INTERMOLECULAR FORCES AND SOME PROPERTIES OF MATTER

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At present it is impossible to calculate the physical properties of matter from first principles. Quantal calculations of the forces acting between molecules are not sufficiently accurate; and, moreover, only in a few simple cases can the methods of statistical mechanics give the exact dependence of the physical properties on such forces. A purely empirical approach is no more successful, for the relation between two different properties is generally too subtle for empirical correlations alone to be useful. The study of intermolecular forces, and the molecular theory of the properties of matter, have therefore proceeded along the following lines. First classical and quantal calculations have been used as a guide to the probable dependance of the forces on the separation of the molecules, and, if relevant, on the angles which define their mutual orientations: an expression for the potential-energy curve may then be deduced which is approximately of the correct shape but contains several unknown parameters. Secondly, the physical properties of a substance formed from these idealised molecules are calculated by the methods of equilibrium statistical mechanics, and that part of non-equilibrium statistical mechanics which is usually called "kinetic theory". Thirdly, these calculated properties are compared with those observed to find out if the assumed model is adequate and, if so, what are the best values of the unknown parameters. Very often it is found that one property may be accounted for by a variety of intermolecular potentials and so it is necessary to make the comparisons between theory and experiment as wide as possible. Different properties test different aspects of a potential; and a potential which will satisfy many properties is probably close to reality. The object, then, of the work reviewed here has been first to find the intermolecular potential energies and then to use them to correlate as many physical properties as possible. Only measurements on simple systems, where quantitative comparison of theory and experiment can usually be made, are discussed. Topics omitted include the properties of metals, all systems in which there are highly specific forces, and those properties which depend primarily on the rate of exchange of internal energy.

London[1] and Margenau[2] have reviewed theoretical calculations of the attractive forces between molecules. Standard works[3, 4] on the use of statistical mechanics for the calculation of the equilibrium properties of

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[1] London, *Trans. Faraday Soc.*, 1937, **33,** 8.

[2] Margenau, *Rev. Mod. Physics*, 1939, **11,** 1.

[3] Fowler and Guggenheim, "Statistical Thermodynamics", Cambridge Univ. Press, 1939.

[4] Mayer and Mayer, "Statistical Mechanics", Wiley, 1940.

matter have recently been supplemented by a review by de Boer.[5] A forthcoming book [6] by Hirschfelder, Curtiss, and Bird will treat exhaustively many of the topics discussed below. Of the omitted topics, Brieglieb [7] describes specific forces of all kinds, and Davies,[8] Kellner,[9] and Donohue [10] have reviewed different aspects of the hydrogen bond.

The Intermolecular Forces

It is a simple deduction from the properties of matter that two molecules attract each other at large distances and repel each other at short distances. It is therefore convenient to represent their potential energy as the sum of two sets of terms, one negative and one positive. The positive terms, due to the overlap and hence the repulsion of the electron clouds, are shown by quantal calculations to be of the form $F(r)e^{-Ar}$ at the comparatively large distances at which intermolecular forces are important. Here $F(r)$ is a polynomial in r, the separation of the molecules, and A is a constant. This energy increases rapidly with decreasing r and is numerically the same, though of opposite sign, as the energy which would lead to chemical combination, if the Pauli principle permitted this. The negative terms in the energy may be of several kinds. If the molecules are not symmetrical then there is the classical electrostatic energy between their two charge distributions. This may be expressed exactly as an infinite series in inverse powers of r. The series converges as long as the charge distributions do not overlap—a condition which is always satisfied. If there are no ions present then the first term in this series, and generally much the largest, is the term in r^{-3}, which is the energy of interaction of the two " point dipoles " of the charge distributions. Higher terms (r^{-4}, r^{-5}, etc.) depend on the details of the charge distributions. All the terms vanish when averaged over all orientations. However, a Boltzmann factor, $e^{-E/kT}$ is larger for negative than for positive energies and so a statistical average of such energies will always be negative leading to a net attractive force. As well as these direct interactions there is a negative contribution to the energy from the interactions between the permanent moments of one molecule and the moments induced in the other. These energies vary as the square of the corresponding direct term and so their leading term is in r^{-6}. Generally they contribute little to the total energy. Finally there are terms from the polarisation of one molecule by the other due to the rapidly oscillating moments of electron clouds. These energies may also be expressed as series of even powers starting with r^{-6} : they can only be described by the methods of quantum mechanics and were first investigated by London [11] who named them " dispersion " energies. Their importance

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[5] de Boer, *Rep. Progr. Physics*, 1949, **12**, 305.

[6] " Molecular Theory of Gases and Liquids ", Wiley, to be published.

[7] Brieglieb, " Zwischenmolekulare Krafte und Molekulstruktur ", Stuttgart, 1937,

[8] Davies, *Ann. Reports*, 1946, **43**, 5.

[9] Kellner, *Rep. Progr. Physics*, 1952, **15**, 1.

[10] Donohue, *J. Phys. Chem.*, 1952, **56**, 202.

[11] London, *Z. physikal. Chem.*, 1930, *B*, **11**, 222.

is threefold. First, they are present in all interactions between atoms and molecules and so can account for the existence of attractive forces between spherically symmetrical molecules. Secondly, they are additive and, for simple molecules, depend little on orientation. By " additive " is meant that the total energy of an assembly of N simple molecules is, to a very good approximation, the sum of the energies of the $N(N-1)/2$ molecular pairs taken separately. Hence such energies can account for the cohesion of argon atoms in a crystal where each atom has twelve nearest neighbours. Neither dipole–dipole nor valency forces could account for such a structure. Thirdly, the dispersion energy is usually the largest of the negative terms. London [1] and Brieglieb [7] give tables of the approximate sizes of the three negative terms for the interaction of various pairs of molecules.

All these attractive terms are small compared with the energies of chemical bonds, and their calculation is often very difficult. For example, the original treatment of the forces between atoms by Heitler and London fails to show the existence of the dispersion forces at all. These appear only when a more exact treatment is made. The precautions which are necessary if one treatment is to give good values for both the valency forces and the dispersion forces were shown by the calculation by Hirschfelder and Linnett[12] of the energy of interaction of two hydrogen atoms. They used a complicated wave-function which gives a reasonable value of the energy at all separations. If the spins of the two electrons are anti-parallel then the atoms may unite to form a stable molecule, for which, with their wave-function, the energy curve has a minimum of 98,000 cal./mole at a separation of 0·761 Å. If the spins are parallel then there is a shallow minimum due to the dispersion energy. This is only 7·4 cal./mole deep at a separation of 4·47 Å. The difference between the two minima, both in depth and position, is here unusually great, but the example illustrates the difficulty of calculating directly the small energy differences which produce the forces between molecules whose valency requirements are saturated. Less accurate calculations have been made for larger atoms.[2, 6] A most useful approximation for the dispersion energy has been derived by Slater and Kirkwood :[13] probably its most accurate form is

$$E(r) = -(3/4)(pa_0\alpha^3)^{1/2}\, e^2\, r^{-6} \quad . \quad . \quad . \quad (1)$$

where p is the number of electrons in the outer shell, a_0 is the Bohr radius of the hydrogen atom (0·529 Å), α is the polarisability of the atom, and e is the electronic charge. This simple result may be tested by comparing the attractive fields of neon, argon, krypton, and xenon. Equation (1) requires that m, the coefficient of r^{-6}, is proportional to $\alpha^{3/2}$. Fig. 1 shows a graph of log m against log α. It is almost a straight line whose mean slope is 1·69, rather larger than this approximate theory would require. The absolute magnitudes of m cannot be determined very accurately, but it is found that equation (1) predicts energies of about the right size. An

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[12] Hirschfelder and Linnett, *J. Chem. Phys.*, 1950, **18**, 130.

[13] Slater and Kirkwood, *Phys. Review*, 1931, **37**, 682 ; Kirkwood, *Physikal. Z.*, 1932, **33**, 57 ; Hellman, *Acta Physicochim, U.R.S.S.*, 1935, **2**, 273.

illustration of the distances at which these attractive forces are balanced by the repulsive forces is provided by Fig. 2, where the intermolecular energy curve is compared with the radial electron distribution within the atom.[14] It is seen that the atoms repel each other as soon as there is any overlapping of their outer shells. (The absolute values of the "collision diameter" and depth of the intermolecular energy shown in Fig. 2 can be determined much more accurately than the coefficient of the r^{-6} term.)

