Parameters of the Morse Potential from Second Virial Coefficients of Gases

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An analytic expression for the second virial coefficient in case of the Morse potential is derived. The parameters of the Morse potential are determined for eighteen species comprising inert gases, diatomic and polyatomic molecules, and mixtures of gases using experimental second virial coefficients. The calculated second virial coefficients based on the obtained Morse potential agree well with the empirical second virial coefficients and their temperature dependence.

1. Introduction

The parameters of various pair potentials, e. g. those of the potentials of Lenard-Jones [1, 2], Buckingham-Corner [3, 4] and others [5], have already been obtained from second virial coefficients or transport phenomena. Contrary to these potentials, the Morse potential has the advantage of enabling analytical solutions of quantum mechanical problems. Knowledge of its parameters would be useful in calculating the vibrational structure of van der Waals molecules, and the cross sections and phase shifts of rainbow scattering and the orbiting resonance scattering [6] in atomic and molecular collisions.

In this work, an analytic expression for the second virial coefficient based on the Morse potential is obtained. This enabled the determination of the parameters of the Morse potential from empirical second virial coefficients for eighteen species comprising inert gas, diatomic and polyatomic molecules, and mixtures of such gases. The assumption was made that diatomic and polyatomic molecules are rigid and spherical.

2. The Second Virial Coefficient for the Morse Potential

By introducing the Morse potential

$$U(r) = -2D\exp[-\alpha(r-r_e)] + D\exp[-2\alpha(r-r_e)] \quad (1)$$

the notations

$$p = D/kT, \quad (2)$$

$$b = \sqrt{p}\exp(\alpha r_e) \quad (3)$$

and

$$x = b\exp(-\alpha r), \quad (4)$$

the second virial coefficient per a mol, $B(T)$, can be written as

$$B(T) = \frac{4\pi N_A}{3\alpha^3}\int_0^b \exp(-x^2+2\sqrt{p}x)\cdot(\sqrt{p}-x)\left(\log\frac{x}{b}\right)^3 dx, \quad (5)$$

where N_A is Avogadro number. For $b\to\infty$, (5) becomes

$$B(T) = \frac{4\pi N_A}{3\alpha^3}\int_0^\infty \exp(-x^2+2\sqrt{p}x)\cdot(\sqrt{p}-x)\left(\log\frac{x}{b}\right)^3 dx. \quad (6)$$

We use the integral [7]

$$\int_0^\infty x^{\nu-1}\exp(-x^2+2\sqrt{p}x)\,dx = \frac{1}{2}\left[\sum_{n=0}^\infty \frac{p^n}{(\frac{1}{2})_n n!}\Gamma\left(\frac{\nu}{2}+n\right) + 2\sqrt{p}\sum_{n=0}^\infty \frac{p^n}{(\frac{3}{2})_n n!}\Gamma\left(\frac{1+\nu}{2}+n\right)\right], \quad (7)$$

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where $(a)_n$ is $\Gamma(a+n)/\Gamma(a)$ for $(1/2)_n$ and $(3/2)_n$. If (7) is divided by b^ν, differentiated three times with respect to ν, and multiplied by b^ν, then

$$\int_0^\infty x^{\nu-1} \exp(-x^2 + 2\sqrt{p}\,x) \left(\log\frac{x}{b}\right)^3 \mathrm{d}x = \frac{1}{16}\left[\sum_{n=0}^{\infty} \frac{p^n}{(\frac{3}{2})_n n!}\,\Gamma\left(\frac{\nu}{2}+n\right) h\left(\frac{\nu}{2}+n, b^2\right) + 2\sqrt{p}\sum_{n=0}^{\infty}\frac{p^n}{(\frac{3}{2})_n n!}\,\Gamma\left(\frac{1+\nu}{2}+n\right) \cdot h\left(\frac{1+\nu}{2}+n, b^2\right)\right] \tag{8}$$

with

$$h(z, y) = (\psi(z) - \log y)^3 + 3(\psi(z) - \log y)\,\psi'(z) + \psi^{(2)}(z)\,, \tag{9}$$

where the function $\psi(z)$ is the logarithmic derivative of the gamma function [8]:

$$\psi(z) = \frac{\mathrm{d}\log\Gamma(z)}{\mathrm{d}z} = \frac{\Gamma'(z)}{\Gamma(z)}\,, \tag{10}$$

$$\psi'(z) = \frac{\mathrm{d}\psi(z)}{\mathrm{d}z} \tag{11}$$

and

$$\psi^{(2)}(z) = \frac{\mathrm{d}^2\psi(z)}{\mathrm{d}z^2}\,. \tag{12}$$

From (6) and (8), the second virial coefficient in case of the Morse potential becomes

