NOTA

INTERMOLECULAR PARAMETERS FOR SIMPLE MOLECULES

Despite its shortcomings the LENNARD-JONES (6,12) intermolecular potential

$$\Phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

is still one of the most widely used in theoretical calculations for both the gaseous and condensed states. This derives partly from its simplicity and from the fact that a great amount of data have been collected or calculated on its basis. However, it has now been established that the real pair-potential is shallower than this at large separations and deeper and steeper near the minimum (1), but luckily in the liquid state, where multi-body interactions are far from negligible, the LENNARD-JONES potential acts as an «effective» potential, giving a satisfactory account of the overall effect.

The molecular parameters ε and σ are usually determined from physical properties like the critical constants, the second virial coefficient, viscosity and crystal properties at OK which, on one hand, can be accurately measured, and whose values, on the other, can be easily calculated from a workable theory. A detailed account of the several methods of determining ε and σ has been given by HIRSCHFELDER, CURTISS and BIRD (2), but it can be readily seen from the quoted tables that these parameters depend, to a sensible extent, on the physical property which was used for their determination. To make things worse it has also been found that if a single property, like the second virial coefficient, is used to evaluated ε and σ, then the resulting values differ according to the temperature range chosen, this giving rise to what appears to be two different sets of molecular parameters: a high-temperature set and a low--temperature one (3). For these reason BELLEMANS, MATHOT and SIMON chose three of the above mentioned properties, namely critical data, viscosity and second virial coefficients, and analysed the resulting values of ε and σ for a series of simple molecules (Argon, Krypton, Nitrogen, Oxygen, Carbon Monoxide and Methane), taking an average of the values calculated from the three different methods as a possible way of minimizing errors (values of ε obtained from viscosity data were discarded in this treatment for lack of the desired accuracy) (4).

For small, light molecules, however, quantum effects must be accounted for, and, to this purpose, de Boer introduced a new parameter Λ which is a measure of the molecule's deviation from classical behaviour (5)

$$\Lambda = \frac{h}{\sigma (m\varepsilon)^{1/2}} \tag{2}$$

where *h* is Planck's constant and *m* the mass of the molecule. Provided that any lack of conformity to the law of corresponding states is due only to quantum effects, which is a reasonable assumption in the case of the rare gases, then reduced thermodynamic quantities should show a smooth variation in Λ or in Λ^2. Failure of these plots, the so-called de Boer plots, to show such a regular dependence while making use of the best available parameters ε and σ, led Boato and Casanova to conclude that the parameters themselves were in error, and so to devise a new method of deriving a self-consistent set of parameters for the *rare gases*, based on accurate vapour pressure data for different isotopic species (6).

It is assumed that the logarithm of the vapour pressure of the liquid is a linear function of 1/T, or, in terms of the reduced quantities

$$\ln \tilde{p} = \alpha \frac{1}{\tilde{T}} + \beta \tag{3}$$

with

$$\tilde{p} = \frac{p}{\varepsilon} \sigma^3 \qquad \tilde{T} = \frac{kT}{\varepsilon} \tag{4}$$

The coefficients α and β are polynomials in Λ^2

$$\alpha = a_1 + b_1 \Lambda^2 + c_1 \Lambda^4 + \ldots \tag{5}$$

$$\beta = a_2 + b_2 \Lambda^2 + c_2 \Lambda^4 + \ldots \tag{6}$$

where a_1, b_1, c_1, a_2, b_2, c_2 are universal constants.

It can then be easily shown that the molecular parameters are given by

$$\frac{\varepsilon}{k} = \frac{A}{a_1 + b_1 \Lambda^2 + c_1 \Lambda^4} \tag{7}$$

$$\ln \frac{\varepsilon}{\sigma^3} = B - a_2 - b_2 \Lambda^2 - c_2 \Lambda^4 \tag{8}$$

where the constants A and B refer to the temperature dependence of the vapour pressure

$$\ln p = A \frac{1}{T} + B \tag{9}$$

and can be obtained from experimental data.

Deviations from the linear dependence expressed by equation (3) do not affect the final values of ε and σ in a significant way, provided that the same general law is valid for all the molecules concerned (principle of corresponding states).

The same treatment can be applied to simple, polyatomic molecules, once their states of vibration and rotation are not affected by the position of their neighbours and the interaction potential is independent of the relative orientation of the molecules (5). This is approximately the case with small diatomic molecules like nitrogen, oxygen and carbon monoxide, and simple spherical molecules like methane and carbon tetrafluoride, although they all have an extra entropy due to rotational degrees of freedom which are, of course, absent in monoatomic molecules. The quantification of rotational energy might eventually alter the coefficients a, b, c (in equations (5) and (6)) which were obtained from a generalization of the law of corresponding states, but it seemed worthwhile to calculate the new intermolecular parameters on the same assumptions. Terry *et. al.* have shown, from accurate measurements of liquid densities, that the rare gases (argon, krypton and xenon), nitrogen and oxygen conform fairly well to the classic law of corresponding states, but methane and carbon dioxide show deviations which seem to be larger than experimental errors can account for (7).