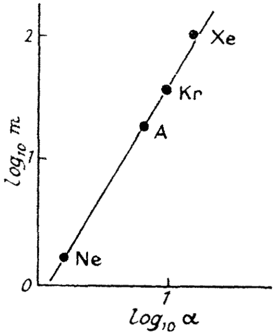

FIG. 1

The variation of m, *the coefficient of the dispersion energy, with* α, *the polarisability, in the rare gases. (Arbitrary units.)*

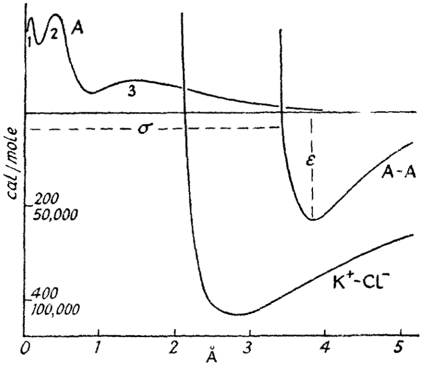

FIG. 2

The intermolecular energy of the pairs A–A (*upper figures in the scale*) *and* K⁺–Cl⁻ (*lower figures in the scale*). *The* A–A *energy is compared with the radial electron distribution within an argon atom. The horizontal scale of the latter has been doubled so that the mutual overlap at any separation is given correctly.* 1, 2, *and* 3 *show the three completed electron shells. The distance* σ *is commonly called the collision diameter of argon.*

Few calculations have been made for molecules. Margenau[15] and de Boer[16] have both calculated the energy of interaction of two hydrogen

[14] See Coulson, "Valence", Oxford Univ. Press, 1952, p. 38.

[15] Margenau, *Phys. Review*, 1943, **63**, 131, 385.

[16] de Boer, *Physica*, 1942, **9**, 363.

molecules as a function of their orientation, and, as would be expected, they find that the total energy behaves roughly as if it arose from the interaction of two " sources " extended along the axes of the molecules. That is, for a given separation of the centres, the negative value of the energy is greater when the molecules are parallel than when they are perpendicular, and greater when they are perpendicular than when they are co-linear. In polyatomic molecules it is often assumed that a substantially correct representation of the field may be obtained by regarding each atom as a separate centre of attractive and repulsive forces.[17] Though an over-simplification, such a treatment is undoubtedly more accurate than the assumption that a polyatomic molecule is a point-centre of force. This simple representation is not possible, however, if the molecules have conjugated double bonds. Coulson and Davies [18] have shown that the dispersion energy between the π-electrons of polyenes is proportional to r^{-6} only at large separations. At shorter distances it varies as a lower power of r and depends, in no simple way, on the orientation of the molecules.

An empirical potential which is roughly of the form suggested by these quantal calculations, and yet is easy to manipulate, is the inverse power potential

$$E(r) = nr^{-12} - mr^{-6} \quad . \quad . \quad . \quad . \quad (2)$$

often called the Lennard-Jones potential. This is more conveniently written, not in terms of the parameters m and n, but of new parameters, σ and ε, with the dimensions of distance (expressed in Å) and energy (expressed in ergs/molecule, cal./mole, or, often more conveniently, by expressing the quotient $\varepsilon/\boldsymbol{k}$ in °K). In terms of these parameters,

$$E(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] \quad . \quad . \quad . \quad . \quad (3)$$

This is the potential drawn for argon in Fig. 2. The choice of the r^{-6} term for the attractive energy is obvious but the choice of the r^{-12} term needs some justification. An exponential repulsion would be more accurate and a few calculations have been based upon it.[3, 19] However, it is difficult to handle mathematically, and, as is shown below, the simpler form of equation (3) is a satisfactory representation of the total potential as long as the kinetic energy of the molecules is not very high. This restriction is satisfied for the physical properties discussed below but not, for example, in " molecular beam " experiments. From these it may be shown that the energy of repulsion at very small separations may not be obtained by extrapolating either a twelfth power or an exponential term from distances near that of minimum energy.[20]

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[17] Corner, *Proc. Roy. Soc.*, 1948, *A*, **192,** 275 ; Trappeniers, *Physica*, 1951, **17,** 501 ; Rowlinson, *J. Chem. Phys.*, 1952, **20,** 337 ; Thomaes, *J. Chim. phys.*, 1952, **49,** 323.

[18] Coulson and Davies, *Trans. Faraday Soc.*, 1952, **48,** 777.

[19] Buckingham, *Proc. Roy. Soc.*, 1938, *A*, **168,** 264 ; Buckingham and Corner, *ibid.*, 1947, *A*, **189,** 118.

[20] Berry, *Phys. Review*, 1949, **75,** 913 ; Amdur, Davenport, and Kells, *J. Chem. Phys.*, 1950, **18,** 525.

The Three States of Matter

Possibly the most obvious question to ask of statistical mechanical theory is whether it can show that matter composed of simple spherical molecules is capable of existing in three phases—gas, liquid, and solid. The answer is that it cannot. The whole question of changes of phase is little understood.[21] Certain hypothetical problems in one or two dimensions

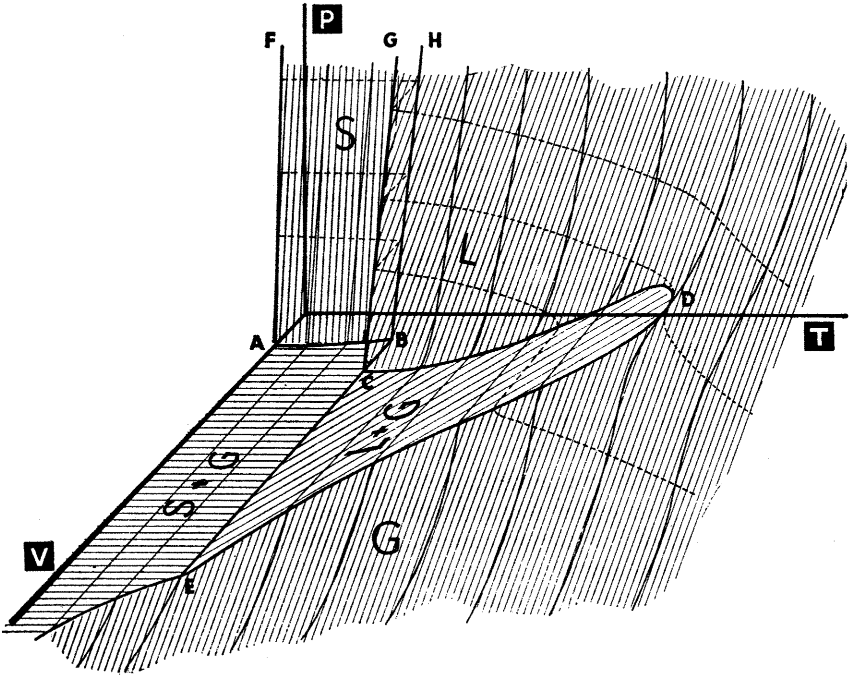

Fig. 3

The equation of state of a simple substance, as a surface in the three dimensions of pressure, volume, and temperature. (Not to scale.) AB *is the vapour pressure curve of the solid. The slope of* AF *shows the compressibility of the solid at absolute zero. The line* BCE *is at the triple-point pressure and temperature, and the letters show, respectively, the volumes of the solid, liquid, and gas at this point.* CD *is the vapour pressure and density of the liquid, and* ED *the density of the coexistent gas. These meet at* D, *the gas–liquid critical point. It is not known if the curves* BH *and* CG *meet at a liquid–solid critical point. The shape of the surface is shown by the isotherms (continuous lines), and by three isobars (dashed lines), one below, one at, and one above the critical pressure.*

may be solved, but a complete treatment of the possible phases of a three-dimensional assembly is still impossible. This is the more to be regretted as experiments so far made do not settle beyond doubt the nature of the transition either at the condensation of a gas to a liquid or at the freezing of a liquid to a solid. Fig. 3 shows schematically the equation of state of a

