A HYBRID POTENTIAL FOR INERT GAS ATOMS

ANIL SARAN

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32.

ABSTRACT. A potential model for inert gas atoms comprising the Morse potential function in the region of potential minimum, molecular beam scattering data in the repulsive region and the experimental $B(T)$ data for large values of intermolecular separation has been suggested. This hybrid potential has been determined for neon, argon and krypton with fairly satisfactory results.

INTRODUCTION

The most commonly used forms of the intermolecular potential are the Lennard-Jones (12:6) and the modified Buckingham exp-6 models which involve two and three unknown parameters respectively. Generally these parameters are determined from a set of experimental data and the same parameters are used to calculate other properties. However, it has been found that even for spherically symmetric molecules it is not possible to represent quite satisfactorily the equilibrium and non-equilibrium properties, in terms of a single set of parameters. This has led several workers to suggest that the intermolecular potential can not be adequately represented over the whole range of intermolecular distances by only two or three parameters.

Guggenheim and McGlashan (1960a) were first to suggest a six-parameter potential to obtain the potential energy curve for interaction between two argon atoms. They have utilized different equations to represent the intermolecular potential at different ranges of intermolecular distances. The potential energy curve thus obtained is much deeper and wider than those on the Lennard-Jones (12 : 6) and the exp-6 models. This result is in agreement with the suggestion of Kihara (1953, 1955) that at least for inert gases the intermolecular potential should be wider than those on the Lennard-Jones (12,6) potential. Barua and Chakraborti (1961) and Chakraborti (1963) have extended the treatment of Guggenheim and McGlashan (1960a) with some modification to the case of Kr and Xe respectively. The results obtained were similar to that of Guggenheim and McGlashan.

Recently Konowalow and Hirschfelder (1961) have used the Morse potential function to interpret the various transport and equilibrium properties of substances. The parameter c of the Morse potential function, which is related to the curvature of the potential at its minimum, makes this potential more flexible than the Lennard-Jones (12:6) potential. Konowalow and Hischfelder have pointed

out that this potential will be better representation near the potential minimum although at small and large separations it may be lead to erroneous results. They have utilized mainly the crystal properties data to determine the force constants for several nonpolar molecules. Saran (1963) has used transport properties data to obtain the parameters on the Morse potential. The two sets of parameters are, however, found to differ considerably from each other and probably this points to the failure of the Morse potential far from the regions of potential minimum which is stressed by crystal properties data. It is seen from Table 1 that the depth (also the width which can be seen by actual drawing of the potentials) on the Morse potential as obtained from crystal properties data is very close to the values obtained on the six-parameter potential. This has led Saran and Barua (1964) to suggest the use of the Morse potential (as obtained from the crystal properties data) near the potential minimum. The amount of data required and the calculations involved will be much less than the six-parameter potential. Consequently, they have proposed the use of following hybrid potential which should be nearly as good as the six-parameter and have successfully applied to the case of xenon.

In the region of the potential minimum, a Morse potential function, for $r < \sigma$, the repulsive energy function as obtained from the scattering experiments and for large value of r, the following expression

$$\phi(r)/k = -\frac{\lambda}{k}\left(\frac{r_m}{r}\right)^6 \qquad \text{(for } r \geqslant 1.4r_m) \qquad \ldots \quad (1)$$

TABLE I

Force constants of Ne Ar, Kr and Xe on Morse, six-parameter and Lennard-Jones (12:6) Models

Subs-tance	Morse potential model			Six-parameter model						L.-J (12 : 6) model	
	c	r_mÅ	ε/k °K	r_mÅ	ε/k °K	$K/k \times$ 10^{-2} °K	$\alpha/k \times$ 10^{-3} °K	$\beta/k \times$ 10^{-4} °K	λ/k °K	r_mÅ	ε/k °K
Ne	5.1	3.152	43 99[a]	3.130	40.6	13.26	5.78	0.578	44.3[b]	3.086	35.60[f]
Ar	5.0	3.855	144.8[a]	3.812	137.5	44.9	19.6	1.96	150[c]	3.826	119.49[g]
Kr	4.5	4.038	182.7[a]	4.074	192.8	65.95	30.74	0	185[d]	4.130	166.67[g]
Xe	4.9	4.420	274.7[a]	4.418	277.7	87.9	38.58	0	255[e]	4.568	225.30[g]

