

CENTRAL POTENTIALS FOR POLYATOMIC MOLECULES: I A SURVEY OF MORSE
POTENTIALS DETERMINED FROM VISCOSITY AND THE SECOND
VIRIAL COEFFICIENT *

by

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ABSTRACT

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The Morse potential function is used to approximate the pair interaction potential for a wide variety of hydrocarbons. The effects of molecular asymmetry (narrowing and deepening of the potential well) are most clearly evident in potentials determined from experimental second virial coefficients. Such potentials are shown to be more realistic than those potentials determined from experimental viscosities which are much less sensitive to asymmetry.

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The study of the gas-phase thermal properties of polyatomic molecules has both practical and theoretical interest. The description of the pair interactions of polyatomic molecules has proved to be such a formidable task that the present state of the art is quite rudimentary. Thus, it is customary to attempt a rough description of the properties of dilute gases in terms of model potential functions containing a few adjustable constants which are fixed empirically.

Of the wide variety of semi-empirical potential functions which have been proposed (5,6,17-19) to predict the properties of dilute gases, the most widely studied has been the two-parameter Lennard-Jones (12-6) model:

$$\psi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

This potential provides a fair compromise between simplicity and accuracy in its application to spherical molecules. It is now well established, however, that the (12-6) model is insufficiently flexible to represent the interaction of asymmetrical molecules. As shown by Pitzer (26) and Balescu (2) the potential well narrows and deepens as the corresponding molecule deviates from spherical symmetry.

These shape effects have been demonstrated quite clearly in some recent investigations of model potentials deduced largely from experimental second virial coefficient data. At least in

part, they are built into the Kihara potential (18) when its hard core is fixed on the basis of molecular structure alone (7,8,12). Even when all their parameters are determined from $B(T)$ data alone, the Kihara as well as other three-parameter potentials (27,29) exhibit the narrowing and deepening of the potential well with increasing molecular asymmetry.

It is the purpose of this survey to assess the sensitivity to molecular shape of potentials determined from the experimental viscosities for a variety of hydrocarbons. It is no essential restriction to confine the study to the Morse potential model,

$$\psi(r) = \epsilon \left\{ \exp \left[-2(c/\sigma)(r-r_m) \right] - 2 \exp \left[-(c/\sigma)(r-r_m) \right] \right\}$$

which has proven moderately successful when applied to spherical molecules (19,20). The parameters ϵ and σ have the same significance as for the (12-6) model. The third parameter, c , is related to the curvature of the potential at r_m through the expression

$$\left. \frac{d^2\psi}{dr^2} \right|_{r=r_m} = \frac{2\epsilon c^2}{\sigma^2}$$

Thus, large values of c correspond to a narrow potential well, while small values of c correspond to a wide one. Apparently,

this model has the requisite flexibility for application to non-spherical molecules.

To confirm this view, the Morse potentials for a few n-alkanes which were determined from $B(T)$ data alone (21,22), are presented in Table I. There it is seen that $\epsilon/k, c$, and σ increase with the increase in chain length about as expected from a consideration of molecular structure (2,26). Next, Morse potentials were fixed by minimizing the rms percentage deviation between the experimental and calculated $\eta(T)$. The latter were found from tables of collision integrals (23) recently developed in this laboratory. These "viscosity-determined" Morse potentials are listed in Table II along with (12-6) potentials which were also determined from viscosity data (16). In view of its greater flexibility, it is no surprise that the Morse potential affords appreciably better agreement with the experimental $\eta(T)$ than does the (12-6) model. However, for neither model do the potentials determined from viscosity afford reasonable agreement with the experimental $B(T)$. The rms percentage errors for $B(T)$ are typically 40 per cent or more, well outside the range of experimental uncertainty. In contrast, as shown in Table I, the Morse potentials determined from $B(T)$ alone fare appreciably better in reproducing the experimental $\eta(T)$. In those cases the errors in $\eta(T)$ are typically under 20 per cent.

For the rare gases, which are essentially structureless, spherical molecules, potentials deduced from $B(T)$ are usually not too different from those found from $\eta(T)$ (17). For the n-alkanes, however, it is evident from the results that a real dichotomy exists between the Morse potentials deduced from each of these properties. An explanation

may be found by examining the structure-dependence of the "virial-derived" and "viscosity-derived" potentials. In accord with the predictions of Pitzer (26) and Balescu (2), the attractive portions of the "virial-derived" potentials deepen and narrow fairly smoothly with increasing chain length (which we equate with increasing asymmetry): those for the "viscosity-derived" potentials do not. Although the same comparison cannot be made for the remaining hydrocarbons we treat, we are able to discern little connection between molecular structure and the parameters of the "viscosity-derived" potentials. It is well known that for all molecules the low-temperature $B(T)$ yields information on the depth as a function of the width of the potential well. It appears that the $B(T)$ for asymmetric molecules is sensitive to their structure in a way that specifies the well shape even more closely. Since this sensitivity to structure seems to be lacking in the $\eta(T)$ data, the "virial-derived" potentials are expected to be more nearly correct. This view is supported by the discussion in the preceding paragraph.

It is not strictly valid to compare potentials determined from these properties singly, since neither one is sufficient to specify the potential in the first place. In an ensuing work (22) it will be shown that it is possible to find compromise Morse potentials which adequately reproduce both $B(T)$ and $\eta(T)$ for a number of hydrocarbons.