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[21] See, *e.g.*, "Les changements de phases", Colloquium of the Société de Chimie Physique, Paris, 1952.

simple substance, as a surface in the three dimensions of pressure, volume, and temperature. The gross features of this surface are easy to find by experiment, but the finer features, such as the curvature near the transition points, are not easily determined. It is seen that the lines separating the " gas " surface and the " liquid " surface converge as the temperature is raised, finally meeting at the gas-liquid critical point. Above that temperature there is no transition, that is, no discontinuity, on the fluid surface. Neither theory nor experiment has yet been able to show whether there is a liquid–solid critical point. It is not known whether the lines in Fig. 3 forming the step which separates the " solid " surface from the " liquid " converge and meet at sufficiently high temperatures and pressures. The present indications are that they do not. It seems that the solid phase, which is resistant to shear and has " long-range order ", differs fundamentally from the fluid phases, which have neither of these properties. For example, solid helium is stable at a temperature of ten times the gas–liquid critical temperature, under a pressure of 3000 times the critical pressure.[22]

The exact nature of the gas–liquid critical point is also unsettled. Simple empirical equations of state, such as that of van der Waals, define the critical point as that point on the P, V, T surface where

$$(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0, \quad (\partial^3 P/\partial V^3)_T < 0 \quad . \quad . \quad (4)$$

Everywhere above this temperature $(\partial P/\partial V)_T$ is negative. Below this temperature two phases can exist together. Fifteen years ago careful experiments [23] seemed to show that there was a small region above the temperature at which the phase boundary disappeared, in which $(\partial P/\partial V)_T$ was still zero. This result was supported by theoretical arguments [4] based on the behaviour of the partition function of a gas at its condensation point. However, there has recently been much painstaking work [24] on the shape of the isotherms near the critical point, which does not, on the whole, support this view. The effect of gravity is thought to have vitiated some of the earlier work. Immediately above the critical point the fluid contains clusters of very large numbers of molecules. This is shown directly by measurements of the light scattered by such a fluid.[25] These clusters tend to settle out to the bottom of the tube and so produce pressure and density gradients which affect the shape of the observed isotherms. Schneider and Weinberger [24] have shown that the shorter the tube containing the fluid, the closer its properties conform to the classical picture of the critical point. It is still uncertain, however, whether the third and higher derivatives of equation (4) may not vanish just at the critical point.

Two substances are said to obey the principle of corresponding states if, by choice of suitable units of P, V, and T, their equations of state (the

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[22] Holland, Huggill, Jones, and Simon, *Nature*, 1950, **163,** 148 ; Domb, *Phil. Mag.*, 1951, **42,** 1316.

[23] Maass, *Chem. Reviews*, 1938, **23,** 17.

[24] Beattie, Douslin, and Levine, *J. Chem. Phys.*, 1951, **19,** 948, and earlier papers ; Schneider and Weinberger, *Canad. J. Chem.*, 1952, **30,** 422, 815, 847, and earlier papers.

[25] Cataldi and Drickamer, *J. Chem. Phys.*, 1950, **18,** 650 ; Babb and Drickamer, *ibid.*, p. 655.

surfaces of Fig. 3) may be made to coincide. This principle has been one of the most fruitful concepts which has come from the work of van der Waals. However, its usefulness really dates from Pitzer's [26] simple derivation, from classical statistical mechanics, of the fact that all substances conform to this principle if their intermolecular energies can be expressed in the form

$$E(r) = \varepsilon_{ii}.f(\sigma_{ii}/r) \qquad . \quad . \quad . \quad . \quad (5)$$

where ε_{ii} and σ_{ii} are two constants, an energy and a distance, which characterise the interaction of two molecules of species i, and where f denotes a function of (σ/r) which is the same for all species. [Equation (3) is a special case of equation (5).] The rare gases, except helium, conform very closely to the principle of corresponding state and so their potential energies must be related by an equation such as (5). Small deviations from this principle are shown by more complicated molecules.[27] The size of the deviations can often be quantitatively related to the departure of the intermolecular potential from the form of equation (5), and this gives us a way of investigating molecular shapes as well as sizes.[28] Helium and hydrogen show deviations which cannot be explained by the departure of their potentials from the form of equation (5). Such deviations occur with light molecules for which quantal effects are important. Byk,[29] and more recently de Boer and others,[30] have shown that the divergence between classical and quantal behaviour is proportional to a dimensionless parameter Λ, defined by

$$\Lambda = hm^{-1/2}\sigma^{-1}\varepsilon^{-1/2} \qquad . \quad . \quad . \quad . \quad (6)$$

where h is Planck's constant and m is the mass of the molecule. This parameter has been used to predict [30] the properties of ^{3}He from those of ^{4}He, and the properties [31] of the isotopes of hydrogen from those of normal hydrogen. Subsequent measurements [32] of the vapour pressure of ^{3}He confirmed the calculations. The properties of the hydrogen isotopes [33] did not agree exactly with those calculated, probably because of a simultaneous departure of the energy from the form of equation (5). Very much greater deviations from the principle of corresponding states are shown by highly polar substances such as ammonia and water. At present little can be said about these.

Imperfect Gases.—Only at low densities do real gases obey the equation of state, $PV = RT$. Departures from this, the equation of perfect gases, is shown in Fig. 3 as a departure of the isotherms from the shape of rectangular hyperbolæ. However, this is not a convenient representation, and Fig. 4 shows PV/RT as a function of $(1/V)$, the molar density. The

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[26] Pitzer, *J. Chem. Phys.*, 1939, **7**, 583.

[27] Guggenheim, *ibid.*, 1945, **13**, 253 ; *Austral. Review Pure Appl. Chem.*, 1953, **3**, 1.

[28] Cook and Rowlinson, *Proc. Roy. Soc.*, 1953, *A*, **219**, 405.

[29] Byk, *Ann. Physik*, 1921, **66**, 167 ; 1922, **68**, 161.

[30] de Boer *et al.*, *Physica*, 1948, **14**, 139, 149, 520, 1101.

[31] Hammel, *J. Chem. Phys.*, 1950, **18**, 228.

[32] Sydoriak, Grilly, and Hammel, *Phys. Review*, 1949, **75**, 303.

[33] Friedman, White, and Johnston, *J. Chem. Phys.*, 1951, **19**, 126.

departures from the equation of perfect gases are seen to be considerable. (Many attempts have been made to fit empirical equations to these curves,[34] but, although of some practical importance, these contribute little to our understanding of the forces responsible for the imperfection of gases.) The calculation of the equation of state of a gas at densities below that of the saturated vapour is one of the few problems in the statistical mechanics of interacting molecules which can be solved exactly.[3–6, 35] The solution leads to an open equation of state

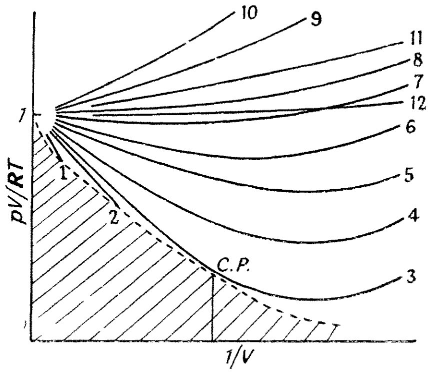

FIG. 4

The equation of state of a gas. (Not to scale.) Curves 1—12 are isotherms at a series of increasing temperatures. The third is the critical isotherm, which just touches the shaded two-phase region. The eighth is the Boyle-point isotherm, at which temperature the second virial coefficient vanishes.

$$PV/RT = 1 + B/V + C/V^2 + D/V^3 + \dots \qquad (7)$$

where B, C, D, etc., are the second, third, fourth, etc., virial coefficients. They are functions of the temperature but not of the density. If the molecules are non-interacting point particles, all the coefficients are zero. For real molecules exact expressions may be obtained in terms of the intermolecular energies. The coefficients are of the greatest importance as they

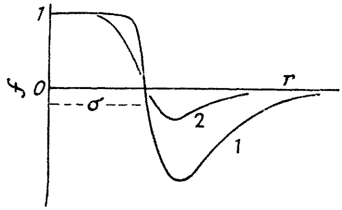

FIG. 5

The function f *of equation* (8), *at a low temperature* (1) *and a high temperature* (2).