[a]Konowalow and Hirschfelder (1961) :
[b]Guggenheim and McGlashan (1960b) :
[c]Guggenheim and McGlashan (1960a) :
[d]Barua and Chakraborti (1961) :
[e]Chakraborti (1963) :
[f]Hirschfelder, Curtiss and Bird (1954) ;
[g]Whalley and Schneider (1955).

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is to be used. σ is the value of intermolecular separation r at which $\phi(r) = 0$. λ/k is a constant to be determined by fitting the experimental second virial data $B(T)$. r_m is the value of r at which the attractive energy is maximum. In this paper, the treatment of Saran and Barua (1964) has been extended to the cases of neon, argon and krypton.

CALCULATIONS AND RESULTS

(i) *Determination of Potential Energy Curve*

In the neighbourhood of the potential minimum, the interaction energy on the Morse potential is expressed as

$$\phi(r) = \epsilon\{\exp[-2c(r^*-r_m^*)]-2\exp[-c(r^*-r_m^*)]\} \qquad \ldots \quad (2)$$

where $\phi(r)$ is the potential energy of two atoms separated by a distance r, ϵ is the depth of the potential at its minimum where $r = r_m$, $r^* = r/\sigma$, $r_m^* = r_m/\sigma$; σ being the value of r for which $\phi(r) = 0$. The parameter c is related to the curvature at the potential minimum. The force constants recorded in Table I were used to get the potential energy curves at the potential minimum region for the above mentioned gases.

When the intermolecular separation is large, the interaction energy is given by eqn. (1). The values of λ/k for the above mentioned gases as obtained by fiting the experimental second virial coefficient data are given in Table II.

Following Chakraborti (1963) in the region $r < \sigma$, we have utilized the potential energy function as determined by Amdur and Mason (1954, 1955a, 1955b) from scattering experiments. Their results may be expressed as

$$\phi(r) = A/r^n \quad \text{erg (for } r < sA^0) \qquad \ldots \quad (3)$$

The values of A, n and s are given in Table II for gases considered here.

TABLE II

Values of the constants A, n, s and λ/k.

Substance	$A \times 10^{10}$		s Å	λ/k °K
Ne	6.07	10.41	2.13	71.0
Ar	13.60	8.33	2.69	180.0
Kr	2.55	5.42	3.14	333.0

The potential energy curves were obtained by joining the points in the different regions of r by smooth lines. The potential energy curves thus obtained on the hybrid potential are shown in Figs. 1-3 for the gases neon, argon and krypton respectively. For the sake of comparison the potential energy curves on the Lennard-Jones (12:6) as well as on six-parameter potentials are also

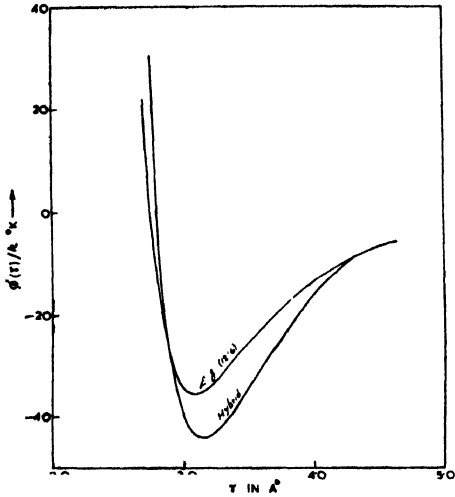shown. The potential energy curve for neon on six-parameter potential has not been shown in Fig. 1.

