TRANSPORT PROPERTIES OF LIQUIDS IN RELATION TO THEIR STRUCTURE

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The subject of transport properties of gases is now comparatively well understood and a general theory is available[1] which can be used with reasonable success to predict these properties for simple gases. For liquids, however, no comparable success has yet been achieved. The present Review considers the state of the theory of transport properties for simple liquid systems and how molecular structure influences these properties for more complex systems. High polymers, their solutions, and electrolytes are not discussed.

1. Origin and sign of the transport coefficients

(a) **Origin of the Transport Phenomena.**—In the approach to equilibrium of a system perturbed by the influence of a concentration, velocity, or temperature gradient, the perturbing influence of the gradient tends to be eliminated by an irreversible flux or flow of molecular properties down the gradient. The flux of mass down a concentration gradient gives rise to the phenomenon of diffusion, the flux of momentum down a velocity gradient to viscosity, and the flux of heat down a temperature gradient to thermal conductivity. Empirical relationships between the fluxes and the forces causing them were proposed by Fick, Newton, and Fourier and are given by the equations

$$J = -D\partial c/\partial x, \quad p' = -\eta \partial v/\partial x, \quad Q = -\lambda \partial T/\partial x \quad . \quad . \quad . \quad (1)$$

The proportionality constants D, η, and λ between the forces or gradients and fluxes are called, respectively, the coefficients of diffusion, viscosity, and thermal conductivity, and $\partial c/\partial x$, $\partial v/\partial x$, and $\partial T/\partial x$ the corresponding gradients in concentration, velocity, and temperature. J, p', and Q are the fluxes of mass momentum and energy per unit time per unit area.

In addition to the direct effects, various "cross-effects" exist in mixtures. Thus mass flow can arise from a temperature gradient and heat flow from a concentration gradient so that additional terms proportional to these gradients must be added to equation (1) where appropriate.

(b) **The Sign of the Transport Coefficients.**—Further general information on the transport coefficients can be obtained from irreversible thermodynamics which provides the framework for non-equilibrium systems corresponding to that which equilibrium thermodynamics provides for a study of equilibrium properties. It therefore shows which results of transport theory are of general validity and independent of assumptions

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[1] Chapman and Cowling, "The Mathematical Theory of Non-uniform Gases," C.U.P., 1939.

about molecular mechanisms or interactions. For the present, attention will be restricted to determining the sign of the transport coefficients.

For an arbitrary change of a system in time dt, the rate of change of entropy can be written as a sum of two terms

$$\mathrm{d}S/\mathrm{d}t = \mathrm{d}_eS/\mathrm{d}t + \mathrm{d}_iS/\mathrm{d}t \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

where d_eS represents the entropy change from external sources and d_iS that from irreversible processes inside the system. This internal entropy production is zero at equilibrium when all gradients in molecular properties have been eliminated, is positive for all other cases, and its rate can be calculated from the fundamental laws of macrophysics. It turns out that the entropy production is a sum of products of fluxes J_i and forces X_i of the form

$$T.\,\mathrm{d}_iS/\mathrm{d}t = \sum_i J_i\, X_i > 0 \quad . \; . \; . \; . \; . \; . \quad (3)$$

which was originally proposed by Onsager.[2] In addition the laws of Newton, Fick, and Fourier suggest linear relationships, at any rate near equilibrium, between the fluxes and forces, called phenomenological equations, which can be generalised in the form

$$J_i = \sum_{k=1}^{n} L_{ik}X_k \; (i = 1, 2, \cdots n) \quad . \; . \; . \; . \; . \quad (4)$$

Where L_{ik} is the phenomenological coefficient. To determine the sign of the transport coefficients the case of two simultaneous irreversible processes can then be considered[3] which may be written according to equation (4) as

$$J_1 = L_{11}X_1 + L_{12}X_2; \;\; J_2 = L_{21}X_1 + L_{22}X_2 \quad . \; . \quad (5)$$

The phenomenological coefficients L_{11} and L_{22} are, for example, related to the coefficients of thermal conductivity and diffusion, and the coefficient $L_{21} = L_{12}$ to the thermal diffusion coefficient. The equivalence of L_{12} and L_{21}, called the reciprocal relations, was proved by Onsager. Combining equations (5) and (3), we have

$$T.\mathrm{d}_iS/\mathrm{d}t = L_{11}X_1{}^2 + (L_{21} + L_{12})X_1X_2 + L_{22}X_2{}^2 > 0 \; . \; . \quad (6)$$

which from the theory of quadratics requires $L_{11}>0$, $L_{22}>0$, $(L_{12} + L_{21})^2 < 4L_{11}L_{22}$. In physical terms this means that the direct transport coefficients, *e.g.*, thermal conductivity and diffusion, are positive whereas the cross-term interference coefficients can be of either sign.

Irreversible thermodynamics does not, however, enable numerical values of the transport coefficients to be calculated. For this purpose statistical theories must be used.

[2] Onsager, *Phys. Review*, 1931, **37**, 405; 1931, **38**, 2265.

[3] Prigogine, "Thermodynamics of Irreversible Processes," Thomas, Springfield, 1955.

2. Statistical theories of transport phenomena

Ideally, calculation of the transport properties of liquids requires a knowledge of: (1) liquid structure, (2) molecular mechanism of the transport process, (3) molecular shape, and (4) molecular force fields. In practice, little of this information is available, so that highly simplified models are generally considered. These can be divided into two broad groups, dense-gas theories and lattice theories, depending on the model of the liquid state assumed.

(a) **Dense-gas Theories.**—In this approach, due to Kirkwood, Born, and Green, and Eisenschitz, an attempt is made to derive expressions for the transport coefficients based on the use of a non-equilibrium distribution function. These theories, which have been recently reviewed,[4] are still in course of development but have as yet yielded little numerical information. It is to be hoped that they will ultimately provide for liquids the corresponding framework that the Chapman–Enskog theory provided for the transport properties of dilute gases. Two additional theories which are also based on the dense-gas approach are due to Enskog[1] and Longuet-Higgins and his co-workers.[5]

(i) *Enskog's theory.* In the kinetic theory of dilute gases the transport of mass momentum and energy is considered to be due to the motion of the molecules between collisions (convective contribution). Compression of the gas increases the collision frequency by a factor χ which Enskog related to the compressibility by the equation

$$(PV/RT - 1) = y = b_0\chi/V = b\rho\chi \quad . \quad . \quad . \quad . \quad (7)$$

where $b_0 = \frac{2}{3}\pi N\sigma^3 = Mb$ is the second virial coefficient, σ the rigid sphere diameter, and M the molecular weight. In addition, compression increases the importance of the collisional contribution to the transfer of energy and momentum when these quantities are transported over the distance separating the colliding molecules at contact during the instantaneous collision. This collisional mechanism cannot affect the diffusion coefficient, which is always controlled by a convective mechanism but affects profoundly the transfer of momentum and heat.