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[34] Partington, " Advanced Treatise on Physical Chemistry ", Longmans, 1950, Vol. 1; Beattie and Stockmayer, *Rep. Progr. Physics*, 1940, **7**, 195.

[35] Rushbrooke, " Introduction to Statistical Mechanics ", Oxford Univ. Press, 1949, Ch. 16.

are the primary source of most accurate knowledge about intermolecular forces. Simple expressions may be written for the second and third coefficients, B and C. If $E(r_{12})$ is the energy of interaction of two molecules, 1 and 2, when separated by a distance r_{12}, a function f_{12} may be defined by

$$f_{12} = 1 - \exp\left[- E(r_{12})/kT \right] \quad . \quad . \quad . \quad . \quad (8)$$

This function is sketched in Fig. 5. Then B and C are given by the following expressions, where the integrations are taken over all values of the separations r_{12}, etc.,

$$B = 2\pi N \int f_{12}\, r_{12}^2\, \mathrm{d}r_{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$C = \frac{8\pi^2 N^2}{3} \iiint f_{12} f_{13} f_{23}\; r_{12} r_{13} r_{23}\; \mathrm{d}r_{12}\, \mathrm{d}r_{13}\, \mathrm{d}r_{23} \quad . \quad . \quad (10)$$

(If the molecules are not spherical, further integrations must be made over all orientations.) It can be seen that B is a measure of the interaction of a pair of molecules and C of the simultaneous interaction of three molecules. Virial coefficients are not easily measured, for the terms they contribute to the right-hand side of equation (7) are small. Little is known, experimentally or theoretically, about the coefficients above C. Guggenheim [27] has recently reviewed the experimental results for B and C and shown that, for simple molecules, they conform well to the principle of corresponding states, and so the potential energies must all be of one kind, as in equation (5). More detailed information about the intermolecular forces may be had by evaluating the integrals of equation (8) for various "model" potentials and then comparing the observed and calculated values. Many such calculations have been made. Probably the most useful, at present, are those [6, 36] for the potential of equation (3). The calculated curves are shown in Fig. 6, together with some experimental points for argon.[37] The agreement is better for B than it is for C. This is always the case, for C is both harder to measure and is much more sensitive to slight variations in the shape of the potential energy curve. The virial coefficients by themselves will not determine the shape of the energy curve but, if its shape is known, or chosen on other evidence, then they will determine the parameters of length and energy with some precision. Parameters derived from equation (3) are listed in the Appendix.

Since equation (3) is a special case of equation (5), it follows from the principle of corresponding states that there is, for such molecules, a universal relation between the critical volume and $(N\sigma^3)$, and between the critical temperature and (ε/k). It is found empirically for the rare gases and other simple molecules that these relations are approximately

$$V_c = 1{\cdot}50 b_0, \quad \text{where } b_0 = (2/3)\pi N\sigma^3,$$
$$T_c = 1{\cdot}25(\varepsilon/k) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

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[36] Beattie and Stockmayer, *J. Chem. Phys.*, 1942, **10,** 476; Bird, Spotz, and Hirschfelder, *ibid.*, 1950, **18,** 1395.

[37] Michels, Wijker, and Wijker, *Physica*, 1949, **15,** 627.

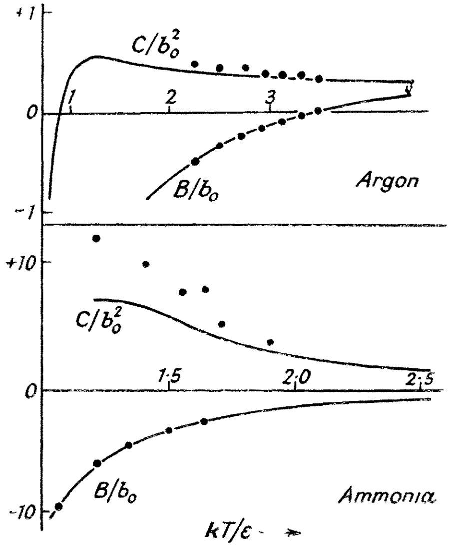

Fig. 6

Experimental values of the second and third virial coefficients of argon and ammonia. The calculated curves for argon are for an energy of the form of equation (3), *and those for ammonia for a similar energy with the addition of a dipole–dipole term* (μ = 1·47D).

No close theoretical check is available for these figures since there is no exact statistical theory of the critical point.

If the molecules are polar then a first approximation to their potential energies is obtained by adding to equation (3) a term which represents the interaction of their dipoles. The second [38] and third [39] virial coefficients have been calculated for this model and are shown in Fig. 6 for a molecule with the dipole moment of ammonia.

The physical meaning of B and C may be seen by comparing Fig. 5 and Fig. 6. At high temperatures B and C are both positive. Here the greatest contribution to the integrals comes from the repulsive forces, at small separations where f is positive. These forces cause the pressure to be higher than in a perfect gas, as would be expected. At lower temperatures B becomes negative. The attractive forces (region of f negative) now predominate, and cause the pressure to diminish as clusters are formed. However, the coefficient C remains positive, and in fact increases, before finally becoming negative at very low temperatures. The positive sign of C means that the simultaneous association of two molecules 1 and 2 with a third molecule, 3, is hindered rather than helped by the mutual interaction of 1 and 2; for the independent associations of 1 with 3, and 2 with 3, are represented by the second virial coefficient. It is seen that this hindering effect is larger for polar molecules than for non-polar, because of the

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[38] Stockmayer, *J. Chem. Phys.*, 1941, **9**, 398; Rowlinson, *Trans. Faraday Soc.*, 1949, **45**, 974; 1951, **47**, 120.

[39] Rowlinson, *J. Chem. Phys.*, 1951, **19**, 827.

dependence of the dipole energy on the orientation. A group of three polar molecules cannot be arranged so that the total energy is as low as is possible in three separate pairs.

The virial expansion, equation (7), is only useful at relatively low pressures because of the difficulty both of measuring and computing the higher coefficients. The point at which the series ceases to converge, and therefore the theoretical limit to its validity, is close to the condensation point. Here the clusters become so large that they contain an appreciable fraction of the molecules in the assembly, and the individual coefficients then depend on the density as well as on the temperature. Unfortunately the nature of this dependence is not understood. At very high temperatures and pressures, such as are reached in explosions, (pV/RT) becomes very large, and the virial expansion less useful. Under these conditions the molecules are forced together so violently that their electronic shells are considerably distorted. The mean increase in the kinetic energy of the electrons and nuclei, from that in the ideal gas state, is given by

$$\overline{\Delta K} = 3\Delta(PV) - \Delta u \quad . \quad . \quad . \quad . \quad (12)$$

where Δu is the change in total energy. The right-hand side of this equation is calculable from compressibility measurements. Michels, de Boer, and Bijl [40] have shown that the increase may be considerable. At 150° C and 3000 atmospheres $\overline{\Delta K}$ is 8 kcal./mole for carbon dioxide. Crude theoretical calculations of this increase have been made by considering the change in the wave-functions of simple systems, such as H and H_2^+, when confined in an energy " box " whose size is the mean volume per molecule.[41] These calculations agree as well as can be expected with the experimental results and Cottrell and Paterson [42] have recently based upon them an equation of state which is of use in interpreting the behaviour of exploding gases.

The transport properties of gases.—The transport properties of a gas or gas-mixture are measured by the coefficients of viscosity, thermal conductivity, and the various coefficients of diffusion. Such coefficients measure, respectively, the rate of transfer through the gas of molecular momentum, energy, and mass. They are the simplest " rate processes " in a gas, and so may be treated theoretically in a much more detailed way than any chemical reaction. While the rate of a reaction is determined primarily by the inter-atomic forces within the molecules, the transport properties are determined by the weaker forces acting between them. If the intermolecular energies have not spherical symmetry, then rotational and vibrational energy may be exchanged in collisions. This complicates the theoretical treatment of the transport properties, but fortunately such energy exchange seems to affect seriously only the thermal conductivity. The coefficient of viscosity (and those of diffusion, which are discussed later, in the section on Solutions) appears to measure an energy averaged over all

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[40] Michels, de Boer, and Bijl, *Physica*, 1937, **4,** 981.

