A critical evaluation of Lennard–Jones and Stockmayer potential parameters and of some correlation methods

FRANK M. MOURITS AND FRANS H. A. RUMMENS

Department of Chemistry, University of Regina, Regina, Sask., Canada S4S 0A2

Received November 10, 1976[1]

FRANK M. MOURITS and FRANS H. A. RUMMENS. Can. J. Chem. **55**, 3007 (1977).

Published values for the potential parameters σ and ε/k of the Lennard–Jones (12–6) and Stockmayer (12–6–3) potentials as based on viscosity measurements are reviewed, with particular reference to the problem of indeterminacy inherent to such calculations. A number of correlation techniques, calibrated on viscosity-based potential parameters, are critically reviewed; where possible, priority rules for the use of these correlations have been developed. In addition, several other criteria (i.e. not based on viscosity data) for the acceptance or rejection of σ and ε/k parameter values are also discussed. Upon application of the various criteria and priority rules it has been possible to give recommended σ and ε/k parameter values for 75 molecules.

FRANK M. MOURITS et FRANS H. A. RUMMENS. Can. J. Chem. **55**, 3007 (1977).

On passe en revue les valeurs publiées pour les paramètres σ et ε/k des potentiels de Lennard–Jones (12–6) et de Stockmayer (12–6–3); les potentiels sont basés sur des mesures de viscosité et on tient particulièrement compte des problèmes d'indéterminations inhérents aux tels calculs. On fait aussi une revue critique d'un certain nombre de techniques de corrélation, calibrées sur des paramètres de potentiel basés sur la viscosité; on a développé, dans les cas qui s'y prêtent, des règles de priorité pour l'utilisation de ces corrélations. De plus, on discute de plusieurs autres critères (qui ne sont pas basés, c'est-à-dire, sur la viscosité) pour l'acceptation ou le rejet de valeurs des paramètres σ et ε/k. Par l'application de divers critères et de règles de priorité, il est possible de présenter des valeurs recommandées pour les paramètres σ et ε/k pour 75 molécules.

[Traduit par le journal]

Introduction

The prediction of bulk properties of matter from molecular level models appears to be a well-developed science. Particularly in gases, properties like the second virial coefficient, viscosity, thermal conductivity *et cetera* can be molded into a unifying framework based on molecular pair interactions (see in particular Hirschfelder, Curtiss, and Bird's book (1a)). These models of pair interactions all start with the assumption that there exists a general potential function, different only for the various different molecules through one, two, or more parameters. Many such functions have been proposed (1b), but perhaps the one most commonly used is the Lennard–Jones (12–6) function of [1]:

$$[1] \quad V(\text{pair}) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where r is the distance between the centres of mass of the two molecules, ε is the maximum depth of the potential well, and σ is the distance

at which $V(\text{pair}) = 0$. Equation 1 can, strictly speaking, only be used for non-polar molecules, but in practice [1] is also used for polar molecules. However, for the latter the Stockmayer (12–6–3) potential of [2] should be preferred:

$$[2] \quad V(\text{pair}) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \delta\left(\frac{\sigma}{r}\right)^{3}\right]$$

where $\delta = \zeta\,\mu^2/4\sigma^3\varepsilon$, $\zeta(\theta_1,\theta_2,\phi)$ being a function to describe the angular dependence of the dipole–dipole interaction energy. Used in their proper integrated forms, [1] or [2] can lead to expressions for transport properties (1c) and equation of state and thermodynamic properties (1d); data-fitting with accurate experimental data on these properties can be used to determine the parameters ε/k and σ. Mixing rules exist (1e) to predict macroscopic properties of binary mixtures. Particularly in engineering the possibility of calculating transport properties of gases has been explored and applied extensively. In our own attempts to construct a molecular model to account for the medium nmr shift of gases and liquids (see following paper (2)) we

---

[1]Revision received May 11, 1977.

have been confronted (as have many others before us) with several major drawbacks of the above outlined approach.

(*i*) Methods to extract the parameters ε/k and σ from different macroscopic properties often lead to substantially different values; this may happen even if the same property is employed.

(*ii*) All too often the ε/k and σ for the molecules of interest are not known, and even the required macroscopic properties may not have been measured. In these cases one has to resort to estimation methods, of which a bewildering collection is available in the literature, thus leaving one with the difficult task of deciding which approximation to believe most.

In this paper we will exclusively discuss ε/k and σ parameters either directly obtained from gas viscosities or estimated by correlation methods which have been calibrated on such viscosity-based parameters. This restriction is a pragmatic one; more parameters are known from viscosity than from all other sources combined. Second virial coefficients apply to a state of equilibrium and therefore potential parameters based on second virial coefficients should, in principle, be more relevant to nmr medium shift applications than those based on viscosity. Second virial coefficient data fits are, however, very sensitive to the choice of potential; in particular shape- and higher-order polarity terms are needed to obtain physically meaningful parameters (3). At present only Lennard–Jones parameters have been calculated from 2nd virial coefficients in any great number and these are notably poor for polar and large non-polar molecules (1*f*).

Directly viscosity-based parameters and their reliability are discussed first. Next some of the more prominent correlation methods will be discussed and several priority rules for the use of these will be proposed. A few extra tests will also be discussed; these are crude correlation guides for ε/k and σ which are nevertheless useful because even the best of the correlation techniques can on occasion produce extremely erroneous results. Finally, this critical analysis has enabled us to recommend best values for σ and ε/k. A list of such recommended parameters for 75 molecules concludes this paper.

Discussion

ε/k and σ Parameters Directly Obtained From Gas Viscosities

Before comparing in detailed fashion the various sets of parameters, it should be pointed out that for some molecules greatly varying parameter values have been reported. Reid and Sherwood (4*a*) have already discussed this in connection with the parameter values for *n*-butane as calculated by Flynn and Thodos and by Svehla, whose calculations were based on the *same* experimental viscosity data.

The explanation of these erratic results has recently been given by Kim and Ross (5). These authors noted that the Lennard–Jones collision integral $\Omega^{(2,2)*}$ in the reduced temperature range $0.4 < T^* < 1.4$ reduced to $1.604(T^*)^{-1/2}$ with an error of less than 0.7%. This has the effect (since $T^* = kT/\varepsilon$) that the Chapman–Enskog equation for the viscosity η is reduced to a simple proportionality with T, out of which only the *product* $\sigma^2\varepsilon^{1/2}$ can be deduced:

$$[3] \qquad \eta = \frac{266.95 \times 10^{-7}(MT)^{1/2}}{\sigma^2\Omega^{(2,2)*}}$$

$$= \frac{166.43 \times 10^{-7}T(Mk)^{1/2}}{\sigma^2\varepsilon^{1/2}} \quad (P)$$

Reichenberg (6) has also studied this matter, reaching virtually the same conclusion, albeit with a slightly different indeterminacy range of $0.39 < T^* < 1.55$. Halkiadakis and Bowrey (7) have applied the same ideas to the Stockmayer potential and its parameters; they found that the range of indeterminacy increases slowly with polarity to become $0.2 < T^* < 1.8$ when δ_{max} reaches $\delta_{max} = 2.5$ ($\delta_{max} = \frac{1}{2}\mu^{*2}$, where $\mu^{*2} = \mu^2/\sigma^3\varepsilon$). Our own analysis confirmed the above, but it was found that in the indeterminate range $\Omega^{(2,2)*}$ for polar molecules reduces to $A(T^*)^{-n}$, where A and n depend strongly on the value of δ_{max}, with the result that η then becomes inversely proportional to the product $P(n) = \sigma^2(\varepsilon/k)^n$. Such indeterminacy is not really serious when viscosities are recalculated; any combination σ, ε/k such that the product $P(n)$ is equal to the experimental value will reproduce viscosities to good precision. Greater errors occur when viscosities of *mixtures* or other properties are calculated. Such errors take on catastrophic dimensions when a property like the nmr Van der Waals intermolecular shift σ_w is calculated, because σ_w is approximately proportional to $\sigma^{-3}\varepsilon$ (8); a σ which is too large combined with too small an ε now add up to give a much too small σ_w value.

Kim and Ross (5) also showed that the collision integral $\Omega^{(2,2)*}$ in the range $0.9 < T^*$

< 5 can be written, with an error of less than 0.1%, as:

$$[4] \qquad \Omega^{(2,2)*} = 0.7616\left(1 + \frac{1.09}{T^*}\right)$$

Equation 4 makes the Chapmann–Enskog equation (eq. 3) equivalent to the empirical Sutherland formula, which can be written as follows:

$$[5] \qquad \eta = \frac{266.95 \times 10^{-7}(MT)^{1/2}}{\sigma_T^2}$$

$$\sigma_T^2 = \sigma_\infty^2\left(1 + \frac{C}{T}\right)$$

In the above stated T^* range the parameters in [3] and [5] are thus related as follows:

$$[6] \qquad \sigma = 1.146\sigma_\infty \quad \varepsilon/k = 0.917C$$

Through [6], therefore, the large compilation by Franck (9) of σ_∞ and C parameters can be converted to σ and ε/k parameters; the latter being just as much subject to indeterminacy, however, as when obtained directly through [3].