Fig. 1.--The potential energy curve of Neon plotted against the internuclear distance on the hybrid and Lennard-Jones (12 : 6) potentials.
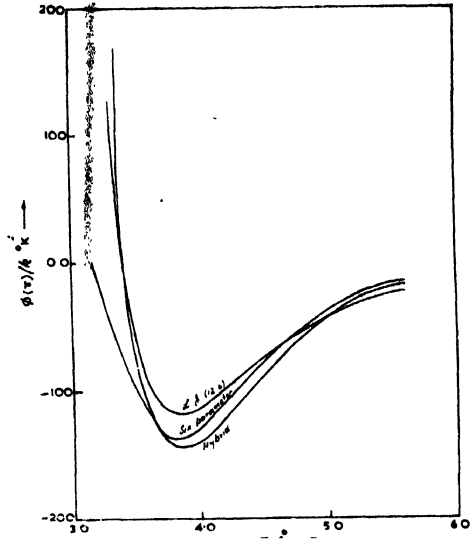

Fig. 2.—The potential energy curve of Argon plotted against the internuclear distance on the hybrid, Lennard-Jones (12 : 6) and six-parameter potentials.
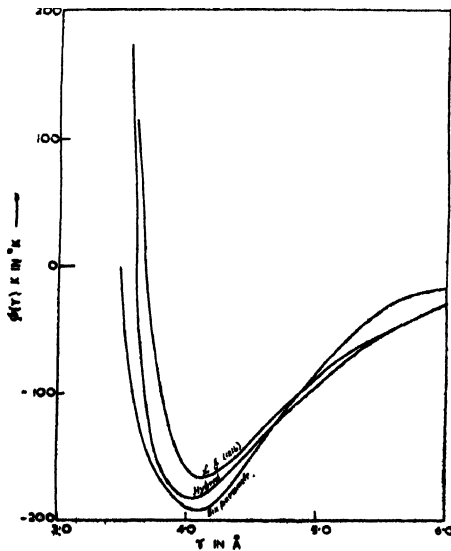

Fig. 3.—The potential energy curve of Krypton plotted against the internuclear distance on the hybrid, Lennard-Jones (12 : 6) and six-parameter potentials.

(ii) *Calculation of Second Virial Coefficient.*

The second virial coefficient $B(T)$ of a gas is expressed as

$$B(T) = 2\pi N \int_0^\infty \{1 - \exp[-\phi(r)/kT]\} r^2 dr, \tag{4}$$

where N is Avogadro's number.

The integral is split up as

$$\int_0^\infty = \int_0^s + \int_s^\sigma + \int_\sigma^{r_1} + \int_{r_1}^\infty \tag{5}$$

where $r_1 = 1.4 r_m$.

In the region $r = 0$ to $r = s$, $\phi(r)$ is very large so that $\exp[-\phi(r)/kT] = 0$. σ is the value of r at which $\phi(r) = 0$ and its value is obtained from potential energy curve. Eqn. (5) now becomes

$$B(T) = \frac{2\pi N}{3} \left[s^3 + \int_s^\sigma \{1 - \exp[-\phi(r)/kT]\} d(r^3) + \int_\sigma^{r_1} \{1 - \exp[-\phi(r)/kT]\} d(r^3) \right.$$

$$\left. \frac{\lambda}{kT} \frac{r_m^6}{r_1^3} \right] \tag{6}$$

The experimental $B(T)$ values of Ne (Michels, Wassenaar and Louwerse, 1960 ; Holborn and Otto, 1925), Ar (Holborn and Otto, 1925 ; Whalley, Lupien and Schneider, 1953) and Kr (Whalley and Schneider, 1954; Beattie, Brierley and Barriault, 1952) are graphically shown in Figs. (4)–(6) respectively along with the calculated values obtained on the hybrid potential. The agreement between the experimental and the calculated values is quite satisfactory.
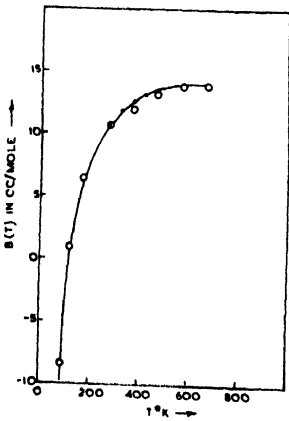