[41] Michels and de Groot, *ibid.*, 1950, **16,** 183 ; Cottrell, *Trans. Faraday Soc.*, 1951, **47,** 337.

[42] Cottrell and Paterson, *Proc. Roy. Soc.*, 1952, *A*, **213,** 214.

orientations, and so gives information about the variation of the energy with distance. This information is a useful supplement to that obtained from the virial coefficients, for the two properties depend in a very different way on the potential energy. At the temperatures at which it is usually measured, the second virial coefficient is mainly a measure of the size of the attractive forces. The coefficient of viscosity is determined by the angle of deflection of two colliding molecules and so depends to a much greater degree on the repulsive part of the potential. The two properties are therefore complementary and between them provide a severe test of any proposed potential energy curve.

The simple treatment of viscosity in terms of the mean free path and similar concepts is not accurate, even for molecules which are rigid spheres, and breaks down completely for real molecules whose potential energies are continuous functions of their separations. However, an exact treatment is possible, though long and difficult. A full account is given in the monograph of Chapman and Cowling,[43] and more elementary accounts by Jeans [44] and Kennard.[45] The correct expression for the coefficient of viscosity for spherical molecules, apart from some very small correction terms which may be ignored, is

$$\eta = \frac{5}{8}\left(\frac{mkT}{\pi}\right)^{1/2}\left[\iint x^3\, \mathrm{e}^{-x}\, y \sin^2 \chi(x, y)\, \mathrm{d}x\, \mathrm{d}y\right]^{-1} \quad . \quad . \quad (13)$$

where m is the molecular mass and $\chi(x,y)$ is the angle of deflection of two molecules in a collision characterised by the two parameters x and y, which are the ratio of the relative kinetic energy to kT and the distance between the two lines of centres before the collision. The integration is an averaging over all collisions. The expression of χ in terms of x, y, and the intermolecular energy is a straightforward problem in classical mechanics. If energies are of the form of equation (5), then equation (13) and the principle of corresponding states implies that the function $[\eta(V_c)^{2/3}N^{1/3}(MRT)^{-1/2}]$ is a universal function of T/T_c. This is found to be so [46] for the viscosities of such simple gases as Ne, A, Xe, N_2, O_2, CO, and CH_4, again showing that their potential energies are of the form of equation (5). If more detailed information is wanted about the potential energy, then, as in the case of the virial coefficients, model potentials must be inserted into equation (13) and the integrations carried out. However, in this case, the calculations are extremely laborious, and for many years the energies were chosen more for their mathematical convenience than for their physical reality. The only calculations now worth consideration are those for an 8-and-4 inverse power potential,[47] a 12-and-6 inverse power potential [48] [that is, equation

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[43] Chapman and Cowling, "Mathematical Theory of Non-Uniform Gases", Cambridge Univ. Press, 2nd edn., 1951.

[44] Jeans, "Kinetic Theory of Gases", Cambridge Univ. Press, 1940.

[45] Kennard, "Kinetic Theory of Gases", McGraw-Hill, 1938.

[46] Rowlinson and Townley, *Trans. Faraday Soc.*, 1953, **49**, 20.

[47] Hassé and Cook, *Proc. Roy. Soc.*, 1929, *A*, **125**, 196.

[48] The most extensive of four independent calculations are those of Hirschfelder, Bird, and Spotz, *J. Chem. Phys.*, 1948, **16**, 968; *Chem. Reviews*, 1949, **44**, 205.

(3)], and a " square-well " potential [49] in which the molecule is represented by a hard core surrounded by a rectangular potential trough. Any of these potentials is capable of representing either the second virial coefficient or the coefficient of viscosity over quite wide temperature ranges, but only equation (3) is capable of representing both coefficients with one pair of parameters. This agreement is strong evidence that the form of potential of equation (3) is close to the correct one. Hirschfelder, Bird, and Spotz [48] compare the parameters derived from the two properties. The empirical equations connecting the parameters derived with the viscosity with the critical constants are [46]

$$V_c = 1{\cdot}46b_0$$
$$T_c = 1{\cdot}28(\varepsilon/\boldsymbol{k}) \quad . \quad . \quad . \quad . \quad (14)$$

These equations are virtually the same as those [equations (9)] derived from the second virial coefficient, so illustrating the agreement which can be obtained with the potential energy of equation (3).

Two important problems in the theory of the transport properties of gases are still unsolved. The viscosity of a polar gas cannot yet be expressed in terms of its dipole moment and intermolecular energy, in the way in which its virial coefficients can. This difficulty is due to the inelastic nature of collisions between molecules with non-central force fields. The second problem is an understanding of the effect of ternary and higher-order collisions on these properties, comparable, say, with our knowledge of the third virial coefficient. In the derivation of equation (13) it is supposed that all but two-body collisions may be ignored. Within the limitations of this assumption, theory requires that the viscosity is independent of the pressure. This is so at pressures near atmospheric. It is not so at very low pressures, when the mean free path is comparable with the size of the apparatus, nor at high pressures when ternary collisions cannot be neglected and when the ratio of the diameter of a molecule to its mean free path is not negligible. The effect of very low pressures is well understood [45] but not the effect of high pressures. Enskog [50] gave an approximate treatment of the special case of molecules which are rigid spheres, but his results do not generally fit the facts, as might be expected for such a crude model.

Liquids.—The liquid state lends itself most readily to exact experimental observation, but it is the most difficult of the three to treat theoretically. At present the observed properties of a liquid cannot be used to give any direct information about the intermolecular forces. The problem rather is to develop a statistical theory which will explain the multitude of experimental observations in terms of intermolecular forces derived from the properties of gases and solids.

The high density of the liquid state and the regularities of its structure, as revealed by X-ray diffraction patterns, show its affinity to the solid state. Most statistical treatments have been based on these similarities. However,

[49] Holleran and Hulbert, *J. Chem. Phys.*, 1951, **19**, 232.

[50] See ref. 43, Ch. 16.

as Fig. 3 shows, there is a continuity of state between liquid and gas, which makes it certain that a satisfactory statistical treatment must consider the fluid state as a whole. Only over a restricted range of volume and temperature can this state subdivide into two fluid phases.

Eyring,[51] and Lennard-Jones and Devonshire [52] are mainly responsible for the lattice, or " disordered solid ", model of the liquid state. They calculated the thermodynamic properties of a liquid by supposing that each molecule is confined to a small cell by its nearest neighbours. Lennard-Jones and Devonshire found the partition function for the motion of the molecule within its cell by using the potential of equation (3). (The partition function is the value of $e^{-E/kT}$ integrated over the cell, where E is the energy of interaction with the neighbours.) By neglecting the possibility of molecules exchanging cells they were able to calculate the partition function, and so the equation of state, of the whole assembly. Such a model shows a gas–liquid transition at all temperatures below ($\boldsymbol{k}T/\varepsilon = 1{\cdot}2$). Above that temperature there is no transition. Thus qualitatively the model behaves as a real fluid. Quantitatively the agreement is not good. The critical temperature comes at about the correct value of ($\varepsilon/\boldsymbol{k}$) but neither the critical pressure and critical volume nor the vapour-pressure curve is given correctly. The model is quite unacceptable at low densities, as would be expected from its derivation from the solid state. For example, it predicts a vanishing second virial coefficient at all temperatures. There have been many ingenious attempts to improve this treatment by allowing the existence of unoccupied cells, whose number and size depend on the volume and temperature. These modifications can be made intuitively more attractive than the original theory and have the merit of giving a reasonable treatment of the gas phase at low densities.[53] However, none of them gives satisfactory values for the critical constants and vapour-pressure curve. De Boer summarised their successes and failures at a recent discussion of the Royal Society.[54]

An entirely different approach [55] to the theory of the liquid state was initiated by Yvon and developed by Kirkwood and by Born and Green. Here the fluid phase is treated as a unity and the whole theory is on a more sound foundation. It is possible to define first, second, third, etc., distribution functions for the fluid; there being as many of these as there are molecules in the assembly. The first is simply the density, the second measures the probability that a pair of molecules are a given distance apart, the third is a similar probability for a group of three molecules, and so on. (The second is the pair or radial distribution function obtained from the X-ray diffraction patterns of liquids.) The theory rests upon the fact that a set of equations may be obtained, each giving the nth distribution function

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[51] Eyring, *J. Chem. Phys.*, 1936, **4,** 283.