The indeterminacy problem thus obliges one to make a judgement on the quality of the experimental viscosity data. In Table 1 the viscosity-based parameters σ are listed as originating from Franck (abbrev. F) (9), Hirschfelder et al. (abbrev. HCB) (1f), Flynn and Thodos (abbrev. FT) (10), Svehla (abbrev. S) (11), Tee, Gotoh, and Stewart (abbrev. TGS) (12), Linakis and Bowrey (abbrev. LB) (13), and Halkiadakis and Bowrey (abbrev. HB) (7). In the column marked HB we have also indicated the total number of viscosity points (N_t) used by HB as well as the number (N_e) of viscosity points outside the indeterminate range. The parameters values of HCB and FT were obtained by a multiple two-point numerical fitting technique, whereas those given by S, TGS, LB, and HB were obtained by direct least-squares fitting on [3]. In Table A the corresponding ε/k values are listed.[2]

For polar molecules (Tables 2 and B)[2] a distinction must be made between parameters calculated following a Lennard–Jones potential [1], and those calculated according to a Stockmayer potential [2]. Only Monschick and Mason (referred to as MM), using a graphical curve-shifting procedure, have used [1] and [2] on the same set of viscosity data (14).

[2]Copies of Tables A, B, and C are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

Because of the important role of the product $P(n) = \sigma^2(\varepsilon/k)^n$, the values of $P(n)$ for all parameter sets listed in Tables 1, 2, A, and B have been calculated; these are given in Tables 3 and 4. In Table 4 the calculated $P(n)$ values based on the Stockmayer potential are given both for the correct value of n (varying between 0.49 and 0.54) as well as for $n = 0.50$. The latter allows comparison with the Lennard–Jones based products $P(n)$, where $n = 0.50$. As will be shown, these products $P(n)$ can be used as a guide in analyzing and judging the various parameter sets. As expected, the $P(n)$ values for indeterminate parameter sets are fairly constant ($\pm 1\%$ or less), although the individual σ and ε/k parameters may vary strongly between the various authors. For determinate situations $P(n)$ is only constant, when the individual σ and ε/k parameters are the same. The $P(n)$ values based on the data of Franck (eq. 6 and ref. 9) were found to be systematically higher than all other $P(n)$ values; hence the corresponding σ and ε/k values were omitted from further consideration.

For the noble gases, N_2, O_2, CO_2, CH_4, C_2H_6, and H_2O the viscosities are known over a very large temperature range; therefore a high percentage of viscosity points falls outside the indeterminate range. Indeed the parameters from HCB, FT, S, TGS, and MM show a good mutual agreement for these molecules. The σ parameters of LB and HB seem to be systematically lower for the noble gases, N_2, O_2, and CO_2 in spite of a high percentage determinacy. We have traced this discrepancy back to their use of presmoothed viscosity data (15), even extrapolating outside the original experimental temperature range (O_2). In the HB study viscosity points outside the indeterminacy range were given a statistical weight 10 times larger than those inside the range, whereas in the LB study virtually the same data points were used but with equal statistical weight. The product $P(n)$ is a useful quantity to discuss the differences between the results of HB and LB. As the tables show, for highly determinate cases the products $P(n)$, as well as the individual σ and ε/k parameters are very similar in the HB and LB studies. The tables show also that the HB and LB products $P(n)$ are almost the same, but with widely different individual σ and ε/k values, for those molecules where the parameters are indeterminate. For molecules whose experimental points are partly inside, partly outside the indeterminate range, several sub-cases

TABLE 1. The Lennard–Jones parameters σ (in Å) for non-polar molecules, based on viscosity and calculated by empirical correlations, and recommended values for σ and ε/k (in K)

#		σ_{visc}									σ_{calc}		σ (recommended)	ε/k (recommended)
		F[a]	HCB[b]	FT[c]	S[d]	TGS[e]	LB[f]	HB[g]	N_t^h	N_e^h	ST Eq.7	TGS Eq.12		
1	Ne	2.578	2.824		2.820		2.664				2.745	2.796	2.822	32.0
2	Ar	3.426	3.442		3.542	3.434	3.320	3.302	13	13	3.460	3.432	3.465	113.5
3	Kr	3.690	3.61		3.655	3.721	3.563	3.539	13	10	3.741	3.677	3.662	178.0
4	Xe	4.068	4.055		4.047	4.049	3.909	3.890	13	9	4.111	4.019	4.050	230.2
5	N₂	3.690	3.715		3.798	3.722	3.606	3.584	13	13	3.687	3.668	3.738	82.0
6	O₂	3.460	3.487		3.467		3.374	3.354	13	13	3.480	3.431	3.480	102.6
7	CO₂	3.953	3.964		3.941	3.881	3.765	3.752	13	9	4.012	3.885	3.943	200.9
8	CS₂	4.526	4.438		4.483						4.748	4.575	4.575	414.6
9	SF₆		5.24		5.128						4.989	4.960	5.199	212.0
10	(CN)₂	4.538	4.38		4.361						5.137	4.571	4.571	275.7
11	F₂	3.644	3.653		3.357		3.534	3.439	5	3	3.362	3.325	3.439	152.1
12	Cl₂	4.217	4.258		4.217		4.235	4.232	21	10	4.380	4.176	4.240	307.2
13	Br₂	4.354	4.268		4.296						4.514	4.266	4.266	437.3
14	I₂	5.099	4.982		5.160		5.095	5.077	6	1	4.867	4.630	4.630	577.4
15	CH₄	3.816	3.809	3.808	3.758	3.774	3.863	3.782	67	51	3.845	3.787	3.790	142.1
16	CF₄				4.662		4.407	4.390	19	19	4.541	4.405	4.486	167.3
17	CCl₄	5.901	5.881		5.947		5.744	5.611	21	4	5.795	5.554	5.611	415.5
18	C₂H₆	4.446	4.418	4.384	4.443	4.480	4.416	4.302	70	30	4.452	4.395	4.407	227.9
19	C₃H₈	5.110	5.061	5.240	5.118	5.136	5.147	4.982	29	9	5.031	4.940	5.114	237.2
20	n-C₄H₁₀	5.248	4.997	5.869	4.687	5.339	5.179	5.176	11	0	5.595	5.405	5.405	305.0
21	i-C₄H₁₀	5.408	5.341	5.819	5.278		5.372	5.370	6	0	5.438	5.392	5.392	295.8
22	n-C₅H₁₂	5.798	5.769	6.099	5.784	6.104	5.989	5.751	44	9	6.260	5.851	5.916	308.3
23	neo-C₅H₁₂				6.464	6.520					6.058	5.757	5.757	312.2
24	n-C₆H₁₄	5.993	5.909	5.916	5.949		6.207	5.923	31	0	6.623	6.269	6.269	341.3
25	n-C₇H₁₆	6.405				7.144	6.543		8	0	7.006	6.650	6.650	351.4
26	n-C₈H₁₈	7.540	7.451	7.407			7.318	7.167	8	0	7.452	7.024	7.024	357.7
27	n-C₉H₂₀	8.433	8.448	8.302			8.467	8.286	4	1	7.883	7.351	7.351	360.3
28	cyclo-C₆H₁₂	6.130	6.093	6.143	6.182						5.984	5.771	5.771	394.8
29	C₂H₄	4.263	4.232	4.066	4.163	4.257	4.240	3.971	30	5	4.419	4.232	4.155	225.6
30	C₃H₆	4.732		4.670	4.678		4.730	4.424	36	1	4.969	4.778	4.778	271.2
31	butene-1	5.305		5.198							5.412	5.274	5.274	302.4
32	i-butene	5.191		4.776							5.451	5.282	5.282	299.6
33	C₂H₂	4.263	4.221	4.114	4.033		4.060	3.964	29	12	4.322	4.131	4.078	221.4
34	C₃H₄	4.790		4.742	4.761						4.787	4.667	4.667	284.7
35	C₆H₆	5.397	5.270	5.628	5.349	5.443	5.398	5.340	30	0	5.699	5.455	5.455	401.2
36	C₆H₅CH₃	6.210		5.932							6.284	5.923	5.923	407.8
37	mesitylene	8.525		7.706							6.995	6.760	6.760	400.5