Fig. 4.—The second virial ocefficient $B(T)$ of Neon plotted as a function of temperature. ● Michels, Wassenaar and Louwerse, 1960; O Holborn and Otto, 1925.
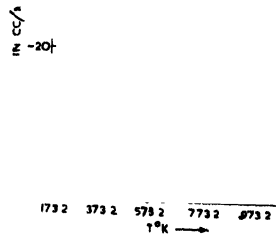
Fig. 5.—The second virial coefficient $B(T)$ of Argon plotted as a function of temperature. ● Holborn and Otto, 1925; O Whalley, Lupien and Schneider, 1953.
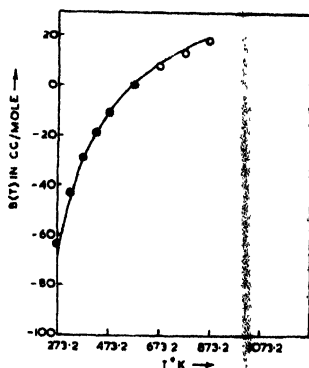
Fig. 6.—The second virial coefficient $B(T)$ of Krypton plotted as a function of temperature. ● Beattie, Brierley and Barriault, 1952; O Whalley and Schneider, 1954.

CONCLUSIONS

In order to have a more realistic representation of the intermolecular potential, the combination of the Morse potential, molecular beam scattering data and the use of second virial data is found to give fairly satisfactory results. It will be interesting to calculate other properties with this hybrid potential.

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REFERENCES

Amdur, I. and Mason, E. A. 1954, *J. Chem. Phys.*, **22**, 670.

Amdur, I. and Mason, E. A. 1955a, *J. Chem. Phys.*, **23**, 415.

Amdur, 1. and Mason, E. A. 1955b, *J. Chem. Phys.*, **23**, 2268.

Barua, A. K. and Chakraborti, P. K. 1961, *Physica*, **27**, 753.

Beattie, J. A., Brierley, J. S. and Barriault, R. J., 1952, *J. Chem. Phys.*, **20**, 1615.

Chakraborti, P. K., 1963, *Physica*, **29**, 227.

Guggenheim, E. A., and McGlashan, M. L. 1960a, *Proc. Roy. Soc.*, *A***255**, 456.

Guggenheim, E. A. and McGlashan, M. L. 1960b, *Mol. Phys.*, **3**, 563.

Hirschfelder, Curtiss and Bird. Molecular Theory of Gases and Liquids. (John Wiley & Sons, Inc., N.Y., 1954).

Holborn, L. and Otto, J. 1925, *Z. Physik*, **33**, 1.

Kihara, T. 1953, *Rev. Mod. Phys.*, **25**, 831; 1955, *ibid.*, **27**, 412.

Konowalow, D. D. and Hirschfelder, J. O. 1961, *Phys. Fluids*, **4**, 629.

Michels, A., Wassenaar, T. and Louwerse, P. 1960, *Physica*, **26**, 539.

Saran, A. 1963, *Ind. J. Phys.*, **37**, 491.

Saran, A. and Barau, A. K. 1964, *Canad. J. Phys.*, **42**, 2026.

Whalley, E., Lupien, Y. and Schneider, W. G. 1953, *Canad. J. Chem.*, **31**, 772.

Whalley, E. and Schneider, W. G. 1954, *Trans. Am. Soc. Mining Met., Engrs*, **76**, 1001.

Whalley, E. and Schneider, W. G. 1955, *J. Chem. Phys.*, **23**, 1644.