In Table I intermolecular parameters for nitrogen, oxygen, carbon monoxide and methane, calculated

Table I

Intermolecular parameters for simple molecules according to BELLEMANS *and to a treatment based on vapour pressure data.*

	BELLEMANS *et al.*			This work			
Molecule	ε/k	σ/A	Λ	ε/k	σ/A	Λ	References
Nitrogen	99.2	3.664	0.226	103.2	3.484	0.233	8 (97 - 125 K)
Oxygen	121.8	3.450	0.203	132.2	2.882	0.233	9 (55 - 100 K)
Carbon Monoxide	104.4	3.671	0.220	110.2	3.435	0.229	10 (93 - 132 K)
Methane	152.1	3.783	0.234	152.4	3.737	0.237	11 (113 - 150 K)

using BOATO and CASANOVA method, are compared with those of BELLEMANS *et. al.*; the source of data is given in the last column, together with the temperature range chosen. Values of ε are significantly larger than those obtained from BELLEMANS' criteria, while the reverse is true for the σ parameters, showing that for these molecules the present treatment originates an intermolecular potential which is deeper and steeper near the equilibrium distance thant it could be predicted from data for the gaseous state.

However, a plot of the reduced critical temperature

$$T_c^* = \frac{kT_c}{\varepsilon} \tag{10}$$

against Λ shows considerable deviations, for oxygen and carbon monoxide, from the smooth curve which can be drawn with the rare gases and other light molecules like hydrogen and deuterium; methane conforms very well to the general trend, and nitrogen shows a small deviation, probably within experimental error. Oxygen shows, therefore, the largest deviation (a change of 16 % in the value of σ from that of BELLEMANS) which could be attributed to dimerization in the liquid, but it should be said that TERRY *et. al.* did not find anything

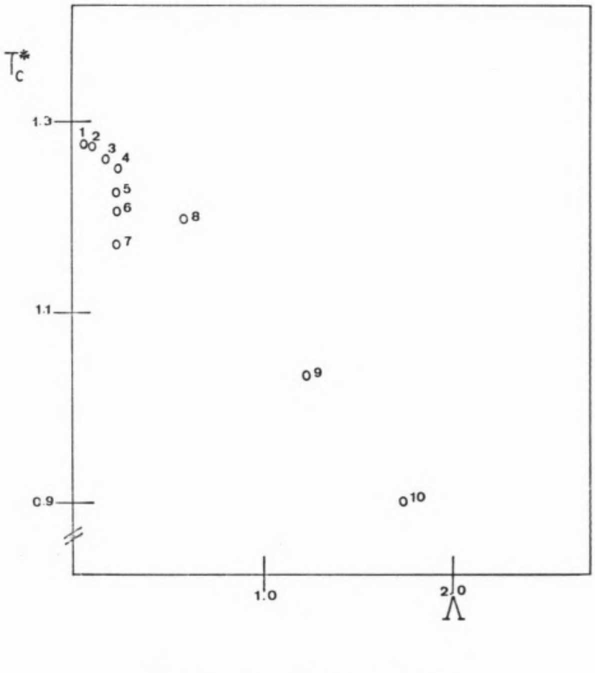

Fig. 1 — Plot of T_c^* against Λ

1—*Xenon;* 2—*Krypton;* 3—*Argon;* 4—*Methane;* 5—*Nitrogen;* 6—*Carbon Monoxide;* 7—*Oxygen;* 8—*Neon;* 9—*Deuterium;* 10—*Hydrogen.*

obviously abnormal in the volume of liquid oxygen which might be an indication of such dimerization taking place (7). On the other hand, the implication that there might be something wrong with the vapour pressure data seems to be out of place since the values of MUIJLWIJK *et. al.* used in this work agree, within ± 0.03 K, with those recommended in a critical review by MULLINS *et. al.* (12) and quoted by ROWLINSON (13). As for carbon monoxide, it is thought that the observed deviation may be due to a greater restraint on the rotation of its molecules, because of their dipole moment and large quadrupole moment (14).

A plot similar to fig. 1 to show the self-consistency of the σ values would necessarily involve the critical volumes but since these are affected by appreciable experimental error, it has been excluded.

REFERENCES

1. Rowlinson, J. S., «Liquids and Liquid Mixtures», 2nd. ed., Butterworths, London, 1969, Chap. 7.
2. Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., «Molecular Theory of Gases and Liquids», John Wiley & Sons, Ltd., New York, 1967.
3. Byrne, M. A., «Ph. D. Thesis», Univ. Oxford, 1966.
4. Bellemans, A., Mathot, V. and Simon M., *Advan. Chem. Phys.*, **11**, *117 (1967)*.
5. de Boer, J., *Physica*. **14**, *139 (1948)*.
6. Boato, G. and Casanova, G., *Physica*, **27**, *571 (1961)*.
7. Terry, M. J., Lynch, J. T., Bunclark, M., Mansell, K. R. and Staveley, L. A. K., *J. Chem. Thermodyn.*, **1**, *413 (1969)*.
8. Michels, A., Wassenaar, T., de Graaf, W. and Prins, C., *Physica*, **19**, *26 (1953)*.
9. Muijlwijk, R., Moussa, M. and van Dijk, H., *Physica*, **32**, *805 (1966)*.
10. Michels, A., Wassenaar, T. and Zwietering, T., *Physica*, **18**, *161 (1952)*.
11. van Itterbeek, Staes, K., Verbeke, O. and Theeuwes, F., *Physica*, **30**, *1896 (1964)*.
12. Mullins, J. C., Ziegler, W. T. and Kirk, B. S., *Advan. Cryog. Eng.*, **8**, *126 (1968)*.
13. Rowlinson, J. S., *Advan. Cryog. Eng.*, **8**, *49 (1968)*.
14. Staveley, L. A. K., *J. Phys. Chem. Solids*, **18**, *46 (1961)*.

M. NUNES DA PONTE

J. C. G. CALADO

Centro de Estudos de Química Nuclear
Instituto Superior Técnico
Lisboa 1 — Portugal