

# THE THERMAL CONDUCTIVITY OF LIQUIDS AND DENSE GASES

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## I. INTRODUCTION

The subject of the thermal conductivity of liquids and dense gases is important for two main reasons: firstly, because its study can help in giving a better understanding of the basic molecular processes involved in transport phenomena in general, and secondly, because of its significance in technological applications. In the present review both experimental and recent theoretical aspects are covered, and data on various types of systems are discussed in the light of existing theories.

## ORIGIN OF THE PHENOMENON

If a system is perturbed from equilibrium by the effect of a temperature gradient  $\partial T/\partial x$ , the perturbation tends to be eliminated by a flux of heat down the gradient, giving rise to the phenomenon of thermal conductivity. The coefficient of thermal conductivity  $\lambda$  is then defined as the proportionality constant between the flux  $J_q$  and the gradient, written in the one dimensional case as

$$J_q = -\lambda \partial T/\partial x \quad (\text{Eq. 1})$$

Equation 1 is called Fourier's law (42). The negative sign indicates that the flux is down the gradient, and it can be shown from irreversible thermodynamics (95) that the coefficient itself is always positive. Typical values of the thermal conductivity of a variety of liquids are given in Table I.

Most organic liquids have thermal conductivities ranging between about  $8$  to  $30 \times 10^{-4}$  joule  $\text{cm.}^{-1}$   $\text{sec.}^{-1}$   $^{\circ}\text{C.}^{-1}$ , lowest values generally occurring for the lower alkyl halides ( $6 \times 10^{-4}$  joule  $\text{cm.}^{-1}$   $\text{sec.}^{-1}$   $^{\circ}\text{C.}^{-1}$ ). Among common liquids, water and ammonia have exceptionally high thermal conductivities, the values of which are also approached by some organosilicon compounds. From Table I, it can be seen that the thermal conductivities of liquid metals are higher by a factor of about 100 than those of normal liquids. For molten salts, values are available only for the alkali nitrates. These range from about  $22$  to  $55 \times 10^{-4}$  joule  $\text{cm.}^{-1}$   $\text{sec.}^{-1}$   $^{\circ}\text{C.}^{-1}$ . Thermal conductivities throughout this review are in the units used above. Conversion factors are given below.

To convert	joules $\text{cm.}^{-1}$ $\text{sec.}^{-1}$ $^{\circ}\text{C.}^{-1}$	to:	
	cal. $\text{cm.}^{-1}$ $\text{sec.}^{-1}$ $^{\circ}\text{C.}^{-1}$		multiply by 0.2390
	kcal. $\text{m.}^{-1}$ $\text{hr.}^{-1}$ $^{\circ}\text{C.}^{-1}$		multiply by 86.042
	B.t.u. $\text{ft.}^{-1}$ $\text{hr.}^{-1}$ $^{\circ}\text{F.}^{-1}$		multiply by 57.780

For simple liquids, the thermal conductivities are about 10 to 100 times greater than those of the corresponding gases at the same temperature (*cf.* Table XI) and about 0.10 to 0.20 smaller than the values of the corresponding solids at the melting point. Figures for liquid and solid argon are, respectively,  $12.60$  and  $17.53 \times 10^{-4}$  joule  $\text{cm.}^{-1}$   $\text{sec.}^{-1}$   $^{\circ}\text{C.}^{-1}$ .

## II. EXPERIMENTAL DETERMINATION OF THERMAL CONDUCTIVITY

## A. BASIC THEORY

For a discussion of the problem of convection and for derivation of the basic equation used in the experimental determination of thermal conductivity, the hydrodynamic equations of change are necessary. These are simply expressions of the conservation laws for mass, momentum, and energy and can be written (126) in Cartesian tensor notation for a viscous, compressible, heat-conducting, isotropic fluid as

$$\frac{D\rho}{Dt} = -\rho \frac{\partial v_k}{\partial x_k} \quad \text{equation of continuity (conservation of mass)} \quad (\text{Eq. 2})$$

$$\rho \frac{Dv_i}{Dt} = \frac{\partial \sigma_{ij}}{\partial x_j} + \rho f_i \quad \text{equation of motion (conservation of momentum)} \quad (\text{Eq. 3})$$

$$\rho \frac{Du}{Dt} = \sigma_{ij} d_{ij} - \frac{\partial q_i}{\partial x_i} \quad \text{energy balance equation (conservation of energy)} \quad (\text{Eq. 4})$$