[a]See ref. 9. [b]See ref. 1f. [c]See ref. 10. [d]See ref. 11. [e]See ref. 12. [f]See ref. 13. [g]See ref. 7. [h]N_t is the total number of viscosity points used by HB; N_e is the number of viscosity points outside the indeterminate range. See text for further details.

need to be considered. If the HB and LB procedures result in substantially different products $P(n)$, then the set of experimental points favored by the HB weighting method (normally the high-temperature points) is inconsistent with the complete set. In fact in such a case the HB parameters should be considered less reliable since even their product $P(n)$ does not optimally fit the

TABLE 2. The Lennard–Jones and Stockmayer potential parameters σ (in Å) for polar molecules, based on viscosity and calculated by empirical correlations, and recommended values for σ and ε/k (in K)

#		μ*²	$\sigma_{visc,L.J.}$				$\sigma_{visc,St.}$					σ_{calc}				σ ε/k (recommended)	
			F[a]	HCB[b]	S[c]	MM[d]	MM[e]	LB[f]	HB[g]	N_t[h]	N_e[h]	ST Eq.7	ST Eq.8	TGS Eq.12	MS Eq.15	σ	ε/k
38	N_2O	0.02	3.724	3.848	3.828			3.613[i]	3.740	29	14	4.059	3.612	3.900	4.009	3.776	248.8
39	CO	0.02	3.701	3.648	3.690				3.633	28	0	3.660	3.558	3.698	3.598	3.698	104.5
40	COS	0.15	4.274	4.13	4.130							4.790	4.076	4.424	4.505	4.424	286.4
41	NO	0.03	3.541	3.535	3.492			3.457	3.428	34	20	3.794	3.039	3.553	3.236	3.489	117.2
42	HI	0.06	4.068	4.123	4.211		4.13	4.238				3.785	4.027	4.080	3.875	4.080	333.6
43	HBr	0.30	3.621		3.353		3.41					3.617	3.761	3.852	4.086	3.852	281.1
44	HCl	0.82	3.392	3.305	3.339		3.36	3.240	3.240	12	0	4.282	3.396	3.771	3.168	3.168	322.6
45	HF	2.33			3.148								3.220			3.148	330.
46	H_2S	0.43	3.644		3.623	3.591	3.49	3.628[i]	3.491	9	0	3.903	3.625	3.840	3.733	3.733	302.4
47	SO_2	0.85	4.251	4.290	4.112	4.026	4.04	4.249	4.017	44	17	4.494	3.893	4.283	4.054	4.102	328.5
48	HCN	2.36	3.254		3.630								4.066			3.630	569.1
49	NH_3	1.52	2.830		2.900		3.15	3.288[i]	3.206	40	15	3.273			3.121	3.215	309.9
50	H_2O	2.46	2.601		2.641		2.71	3.086	3.067	25	19	3.003			2.708	2.71	506.
51	$CHCl_3$	0.14	5.431	5.430	5.389		5.31	5.157	5.163	14	3	5.052	4.872	5.179	5.114	5.179	381.7
52	CH_2Cl_2	0.43	4.847	4.759	4.898	4.748	4.52	4.759	4.830	5	2	5.033	4.537	4.906	4.998	4.752	403.5
53	CH_3Br	0.71	4.423		4.118		4.25						4.306	4.278		4.306	416.2
54	CH_3Cl	0.97	4.091	3.375	4.182	4.151	3.94	4.047	4.057	21	2	4.693	4.067	4.419	4.296	4.296	328.1
55	C_2H_5Cl	0.83			4.898		4.45						4.583		4.490	4.490	402.9
56	$n\text{-}C_3H_7OH$	0.37	4.813		4.549		4.71	5.377	4.570	7	0	5.843	4.724	5.543	4.867	4.867	480.2
57	$i\text{-}C_3H_7OH$	0.41	4.961				4.64					6.003	4.739	5.623	4.491	4.739	456.0
58	C_2H_5OH	0.57	4.526	4.455	4.530	4.370	4.31	4.755[i]	4.756	15	9		4.323		4.317	4.317	450.2
59	CH_3OH	1.11	3.724	3.585	3.626	3.666	3.69	3.959	3.930	14	5		3.850		3.657	3.657	385.2
60	$(C_2H_5)_2O$	0.16	5.133		5.678	5.539	5.49	5.825	5.813	22	8	6.091	5.136	5.711	5.553	5.553	348.0
61	$(CH_3)_2O$	0.46	4.560		4.307	4.264	4.21	4.736[i]	4.359	14	0	4.425	4.513	4.718	4.230	4.230	352.3
62	$CH_3CO_2C_2H_5$	0.33	5.397		5.205	5.163	5.24					6.427	5.172	5.888	5.841	5.65	372.
63	$CH_3CO_2CH_3$	0.41	5.007		4.936	5.054	5.04					5.903	4.796	5.421	5.141	5.141	389.4
64	$(CH_3)_2CO$	1.35	4.778		4.600	4.669	4.50	4.601	4.601	9	0		4.659		4.599	4.599	458.0
65	CH_3CHO	1.56						3.972	3.972	4	0		4.332		3.883	4.332	413.5

[a] See ref. 9. [b] See ref. 1f. [c] See ref. 11. [d] Lennard–Jones parameters of ref. 14. [e] Stockmayer parameters of ref. 14. [f] See ref 13. [g] See ref. 7. [h] See footnote h of Table 1. [i] Total number of data points used less than N_t.

data points in the indeterminate range. On the other hand the LB *product P(n)* is more reliable. It would have been better to employ the HB method, but with the LB product *P(n)* kept as a fixed constant. Examples are C_3H_8, C_2H_4, N_2O, NH_3, and SO_2. If the HB and LB products *P(n)* are essentially the same, when the individual σ and ε/k parameters are different, then one should prefer the HB parameters. Examples are F_2 and CCl_4. If the HB and LB products *P(n)* and the σ and ε/k parameters are virtually the same, then apparently the case is already effectively determinate (noble gases, N_2, O_2, CO_2, NO). The fourth possibility relates to cases where N_e is very small. If these few points fall in a *narrow T** range (as they normally will do), then the extracted HB parameters may become effectively indeterminate (constant *P(n)*) again, as was pointed out already by Reichenberg (6). Examples are CH_3Cl, $CHCl_3$, C_2H_5OH, CH_3OH, and $(C_2H_5)_2O$. Although the degree of indeterminacy as indicated in Tables 1 and 2 refers, strictly speaking, only to the work of HB, it gives in general also a good indication of the indeterminacy of the parameters of the *other* authors for these same molecules, since the sources of viscosity data were largely the same. In addition, the latter data are for the most part

TABLE 3. The product $P(n)$ for the non-polar molecules of Table 1 with $n = 0.50$

#		P_{visc}[a]							P_{calc}		P_{ave}	P_{rec}	% dev.
		F	HCB	FT	S	TGS	LB	HB	ST Eq.7	TGS Eq.12			
1	Ne	72	45		46		55		46	43	48	45	
2	Ar	134	130		121	130	133	134	129	130	130	127	
3	Kr	179	180		179	178	177	178	174	176	178	179	
4	Xe	252	249		249	249	248	248	244	247	249	249	
5	N_2	134	128		122	128	134	134	133	134	129	126	
6	O_2	128	122		124		127	128	129	131	125	123	
7	CO_2	218	221		217	221	221	221	221	221	220	220	
8	CS_2	439	417		434				422	426	426	426	− 0.1
9	SF_6		388		392				365	365	389	389	
10	$(CN)_2$	358	353		355				418	347	354	347	+ 2.0
11	F_2	144	141		120		144	146	143	118	138	146	
12	Cl_2	319	315		316		312	312	310	313	314	314	
13	Br_2	419	415		416				377	381	415	381	+ 8.4
14	I_2	594	582		580		581	581	512	515	581	515	+11.3
15	CH_4	178	172	172	172	171	166	169	175	177	171	171	
16	CF_4				252		262	263	248	249	259	259	
17	CCl_4	637	635		635		640	642	614	618	638	642	
18	C_2H_6	301	296	295	290	290	292	294	292	295	293	293	
19	C_3H_8	417	408	394	403	400	401	405	400	403	402	402	
20	$n\text{-}C_4H_{10}$	512	506	497	506	502	507	506	507	510	504	510	− 1.3
21	$i\text{-}C_4H_{10}$	514	505	499	506		504	505	498	500	504	500	+ 0.7
22	$n\text{-}C_5H_{12}$	630	618	610	618	602	610	614	616	618	612	612	
23	$neo\text{-}C_5H_{12}$				581	575			581	586	578	586	− 1.3
24	$n\text{-}C_6H_{14}$	718	710	720	707		711	714	726	726	712	726	− 1.9
25	$n\text{-}C_7H_{16}$	829				818		829	832	829	823	829	− 0.7
26	$n\text{-}C_8H_{18}$	1000	993	1001			992	994	941	933	995	933	+ 6.2
27	$n\text{-}C_9H_{20}$	1132	1106	1124			1128	1121	1039	1026	1120	1026	+ 8.4
28	$cyclo\text{-}C_6H_{12}$	674	668	668	659				658	662	665	662	+ 0.5
29	C_2H_4	261	256	251	256	257	261	264	261	264	258	258	
30	C_3H_6	385		378	378		377	378	373	376	378	376	+ 0.6
31	butene-1	489		483					481	484	483	484	− 0.2
32	i-butene	475		470					481	483	470	483	− 2.7
33	C_2H_2	245	242	246	248		248	250	253	255	247	247	
34	C_3H_4	366		363	360				366	368	361	368	− 1.7
35	C_6H_6	591	583	580	581	583	584	583	593	596	582	596	− 2.4
36	$C_6H_5CH_3$	711		683					706	708	683	708	− 3.7
37	mesitylene	812		908					902	915	908	915	− 0.7