[52] Lennard-Jones and Devonshire, *Proc. Roy. Soc.*, 1937, *A*, **163,** 53.

[53] Rowlinson and Curtiss, *J. Chem. Phys.*, 1951, **19,** 1519.

[54] de Boer, *Proc. Roy. Soc.*, 1952, *A*, **215,** 1—66.

[55] (*a*) Kirkwood and Boggs, *J. Chem. Phys.*, 1942, **10,** 394; Kirkwood, Maun, and Alder, *ibid.*, 1950, **18,** 1040; Kirkwood, Lewinson, and Alder, *ibid.*, 1952, **20,** 929. (*b*) Born and Green, " Kinetic Theory of Liquids ", Cambridge Univ. Press, 1949.

in terms of the $(n + 1)$th. If soluble, this set of equations would give exactly the equation of state and other thermodynamic properties of gases, liquids, and solids. However, it is not soluble at present and so the so-called " superposition approximation " has been introduced. It is supposed that the probability of a given array of three molecules is simply related to the " superposition " of the probabilities of the three-pair configuration occurring independently. In this way the set of equations is " closed ", and the equation for the pair distribution function is soluble without a knowledge of the triplet and higher functions. Even so, its solution is exceedingly difficult and has only been achieved by numerical methods. The results so far obtained show that this treatment is superior to the cell theories at densities up to and including the critical. At higher densities the superposition approximation becomes less accurate. This is well illustrated by Rushbrooke and Scoins [56] who have shown that if this theory, with the superposition approximation, is used to calculate the virial coefficients, then the second and third are given correctly but the fourth is not. An exact theory of the liquid state is still a distant goal.

While the equilibrium properties are still so imperfectly understood it is not to be expected that the theory of the transport properties is very far advanced.[54] Neither the treatment of the cell model by Eyring [57] nor that of the pair distribution function by Kirkwood [58] has yet given any quantitative account of the part that intermolecular forces play in the transport properties of liquids. However, the latter has established the useful result that the coefficient of shear viscosity of any fluid, gas, or liquid consists of two parts, which may be called a " kinetic " term and an " intermolecular force " term. These correspond to the carrying of molecular momentum by the motion of the molecules themselves and by the direct action of their intermolecular energies, which enable a force to be transmitted over larger distances than the molecules actually move. Only the first term is important in a gas at low pressures while the second is predominant at the density of a normal liquid. In the supercritical fluid both are important. As the two terms are quite different in form, there is no reason to expect much correlation between gas and liquid viscosities, as indeed, is the case.

Solids.—The physical properties of a simple solid formed of monatomic molecules (excluding metals) or univalent ions can be expressed rigorously in terms of the intermolecular energies, as long as the temperature is close to absolute zero. Conversely, measurements of these properties can give direct and accurate information about the potential energy curves, or, more precisely, about their shape and depth near the position of minimum energy.[59] If the molecules are not spherical then the situation is different.

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[56] Rushbrooke and Scoins, *Phil. Mag.*, 1951, **42**, 582 ; *Proc. Roy. Soc.*, 1953, *A*, **216**, 203.

[57] Glasstone, Laidler, and Eyring, " The Theory of Rate Processes ", McGraw-Hill, 1941.

[58] Kirkwood, Buff, and Green, *J. Chem. Phys.*, 1950, **18**, 901, and earlier papers. See also ref. 55 (*b*).

[59] Fowler, " Statistical Mechanics ", Cambridge Univ. Press, 2nd Edn., 1936, pp. 312—337.

The structure, lattice energy, etc., of a crystal of polyatomic molecules, unlike the properties of the fluid phases, depend on the fine details of the variation of the intermolecular energy with the orientation of the molecules. Only rarely does a knowledge of the crystal constants help in determining the potential energy curve. This situation may improve as more becomes known about the forces between polyatomic molecules, but before much systematic progress can be expected there is one theoretical problem that must be solved. This is to obtain a general relation between the symmetry of an intermolecular energy surface and the symmetry of the corresponding crystal structure. At present, however, almost nothing is known about such relations, and therefore only the simplest structures, those of the rare gases and the alkali halides, are discussed in this section.

The forces between the atoms of the rare gases are entirely independent of their orientation, indeed the concept of orientation has no meaning here, and so it is possible to calculate *a priori* the structure of lowest energy. Lennard-Jones and Ingram [60] showed that the face-centred cubic lattice is more stable than the body-centred, and both are more stable than the simple cubic lattice. Prins, Dumoré, and Tjoan [61] have, however, recently found that, for all reasonable forms of the intermolecular energy, the hexagonal close-packed lattice is even more stable than the face-centred cubic. The energy difference is small, about 1 part in 14,000, and it is observed experimentally that the rare gases crystallise in the less stable structure. The reason for this is not known. Several effects could produce energy differences of this size. Possibly the zero-point energies of the two structures differ appreciably, or possibly the energy of the assembly of N atoms may not be accurately the sum of the energies of the $N(N-1)/2$ intermolecular pairs, as has been assumed in the calculations. This last effect has been discussed by Axilrod and Teller,[62] who find that there may be differences of up to 9% between the actual energy of a cluster of three molecules and the energies of the three pairs taken separately.

However, since the face-centred lattice is an experimental fact, measurements of the crystal spacing and the latent heat of sublimation (both corrected for the zero-point energy and extrapolated to absolute zero) can be used to obtain precise information about the position and depth of the minimum of the energy curve. A thorough treatment of this kind has been given by Corner [63] who, by combining information derived from the crystals with that derived from the second virial coefficients, has calculated energy curves for the rare gases which are probably the most reliable known. At temperatures well above absolute zero, and towards the melting point of the solid, it becomes increasingly difficult to relate the intermolecular energy and the physical properties.[64]

The attractive forces hitherto discussed play a very minor role in ionic

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[60] Lennard-Jones and Ingram, *Proc. Roy. Soc.*, 1925, *A*, **107**, 636.

[61] Prins, Dumoré, and Tjoan, *Physica*, 1952, **18**, 307.

[62] Axilrod and Teller, *J. Chem. Phys.*, 1943, **11**, 299; 1951, **19**, 719, 724.

[63] Corner, *Trans. Faraday Soc.*, 1948, **44**, 914.

[64] Rice, *J. Chem. Phys.*, 1944, **12**, 289; 1946, **14**, 321, 518.

crystals. The stable configuration of these structures is determined primarily by the balance between the repulsive (overlap) energy and the simple Coulomb energy between the ions. The NaCl lattice is the most stable for uni-univalent salts if the repulsive energies of each of the three kinds of interaction (+ +, + —, and — —) are the same, that is, if the ions are the same " size ". If the dispersion energy is not negligible, or if the repulsive energies are not the same, then this lattice may not be the most stable. In this way the adoption of the cæsium chloride structure by certain of the alkali halides was explained by Mayer and others.[65] It is possible, for these simple crystals, to calculate the lattice energy directly from the lattice spacing, the ionic polarisabilities, and the coefficient of compressibility. The electrostatic energies can be summed over the whole crystal by the method of Madelung, or some modification of it.[59] The ionic polarisabilities give approximate values of the dispersion energy by using the equation of Slater and Kirkwood,[1] and the curvature of the potential at its minimum may be derived from the coefficient of compressibility. This curvature enables the shape of the repulsion energy to be found. This varies as r^{-8} or r^{-9} for the alkali halides. This is a significantly lower power of r than the r^{-12} used for the rare gases. The difference is due mainly to the fact that the minimum of the energy occurs at a smaller separation, owing to the great strength of the ionic energy. This is illustrated in Fig. 2 where the energy of interaction of two argon atoms is compared with that of the iso-electronic pair, K^+ and Cl^-. The energy scales differ by a factor of 250. The differences in the shapes and positions of the minima are very obvious. In both cases an exponential repulsion is more satisfactory, for this will fit the curves at both separations.