With these assumptions Enskog, using an extension of the dilute-gas treatment, derived the transport coefficients in terms of the corresponding dilute-gas coefficients η_0, λ_0, and D_0 to which they reduce in the low density limit as

$$\eta V/\eta_0 b_0 = 1/y + 0{\cdot}8 + 0{\cdot}7614\,y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$
$$\lambda V/\lambda_0 b_0 = 1/y + 1{\cdot}2 + 0{\cdot}7574\,y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$
$$D_{11} V/D_0 b_0 = 1/y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

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[4] Cole, *Rep. Prog. Physics.*, 1956, **19**, 1.

[5] Longuet-Higgins and Pople, *J. Chem. Phys.*, 1956, **25**, 884; Longuet-Higgins and Valleau, *Mol. Phys.*, 1958, **1**, 284; Valleau, *ibid.*, p. 63.

Equations (8) and (9) show that η/ρ and λ/ρ plotted as a function of the density ρ pass through minima at $y = 1{\cdot}146$ and $1{\cdot}151$, respectively, with values

$$[\eta/\rho]_{\mathrm{min.}} = b\eta_0 2{\cdot}545,\ [\lambda/\rho]_{\mathrm{min.}} = b\lambda_0 2{\cdot}938 \quad . \quad . \quad . \quad (11)$$

Fig. 1(*a*) gives theoretical curves for a rigid-sphere gas, and Fig. 1(*b*) experimental results for carbon dioxide[6] for which all three coefficients have been measured. The changing mechanism in heat and momentum transfer causes the thermal conductivity and viscosity curves to pass through minima, while in self-diffusion, where no change in mechanism can take place, the curve falls continuously with increasing compression. The small region in the centre of the thermal conductivity curve for carbon dioxide is anomalous (see p. 251) and thermal conductivity data for other dense gases away from the critical region exhibit smooth minima.

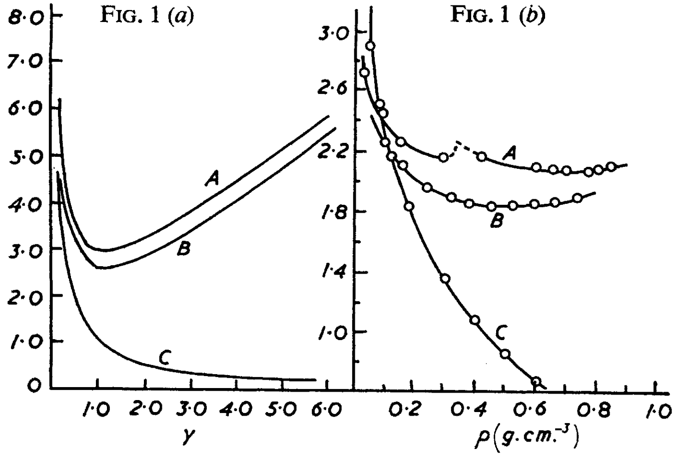

FIG. 1. *Theoretical and experimental curves on the Enskog theory.*
1 (*a*) Ordinate: curve *A*, reduced thermal conductivity $\lambda v/\lambda_0 b_0$;
curve *B*, reduced viscosity $\eta v/\eta_0 b_0$;
curve *C*, reduced self-diffusion coefficient $D_{11}V/D_0 b_0$.
(Copied substantially from Hirschfelder, Curtiss, and Bird, "Molecular Theory of Gases and Liquids," Wiley, N.Y., 1954.)
1 (*b*) Ordinate: curve *A*, log $(\lambda/\rho) \times 10^{-2}$ (erg cm.$^{-4}$ g.$^{-1}$ sec.$^{-1}$ °c^{-1});
curve *B*, log $(\eta/\rho) \times 10^{5}$ (cm.^{2} sec.$^{-1}$);
curve *C*, log $(D_{11}/\rho) \times 10^{4}$ (cm.^{5} g.$^{-1}$ sec.$^{-1}$).

To apply equations (8), (9), and (10) to calculating the transport properties of real gases, Enskog suggested that the effects of molecular shape and force field could be taken into account empirically by fitting *b* in equation (11) to the experimental minima and replacing the pressure *P*

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[6] Robb and Drickamer, *J. Chem. Phys.*, 1951, **19**, 1504; Lenoir and Comings, *Chem. Eng. Prog.*, 1951, **47**, 223; Warburg and Von Babo, *Wiedemann's Annalen*, 1882, **17**, 390.

$$P = T(\partial P/\partial T)_V - (\partial U/\partial V)_T \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

as defined in thermodynamics, where U is the internal energy by the kinetic pressure, as $(\partial U/\partial V)_T$ is zero for a rigid-sphere gas. Such methods reproduce the experimental curves satisfactorily.

(ii) *Theories of Longuet-Higgins, Pople, and Valleau.* Longuet-Higgins and Pople[5] also considered the collisional contribution to viscosity and thermal conductivity in a dense gas of rigid spheres and derived the expressions

$$\eta = \frac{2\sigma}{5}\left(\frac{mkT}{\pi}\right)^{\frac{1}{2}}\left(\frac{P}{kT} - \frac{N}{V}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\lambda = \sigma k\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}}\left(\frac{P}{kT} - \frac{N}{V}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which neglect the convective contribution included by Enskog. The expression for the self-diffusion coefficient D_{11},

$$D_{11} = \frac{\sigma}{4}\left(\frac{\pi kT}{m}\right)^{\frac{1}{2}}\left(\frac{PV}{RT} - 1\right)^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

was derived starting from the random-walk diffusion equation $D_{11} = \langle r^2 \rangle / 6t$ where r is the distance travelled by a molecule in a time t long compared with the time between collisions. As the mechanism of diffusion is purely convective, equation (15) reduces to the dilute-gas expression, for a gas of rigid spheres, in the low-density limit while (13) and (14) which neglect the convective contribution do not.

Longuet-Higgins and Valleau[5] extended the method to a system of molecules interacting with a square-well potential, and Valleau[5] to rough spherical molecules which permit rotational-energy exchange on collision. On the latter theory λ is twice the smooth rigid-sphere value and the viscosity equation contains an additional rotational term. This rotational viscosity does not attain values greater than about half the shear viscosity and vanishes for small moments of inertia, *i.e.*, it can only be important for large molecules.

(iii) *Comparison of dense gas theories.* The main achievement of the Enskog theory is the prediction of the minima in the viscosity and thermal conductivity curves (Fig. 1). The models, although indicating the general behaviour of the transport coefficients, are not correct in detail. For example, the thermal conductivity of simple liquids generally has a less steep temperature dependence than viscosity, whereas both theoretical approaches predict the same temperature dependence for each coefficient.