[a]For references see Table 1.

fairly old and are consequently not likely to be more accurate than 0.7%. It should be kept in mind, however, that recent viscosity data, particularly when measured with the rotating disc technique may be as precise as 0.1% (15), thereby narrowing or even eliminating the in-determinacy range. Except for the noble gases, N_2, O_2, and CO_2 no such accurate data appear to be available at this time.

As far as the fit on viscosity data of polar molecules is concerned, no significant improvement is obtained by replacing the Lennard–Jones

TABLE 4. The product $P(n)$ for the polar molecules of Table 2

#		$P_{visc,L.J.}$[a]				$P_{visc,St.}$[a]				P_{calc}				P_{ave}	P_{rec}	% dev.
		F	HCB	S	MM	MM	LB	HB	n	ST Eq.7	ST Eq.8	TGS Eq.12	MS Eq.15			
38	N$_2$O	235	224	223			229	221	0.50	228	217	230	237	224	224	
39	CO	132	132	130				135	0.50	139	138	140	136	132	140	− 5.6
40	COS	318	312	313					0.50	327	305	331	337	312	331	− 6.2
41	NO	136	127	132			136	134	0.50	130	117	125	129	131	131	
42	HI	313	306	301		302	299		0.50	303	316	304	288	302	304	− 0.6
43	HBr					224			0.49							
		243		238		237			0.50	248	255	249	262	238	249	− 4.6
44	HCl					193	193	193	0.49							
		210	207	207		204	204	204	0.50	219	197	222	180	204	180	−11.8
45	HF			180					0.50		211				180	
46	H$_2$S					213	217	218	0.49							
		231		228	227	226	230	231	0.50	247	240	249	242	228	242	− 6.2
47	SO$_2$					287	285	289	0.49							
		303	292	310	309	304	301	306	0.50	317	298	317	303	304	304	
48	HCN	304		314					0.50						314	
49	NH$_3$	192		199		188	181	176	0.50		204		190	181	181	
50	H$_2$O					212	198	196	0.54							
		201		198		165	158	156	0.50		217		184	160	165	
51	CHCl$_3$	546	533	536		531	541	542	0.50	524	521	524	522	537	524	+ 2.3
52	CH$_2$Cl$_2$					422	428	426	0.49							
		464	456	453	450	449	454	452	0.50	459	440	461	472	452	452	
53	CH$_3$Br					333			0.49							
		365		359		353			0.50		378			353	378	− 7.2
54	CH$_3$Cl					297	299	300	0.49							
		337	333	327	325	316	317	318	0.50	339	320	343	334	317	334	− 5.4
55	C$_2$H$_5$Cl					383			0.49							
				416		407			0.50		427		405	407	405	+ 0.6
56	n-C$_3$H$_7$OH					464	458	464	0.49							
		504		497		494	484	494	0.50	539	490	518	519	492	519	− 5.4
57	i-C$_3$H$_7$OH					460			0.49							
		506				490			0.50	534	480	508	462	490	480	+ 2.1
58	C$_2$H$_5$OH					363	356	356	0.49							
		396	392	391	389	386	377	377	0.50		402		395	380	395	− 4.2
59	CH$_3$OH					262	261	257	0.49							
		293	289	289	286	278	276	272	0.50		318		262	276	262	+ 4.7
60	(C$_2$H$_5$)$_2$O	507		571	575	573	568	565	0.50	581	540	582	575	570	575	− 0.8
61	(CH$_3$)$_2$O					347	353	347	0.49							
		370		369	369	368	374	368	0.50	378	386	377	336	370	336	+ 9.1
62	CH$_3$CO$_2$C$_2$H$_5$					576			0.49							
		626		619	614	613			0.50	639	579	637	653	615	615	
63	CH$_3$CO$_2$CH$_3$					489			0.49							
		538		528	522	519			0.50	538	490	539	522	523	522	+ 0.3
64	(CH$_3$)$_2$CO	509		501	497	474	475	474	0.50		463		453	475	453	+ 4.6
65	CH$_3$CHO					330	330		0.50		382		323	330	382	−15.8

[a]For references see Table 2.

(12–6) potential by a Stockmayer (12–6–3) potential (14). Indeed as MM stated (14), even more primitive potentials would have been equally successful. Klein and Hanley (16) analyzed this problem from a theoretical viewpoint and came to the important conclusion that within the range $2.0 < T^* < 5.0$ little can be learned about the precise nature of the potential function. One must have viscosity data of at least 0.5% accuracy and then either at $T^* < 2.0$ or $T^* > 5.0$ or both in order to distinguish between the various proposed potential func-

tions. The above does not imply, however, that the *parameter* sets for the Lennard–Jones and Stockmayer potentials would have to be the same. Inspection of the two MM columns of Tables 2 and B reveals in fact considerable, but non-systematic differences. Comparing each of the corresponding MM $P(n)$ values with the other $P(n)$ values for the same potential (Table 4), it is evident that all cases except SO_2 are effectively indeterminate. Although therefore no conclusion can be drawn regarding the relative merit of the two potentials with respect to their σ and ε/k parameters, it is evident from Table 4 that the Stockmayer $P(n)$ values are systematically smaller than the Lennard–Jones $P(n)$ values. Analysis of the collision integral $\Omega^{(2,2)*}$ as a function of δ_{max} has shown us that there are, to a good approximation, explicit relations between Stockmayer and Lennard–Jones parameters. Up to $\delta_{max} = 0.25$ the differences are negligible. Going from $\delta_{max} = 0.25$ to $\delta_{max} = 2.5$ the Stockmayer σ values decrease up to 5%, while the Stockmayer ε/k values decrease up to 51% relative to the Lennard–Jones ε/k; as a result Stockmayer $P(n)$ values are substantially smaller than Lennard–Jones $P(n)$ values for $\delta_{max} > 0.25$. This latter trend can be clearly observed in Table 4. The general conclusion therefore is, that, apart from indeterminacy problems, Stockmayer potential parameters are to be preferred for molecules with δ_{max} larger than 0.25.

ε/k and σ Parameters Obtained by Correlation Techniques

Stiel and Thodos (abbrev. ST) (17) have developed the following empirical relationship for non-polar molecules:

$$[7] \qquad \sigma = 0.1866 V_c^{1/3} Z_c^{-6/5}$$
$$\varepsilon/k = 65.3 T_c Z_c^{18/5}$$

and similarly for polar, but non-hydrogen bonding molecules (18):

$$[8] \qquad \sigma = 0.785 V_c^{1/3}, \quad \varepsilon/k = 0.897 T_c$$

Here V_c is the critical volume (cm^3), T_c is the critical temperature (K) and Z_c is the critical compressibility. Selected values for Z_c, V_c, P_c, T_c, as well as for the dipole moment μ are given in Table C.[2] Equation 7 was calibrated on the viscosity-based Lennard–Jones (12–6) parameters of FT (10) and of HCB (1f). Equation 8 was calibrated on the viscosity-based Stock-

mayer parameters of MM (14). More recently, HB (7) have developed similar relations. For non-polar molecules only, they find:

$$[9] \quad \sigma = 0.386 V_c^{1/3} Z_c^{-0.59}, \quad \varepsilon/k = 2.80 T_c Z_c^{0.97}$$

whereas for non-polar and polar molecules combined, they find:

$$[10] \quad \sigma = 0.813 V_c^{1/3}, \quad \varepsilon/k = 0.404 T_c Z_c^{-0.53}$$

HB calibrated [9] and [10] on their own set of calculated viscosity-based Lennard–Jones (12–6) and Stockmayer (12–6–3) potential parameters.