Solutions of non-electrolytes.—The study of solutions [66] is of interest from two points of view. In the first place, it is the only way of investigating the forces between molecules of different species. It is not usually possible to measure the effects of these forces directly, for the properties of a solution generally depend on the difference between these forces and some average of the forces between molecules of like species. However, two special cases in which the effects of the unlike forces may be measured directly are noted below. In the second place, the phase equilibria of solutions have many interesting features which are not encountered with pure substances. Two fluid phases of a pure substance in equilibrium at a given pressure and temperature differ only in their densities. In solutions the difference can also be one of composition, and this extra degree of freedom is responsible for a host of new phenomena. The physical explanation of some of these is far from simple. Azeotropy, incomplete miscibility of liquids, and the occurrence of critical solution points, retrograde condensation, and the solubility of solids in compressed gases, are examples. Most work on solutions, both experimental and theoretical, has been concerned with this

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[65] Born and Mayer, *Z. Physik*, 1932, **75**, 1 ; Mayer and Helmholtz, *ibid.*, p. 19. See also ref. 1.

[66] (*a*) Hildebrand and Scott, "The Solubility of Non-Electrolytes ", Rheinhold, 3rd Edn., 1950. (*b*) *Discuss. Faraday Soc.*, 1953, **15.**

second aspect, that is with trying to measure and understand these new properties, and has not been concerned directly with the measurement of intermolecular forces. Here the emphasis is on the first aspect.

In a mixture of two components, i and j, there are three kinds of molecular interaction to be considered. These are denoted here by the subscripts ii, ij, and jj. If there are only dispersion forces between the molecules then the parameters of the ij interaction usually lie between those of the ii and the jj. Measurements on imperfect gases are the most direct way of finding the relative sizes of the three sets of parameters.[67, 68] These have shown that for simple molecules the parameters of an energy of the form of equation (5) are related approximately by the equations,

$$\sigma_{ij} = \tfrac{1}{2}\sigma_{ii} + \tfrac{1}{2}\sigma_{jj} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\varepsilon_{ij} = \varepsilon_{ii}^{1/2} . \varepsilon_{jj}^{1/2} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

These equations are empirical but seem to apply to a surprisingly wide range of molecules. If the three interactions can be expressed in the common form of equation (5), then it seems as if there should be some extension of the principle of corresponding states which would cover mixtures as well as pure substances. Such an extension may be made exactly if the mixture is a gas at such low density that all virial coefficients above the second may be neglected.[68] The extension cannot be made exactly at higher densities where clusters of three molecules and more contribute to the imperfection of the gas. However, an approximate extension may be made [69] if the ratios of the three parameters are close to unity. Furthermore, if this condition is satisfied, Longuet-Higgins [70] has shown that the principle of corresponding states may be extended to all solutions—solid, liquid, and gas, and even to the critical state.[71] That is, the deviations from ideality of the thermodynamic properties of these solutions may be calculated from the thermodynamic properties of either of the pure components and two dimensionless parameters, $(2\sigma_{ij} - \sigma_{ii} - \sigma_{jj})/\sigma_{ii}$ and $(2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj})/\varepsilon_{ii}$, as long as these parameters are small. This condition is satisfied if equations (15) and (16) hold even roughly. This treatment allows rigorous proofs of some statements about liquid solutions which are intuitively obvious. If ε_{ij} is smaller than the arithmetic mean of ε_{ii} and ε_{jj} then the solution will show positive deviations from Raoult's law. If ε_{ij} is smaller than both ε_{ii} and ε_{jj} then the solution will form a positive azeotrope. This is quite natural, for if the ij forces are weak then the volatility of the mixture will be greater than that of the pure components. Similarly, if ε_{ij} is large there will be negative deviations from Raoult's law and, in the extreme case, negative azeotropy. It is found that many more solutions show positive deviations than negative, and so ε_{ij} is generally less than the

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[67] Hirschfelder and Roseveare, *J. Phys. Chem.*, 1934, **43,** 15.

[68] Guggenheim and McGlashan, *Proc. Roy. Soc.*, 1951, *A*, **206,** 448 ; Fox and Lambert, *ibid.*, 1951, **210,** 557.

[69] Rowlinson, Sumner, and Sutton, *Trans. Faraday Soc.*, 1954, **50,** 1.

[70] Longuet-Higgins, *Proc. Roy. Soc.*, 1951, *A*, **205,** 247.

[71] Cook and Longuet-Higgins, *ibid.*, 1951, **209,** 28.

arithmetic mean of ε_{ii} and ε_{jj}. Probably solutions of spherical molecules never show negative deviations.

This approach to the theory of liquid solutions is limited by two restrictions. It is not accurate if the ratios of the three energies and distances are not close to unity and, of course, it is not applicable if the three potentials cannot be put in the form of equation (5). In practice, the last restriction means that none of the potentials must depend appreciably on orientation. Unfortunately the majority of solutions fall into one or both of these excepted classes, even if the extreme case of polymer solutions is excluded. At present, theories of such solutions are based upon cell models of the liquid state.[72, 73] Their qualitative success is considerable, but quantitatively these theories can be no better than the corresponding theory of pure liquids.[74] The most striking effect of dissimilar energies and strong orientational forces is the incomplete miscibility of some liquids. Two liquids may be immiscible over the whole liquid range from melting point to critical point, or they may show one or two critical solution points. Upper critical temperatures, above which the liquids are completely miscible, are more common than lower critical temperatures. A few systems, of which nicotine–water is the classical example, show both. It appears that the causes of the two critical points are quite different. An upper critical point can occur even with spherical molecules if the ratio $(2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj})/\boldsymbol{k}\boldsymbol{T}$ is large and negative, that is, when the *ii* and *jj* interactions are favoured and when the thermal agitation is only just great enough to keep the mixture homogeneous. At lower temperatures, there is separation into two phases. Almost every mixture of a hydrocarbon and a fluorocarbon shows an upper critical temperature, and in two cases it has been confirmed that ε_{ij} is unusually small by indirect measurements of the heats of mixing.[75] An upper critical temperature is often shown by a mixture of one polar and one non-polar substance, for example, the system aniline–*cyclo*hexane. Lower critical temperatures are rare and apparently occur only when the *ij* interaction can form a hydrogen bond, which is a particularly strong force and one that varies rapidly with changing orientations. Theory indicates that mixtures of spherical molecules cannot show a lower critical point.[72c, 76] The *ij* hydrogen bond leads to a loss of rotational entropy [77] which allows the liquids to mix only if the temperature is low enough for the bond to be stable ; the energy change can then compensate for the loss of entropy.

The non-equilibrium properties of a liquid mixture are little understood, but those of a gas mixture are quite tractable. The viscosity of the mixture,

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[72] (*a*) Guggenheim, "Mixtures", Oxford Univ. Press, 1952. (*b*) Prigogine and Mathot, *J. Chem. Phys.*, 1952, **20,** 49. (*c*) Rowlinson, *Proc. Roy. Soc.*, 1952, *A*, **214,** 192.

[73] Munster, *Trans. Faraday Soc.*, 1950, **46,** 165 ; Barker, *J. Chem. Phys.*, 1952, **20,** 794, 1526 ; Tompa, *ibid.*, 1953, **21,** 250.

[74] Rowlinson, ref. 66(*b*).

[75] Simons and Dunlap, *J. Chem. Phys.*, 1950, **18,** 335 ; Simons and Mausteller, *ibid.*, 1952, **20,** 1516.

[76] Prigogine, ref. 21 ; Bellemans, ref. 66(*b*).

[77] Copp and Everett ; Barker and Fock, ref. 66(*b*).

like most of the equilibrium properties, depends upon all three kinds of interaction and so does not give directly the size of the *ij* parameters.[48] However, if the molecules are similar in energy, size, and mass then the variation of the viscosity with composition shows immediately [46] the deviations from the empirical equations (15) and (16). Binary mixtures chosen from N_2, O_2, NO, and CO conform closely to these equations.