As the absolute expressions could not give good agreement with experiment owing to neglect of the attractive forces, transport coefficient ratios would be expected to be in better agreement with experimentally determined ratios. On the Enskog basis the dimensionless quantity $m\lambda/k\eta$ equals 3·75, neglecting the ratio of the quadratic terms, while on the Longuet-Higgins and Pople theory this ratio is 2·5. Table 1 shows some

TABLE 1. *Comparison between experimental and calculated values of the transport coefficients of simple liquids.**

		Viscosity ($\eta \times 10^3$, poise)			Thermal conductivity ($\lambda \times 10^{-3}$, erg cm.$^{-1}$sec.$^{-1}$°C^{-1})				Self-diffusion ($D_{11} \times 10^5$, cm.^{2}sec.$^{-1}$)		
Liquid	Temp. (°K)	Exp.	E	McL	Exp.	B	H and McL	Exp. ratio of $m\lambda/k\eta$	Exp.	E	McL
Benzene	288·2	6·98	10·69	7·16	14·94	20·11	12·26	2·016	1·88	3·10	1·61
	298·2	6·01	7·86	6·13	14·63	19·26	11·71	2·28	2·15	3·80	1·95
	308·2	5·24	6·05	5·30	14·24	18·43	11·24	2·55	2·40	4·54	2·33
	318·2	4·62	4·84	4·60	13·89	17·56	10·78	2·83	2·67	5·24	2·76
Carbon tetrachloride	298·2	9·00	5·65	7·45	10·64	12·90	10·18	2·19	1·41	2·97	1·49
	308·2	8·03	4·36	6·38	10·51	12·37	9·77	2·42	1·75	3·48	1·81
	318·2	6·90	3·43	5·53	10·39	11·85	9·42	2·78	1·99	4·13	2·15
Argon	84·2	2·80	4·54	3·17	12·60	27·77	9·92	2·16	2·07	3·07	1·69
	87·3	2·52	3·89	2·75	12·16	26·71	9·28	2·31			
Nitrogen	69·1	2·31	5·12	2·01	15·11	27·33	10·28	2·20			
	71·4	2·09	4·19	1·79	14·80	26·40	9·77	2·39			
	77·3	1·58	2·64	1·40	13·96	23·94	8·49	2·98			
Carbon monoxide	72·0	2·44	4·39	2·35	15·89	—	7·70	2·19			
	77·7	1·92	3·09	1·82	15·05	—	6·59	2·64			
	80·8	1·71	2·71	1·61	14·21	—	5·96	2·80			
Methane	93·2	1·88	5·55	2·88	21·53	42·50	17·24	2·21			
	103·2	1·42	3·56	1·99	20·27	39·68	15·27	2·75			
	108·2	1·27	2·92	1·70	19·64	38·77	14·36	2·98			

This Table is taken from refs. 13 and 14. Gaps indicate absence of experimental data.

* E, Eyring; McL, McLaughlin; B, Bridgman; H, Horrocks.

experimental values of this ratio which are in better agreement with the latter value, but as both theories give η and λ the same temperature dependence neither predicts the temperature dependence of the ratio.

(b) **Quasi-crystalline Models.**—In the many theories proposed based on the quasi-crystalline model of a liquid, attention has generally been directed to deriving an equation for the transport process based on an assumed molecular mechanism, leaving as disposable parameters in the final equations terms dependent on the molecular force field and the liquid quasi-lattice geometry. In tests of these theories empirical methods are used to estimate unknown parameters. Of these theories that due to Eyring[7] has been most widely used for viscosity and diffusion, and that of Bridgman[8] for thermal conductivity. Andrade's theory[9] of viscosity is usually applied to metals at their melting point.

(i) *Bridgman's theory of thermal conductivity.* Bridgman assumed that in a liquid subjected to a temperature gradient the energy difference between successive molecules in adjacent layers was transmitted with the velocity of sound, and derived the equation

$$\lambda = 3kU_s\,(N/V)^{\frac{2}{3}} \qquad \ldots\ldots\ldots \quad (16)$$

As no specific molecular force field or lattice geometry was assumed for the liquid, the energy difference between successive layers was taken as $3ka.\mathrm{d}T/\mathrm{d}x$ using the theorem of equipartition, and a the intermolecular distance was approximated to by $(V/N)^{\frac{1}{3}}$

Experimental and calculated values as given in Table 1 agree within about 35%. This expression was subsequently modified by Kincaid and Eyring,[10] using the Eucken factor to take account of the role of the internal degrees of freedom, and good agreement with experimental data was obtained for a series of polar molecules.

(ii) *Andrade's theory.* In 1934 Andrade derived the expression

$$\eta = 4\nu m/3a \qquad \ldots\ldots\ldots \quad (17)$$

for the viscosity of a liquid on the basis of a vibrational mechanism for the transfer of momentum. As in Bridgman's theory, no specific assumptions regarding geometry of the liquid quasi-lattice or molecular force fields were made, so that ν, the vibrational frequency, and a have to be estimated empirically. For metals it was assumed that ν could be taken from the Lindemann formula which relates it to the melting point, atomic weight M, and atomic volume V, so that equation (17) can be rewritten

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

[8] Bridgman, "The Physics of High Pressure," Bell, London, 1931.

[9] Andrade, *Phil. Mag.*, 1934, **17**, 497.

[10] Kincaid and Eyring, *J. Chem. Phys.*, 1938, **6**, 620.

$$\eta = \frac{4C}{3N^{\frac{2}{3}}} \cdot \frac{(MT_f)^{\frac{1}{2}}}{V^{\frac{2}{3}}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

where $C = 3{\cdot}1 \times 10^{12}$ is the constant of the Lindemann formula. As in Bridgman's theory, a was taken as $(V/N)^{\frac{1}{3}}$. Calculated and experimental values of the viscosities which are within about 6% are given in Table 2 for some metals. However, recent experimental work on the viscosities of metals close to the melting point shows that the viscosity rises to anomalously large values that do not agree with values extrapolated from higher temperatures. For example, Yao and Kondic[11] find a value for tin of 0·0271 poise at the melting point, compared with a value extrapolated from high-temperature data of 0·019 poise which compares favourably with the calculated value in Table 2. This suggests that the vibrational picture neglects other factors which can operate under certain conditions (see p. 249).

TABLE 2. *Viscosities of liquids on Andrade's theory.*

	Metals at T_f		Organic molecules at 25°		
Metal	$\eta \times 10^3$ (poise) (exp.)	$\eta \times 10^3$ (poise) (calc.)	Organic liquid	$\eta \times 10^3$ (poise) (exp.)	$\eta \times 10^3$ (poise) (calc.)
Lithium	6·02	5·62	n-Pentane	2·24	2·60
Sodium	6·95	6·23	Isopentane	2·14	2·34
Potassium	5·37	4·99	n-Hexane	2·98	3·64
Rubidium	6·74	6·20	n-Heptane	3·96	4·79
Cæsium	6·86	6·57	Cyclopentane	4·15	3·31
Copper	40·5	41·8	Benzene	6·01	4·18
Silver	38·8	40·7			
Gold	53·6	57·6			
Indium	19·4	20·1			
Tin	21·4	21·3			

Experimental and calculated viscosities of metals from E. N. da C. Andrade, *Proc. Roy. Soc.*, 1952, *A*, **215**, 36. Experimental viscosities of hydrocarbons from A.P.I. Project 44, 1948-52.