For non-polar molecules an alternative was recently introduced by TGS (12). The method does not require knowledge of the often inaccurate V_c parameter, but utilizes P_c, T_c, and Pitzer's acentric factor ω, where ω is defined by

$$[11] \qquad \omega + 1 = -\log_{10} \frac{P}{P_c} \bigg|_{T_r = 0.7}$$

with P being the vapour pressure at the reduced temperature $T_r = 0.7$. Calibrating on their own set of viscosity-based Lennard–Jones (12–6) parameters, they found:

$$[12] \quad \sigma = (2.3454 + 0.2972\omega)\,(T_c/P_c)^{1/3}$$
$$\varepsilon/k = (0.8082 - 0.4504\omega)\,T_c$$

The parameter ω can be calculated (eq. 11) from vapour pressure data or, if the latter are not available, be estimated within 5% from the following semi-empirical relation (19):

$$[13] \qquad \omega + 1 = \frac{3\theta}{7(1 - \theta)} \log_{10} P_c$$
$$\theta = T_b/T_c$$

where T_b (K) is the boiling point temperature.

Malek and Stiel (abbrev. MS) (20) have attempted to expand the TGS method to *polar* compounds, introducing a fourth parameter x to account for the polar interactions:

$$[14] \quad x = \log_{10} \frac{P}{P_c} \bigg|_{T_r = 0.6} + 1.70\omega + 1.552$$

Calibrating on MM's set of Stockmayer parameters (14), they obtained the following relations:

$$[15] \quad \sigma = (2.3454 + 0.2972\omega - 40.4271x$$
$$+ 61.7675\omega x - 15.8248x^2$$
$$- 0.9706\omega^2)\,(T_c/P_c)^{1/3}$$
$$\varepsilon/k = (0.8082 - 0.4504\omega + 27.3866x$$
$$- 48.9402\omega x - 48.7293x^2 + 0.8784\omega^2)\,T_c$$

We have calculated ω and x values for all molecules concerned, directly from the best vapour pressure data available. These are given in Table 5. The right-hand side of Tables 1–4, A and B show calculated values of σ, ε/k and $P(n)$ as based on the critical values of Table C and our own set of ω and x parameters of Table 5.[2]

Critical Comparison of ε/k and σ Parameter Values

In Tables 1–4, A, and B we have italicized those values which we have used to arrive at the *recommended* values. For the values of σ(visc) and ε/k(visc) this judgement was arrived at by searching the original literature on the viscosity measurements as used by the various authors. Generally, when about 30% or more of the experimental points were outside the indeterminate range, the parameters were considered reliable, at least if and when the latter conformed with the criteria regarding $P(n)$ as discussed in the previous section. These preferred σ(visc) and ε/k(visc) values form a basis set against which the σ(calcd) and ε/k(calcd) can be compared.

Discussing first the non-polar molecules (Table 1), it may be seen that the σ(calcd) values according to [7] are not unreasonable but nevertheless slightly too large on the average. It is believed that this is due to the calibration of [7], which included many σ(visc) values now considered to be unreliable. Re-calibrating would be a possibility, but at this stage this would be rather unsatisfactory due to the lack of reliable σ(visc) data for *larger* molecules. Furthermore the strong dependence on the, usually inaccurately known, parameter V_c makes the ST method less attractive, particularly since the TGS method (see below) does not require V_c at all. The correlations given by HB (eqs. 9 and 10) show a lesser dependence on V_c. The σ(calcd) values obtained by [9] are reasonable, but in general somewhat too small. Equation 10 has in principle the great advantage of avoiding the discrimination between polar and non-polar molecules, but for non-polar molecules at least the results are often much too low.

The TGS results (eq. 12) show a very good agreement with our selected σ(visc) and ε/k(visc) parameters despite the fact that the original TGS calibration included some indeterminate parameters. Since the TGS method does not require

knowledge of V_c but rather of the vapour pressure, which is usually accurately known, we prefer the TGS method over those of ST and HB. Based on this preference we have accepted as best values for those molecules, for which no sufficiently determinate σ(visc) and ε/k(visc) were available, the σ(calcd) and ε/k(calcd) calculated with [12]. The last two columns of Table 1 show the selected parameters σ and ε/k for all non-polar molecules; the ε/k values have, in all instances, been selected in conformity with the selection of σ values (see Table B).[2] Where more than one acceptable value was available, the *average* of these is given.

For slightly polar molecules (i.e. $\mu^* \leq 0.3$) [7] gives σ(calcd) values which are too high (as was already noticed for non-polar molecules), whereas the σ(calcd) values according to [8] are too low. Taking the *average* of the results of [7] and [8] gives good agreement for this μ^{*2} range. However, the HB method of [9] gives also good results, comparable with the above mentioned average. For polar molecules with $\mu^{*2} > 0.3$ reasonably good values are obtained with [8]. This is rather remarkable since the calibration of [8] included only one molecule (SO_2) with a large degree of determinacy in its parameters. Equation 10, being a correlation for non-polar and polar molecules combined shows systematic deviations; σ(calcd) is generally too low for slightly polar molecules and too high for polar molecules. It follows therefore that it is impossible to find a universal correlation based on critical constants, which gives good results for molecules of both low and high polarity. The claim of HB that [10] is superior to ST's [7] is irrelevant as far as polar molecules are concerned because the latter equation is designed to correlate non-polar molecules only!

The ω,x method of MS (eq. 15) is potentially the most powerful correlation, since it relates directly the potential parameters to the size and the degree of polarity of the molecule. However, because of the way in which ω and x are defined, these size and polarity factors are not separated, resulting in the need for a cross-term ωx and higher order terms such as ω^2. Ideally, such a method with well-separated parameters would correlate polar and non-polar molecules without discontinuity. However, because of the noted non-separation, one has to arbitrarily set ω^2 and x equal to zero for non-polar molecules (to reduce [15] to [12]), but also for slightly polar

TABLE 5. Values of ω and x for the molecules of Tables 1 and 2

θ		ω^a	θ		ω	x	ω^f	x^f
1	Ne	0	38	N_2O	0.160^g	-0.003^g	0.160^l	-0.003^l
2	Ar	-0.002	39	CO			0.049^m	0.002^m
3	Kr	-0.002	40	COS			0.099^n	-0.002^n
4	Xe	0.002	41	NO	0.577^g	-0.045^g	0.581^o	-0.025^o
5	N_2	0.040	42	HI			0.047^p	0.003^p
6	O_2	0.021	43	HBr	0.083^g	0.011^g	0.076^p	-0.004^p
7	CO_2	0.225^b	44	HCl	0.126^h	0.008^h	0.130^q	0.011^q
8	CS_2	0.127^c	45	HF			0.377^r	0.127^r
9	SF_6	0.257	46	H_2S			0.096^s	0.002^s
10	$(CN)_2$	0.270^d	47	SO_2	0.262^i	0.005^i	0.254^t	0.003^t
11	F_2	0.043^e	48	HCN	0.409^g	0.080^g	0.372^u	0.055^u
12	Cl_2	0.074	49	NH_3	0.252^j	0.013^j	0.256^v	0.013^v
13	Br_2	0.132	50	H_2O	0.344^g	0.023^g	0.344^w	0.023^w
14	I_2	0.229	51	$CHCl_3$			0.215^x	-0.001^x
15	CH_4	0.011	52	CH_2Cl_2			0.197^y	-0.003^y
16	CF_4	0.191	53	CH_3Br			0.232^z	
17	CCl_4	0.191^c	54	CH_3Cl	0.152^g	0.007^g	0.152^{aa}	0.001^{aa}
18	C_2H_6	0.097	55	C_2H_5Cl	0.191^g	0.005^g	0.192^{bb}	0.007^{bb}
19	C_3H_8	0.154	56	$n\text{-}C_3H_7OH$	0.626^j	-0.057^j	0.621^{cc}	-0.050^{cc}
20	$n\text{-}C_4H_{10}$	0.201	57	$i\text{-}C_3H_7OH$	0.663^j	-0.053^j	0.665^{cc}	-0.055^{cc}
21	$i\text{-}C_4H_{10}$	0.185	58	C_2H_5OH	0.641^h	0.003^h	0.635^{cc}	0.001^{cc}
22	$n\text{-}C_5H_{12}$	0.252	59	CH_3OH	0.556^j	0.037^j	0.565^{cc}	0.038^{cc}
23	$neo\text{-}C_5H_{12}$	0.196	60	$(C_2H_5)_2O$	0.275^j	-0.003^j	0.280^{dd}	-0.000^{dd}
24	$n\text{-}C_6H_{14}$	0.301	61	$(CH_3)_2O$	0.206^j	0.002^j	0.202^{ee}	0.007^{ee}
25	$n\text{-}C_7H_{16}$	0.350	62	$CH_3CO_2C_2H_5$			0.360^{ff}	-0.006^{ff}
26	$n\text{-}C_8H_{18}$	0.398	63	$CH_3CO_2CH_3$	0.326^k	0.005^k	0.323^{ff}	0.001^{ff}
27	$n\text{-}C_9H_{20}$	0.449	64	$(CH_3)_2CO$	0.304^g	0.013^g	0.307^{gg}	0.013^{gg}
28	$cyclo\text{-}C_6H_{12}$	0.210	65	CH_3CHO	0.281^k	0.019^k		
29	C_2H_4	0.086						
30	C_3H_6	0.145						
31	butene-1	0.194						
32	i-butene	0.203						
33	C_2H_2	0.189						
34	C_3H_4	0.223						
35	C_6H_6	0.210						
36	$C_6H_5CH_3$	0.264						
37	mesitylene	0.399						