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Table I

Morse potentials determined from B(T) alone.^a

Substance	ϵ/k (°K)	σ (Å)	c	S(B) cm ³ /mole	P(B)	P(η)
methane	203.50	3.6453	5.374	1.3	7.2	5.8
ethane	469.01	3.7417	6.721	0.96	1.2	11.3
propane	527.81	4.3212	6.496	3.0	1.9	8.6
n-butane	640.68	5.1385	7.783	6.2	2.4	3.5
n-pentane	822.23	4.7471	7.462	6.3	1.4	16.9
n-hexane	966.02	4.9418	8.055	8.5	0.64	25.6
benzene	733.45	5.5923	7.455	9.4	1.5	18.1

^a For the sources of the experimental data see the appropriate entries in Table II.
Potential parameters taken from Ref. 22.

Table II

Comparison of Morse and Lennard-Jones potentials determined from viscosity data.

Substance	Potential ^a		σ (Å)	c	P(η)	P(B)	Data Sources ^b	
	M	LJ					ϵ/k (°K)	η (T)
methane	M	194.95	3.613	5.994	0.24	250.	30-a	14, 28, 31
	LJ	140.	3.808	...	0.82	85.3		
ethane	M	272.	4.289	5.820	0.25	48.6	30-b	13
	LJ	236.	4.384	...	1.28	5.0		
propane	M	196.	5.406	5.000	0.62	74.8	30-c	13, 24
	LJ	206.	5.240	...	3.06	46.5		
n-butane	M	311.	5.316	4.630	0.11	28.3	30-d	9, 13, 24
	LJ	208.	5.869	...	1.06	55.4		
n-pentane	M	278.5	6.023	4.440	0.13	40.0	32, 33	3, 13, 24
	LJ	269.	6.099	...	1.30	41.3		
n-hexane	M ^c	423.	5.916	5.30	0.53	44.6	30-e	24
	LJ	423.	5.916	...	1.69	22.6		
n-heptane	M	377.	6.726	4.980	0.49	44.4	25	13, 24
	LJ ^d	282.	8.88	...	34.6	9.3		
n-octane	M	345.	7.371	5.240	0.58	60.0	25	7, 24
	LJ	333.	7.407	...	0.68	39.9		
benzene	M	440.	5.270	5.000	0.50	37.4	30-f	1, 4, 7, 10, 13
	LJ	335.	5.628	...	1.11	40.3		

Table II (cont'd)

Comparison of Morse and Lennard-Jones potentials determined from viscosity data.

Substance	Potential ^a ϵ/k		σ (Å)	c	P(η)	P(B)	Data Sources ^b	
	(°K)	(°K)					$\eta(T)$	B(T)
n-nonane	M	232.	8.549	5.104	0.49	...	25	...
	LJ	266.	8.302	...	0.48
iso-butane	M	232.	5.700	4.500	0.37	...	33	...
	LJ	217 _f	5.819	...	0.90
2,2,3-tri- methyl butane	M	185.	7.586	6.103	0.93	...	15	...
	LJ	178.	7.621	...	1.23
ethylene	M	187.	4.370	4.220	0.50	...	33	...
	LJ	230.	4.066	...	6.70
propylene	M	369.	4.466	5.189	0.70	...	33	...
	LJ	303.	4.670	...	0.71
butene-1	M	307.	5.228	4.831	0.13	...	33	...
	LJ	319.	5.198	...	0.41
butene-2	M	274.	5.382	4.465	0.15	...	33	...
	LJ	259.	5.508	...	0.76
iso butylene	M	181.	5.767	3.677	0.05	...	33	...
	LJ	425.	4.776	...	0.77

Table II (cont'd)

Comparison of Morse and Lennard-Jones potentials determined from viscosity data

Substance	Potential ^a		σ (Å)	c	P(η)	P(B)	Data Sources ^b	
	ϵ/k (°K)	σ (Å)					(T)	B(T)
iso amylene	M	250.	5.910	4.000	0.67	...	33	...
	LJ	283.	5.829	...	0.88
ethyne	M	150.	4.410	4.800	0.33	...	33	...
	LJ	212.	4.114	...	0.56
propyne	M	206.	4.966	4.709	0.17	...	33	...
	LJ	261.	4.742	...	0.88

a M = Morse potential. LJ = Lennard-Jones potential determined from viscosity (Ref. 16).

b Refs. 13 and 30 are compilations of data. References to the original sources are listed there. See Ref. 22 for a listing of the B(T) data used. In a number of cases the values obtained from different sources disagree by 50 cm³/mole or more.

c Incompletely minimized.

d Potential determined from B(T), see Ref. 17. Note the poor agreement with the experimental viscosity.

Notation

$B(T)$	=	second virial coefficient
c	=	Morse parameter governing width of potential well.
k	=	Boltzmann's constant
r	=	separation between molecular centers
r_m	=	separation at the energy minimum
$P(B), P(\eta)$	=	rms percentage deviations
$S(B), S(\eta)$	=	rms deviations
T	=	absolute temperature
T_c	=	critical temperature
ϵ	=	depth of potential
$\eta (T)$	=	viscosity
σ	=	finite separation of molecular centers at zero potential energy
$\psi(r)$	=	potential energy function

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