Justification for using solid-state vibration frequencies for liquid metals at the melting point lies in the small volume and heat capacity changes on fusion; however, alternative methods of evaluating the vibrational frequency in the liquid state may be used to evaluate η from equation (17). Table 2 includes values at 25° for the viscosities of some hydrocarbons which were calculated by using vibrational frequencies in the liquid determined by Barrer[12] from entropy considerations. In this case agreement

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[11] Yao and Kondic, *J. Inst. Metals*, 1952, **81**, 17.

[12] Barrer, *Proc. Chem. Soc.*, 1957, 143.

is within about 20%. Calculation of the temperature dependence of viscosity on a vibrational mechanism, however, gives too small a temperature coefficient.

(iii) *The theory of Eyring.* In this treatment a liquid is considered as a quasi-crystalline lattice with a number of holes. The transport process is assumed to be due to movement of a molecule from one lattice site to a neighbouring vacancy in its own layer. The jump process can then be treated by rate-theory methods and the resulting equations for η and D_{11} are given by

$$\eta = \frac{a_2}{a_1{}^2 a_3 a_4} (2\pi mkT)^{\frac{1}{2}} v_f{}^{\frac{1}{3}} \exp (e_0/kT) \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and

$$D_{11} = \frac{a_1{}^2}{v_f{}^{\frac{1}{3}}} \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \exp (-e^1{}_0/kT) \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The quantities a_1, a_2, a_3, and a_4 are distances within and between the planes of molecules in the liquid, v_f is the free volume which is related to the fraction of free space in the liquid, and e_0 and $e^1{}_0$ are activation energies per molecule for molecular movement. In the derivation of equation (19) it is shown that η depends on the applied shearing force; *i.e.*, the flow in general is non-Newtonian; however, for small shearing forces the approximation given by equation (19) is obtained. Equation (20) for the self-diffusion coefficient is derived as the limiting case of mutual diffusion in a binary mixture.

Again owing to lack of specific assumptions about the nature of the intermolecular forces and lattice structure, e_0, $e^1{}_0$, v_f, and the various a's which depend on them have to be estimated empirically. By assuming the usual relationship for a, taking e_0 and $e^1{}_0$ as fixed fractions of the heat of vaporisation of the liquid, and calculating free volumes from an approximate relationship with the sonic velocity, η and D_{11} have been calculated for a series of simple liquids. The results are given in Table 1, and although the agreement is not very precise this theory, in one of its more empirical forms, can be used to estimate η within about 100% for the majority of liquids.

(iv) *Theories involving assumed molecular force fields and lattice geometry.* In a recent attempt[13] to calculate the coefficients η and D_{11} for simple liquids, two assumptions were made initially about the structure of the liquid quasi-lattice and the molecular force field to avoid empirical determination of quantities dependent on these parameters in the final equations for the transport coefficients. The lattice was assumed to be face-centred cubic, so that relationships between intermolecular distances in the liquids are known, and the intermolecular interaction was represented by a Lennard-Jones 12:6 potential, enabling molecular diameters σ and

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[13] McLaughlin, *Trans. Faraday Soc.*, 1959, **55**, 28.

force contants ϵ/k to be obtained from the transport properties of the molecules in the gas phase.

Diffusion in the liquid was considered due to a convective or hopping mechanism governed by the presence of nearest-neighbour holes. The derived equation for D_{11} may be written

$$D_{11} = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{a^2}{v_f^{\frac{1}{3}}} \frac{n_h}{N} \exp\left(-\Phi_0/3NkT\right) \quad . \; . \; . \; . \; . \quad (21)$$

The fraction of holes n_h/N, free volume v_f, intermolecular distance a, and lattice energy Φ_0 were then calculated from the Lennard-Jones and Devonshire theory of liquids and require only a knowledge of ϵ/k, σ, and ρ. The coefficient of viscosity η was then obtained by using the modified Stokes–Einstein expression $\eta = kT/2\pi\sigma D$ (see p. 246). Calculated and experimental values for a series of simple molecules which conform approximately to the Lennard-Jones 12:6 potential are given in Table 2 and agree with experimental values within about 10%.

The coefficient of thermal conductivity of a similar liquid was calculated[14] as the sum of two independent contributions, one vibrational and the other convective. The frequency of convective movement was assumed to be the same as that operative in self-diffusion, and the frequency for vibrational transfer ν that given by Corner for an assembly of spherical molecules interacting with a Lennard-Jones 12:6 potential. Calculation of the separate contributions showed the convective term to be small ($\frac{1}{2}$% of the experimental value for argon at its boiling point). The values given in Table 1 are therefore purely vibrational $\lambda_{\text{vib.}}$ and are calculated from the equation

$$\lambda \simeq \lambda_{\text{vib.}} = \left[\frac{\epsilon}{\pi^2 r_0^{\,2} m}\left\{11C_{14}\left(\frac{r_0}{a}\right)^{14} - 5C_8\left(\frac{r_0}{a}\right)^{8}\right\}\right]^{\frac{1}{2}} C_v\sqrt{2}(1-n_h/N)/a \quad (22)$$

where C_v is the specific heat per molecule and n_h/N is the fraction of holes which is small compared with unity in the normal liquid range. C_{14} and C_8 are lattice summation constants and $r_0 = \sigma 2^{\frac{1}{6}}$. Agreement with experiment is within about 20%.

By way of summary it may be said that at present no completely satisfactory statistical theory of the transport properties of pure liquids exists. The condensed state can, like the gas phase, have only one mechanism of mass transport which is convective; however, heat and momentum could be transferred by convective, rotational, and vibrational mechanisms. Present indications suggest that heat is mainly transferred by a vibrational process but that momentum can be transferred by a variety of mechanisms dependent on the molecular type (see p. 251). As for the case of gases, little progress will be made without the introduction of specific molecular force fields as basic postulates.

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[14] Horrocks and McLaughlin, *Trans. Faraday Soc.*, 1960, 56, 206.

3. Relationships between the transport coefficients

As the transport coefficients are all concerned with the flux of molecular properties, it might be expected that they are interconnected by various relationships. Longuet-Higgins and Pople, as pointed out earlier, predicted the relationship $m\lambda/k\eta = 2{\cdot}5$, which, although it turns out experimentally to be dependent on temperature, is quite well obeyed for a series of simple liquids.

One of the most widely used relationships in the transport properties of liquids is the Stokes–Einstein expression $kT/D\pi r\eta = \text{const.}$, where r is the radius of a diffusing particle in a medium of viscosity η. When r is large compared with the size of the molecules in the medium (Brownian particle) the constant has its Stokes value of 6. For this case the inverse relationship between viscosity and diffusion has been derived by the methods of irreversible thermodynamics[15] and is therefore of general validity. However, for application to systems where r is comparable with the radii of the molecules of the medium, the Stokes equation does not hold. In this case a value of 4 for the constant is preferred but the relationship is then in practice found to be dependent on temperature and concentration The pressure dependence has recently been tested for liquid mercury by Nachtrieb and Petit.[16] If r is assumed independent of pressure, then at constant temperature $D_P/D_1 = \eta_1/\eta_P$ where the subscripts 1 and P refer to 1 kg.cm.$^{-2}$ and P kg. cm.$^{-2}$ pressure respectively. The good agreement between these quantities is illustrated below and shows that the relationship is not very sensitive to pressure.