[a] The molecular parameters ω for the hydrocarbons were calculated from the API–44 vapour pressure data (28). The ω parameters for the inorganic gases, taken from Reid and Sherwood's tabulation (4b) are experimentally determined or calculated. Their value for CO_2 ($\omega = 0.420$) is clearly in error. [b] K.S. Pitzer, et al. J. Am. Chem. Soc. 77, 3433 (1955). [c] Calculated from vapour pressures given by Boublik and Aim (29). [d] Calculated from vapour pressures given by Edwards (26). [e] J.-H. Hu, D. White, and H.L. Johnston. J. Am. Chem. Soc. 75, 5642 (1953). [f] Calculated (this paper) from vapour pressure data as referenced below. [g] R.L. Halm and L.I. Stiel. AIChE J. 13, 351 (1967). [h] G.K. Stipp, S.D. Bai, and L.I. Stiel. AIChE J. 19, 1227 (1973). [i] T.-F. Yuan and L.I. Stiel. Ind. Eng. Chem. Fundam. 9, 393 (1970). [j] R.L. Halm and L.I. Stiel. AIChE. J. 16, 3 (1970). [k] See ref. 20. [l] E.J. Couch, K.A. Kobe, and L.J. Hirth. J. Chem. Eng. Data 6, 229 (1961); H.J. Hoge. J. Res. Natl. Bur. Standards 34, 281 (1945). [m] A. Michels. T. Wassenaar, and Th. N. Zwietering. Physica 18, 160 (1952); J.O. Clayton and W.F. Giauque. J. Am. Chem. Soc. 54, 2610 (1932). [n] J.D. Kemp and W.F. Giauque. J. Am. Chem. Soc. 59, 79 (1937). [o] H.L. Johnston and W.F. Giauque. J. Am. Chem. Soc. 51, 3194 (1929). [p] See ref. 26. [q] W.F. Giauque and R. Wiebe. J. Am. Chem. Soc. 50, 101 (1928); W. Thomas. Progr. Intern. Res. Thermod. Transp. Prop. ASME Second Symposium, 1962, 166–171; E. Cardoso and A.F.O. Germann. J. chim. phys. 11, 632 (1913); O. Maass and D. McIntosh. Trans. Roy. Soc. Canada III, VIII, 65 (1914). [r] R.L. Jarry and W. Davis Jr. J. Phys. Chem. 57, 600 (1953). [s] W.B. Kay and G.M. Rambosek, Ind. Eng. Chem. 45, 221 (1953); W.F. Giauque and R.W. Blue. J. Am. Chem. Soc. 58, 831 (1936). [t] W.F. Giauque and C.C. Stephenson. J. Am. Chem. Soc. 60, 1389 (1938); K. Clusius, K. Schleich, and R.B. Bernstein. Helv. Chim Acta 45, 258 (1962); T. Toriumi and R. Hara. J. Soc. Chem. Ind. Japan 47, 502 (1944); E. Cardoso and U. Fiorentino. J. chim. phys. 23, 841 (1926). [u] H. Sinosaki, R. Hara, and S. Mitsukuri. Tech. Repts. Tohoku Imp. Univ. 4, 145 (1924). [v] International Critical Tables, Vol. III (1928). McGraw-Hill Book Company Inc., New York. [w] ASME Steam Tables 1967. The Am. Soc. of Mech. Eng. United Engineering Centre, New York. [x] M.A. Zmaczynski. J. chim. phys. 27, 503 (1930). [y] See ref. 29; L.S. Dzung. The Brown Boveri Review 33, 158 (1946). [z] C.J. Egan and J.D. Kemp. J. Am. Chem. Soc. 59, 1265 (1937); ibid. 60, 2097 (1938). [aa] G. Holst. Commun. Leiden, 144 b.c.d. (1913–1914). [bb] J. Gordon and W.F. Giauque. J. Am. Chem. Soc. 70, 1506 (1948); A. Berthoud. J. chim. phys. 15, 3 (1917). [cc] D. Ambrose, J.H. Ellender, and C.H.S. Sprake. J. Chem. Thermodynamics 6, 909 (1974). [dd] D. Ambrose, C.H.S. Sprake, and R. Townsend. J. Chem. Thermodynamics 4, 247 (1972). [ee] E. Cardoso and A. Bruno. J. chim. phys. 20, 347 (1923); R.M. Kennedy, M.Sagenkahn and J.G. Aston. J. Am. Chem. Soc. 63, 2267 (1941). [ff] J. Polak and I. Mertl. Coll. Czech. Chem. Comm. 30, 3526 (1965). [gg] D. Ambrose, C.H.S. Sprake, and R. Townsend. J. Chem. Thermodynamics 6, 693 (1974).
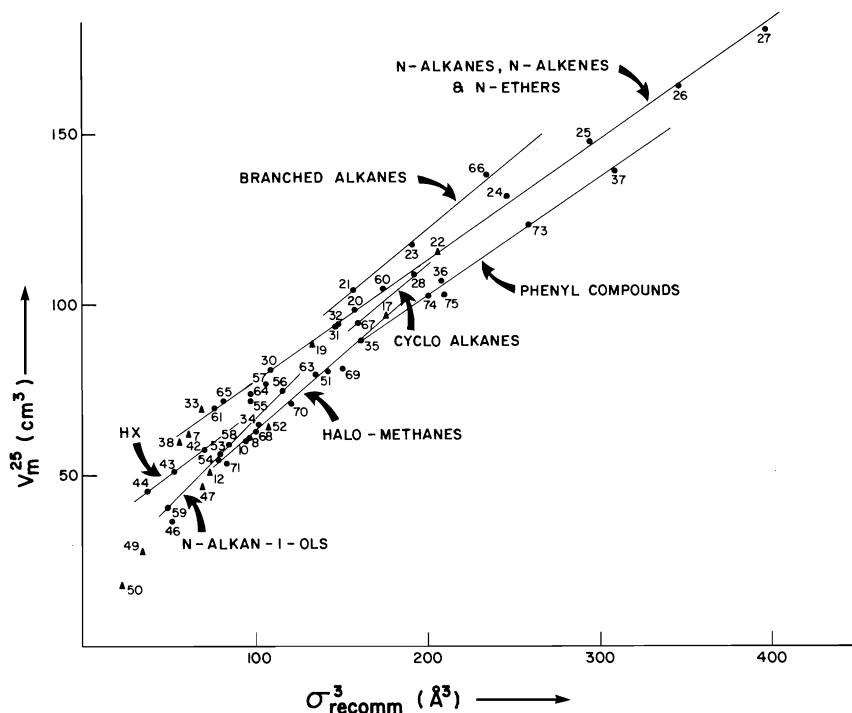
FIG. 1. Empirical correlation between the molar volume V_m^{25} and $\sigma^3(\text{rec})$ values of Tables 1, 2, and 6. $\sigma(\text{rec})$ values, based on determinate $\sigma(\text{visc})$ values are indicated by ▲; filled circles ● indicate $\sigma(\text{rec})$ values based on correlation techniques. Solid lines tie points within classes of compounds.

molecules (the limit appears to be at $\mu^{*2} = 0.3$). Another disadvantage of the MS method is that it requires extremely accurate vapour pressure data (vide infra). Finally it appears that for molecules with $|x| > 0.035$ grossly erroneous results may occur. Examples are HF, HCN, CH_3NO_2, and CH_3CN. In conclusion we prefer the MS method of [15] for polar molecules with $\mu^{*2} > 0.3$ whenever very accurate vapour pressure data are available. If with [15] physically unacceptable results are obtained according to supplementary tests (vide infra) (for example due to inaccurate vapour pressure data), it is recommended to use the ST method of [8]. For slightly polar molecules ($\mu^{*2} \leq 0.3$) it is recommended to use the TGS method of [12], to be consistent with the preference expressed with respect to non-polar molecules. Based upon the above recommendations, preferred σ and ε/k values (or their average) are given in the last columns of Table 2. Table B gives all the corresponding ε/k values for polar molecules.[2]

In Table 3 (non-polar molecules) $P(\text{av})$ is the average of all $P(\text{visc})$ values (except those of F),

while $P(\text{rec})$ is the product based on $\sigma(\text{rec})$ and $\varepsilon/k(\text{rec})$. For the indeterminate cases (where η is only a function of $P(n)$), $P(\text{av})$ will give the best fit on all viscosity data combined. The deviation of $P(\text{rec})$ from $P(\text{av})$ is therefore a direct measure of the error if viscosities were recalculated on the basis of $P(\text{rec})$. These percentage deviations have been given in the last column of Table 3. In the determinate cases $P(\text{rec})$ is always taken from one or more $P(\text{visc})$ data and therefore will, of course, already constitute the best fit over the combined viscosity data.

