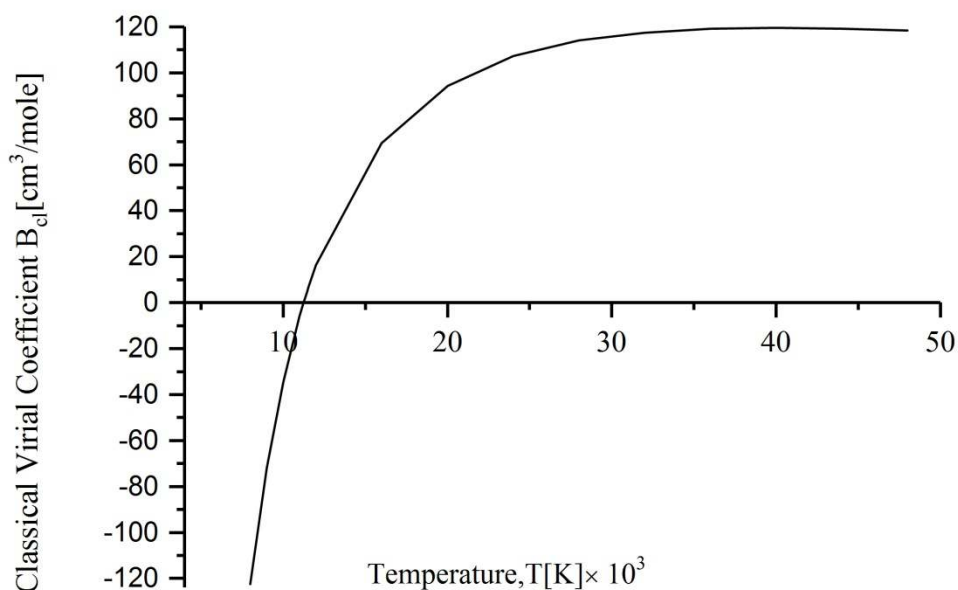


Figure1: The classical second virial coefficient  $B(T)$  [ $\text{cm}^3/\text{mole}$ ] as a function of temperature  $T$  [K], for the EHFACE potential.

Table 5: The critical temperature  $T_c$  [K] for the Morse and EHFACE potentials. Previous results are included for comparison purposes.

critical temperature [K]	(a)	(b)	(c)	(d)	(e)
$T_c$	2230	2490	2093	2100	2190

<sup>a</sup> and <sup>b</sup> are our results for the EHFACE and Morse potentials, respectively; <sup>c</sup>(Dillon *et al.*, 1966); <sup>d</sup>(Morris, 1964); <sup>e</sup>(Grosse, 1960).

#### 4. Conclusion

This work has addressed the classical second virial coefficient  $B_{cl}$  of  $^{87}\text{Rb}$  gas, using the Morse and EHFACE potentials, in the temperature-range 1000-40000K and beyond. Also, the Boyle and critical temperatures have been determined. The agreement with previous results is good. We have recently studied thoroughly the full-fledged *quantum* second virial coefficient  $B_q$  for this system, and our results will be published elsewhere.

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