P (kg. cm.$^{-2}$)	1	1950	3798	6079	8366
D_P/D_1	1	0·957	0·908	0·877	0·828
η_1/η_P	1	0·958	0·916	0·869	0·825

While viscosity and diffusion in metals do not exhibit exceptional behaviour compared with that in organic substances, thermal conductivity does. The problem of the anomalously large thermal conductivity of metals was largely solved by Lorentz[1] who attributed it to conduction due to free electrons. He derived expressions for the thermal (λ) and electrical (σ_e) conductivities which, although they could not be evaluated explicitly, give a simple ratio

$$\frac{\lambda}{\sigma_e T} = \frac{\pi^2 k^2}{3e^2} = 0{\cdot}245 \text{ erg ohm sec.}^{-1}\ {}^\circ\text{K}^{-1}\ {}^\circ\text{C}^{-1}$$

where e is the electronic charge. This equation implies that the ratio of the thermal to the electrical conductivity is the same for all metals at a given temperature and is directly proportional to the temperature. The constancy of this ratio was first discovered experimentally by Wiedemann and Franz and is confirmed by recent accurate data on a number of metals.

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[15] Onsager, *Ann. New York Acad. Sci.*, 1945, **46**, 241.

[16] Nachtrieb and Petit, *J Chem. Phys.*, 1956, **24**, 746.

Measurements of electrical resistance may therefore be used do determine thermal conductivities of metals which are difficult to measure.

While the bulk of the thermal conductance in metals is due to free electrons, it is of interest to examine the magnitude of the lattice contribution λ_v. This has been done below for a series, Bridgman's theory being used:

Metal	Na	Cd	Sn	Pb	Bi
λ_v/λ, experimental (%)	1·1	2·6	3·0	4·4	5·9
Electrical resistivity, μ (ohm. cm.)	10	33	48	95	128

The data show that the percentage contribution of lattice terms to the total thermal conductivity is greatest for the poorest electrical conductors, and lowest for the best, as would be expected. It is obvious that for the case of metals the ratio $m\lambda/\boldsymbol{k}\eta = 2{\cdot}5$ will not hold.

4. Temperature and pressure dependence of the transport coefficients

(a) **Temperature Dependence.**—In the gas phase the coefficients of viscosity, diffusion, and thermal conductivity increase with increase of temperature, but condensation to the liquid destroys this uniformity of behaviour. In a liquid the coefficient of diffusion increases with temperature, viscosity decreases, and thermal conductivity, although generally decreasing with increase of temperature, often increases for complicated structures. This diversity of behaviour in the liquid may be indicative of non-singularity in the transport mechanism. For diffusion alone where the same and only mechanism of convective motion is operative in any phase, does the temperature dependence have the same sign.

(i) *Simple molecules.* The experimentally determined temperature dependence of D and η of many simple liquids can often be best represented by equations of the form

$$\eta = \eta_k \exp E\eta/\boldsymbol{R}T; \quad D = D_k \exp(-E_D/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad (23)$$

where η_k and D_k are constants for a particular species and $E\eta$ and E_D are temperature-independent activation energies per mole for viscous flow and self-diffusion respectively. If the Stokes–Einstein ratio is independent of temperature, differentiation and use of eqn. (23) gives $E\eta + \boldsymbol{R}T = E_D$; but, while the difference is generally of this magnitude, $E\eta$ is often the greater. This derivation is not, however, strictly valid, as the Stokes–Einstein equation for small particles is temperature dependent.

If the molecular processes of mass and momentum transfer involve movement over a potential barrier and viscosity is independent of the applied shearing force, then barrier heights would be the same for each process and decrease with increase of temperature due to lattice expansion. Both η_k and D_k which also depend on lattice geometry should also be temperature dependent. These features are possible with the lattice model of 2(*b*)(iv). However, it shows that compensation between the preexponential factor and activation energy occurs which renders plots of log η and log D linear in $1/T$, in agreement with equation (23). This suggests that activation energies defined by equation (23) are not true activation energies for the molecular process but composite quantities.

(ii) *Complicated structures.* The transport coefficients of complicated molecules often do not follow the behaviour of simple systems. Equations such as (23) may, however, be used as a norm, and departures in behaviour from them analysed in terms of the system considered. For many polar liquids activation energies defined by equation (23) rise continuously as the temperature is lowered. This behaviour is generally attributed to association, with consequent increased size of units involved in molecular motion. Such a hypothesis can readily be tested[17] for closely related pairs of molecules like *o*-terphenyl and triphenylene.

Curve 2 in Fig. 2 illustrates the viscosity of *o*-terphenyl as a function of temperature, which obeys equation (23) at high temperatures only. The progressive increase in viscosity as the freezing point is approached and traversed into the supercooled region can be attributed to the non-planar shape which facilitates interlocking. Joining of the *ortho*-rings to make the planar triphenylene molecule should then remove the associative capacity and equation (23) should be obeyed. This is illustrated by curve 1 in Fig. 2

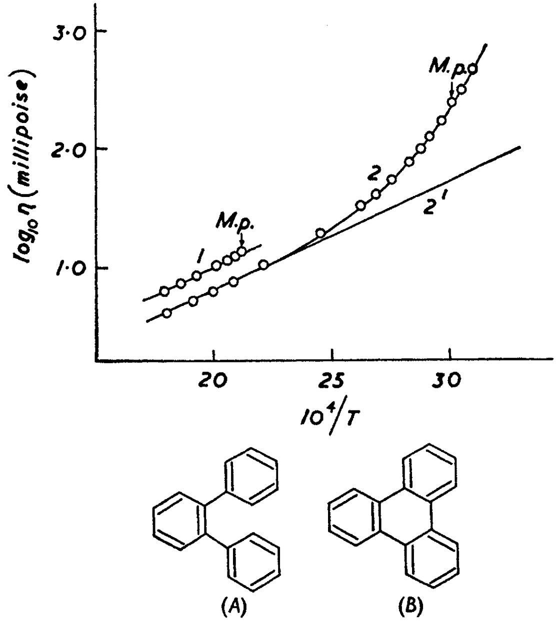

FIG. 2. *Viscosities of* o-*terphenyl* (*A*, *curves* 2 *and* 2′) *and triphenylene* (*B*, *curve* 1). (Copied from McLaughlin and Ubbelohde, *Trans. Faraday Soc.*, 1958, 54, 1804.)