$\rho$  is the fluid density,  $u$  the internal energy per unit mass,  $v_i$  its hydrodynamic (*i.e.*, center of mass) velocity, and  $f_i$  the body force per unit mass due to an external field such as the gravitational field.  $q_i$  is the heat flux vector. The derivative  $D/Dt$  given by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + v_k \frac{\partial}{\partial x_k} \quad (\text{Eq. 5})$$

is generally called the substantial time derivative and measures the rate of change of a property of the fluid as "seen" by an observer seated at the center of mass of any element of fluid considered.  $\sigma_{ij} = \sigma_{ji}$  is the symmetric stress tensor related to the thermodynamic pressure  $p$  and the viscosity coefficients of the fluid, by the generalized form of Newton's viscosity equation known as the Cauchy-Poisson law.

$$\sigma_{ij} = \left\{ -p + \left( \eta' + \frac{2}{3} \eta \right) d_{kk} \right\} \delta_{ij} + 2\eta \Delta_{ij} \quad (\text{Eq. 6})$$

$\eta'$  is the second coefficient of viscosity and  $\eta$  the first or shear coefficient of viscosity. The sum  $(\eta' + 2\eta/3)$  is the coefficient of bulk viscosity (for a discussion of the coefficient of bulk viscosity and its relationship to

TABLE I  
THE THERMAL CONDUCTIVITIES OF SOME LIQUIDS AT 1 ATM. PRESSURE

Temp., $^{\circ}\text{K.}$	Argon	Benzene	Glycerol	Water	Potassium nitrate	Aq.	Sodium	Mercury
						potassium chloride (1 mole/l.)		
$\lambda \times 10^4$ joules, $\text{cm.}^{-1}$ $\text{sec.}^{-1}$ $^{\circ}\text{C.}^{-1}$	84.2	295.9	293.2	293.2	683.0	293.2	573.2	303.2
	12.6	14.3	28.8	60.0	42.5	58.6	1146	860

sound absorption, see ref. 82 and 128) and  $\delta_{ij}$  is the Kronecker delta symbol,  $\delta_{ij} = 1, i = j, \delta_{ij} = 0, i \neq j$ .  $d_{jj}$  and  $\Delta_{ij}$  are related to the symmetrical rate of strain tensor  $d_{ij}$ , given by

$$d_{ij} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (\text{Eq. 7})$$

by the equation

$$d_{ij} = \frac{1}{3} d_{kk} \delta_{ij} + \Delta_{ij} \quad (\text{Eq. 8})$$

In Eq. 4 the term  $\sigma_{ij} d_{ij}$  can be rewritten in terms of the reversible rate of internal energy increase per unit volume by compression  $p d_{jj}$  and the irreversible rate of internal energy production per unit volume due to viscous dissipation  $\Phi$ , by the equation

$$\sigma_{ij} d_{ij} = -p d_{jj} + \Phi \quad (\text{Eq. 9})$$

where  $\Phi$ , called the dissipation function, is given by

$$\begin{aligned} \Phi &= \left( \eta' + \frac{2}{3} \eta \right) d_{jj}^2 + 2\eta \Delta_{ik} \Delta_{ik} \\ &= \eta' d_{jj}^2 + 2\eta d_{ik} d_{ik} \end{aligned} \quad (\text{Eq. 10})$$

#### B. THE ENERGY BALANCE EQUATION IN TERMS OF THE TEMPERATURE

To introduce the coefficient of thermal conductivity into the energy balance (Eq. 4) use is made of Fourier's law

$$q_i = -\lambda \partial T / \partial x_i$$

The resulting equation involving the specific internal energy is not, however, in a useful form for the experimental determination of the thermal conductivity and is therefore transformed in terms of the temperature, which is a more readily measurable quantity. This transformation is made by using the thermodynamic equation

$$du = -\frac{1}{\rho^2} \left[ -p + T \left( \frac{\partial p}{\partial T} \right)_\rho \right] d\rho + C_v dT \quad (\text{Eq. 11})$$

where  $C_v$  is the specific heat at constant volume. The resulting equation is

$$\rho C_v \frac{DT}{Dt} = \frac{\partial}{\partial x_i} \left( \lambda \frac{\partial T}{\partial x_i} \right) - T \left( \frac{\partial p}{\partial T} \right)_\rho \frac{\partial v_k}{\partial x_k} + \Phi \quad (\text{Eq. 12})$$

or in terms of the specific heat at constant pressure  $C_p$

$$\rho C_p \frac{DT}{Dt} = \frac{\partial}{\partial x_i} \left( \lambda \frac{\partial T}{\partial x_i} \right) + T \alpha \frac{Dp}{Dt} + \Phi \quad (\text{Eq. 13})$$

by using the equation of continuity and the relationship

$$C_p - C_v = \frac{\alpha T}{\rho} \left( \frac{\partial p}{\partial T} \right)_\rho \quad (\text{Eq. 14})$$

where  $\alpha$  is the coefficient of thermal expansion. Equations 12 and 13 are equivalent expressions for the energy balance equation for a compressible, viscous, heat-conducting, isotropic fluid in nonisothermal flow.