For polar molecules (Table 4) with $\delta_{max} \leq 0.25$, $P(\text{av})$ is the average over the Lennard–Jones and Stockmayer $P(\text{visc})$ values; Stockmayer $P(\text{visc})$ values were used to calculate $P(\text{av})$ when $\delta_{max} > 0.25$. For reasons of consistent comparison all $P(\text{calcd})$, $P(\text{av})$, and $P(\text{rec})$ values have been calculated with $n = 0.50$. It should be noted that for indeterminate cases the determinate product $P(n)$ may have a value of n, different from 0.50; in these cases also $P(\text{visc})$ values for $n = 0.50$ were calculated to make comparison possible. As before, the % dev. column indicates the error

level in viscosities, recalculated on the basis of the recommended parameters.

Supplementary Test Methods for σ

In addition to already existing non-viscosity-based correlation techniques (1, 11) we have found three additional estimation methods. Figure 1 shows that there is a reasonable correlation between σ^3(rec) and V_m^{25}, the molar volume at 25°C. In fact, for chemically closely related molecules (such as the n-alkanes, the methyl benzenes and the n-alkan-1-ols) very good straight-line relationships exist. In principle a correlation between σ^3 and V_m^b (molar volume at boiling point) would be better; however, V_m^b is not available in many cases, whereas V_m^{25} is much more often available from literature sources. For low-boiling compounds the reverse is often true. An application of the above correlations is ethyl acetate which with the MS method appeared to give too high a value for σ. Using Fig. 1, an estimated σ(rec) = 5.65 was arrived at. Points which would fall clearly outside the indicated correlation band of Fig. 1 must be considered erroneous. In fact this criterion was used in the foregoing discussions; it did confirm that certain σ(visc) values (such as for mesitylene, n-hexane, neopentane, cyclohexane, CCl_4, and propanal) were not only indeterminate, but indeed erroneous.

A second test is based on the σ and ε/k parameters obtained by Wilhelm and Battino (abbrev. WB) (21) from the solubility of certain gases (He, Ne) in liquids. As Fig. 2 shows, there is an excellent straight-line relation between the WB σ values and our σ(rec) values. This relation formed an additional argument to accept the TGS method, particularly because of the excellent correlation for the higher n-alkanes. The only deviating point is that for acetone; since σ(rec) is based on highly accurate P_c, T_c, and vapour pressure data and since in Fig. 1 acetone falls well inside the correlation band, it is suspected that this deviation is caused by an error in the solubility measurements. The WB method in principle provides also ε/k values, but these seem to be rather inaccurate.

A third test is provided by the σ values, obtained by Goldman (22) by fitting a thermodynamic perturbation theory to experimental vapour pressure data. Figure 3 shows an excellent correlation between Goldman's σ and our σ(rec) values.
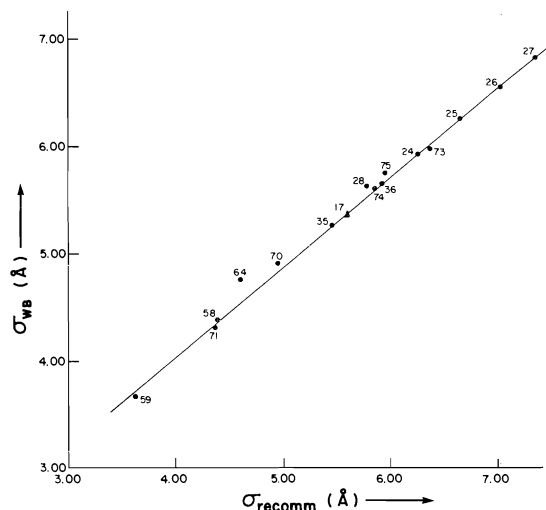

FIG. 2. Empirical correlation between the σ values based on noble gas solubility as given by Wilhelm and Battino (21) and the σ(rec) values of Tables 1, 2, and 6. σ(rec) values, based on determinate σ(visc) values are indicated by ▲; filled circles ● indicate σ(rec) values based on correlation techniques.

Whenever these test methods are used to *estimate* σ values, the problem of finding the corresponding ε/k value still remains. However, in these cases an accurate product $P(n)$ may be available, from which, in combination with the estimated σ value, the ε/k value can be abstracted (example: ethyl acetate).

Auxiliary Parameters

In all correlation techniques discussed above, critical constants are needed. Compilations of experimental critical constants are available (23–26). For molecules where such experimental data are not available, these can be calculated with good precision according to a method described by Curl and Pitzer (27). This method requires knowledge of the boiling temperature, the temperature at which the vapour pressure is 100 Torr and the density at some temperature below the boiling point, all of which data are usually easily accessible.

The TGS and MS methods require in addition knowledge of vapour pressures for the calculation of ω (and x). The potential parameters calculated according to TGS are not very sensitive to small (± 5%) changes in ω. Therefore almost any source of vapour pressures (26, 28–32) at $T_r = 0.7$ is normally accurate enough as are values of ω estimated with the Edmister formula [13]. The situation is more complicated,
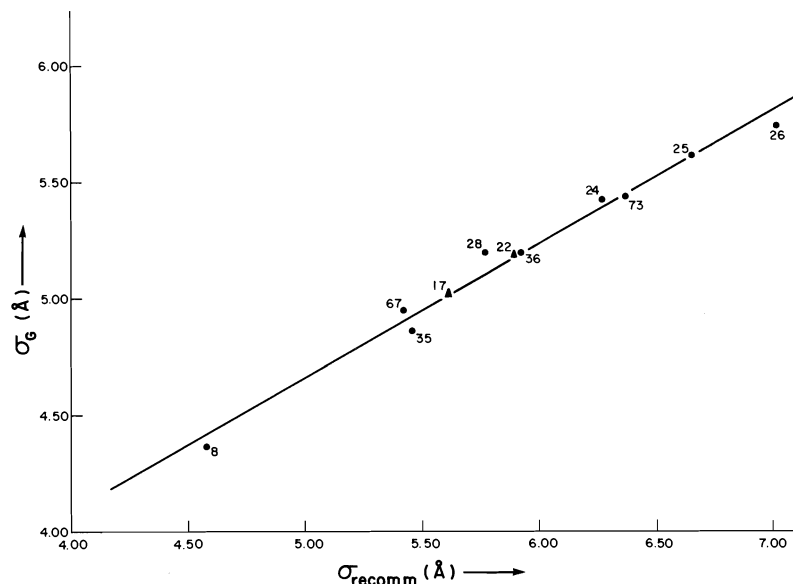
FIG. 3. Empirical correlation between the σ values of Goldman (22) and the σ(rec) values of Tables 1, 2, and 6. σ(rec) values based on determinate σ(visc) values are indicated by ▲; filled circles ● indicate σ(rec) values based on correlation techniques.

however, when the ω and x parameters of the MS method are to be determined. In their original paper, MS calculated Stockmayer parameters for 13 molecules for which, in their words, "reliable values of ω and x were available", without disclosing either their methods or their sources. In Table 5 we have listed the most recent values of ω and x used in other work of Stiel and co-workers. The fact that some of these values were revised several times reflects already the problems encountered when determining such parameters. With the above ω and x parameters we calculated σ and ε/k according to [15], but many of these were clearly unacceptable on the basis of the V_m^{25} or V_m^{b} test (example ethanal) or on the basis of a lacking consistency in homologous series (for example the σ(MS) for HBr and HCl). Partly because of the above we felt compelled to re-evaluate the ω,x method and to develop suitable criteria. Extensive trials have shown us that, in order to obtain reasonable σ and ε/k parameters through the MS method, one needs vapour pressures accurate to ±0.01 Torr (corresponding to a temperature accuracy of ±0.001°C), over an extended pressure range (normally between 0.1 and 2 atm) covering at least the $T_r = 0.6$ point but preferably also the $T_r = 0.7$ point. The requirement of highly accurate vapour pressure data is a direct result

of the extreme sensitivity of σ and ε/k towards ω and x. In order to find the needed vapour pressures at reduced temperatures $T_r = 0.6$ and $T_r = 0.7$, it is necessary to fit experimental data into a vapour pressure equation. One of these is the Antoine equation [16]:

[16] $$\log_{10} P = A - \frac{B}{t + C}$$

Several compilations of Antoine parameters are available (28, 29, 31). The closeness of the data fit over the experimental range should be ±0.03% or less and the calculated critical pressure should be about 8% too low (33). If raw vapour pressure data were available, or if the Antoine equation was not adequate, we have successfully employed the following expression:

[17] $$\log_{10} P = A - \frac{B}{T} + C \log T + DT$$

In our experience, [17] is at least equivalent in quality to the Antoine equation and in certain cases (such as alcohols) definitely superior; in addition, [17] is more easily adaptable to computerized least-squares fitting. Most of our own ω,x values (last two columns of Table 5) were obtained through the vapour pressure equation [17].

TABLE 6. Potential parameters σ and ε/k calculated by correlation techniques for some selected molecules

No.	Compound	μ^{*2}	$V_c{}^a$ (cm³)	$T_c{}^a$ (K)	$P_c{}^a$ (atm)	ω^c	x^c	σ (Å)	ε/k (K)
66	$Si(CH_3)_4$	0	372^b	448.1^b	26.9^b	0.233^d		6.167^m	315.1^m
67	c-C_5H_{10}	0	260	511.6	44.5	0.196^e		5.423^m	368.1^m
68	CH_3I	0.48	173^b	537.7^b	71.7^b	0.123^f	0.005^f	4.656^m	405.5^m
69	CH_2I_2	0.11	249^b	756.1^b	69.0^b	0.185^g	0.011^g	5.327^m	550.5^m
70	$(CH_3)_2SO$	1.56	227^b	754.1^b	73.6^b	0.263^h	0.003^h	4.940^o	602.5^o
71	CH_3NO_2	1.97	173	588	62.3	0.346^i	0.038^i	4.374^n	527.4^n
72	CH_3CN	2.70	173	548	47.7	0.320^j	0.033^j	4.374^n	491.6^n
73	p-Xylene	0	379	616.2	34.7	0.321^e		6.371^m	408.8^m
74	C_6H_5Cl	0.25	308	632.4	44.6	0.249^k	0.004^k	5.856^m	440.2^m
75	$C_6H_5NO_2$	1.15	335^b	758.3^b	50.0^b	0.270^l	0.006^l	5.95^p	534^p

^{a}Taken from ref. 24, unless indicated otherwise. ^{b}Calculated by method of Curl and Pitzer (27). ^{c}Vapour pressures were fitted with [17] except where indicated otherwise. $^d P(t)$ data from J. G. Aston et al. J. Am. Chem. Soc. 63, 2343 (1941). ^{e}From Antoine constants of ref. 28. $^f P(t)$ data from ref. 29. ^{g}From Antoine constants of ref. 31. ^{h}From Antoine constants given by J. Heinrich and J. Surovy. Sb. Pr. Chem Fak. SVST. 207 (1966). $^i P(t)$ data of McCullough; see ref. 30. $^j P(t)$ data of Heim; see ref. 30. $^k P(t)$ data of Zmackzymski; see ref. 30. $^l P(t)$ data of Brown and of Maksimov; see ref. 30. ^{m}Calculated according to TGS method, eq. 12. ^{n}Calculated according to ST method, eq. 8; MS method rejected on the basis of $V_m{}^{25}$ and WB tests. ^{o}Calculated according to MS method, eq. 15. ^{p}MS and ST methods rejected on the basis of $V_m{}^{25}$ and WB tests; σ estimated from Figs. 1 and 2, ε/k calculated from product $\sigma^2\varepsilon^{1/2}$.

Some Further Applications

As mentioned above, for many molecules of interest no viscosity-based potential parameters are available at all. In such cases one has to rely exclusively on the correlation techniques as recommended in this paper. For some molecules, which were of particular interest to our nmr intermolecular interaction studies, we have thus calculated σ and ε/k values as given in Table 6.

Acknowledgement

1. (a) J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD. Molecular theory of gases and liquids. 2nd ed. John Wiley and Sons Inc., New York, NY. 1964; (b) Chapt. 3; (c) Chapt. 8.4; (d) Chapt. 4.7; (e) pp. 222–223; (f) pp. 1110–1112 and pp. 1212–1214.
2. F. H. A. RUMMENS and F. M. MOURITS. Can. J. Chem. This issue.
3. J. R. JOHNSON and P. T. EUBANK. Ind. Eng. Chem. Fundam. 12, 156 (1973).
4. (a) R. C. REID and T. K. SHERWOOD. The properties of gases and liquids. 2nd ed. McGraw-Hill Book Company, New York, NY. 1966. pp. 38–42; (b) Appendix A.
5. S. K. KIM and J. ROSS. J. Chem. Phys. 46, 818 (1967).
6. D. REICHENBERG. AIChE J. 19, 854 (1973).
7. E. A. HALKIADAKIS and R. G. BOWREY. Chem. Eng. Sci. 30, 53 (1975).
8. F. H. A. RUMMENS, W. T. RAYNES, and H. J. BERNSTEIN. J. Phys. Chem. 72, 2111 (1968).
9. E. U. FRANCK. Landolt-Börnstein. Physikalisch-Chemische Tabellen. Vol. 1, Part 1. 6th ed. Springer Verlag, Heidelberg. 1950.
10. L. W. FLYNN and G. THODOS. AIChE J. 8, 362 (1962).
11. R. A. SVEHLA. NASA Technical Report R-132. 1962.
12. L. S. TEE, S. GOTOH, and W. E. STEWART. Ind. Eng. Chem. Fundamentals, 5, 356 (1966).
13. K. N. LINAKIS and R. G. BOWREY. Aust. Chem. Eng. 14, 3 (1973).
14. L. MONSCHICK and E. A. MASON. J. Chem. Phys. 35, 1676 (1961).
15. G. C. MAITLAND and E. B. SMITH. J. Chem. Eng. Data, 17, 150 (1972).
16. M. KLEIN and H. J. M. HANLEY. Trans. Faraday Soc. 64, 2927 (1968).
17. L. I. STIEL and G. THODOS. J. Chem. Eng. Data, 7, 234 (1962).
18. L. I. STIEL and G. THODOS. AIChE J. 10, 266 (1964).
19. W. C. EDMISTER. Pet. Refiner, 37, 173 (1958).
20. K. R. MALEK and L. I. STIEL. Can. J. Chem. Eng. 50, 491 (1972).
21. E. WILHELM and R. BATTINO. J. Chem. Phys. 55, 4012 (1971).
22. S. GOLDMAN. J. Phys. Chem. 80, 1697 (1976).
23. J. F. MATHEWS. Chem. Rev. 72, 71 (1972).
24. A. P. KUDCHADKER, G. H. ALANI, and B. J. ZWOLINSKI. Chem. Rev. 68, 659 (1967).
25. K. A. KOBE and R. E. LYNN. Chem. Rev. 52, 117 (1953).
26. D. G. EDWARDS. Vapour pressures of 30 inorganic liquids between one atmosphere and the critical point. University of California Radiation Laboratory (Livermore, California). Technical Report UCRL-7167 (Rev. 1). 1964.
27. R. F. CURL and K. S. PITZER. Ind. Eng. Chem. 50, 265 (1958).
28. Selected values of properties of hydrocarbons and related compounds. American Petroleum Institute Research Project 44. Thermodynamics Research Centre, Department of Chemistry, Texas A & M University, College Station, TX.
29. T. BOUBLIK and K. AIM. Coll. Czech. Chem. Commun. 37, 3513 (1972).
30. J. TIMMERMANS. Physico-chemical constants of pure organic compounds. Vol. 1 (1950) and Vol. 2 (1965). Elsevier Publ. Cie. New York, NY.
31. Advances in chemistry; physical properties of chemical compounds. Vol. 15 (1955), Vol. 22 (1959), and Vol. 29 (1962). The American Chemical Society, Washington, DC.
32. D. R. STULL. Ind. Eng. Chem. 39, 517 (1947).
33. G. W. THOMSON. Chem. Eng. Progr. 45, 153 (1949).