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[17] McLaughlin and Ubbelohde, *Trans. Faraday Soc.*, 1958, **54**, 1804.

and confirms the mechanism of the associative process. As $E\eta$ at high temperatures for both molecules is the same, extrapolation of the high-temperature data for *o*-terphenyl to lower temperatures (curve 2′) permits the increase in viscosity at any temperature due to association to be evaluated as the difference between curves 2 and 2′. This excess viscosity has been analysed in terms of the fraction of liquid associated, the theory of the viscosity of suspensions being used, and provides a semi-quantitative picture of the origin of the excess viscosity.

Such comparative "chemical" methods can be extended to other systems and with other transport property measurements should provide further information on the origins of deviations from normal behaviour by complex systems.

(b) **Pressure Dependence of the Transport Properties.**—For liquids, the theories outlined in 2(*b*)(iii) and 2(*b*)(iv) indicate an exponential dependence of η and D on pressure at constant temperature owing to work done againt the external pressure in forming a hole which is a pre-requisite for convective molecular motion. For many simple liquids this type of behaviour is confirmed. Fig. 3 illustrates the fluidity ($1/\eta$) of argon as a function of temperature[18] for various constant densities. The small temperature coefficient compared with that at constant pressure tends to confirm the view that the viscosity of simple liquids is controlled mainly by the number of holes and does not change appreciably with temperature provided this number is kept constant.

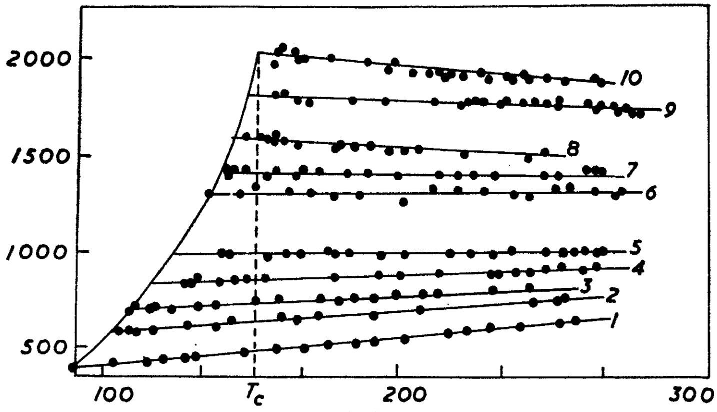

FIG. 3. *Fluidity of argon as a function of temperature at constant density.*
Densities (g. cm.$^{-3}$) are for curves: (1) 1·37, (2) 1·31, (3) 1·22, (4) 1·16, (5) 1·10, (6) 1·02, (7) 0·95, (8) 0·88, (9) 0·78, (10) 0·70.
(Copied substantially from Zhadanova, *Z. Exp. Theor. Phys. U.S.S.R.*, 1956, **31**, 724.)

The change of slope in Fig. 3 accompanies the gas-to-liquid transition which is dealt with successfully by the Enskog treatment. However, the

[18] Zhadanova, *J. Exp. Theor. Phys. U.S.S.R.*, 1956, **31**, 724.

Enskog expressions at high densities indicate that $\eta/\eta_0 \simeq \lambda/\lambda_0$, while experimental data show that the relative viscosity is greatest for the most complex molecules but the relative thermal conductivity is not sensitive to molecular type. For methyl and isopentyl alcohol[19] at 11,000 atm., η/η_0 is 9·95 and 895 respectively, whereas λ/λ_0 is 2·10 and 2·07. In addition, while the temperature coefficient of λ for simple liquids is negative, and for some more complicated liquids like water positive, the pressure coefficient, for all liquids so far examined, is positive, being greatest for the most compressible liquids. These results indicate that increasing pressure favours heat transfer by bringing the molecules closer together for vibrational exchange which is relatively insensitive to molecular type.

It is not necessary to distinguish between collisional and vibrational transfer mechanisms, as the largest portion of thermal energy transferred in a vibration is over the distance between molecular centres at collision which should be greater than the distance between molecular edges at the beginning of the vibration.

Sensitivity of viscosity and diffusion to pressure again brings out the close parallel in behaviour. This is to be expected since both processes involve the breaking off of the intermolecular forces. In diffusion this occurs as the molecule moves from site to site, and in viscosity as adjacent layers are moving with different hydrodynamic velocities under the influence of the applied shearing force, which necessitates continual breaking of the intermolecular attractions between molecules in the adjacent layers.

5. The principle of corresponding states

While statistical theories aim at calculating transport properties from molecular models, it is possible also to correlate behaviour by using the principle of corresponding states. On this basis any group of similar molecules should have the same values of reduced transport coefficients at corresponding temperatures and pressures.

For molecules interacting with central forces we can write[20]

$$\frac{D}{D^*} = \sigma\sqrt{\frac{\epsilon}{m}}, \quad \frac{\eta}{\eta^*} = \frac{\sqrt{m\epsilon}}{\sigma^2}, \quad \frac{\lambda}{\lambda^*} = \frac{k}{\sigma^2}\sqrt{\frac{\epsilon}{m}} \quad . \quad . \quad (24)$$

where the dimensionless groups D^*, η^*, and λ^* are functions of kT/ϵ and $V/N\sigma^3$ only. Little attempt has been made to correlate behaviour on this basis owing to lack of data on simple systems interacting with central force fields.

Alternatively, as ϵ/k and σ are related to T_c and V_c, the critical temperature and volume respectively, reduction can be made with respect to critical properties as in the generalised viscosity plots of Hougen and Watson.[20]

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[19] Hamann, "Physico-chemical Effects of Pressure," Butterworths, London, 1956.

[20] *cf.* Hirschfelder, Curtiss, and Bird, "Molecular Theory of Gases and Liquids," Wiley, N.Y., 1954.

However, there are indications that at the critical point viscosities[21] and thermal conductivities[22] reach anomalously large values owing to the presence of large clusters of molecules. This phenomena has been detected in carbon dioxide and is shown in Fig. 1(*b*) for the thermal conductivity plot which is closer to the critical isotherm than the viscosity plot. As the transport mechanism for heat and momentum is altering in the critical region, the boiling point may be a better reference temperature. For example, the viscosities of the normal paraffins C_5 to C_{20} are all about two millipoises at the boiling point.[23]

6. The transport properties of isotopic species

As the transport properties are influenced by molecular mass, it is of interest to compare the properties of isotopic species. Isotopic substitution has a negligible effect on $\epsilon/\boldsymbol{k}$ and σ, so that D^*, η^*, and λ^* in eqn. (24) are unaltered; therefore

$$\frac{\lambda}{\lambda_i} = \frac{\eta_i}{\eta} = \frac{D}{D_i} = \sqrt{\frac{m_i}{m}} \; . \qquad \ldots \ldots \quad (25)$$

where the subscript *i* refers to properties of the isotopically substituted species. This ratio is also predicted by the theory of section 2(*b*)(iv). No measurements have yet been made on self-diffusion coefficients of isotopically substituted molecules, but this should now be possible by using the spin echo technique for pairs such as CH_4–CHD_3 and $H_2{}^{16}O$–$H_2{}^{18}O$ (see section 8).