$$B(T) = -\frac{\pi N_A}{4\alpha^3}\left[\sqrt{\pi p}\sum_{n=0}^{\infty}\frac{p^n}{n!}\,g\left(\frac{1}{2}+n, b^2\right) + \sum_{n=1}^{\infty}\frac{p^n}{(\frac{1}{2})_n}\,g(n, b^2) + \frac{1}{3}\,h(1, b^2)\right], \tag{13}$$

where

$$g(z, y) = \frac{1}{z}\left[(\psi(z) - \log y)^2 + \psi'(z)\right]. \tag{14}$$

3. Parameters of the Morse Potential for Various Species

For eighteen species, the parameters, D, r_e and α of the Morse potential were determined by the least squares method using the experimental second virial coefficients, B, at n temperatures [9] and minimizing the average deviations,

$$1/n\sum_{i=1}^{n} |(B - B(T))/B|\,100$$

($n = 8$ except Xe–H_2, where $n = 4$).

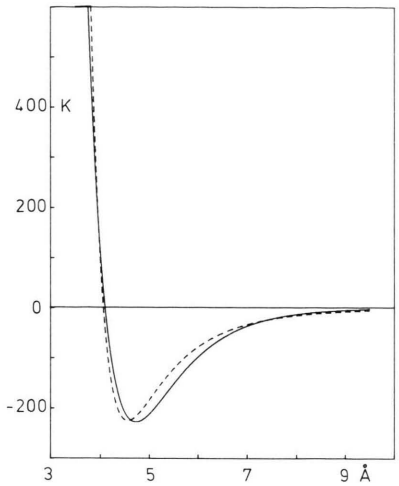

Fig. 1. Pair potential (in K) for Xe vs. internuclear distance (in Å). Solid curve: Morse potential (this work); dashed curve: Lenard-Jones (12, 6) potential.

These deviation are very small, as shown in Table 1. The obtained energy depths, D, and internuclear distances, r_e, agree well with those of ε and r_e of Lenard-Jones (12, 6) potentials except for Ne, H_2, D_2 and O_2. Morse and Lenard-Jones (12, 6) potentials for Xe are shown in Figure 1. Thus, the Morse potential could be used as intermolecular potential though $U(r = 0)$ is not infinity.

The eigenvalues for the Morse potential, E_n, are

$$E_n = -D + 2\alpha\hbar\sqrt{\frac{D}{2m}}\left(n+\frac{1}{2}\right) - \frac{\alpha^2\hbar^2}{2m}\left(n+\frac{1}{2}\right)^2, \tag{15}$$

$$E_n = -D + \omega_e\left(n+\frac{1}{2}\right) - \omega_e\chi_e\left(n+\frac{1}{2}\right)^2,$$

$$n = 0, 1, 2, 3, \ldots, \tag{16}$$

where m is reduced mass and ω_e and $\omega_e\chi_e$ are spectroscopic constants. From (15) and (16),

$$D = \omega_e^2/4\,\omega_e\chi_e\,. \tag{17}$$

Table 1. Parameters of the Lenard-Jones potential and the Morse potential (this work), and average deviations of the calculated from empirical second virial coefficients.

System	L-J (12, 6) Potential [a]		Morse potential			Average deviation
	ε/k K	r_e Å	D/k K	r_e Å	α Å^{-1}	%
He	10.8	2.88	12.6	2.92	2.197	0.6
Ne	35.6	3.09	51.3	3.09	2.036	1.1
Ar	119	3.83	118.1	4.13	1.253	4.0
Kr	166.7	4.13	149.0	4.49	1.105	2.6
Xe	225	4.57	226.9	4.73	1.099	0.4
H_2	29.2	3.22	49.4	3.29	1.923	0.3
D_2	31.1	3.22	47.5	3.31	1.844	0.2
N_2	95.9	4.16	93.4	4.43	1.166	1.1
O_2	118	3.88	152.4	3.75	1.542	0.2
CO	100.2	4.22	100.3	4.27	1.136	2.5
NO	131	3.56	131.8	4.22	1.309	1.8
CO_2	189	5.03	196.7	5.18	1.020	2.0
NO_2	193.6	5.15	193.6	5.31	0.978	1.4
CH_4	148.2	4.28	149.1	4.50	1.166	0.3
C_2H_4	199.2	5.07	206.7	5.26	1.004	0.5
C_6H_6			927.7	4.46	1.400	0.2
$Ar-H_2$			64.9	3.73	1.389	3.2
$Xe-H_2$			89.7	3.90	1.395	1.0

[a] Ref. [5] except inert gases. Ref. [11] for He, Ne and Ar; Ref. [12] for Kr and Xe.