The rate of diffusion of one gas into another is a more useful property as it depends, to a very good approximation, only on the *ij* forces and not on the *ii* or the *jj*. Diffusion coefficients are difficult to measure accurately but, as more measurements are made over an adequate range of temperature, will probably become the most useful way of measuring the *ij* forces.[48] Direct tests of equation (15) and (16) may be made by comparing these coefficients with the coefficients of self-diffusion, found by using isotopic tracers.[46, 78]

A temperature gradient in a gas mixture causes some separation which is measured by the coefficients of thermal diffusion.[79] There is no simple explanation of this separation. It was not detected experimentally until after its prediction on purely theoretical grounds by Chapman and Enskog.[43] However, many experimental investigations have now been made, especially since, in 1938, Clusius and Dickel [80] showed that thermal diffusion, when combined with convection, provided one of the most rapid ways of separating isotopes. These coefficients are much more sensitive than the other transport properties to small changes in the shape of the intermolecular energy curves, and so provide a severe test for any molecular model. However, like ordinary diffusion coefficients, they are hard to measure accurately, and all that can be said at present is that the energy of equation (3) is the most successful that has yet been tried.[79] Calculations of these coefficients for an energy with an exponential repulsion are now being made.[81]

Solid solutions have not been discussed in this section. It is rare to find two solids, other than metals, which are at all miscible. The high degree of order and the rigidity of a crystal lattice will allow the replacement of a molecule of one species by one of another only if their potential energy curves are almost identical. Moreover, even when a solid solution is formed it is difficult to be sure that it is homogeneous and at equilibrium, and so thermodynamic measurements are hard to make. However, one system in which the solid state plays a part has recently aroused some interest. This is the equilibrium between a pure solid, its vapour, and an added gas. The effect of the added gas on the apparent vapour pressure of the solid may be expressed in terms of certain of the virial coefficients. The first term is B_{ij}, the second coefficient for the interaction in the gas phase of one molecule from the solid and one of the added gas. Measurements of this coefficient thus provide a second way of measuring directly the effects of the *ij* forces.[82]

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[78] Amdur, Irvine, Mason, and Ross, *J. Chem. Phys.*, 1952, **20**, 436.

[79] Grew and Ibbs, "Thermal Diffusion in Gases", Cambridge Univ. Press, 1952.

[80] *Naturwiss.*, 1938, **26**, 546.

[81] Hirschfelder, personal communication.

[82] Robin and Vodar; Ewald, Jepson, and Rowlinson, ref. 66(*b*).

Again equations (15) and (16) are found to be approximately true, even for such dissimilar molecules as ethylene and naphthalene.

Conclusion

The object of a molecular theory of the physical properties of matter is to give exactly the relations between these properties and intermolecular forces. At present this can only be done for the two extreme cases of gases at low densities and solids at low temperatures—the limits of complete disorder and complete order. Experimental knowledge of intermolecular forces is derived from observations of these extreme cases, and even here the interpretation of the results is difficult for all but monatomic systems. Our understanding of intermediate cases, and in particular of the liquid state, is not yet far enough advanced for the direct interpretation of the properties in terms of the intermolecular forces. However, many less complete correlations, which give some information about these forces, have been based upon secure statistical foundations. Probably the most useful of these are the principle of corresponding states, its recent extension to mixtures, and attempts to relate deviations from this principle to the intermolecular forces.

It is doubtful if much more progress will be made in the direct interpretation of the behaviour of monatomic systems until there is an exact statistical treatment of the liquid phase. More rapid progress can reasonably be expected in bringing the interpretation of polyatomic systems up to the standard of that of monatomic systems.

I wish to thank Imperial Chemical Industries for a Research Fellowship, during the tenure of which this review has been written.

Appendix

The " collision diameter " of a molecule is a distance often used to calculate collision rates in a gas by those working on the kinetics of reactions. The values used are generally derived from the viscosities of the gases by means of an inaccurate equation and by assuming that the molecules are rigid spheres. In most cases these approximations do not matter much as little more than the orders of magnitude of the collision rates are needed. However, it is probably worth while tabulating some collision diameters so that these calculations can be improved.

The viscosity of a gas is a function of the average deflections of two colliding molecules [see equation (13)]. There is no simple relation between this quantity and the size of the molecules. A more useful measure of size in chemical kinetics would be a collision diameter which, when used in the usual equations, would give the number of collisions in which the centres of the molecules approached nearer than some given distance. The distance of approach will probably be a more important factor than the angle of deflection in governing the rate of reaction. Fortunately one such diameter can be given at once for molecules with central force-fields, the diameter which is denoted σ in equation (3). Fig. 2 shows that the centres of two molecules which collide head-on approach to a distance of σ or less, according to their kinetic energy. It can be proved more generally that all occasions in which the initial separation of the lines of centres of two approaching spherical molecules is less than σ result in collisions in which the centres approach closer than σ, and *vice versa.* Hence if σ is used in the usual expressions for the collision rates of rigid spheres there will be obtained the number of collisions in which the centres approach to less than this distance. For collisions between two molecules of different species the arithmetic mean diameter of equation (15) is recommended.

This diameter may be found from the second virial coefficient, from the viscosity [by fitting the experimental results to equation (13) with the appropriate values of the angles of deflection], or less exactly from the critical volumes by using equation (11) or equation (14). The last method is used only when the virial coefficient and the viscosity are not known over a wide enough range of temperature. The diameters in the first group in the Table below are mean values from the virial coefficients and the viscosities. For interest, values of ε/k are also given. Quantal corrections to equations (9) and (13) have been made for helium and hydrogen. The diameters in the second group are calculated from the critical volume by using the mean of equations (11) and (14), and the volumes recommended by Kobe and Lynn.[83] The molecules in this group are far from spherical and the significance of σ is doubtful. However, it must be an average over all orientations and should give collision rates which are of the correct relative sizes. The values of σ are not very sensitive to the assumed form of the intermolecular energy. Strongly polar compounds cannot be included in these lists.

Group 1

Helium (2·56 Å, 10·2° K), Neon (2·78 Å, 44·5° K), Argon (3·42 Å, 120° K), Krypton (3·61 Å, 165° K), Xenon (4·0 Å, 220° K), Hydrogen (2·93 Å, 37° K), Nitrogen (3·68 Å, 95° K), Oxygen (3·44 Å, 118° K), Methane (3·85 Å, 150° K), Carbon tetrafluoride (4·70 Å, 153° K).

Group 2

Carbon monoxide (3·66 Å), Carbon dioxide (3·73 Å), Nitrous oxide (3·74 Å), Ethane (4·30 Å), Ethylene (4·05 Å), Acetylene (3·92 Å), Propane (4·75 Å), Propylene (4·59 Å), *cyclo*Propane (5·15 Å), *n*-Butane (5·18 Å), *iso*Butane (5·20 Å), *n*-Pentane (5·50 Å), *iso*Pentane (5·48 Å), *neo*Pentane (5·45 Å), *n*-Hexane (5·82 Å), *cyclo*Hexane (5·50 Å), *n*-Heptane (6·11 Å), *n*-Octane (6·40 Å), Benzene (5·28 Å), Toluene (5·55 Å), Methyl ether (4·67 Å), Ethyl ether (5·33 Å), Chloroform (5·05 Å), Carbon tetrachloride (5·28 Å), Chlorobenzene (5·48 Å), Carbon disulphide (4·50 Å).

The equivalent diameter of two colliding hydrogen atoms ($^3\Sigma$ state) is shown by quantal calculations [12] to be 3·97 Å. This great size is due to the unusually weak dispersion forces.

The diameters in this Table are smaller than most of those commonly used in work on chemical kinetics. The latter probably correspond more closely with the equilibrium separations, that is, with the minimum of the

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[83] Kobe and Lynn, *Chem. Reviews*, 1953, **52**, 117.

energy curve in Fig. 3. These are about 12% greater than σ ; for example, the potential of equation (3) would give for the minimum, ethylene 4·6 and benzene 5·9 Å. Probably the diameter σ is the more suitable of the two. The use of equilibrium diameters in the expression for the collision rate does not give the number of molecules which approach closer than the equilibrium separation. This is a property peculiar to the distance σ.

The correct way of calculating rates of diffusion from these diameters and the corresponding energies is given in the publications of Hirschfelder and his associates.[6, 48]