Table 3 gives all the known viscosity, thermal conductivity, and square roots of the mass ratios for various pairs of molecules. For the non-polar pairs with methane and cyclohexane the viscosity ratio is in good agreement with the square root of the mass ratio. For benzene the deviation is probably due to non-central forces (see below). The deviation for the pair H_2–D_2 is due to quantum effects which also influence the thermal conductivity ratio.

Pople has pointed out, however,[24] that the viscosity ratio is not given by (25) if the intermolecular forces are non-central except in the special case when *all* the atomic masses in the molecule are altered by the same ratio. The results in Table 3 show that for water the viscosity ratio is in closer agreement with the square roots of the moments of inertia which are $\sqrt{(I_{Ai}/I_A)} = 1{\cdot}340$, $\sqrt{(I_{Bi}/I_B)} = 1{\cdot}414$, and $\sqrt{(I_{Ci}/I_C)} = 1{\cdot}390$. Pople suggests that for water angular rotations of the water molecules contribute appreciably to momentum transfer. On the other hand, agreement of the thermal conductivity ratio with equation (25) indicates that rotational motion is not important for heat transfer in water.

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[21] Michels, Botzen, and Schuurman, *Physica*, 1957, **23**, 95

[22] Guildner, *Proc. Nat. Acad. Sci.*, 1958, **44**, 1149.

[23] Nissan, *Phil. Mag.*, 1941, **32**, 441.

[24] Pople, *Physica*, 1953, **19**, 668.

TABLE 3. *Transport coefficient ratios for isotopic molecules*

Molecules	T(°K)	η_i/η	$(m_i/m)^{\frac{1}{2}}$	Molecules	T(°K)	η_i/η	λ/λ_i	$(m_i/m)^{\frac{1}{2}}$
CH_4, CD_4	90·1	1·113	1·119	H_2O/D_2O	293·2	1·245	1·043	1·054
C_6H_6, C_6D_6	293·2	1·065	1·038		313·2	1·202	1·053	
	311·0	1·062			333·2	1·178	1·060	
	332·2	1·058			353·2	1·164	1·050	
C_6H_{12}, C_6D_{12}	293·2	1·064	1·070	H_2/D_2	20·3	3·216	0·936	1·414
	311·0	1·062						
	333·2	1·060						

References to experimental data: methane[25], benzene and cyclohexane[26], η for water[27], λ for water[28], hydrogen[29].

From the mechanistic point of view agreement of transport coefficient ratios with the square root of the masses does not differentiate between a purely convective and a purely vibrational mechanism since both are governed by the same equation of motion.

7. The transport properties of mixtures

While transport properties of one-component systems are fundamentally a function of the force constant of the molecular interaction, molecular diameter mass, temperature, and volume, yet complications arise in mixtures owing to differences in the properties and the introduction of concentration effects. For the present, attention will be restricted to binary systems. Of these the simplest are mixtures of isotopic species where mass effects will be predominantly important. Experimental data on such mixtures and the pure components are, however, rare and most work is confined to heteromolecular systems.

(a) **Viscosity of a Binary Mixture.**—No statistical theory is at present available which can be used to calculate the viscosity of a binary mixture successfully, so that results are generally represented by empirical laws of the form

$$\mathrm{f}\,(\eta_{\mathrm{mix.}}) = x\,\mathrm{f}\,(\eta_{11}) + (1 - x)\,\mathrm{f}\,(\eta_{22}) \quad . \; . \; . \; . \; . \quad (26)$$

where x and $1 - x$ are the mole fractions. However, the viscosities of most binary systems cannot be adequately represented by equation (26) when $\mathrm{f}(\eta)$ is η itself, $\log \eta$, or $1/\eta$. Although $\eta_{\mathrm{mix.}}$ is sometimes cubic in x, the usual behaviour is quadratic, which suggests equations of the form

$$\eta_{\mathrm{mix.}} = x^2\eta_{11} + 2x(1 - x)\eta_{12} + (1 - x)^2\eta_{22} \quad . \; . \quad (27)$$

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[25] Bresler and Landermann, *J. Exp. Theor. Phys. U.S.S.R.*, 1940, **10**, 250.
[26] Schiessler and Dixon, *J. Phys. Chem.*, 1954, **58**, 430.
[27] Hardy and Cottingham, *J. Res. Nat. Bur. Stand.*, 1949, **42**, 572.
[28] Challoner and Powell, *Proc. Roy. Soc.*, 1956, *A*, 238, 90.
[29] Powers, Mattox, and Johnston, *J. Amer. Chem. Soc.*, 1954, **76**, 5972, 5974.

where η_{12} is associated with the heteromolecular interaction. Some mixtures have been analysed[30] by using equation (27) and η_{12} found to be independent of x but subject to the usual temperature dependence law (equation 23).

(b) **Thermal Conductivity of Binary Mixtures.**—As for viscosity, experimental data on the thermal conductivity of simple mixtures is usually quadratic in x rather than linear. An expression has been derived by Bearman[31] on the basis of the distribution function type of treatment and for a regular solution can be written as

$$\lambda_{\text{mix.}} \simeq x\lambda_{11}\left(\frac{V_1}{V}\right)^2\frac{D_{1x}}{D_{11}} + (1-x)\left(\frac{V_2}{V}\right)^2\frac{D_{2x}}{D_{22}} \quad . \; . \; . \quad (28)$$

where λ_{11}, λ_{22}; D_{11}, D_{22}; V_1, V_2, are the thermal conductivities, self-diffusion coefficients, and molar volumes of the pure species 1 and 2 respectively. V is the mean molar volume and D_{1x} and D_{2x} are self-diffusion coefficients of species 1 and 2 in the mixture. The equation was applied to the carbon tetrachloride–benzene system, and although giving the general shape of the curve it fails to reproduce it quantitatively even when fitted at the extremes for the pure constituents.

(c) **Diffusion in a Binary Mixture.**—While the subjects of viscosity and thermal conductivity of binary mixtures are still undeveloped from the theoretical point of view, more progress has been made for the case of diffusion. The coefficient of self-diffusion, which is, in reality, the property of an equilibrium system, is given by the theory of random processes as $D_{11} = \langle r^2 \rangle / 6t$, where $\langle r^2 \rangle$ is the mean square displacement of a particle in a time t long compared with the time between collisions. It is usual in measuring so called self-diffusion coefficients, however, to use isotopically labelled molecules which differ effectively only in mass from the parent substance and then define the diffusion coefficient in terms of Fick's law.

According to equation (4) there are n^2 diffusion coefficients in an n-component system. Onsager showed that of these only $(n-1)^2$ are independent, so that diffusion in a binary mixture can be represented by a single diffusion coefficient called the mutual diffusion coefficient. Attempts have been made to relate the various diffusion coefficients in a mixture to the mutual diffusion coefficient D. Hartley and Crank[32] derived the equation

$$D = V_1 c_1 D_2 + V_2 c_2 D_1 \quad . \; . \; . \; . \; . \quad (29)$$

where D_1 and D_2 are the intrinsic diffusion coefficients, c_1 and c_2 the concentrations, and V_1 and V_2 the partial molar volumes of species 1 and 2.