The dissociation energy, D_0, becomes

$$D_0 = -E_0 = D - \frac{1}{2}\omega_e + \frac{1}{4}\omega_e\chi_e . \tag{18}$$

The eigenfunctions for the Morse potential, $\Psi_n(z)$, are

$$\Psi_n(z) = N_n \exp(-z/2)\, z^{k_n} L_n^{(2k_n)}(z) \tag{19}$$

with

$$N_n = \sqrt{\frac{\alpha(2a-1-2n)\,n!}{\Gamma(2a-n)}} , \tag{20}$$

where $L_n^{(2k_n)}(z)$ is the n-th associated Lagguerre polynomial,

$$z = 2a \exp[-\alpha(r-r_e)], \tag{21}$$

$$a = \sqrt{2mD}/\alpha\hbar \tag{22}$$

and

$$k_n = \sqrt{-2mE_n}/\alpha\hbar = a - \left(n+\frac{1}{2}\right) > 0 . \tag{23}$$

From (23), the maximum value of n, n_m is given by

$$n_m < a - \frac{1}{2} = \frac{2D}{\omega_e} - \frac{1}{2} . \tag{24}$$

Table 2. Parameters of the Morse potential for various species.

System	D meV	r_e Å	D_0 meV	ω_e cm^{-1}	$\omega_e\chi_e$ cm^{-1}	n_m	r_0 Å
He	1.09	2.92	0.01	37.76	40.67	0	
Ne	4.44	3.09	2.70	31.51	6.93	1	3.28
Ar	10.18	4.13	8.93	20.86	1.33	7	4.21
Kr	12.84	4.49	11.97	14.26	0.49	14	4.54
Xe	19.55	4.73	18.69	13.98	0.31	22	4.76
H_2	4.26	3.29	0.46	92.14	61.85	0	4.54
D_2	4.09	3.31	1.66	61.20	28.47	0	3.92
N_2	8.05	4.43	6.82	20.62	1.64	5	4.54
O_2	13.13	3.75	11.19	32.57	2.50	6	3.83
CO	8.64	4.27	7.33	21.97	1.73	5	4.38
NO	11.36	4.22	9.77	26.56	1.92	6	4.30
CO_2	16.95	5.18	15.68	20.88	0.80	12	5.24
N_2O	16.68	5.31	15.47	19.85	0.73	13	5.36
CH_4	12.92	4.50	10.87	34.50	2.86	5	4.61
C_2H_4	17.81	5.26	16.21	26.38	1.21	10	5.33
C_6H_6	79.94	4.46	77.07	46.72	0.85	27	4.48
$Ar-H_2$	5.59	3.73	2.69	55.26	16.94	1	4.16
$Xe-H_2$	7.73	3.90	4.26	64.17	16.51	1	4.24

The expectation value of r in E_0, r_0, which represents the internuclear distance in the vibrational ground state, is

$$r_0 = \langle \Psi_0 \,|\, r \,|\, \Psi_0 \rangle$$

$$= r_e + \frac{1}{\alpha}[\log 2a - \psi(2a-1)] , \tag{25}$$

where $\psi(z)$ is the logarithmic derivative of the gamma function in (10).

From (15), (16), (18), (20) and (25), the values of D, r_e, D_0, ω_e, $\omega_e\chi_e$, n_m and r_0 are shown in Table 2.

In the following, for the inert gases the spectroscopic data [10] are listed up to be compared with this work: $D = 0.90$ meV and $r_e = 2.97$ Å, for He, $D_0 = 2.02$ meV, $\omega_e = 13.7\ \mathrm{cm}^{-1}$ and $r_e = 3.15$ Å for Ne, $D_0 = 10.51$ meV, $\omega_e = 25.74\ \mathrm{cm}^{-1}$ and $r_e = 3.758$ Å for Ar, $D_0 = 15.7$ meV, $\omega_e = 24.18\ \mathrm{cm}^{-1}$, $\omega_e\chi_e = 1.34\ \mathrm{cm}^{-1}$ and $r_e = 4.03$ Å for Kr, and $D_0 = 23.0$ meV, $\omega_e = 21.12\ \mathrm{cm}^{-1}$, $\omega_e\chi_e = 0.65\ \mathrm{cm}^{-1}$ and $r_e = 4.361$ Å for Xe. For helium, D_0 is nearly equal to zero and the van der Waals molecule of He seems not to have a bound state, while the maximum number of energy levels for Ne, Ar, Kr and Xe is 2, 8, 15, and 23, respectively.

The van der Waals molecules of H_2 and D_2 only exist in the ground state. For the van der Waals molecules of Ne, H_2, D_2 and etc., which have not many energy levels, the internuclear distance in the ground state, r_0, tends to become larger than r_e.

For the mixtures of gases, the energy depth, D, is 5.59 meV and r_e is 3.73 Å for Ar–H_2, and D is 7.73 meV and r_e is 3.90 Å for Xe–H_2 in this work while the energy depth is 6.303 meV and r_e is 3.574 Å for Ar–H_2, and the energy depth is 8.17 meV and r_e is 3.394 Å for Xe–H_2 in the Buckingham-Corner potential from the results of orbiting resonance scattering [6].

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