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[30] Hind, McLaughlin, and Ubbelohde, *Trans. Faraday Soc.*, 1960, **56**, 328.
[31] Bearman, *J. Chem. Phys.*, 1958, **29**, 1278.
[32] Hartley and Crank, *Trans. Faraday Soc.*, 1949, **45**, 801

This equation takes account of the phenomenon of mass flow across a section fixed relative to the ends of the diffusion vessel first treated by Darken,[33] and is due to relief of the pressure gradient built up by the different mobilities of the two particles. This equation, however, assumes no volume change on mixing. The intrinsic diffusion coefficient which is defined with reference to a cross-section moving with the mass flow velocity is connected with the mobility of the particle ω_j in the mixture by a thermodynamic term

$$D_j = \omega_j kT \frac{\mathrm{d} \ln a}{\mathrm{d} \ln x_j} \cdot \frac{x_j}{V_i c_j} \qquad \text{. . . . . . . (30)}$$

when the assumptions are made that a molecule moves with a velocity proportional to the diffusion force given by $v_j = \omega_j . \mathrm{d}\mu_j/\mathrm{d}x$ and the Fick diffusion coefficient D_j is defined by $J_j = c_j v_j = - D_j, \mathrm{d}c_j/\mathrm{d}x$. It is assumed here that the gradient of chemical potential $\mathrm{d}\mu_j/\mathrm{d}x$ is the force causing diffusion rather than the concentration gradient. This can be shown to be a direct consequence of the extension of the second law of thermodynamics to non-equilibrium systems. a_j in equation (30) is the activity. Combining equations (29) and (30), we have

$$D = \frac{\mathrm{d} \ln a_1}{\mathrm{d} \ln x_1} \left[x_2 \omega_1 kT + x_1 \omega_2 kT \right] \qquad \text{. . . . (31)}$$

when the Duhem–Margules equation is used. Equation (31) has been tested[34] for some binary systems with $\omega_j kT$ replaced by the tracer self-diffusion coefficient in the mixture and gives the general shape of the experimental curve. It has also been modified by assuming that the mobilities, which are the inverse of the friction coefficients, are determined mainly by the viscous forces.

At present, although diffusion in mixtures has not been successfully treated statistically, the thermodynamic approach outlined has provided some insight into the phenomenon. Equation (29) shows that the mutual diffusion coefficient depends on concentration, because D_1 and D_2 are not in general equal, and in addition tends to the self-diffusion coefficient of the species present in vanishingly small concentration. In tracer measurements therefore from equation (29) $D \rightarrow D_{11}$, as c_1, the tracer concentration is small, so that the self-diffusion coefficient of the non-isotopic species should be corrected for the mass effect by using equation (25).

The above treatment of mutual diffusion still assumes that the flux of a particular species is dependent on its own gradient of chemical potential alone and not as in the Onsager equation (4). Application of equilibrium thermodynamics to correct for non-ideality is not likely to be seriously in error for small gradients.

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[33] Darken, *Trans. Amer. Inst. Mining, Met. Eng.*, 1948, **175**, 184.

[34] Carman and Miller, *Trans. Faraday Soc.*, 1959, **55**, 1831.

(d) **The Soret and Dufour Effects.**—On the basis of equation (4) it can be seen that coupling effects can occur in transport processes in mixtures. By Curie's theorem[35] such coupling can only occur between quantities of the same tensorial character so that, while diffusion forces and heat fluxes can couple and *vice versa*, neither can be coupled with viscous processes. In non-electrolyte systems therefore two effects exist due to the coupling of diffusion and heat conduction. In the first case, a concentration gradient is set up in the mixture as the result of a temperature gradient (Soret effect or thermal diffusion) and a temperature gradient is set up when two substances diffuse into each other (Dufour effect). These coefficients are given[35] by $S_T = D^1/D$ and $D_e \simeq D^1/\lambda$, where D^1 is the diffusion coefficient due to the temperature gradient. Although both effects have been found in gases, the Dufour effect has not been found in liquids. This arises because D for gases is about 10^5 times larger than for liquids whereas the Soret coefficient for both states is of the same order of magnitude. In addition, λ for liquids is about 10—100 times greater than the gas value so that the Dufour effect is 10^6—10^7 times smaller in the liquid phase. Moreover, the heat of mixing and the time lag before the maximum temperature gradient is formed would tend to make the effect difficult to observe.

Molecular kinetic theories have been proposed for the thermal diffusion process. The theory of Hibby and Wirtz[36] is developed by considering the relative tendency of a molecule to undergo diffusion by an activated process in a liquid mixture subjected to a temperature gradient and thus causing a concentration gradient to be set up. The equation derived may be written

$$S_T = \frac{(q_{\mathrm{H}1} - q_{\mathrm{L}1}) - (q_{\mathrm{H}2} - q_{\mathrm{L}2})}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where $q_{\mathrm{H}1}$ and $q_{\mathrm{L}1}$ are component parts of the activation energy for the process due respectively to the energy necessary to detach a molecule from its neighbours to allow flow to occur and to the energy to create a hole necessary to accommodate it. Prigogine and his co-workers[37] derived a similar equation with $q_{L1} = q_{L2}$. Denbigh[38] has given a thermodynamic treatment which results in an equation formally similar to (32), showing that S_T is independent of concentration for ideal mixtures. This has been confirmed by Prigogine's experimental results.

8. New experimental techniques

Recent developments in the field of piezoelectric crystals and nuclear magnetic resonance have provided new experimental techniques for the study of transport properties. In the former, developed principally by Mason,[39] the effects of a viscous medium on the electrical characteristics of

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[35] de Groot, "Thermodynamics of Irreversible Processes," N.H.P., Amsterdam, 1958.
[36] Hibby and Wirtz, *Z. Physik*, 1943, **44**, 369; Wirtz, *Z. Naturforsch.*, 1948, **30**, 672.
[37] Prigogine, de Bouckère, and Amand, *Physica*, 1950, **16**, 577.
[38] Denbigh, *Trans. Faraday Soc.*, 1952, **48**, 1.
[39] Mason, *Trans. Amer. Soc. Mech. Eng.*, 1947, **69**, 359.

a torsionally excited quartz crystal have been developed for measuring viscosity at high shearing rates and should provide important information on shear relaxation phenomena in liquids.

In the nuclear magnetic resonance field the spin echo phenomenon has been analysed in terms of a diffusion process and applied to the measurement of self-diffusion coefficients by McCall and his co-workers.[40] In this case it is possible to measure directly the self-diffusion coefficient since only nuclear properties are involved in differentiating the diffusing particles. In both techniques pressure can be varied as readily as temperature so that significant new information should be obtained.

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[40] Douglass and McCall, *J. Phys. Chem.*, 1958, **62**, 1102.