#### C. EQUATION FOR THE EXPERIMENTAL DETERMINATION OF THERMAL CONDUCTIVITY

In the experimental determination of thermal conductivity, conditions are required under which convection is absent; *i.e.*, heat is transferred by pure conduction and no contribution to transport arises from the bulk motion of elements of the fluid from hotter to colder regions. In such a state  $v_i = 0$  and the energy balance Eq. 13, for small temperature gradients, where  $\lambda$  can be considered effectively as a constant, reduces to

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + T \alpha \frac{\partial p}{\partial t} \quad (\text{Eq. 15})$$

In principle the thermal conductivity of a fluid can be measured in any apparatus which provides boundary conditions to Eq. 15. The standard reference work for solutions with various boundary conditions is by Carslaw and Jaeger (14). Steady-state, *i.e.*, time-independent, methods are generally preferred since, at constant pressure, Eq. 15 reduces to Laplace's equation

$$\nabla^2 T = 0 \quad (\text{Eq. 16})$$

the solution of which, together with information on the heat flux at the boundaries is sufficient to evaluate the thermal conductivity without recourse to the density, specific heat, and coefficient of expansion. In addition, time-independent temperatures are easier to measure.

##### 1. Steady-State Methods

In practice a steady-state temperature is maintained by an internal heat source, and methods can be classified according to the cell geometry in which this is achieved. The two most important types are linear and radial systems. In the former the parallel plate apparatus is the commonest, and in the radial systems, either concentric cylinders or concentric spheres are used.

The appropriate solutions to Eq. 16 for these systems with the assumption of constant pressure are

$$\lambda = \frac{qd}{A(T_2 - T_1)} \quad (\text{parallel plates}) \quad (\text{Eq. 17})$$

$$\lambda = \frac{q \ln \frac{b}{a}}{2\pi l(T_2 - T_1)} \quad (\text{concentric cylinders}) \quad (\text{Eq. 18})$$

$$\lambda = \frac{q(b-a)}{4\pi ab(T_2 - T_1)} \quad (\text{concentric spheres}) \quad (\text{Eq. 19})$$

$q$  is the heat lost by conduction from the hotter surface at a temperature  $T_2$  to the colder surface at temperature  $T_1$ . For concentric cylinders and spheres the inner surface is generally made the hotter for convenience in thermostating, and for the parallel plate arrangement, heat is usually supplied uniformly from above as the system is then theoretically free from convection.  $d$  is the plate spacing,  $a$  and  $b$  are the inner and outer radii of the cylinders or spheres,  $l$  is the cylinder length,

and  $A$  is the effective area over which heat is conducted in the plate arrangement.

In the plate and cylinder arrangements elaborate precautions are necessary to avoid distortion of the temperature profile at the ends due to heat leakage. These "end" effects, which could lead to convection (see section IIE) unless compensated, can be avoided by using concentric spheres.

In general, with all three types, the geometrical factors enter the equation so that precision in construction is essential. Corrections can be applied for such things as eccentricity and heat conduction along spacing pieces and connections. These should however be minimized. Suitable forms of these arrangements can be found in the following references: flat plates, Chalonner and Powell (17) and Michels, Sengers, and Van der Gulik (87); concentric cylinders, Ziebland and Burton (148) and Riedel (113); concentric spheres, Riedel (113) and Richter and Sage (107).

## 2. Transient Methods

Nonsteady-state measurements have generally been restricted to hot wire cells. In this case the development of temperature is observed in an electrically heated wire, immersed axially in a liquid, in a cylindrical cell which is initially in thermal equilibrium. This system to a first approximation can be treated as an infinite line source of constant heat generation in an extended medium. If the pressure is assumed constant (see section IIE) the solution of Eq. 15 is

$$T_{\infty}(r,t) = \frac{-q/l}{4\pi\lambda} \left\{ \text{Ei} \left( \frac{-r^2}{4K_m t} \right) \right\} \quad (\text{Eq. 20})$$

where  $q/l$  is the heat conducted per unit length away from the wire,  $T_{\infty}(r,t)$  is referred to the initial temperature,  $K_m = \lambda/\rho C_p$  is called the thermal diffusivity, and  $\text{Ei}(-x)$  is the exponential integral. Expanding  $\text{Ei}(-x)$  gives the temperature at a radial distance  $r'$  as

$$T_{\infty}(r',t) = \frac{q/l}{4\pi\lambda} \left\{ \ln t + \ln \frac{4K_m}{r'^2\gamma} + \frac{r'^2}{4K_m t} + \dots \right\} \quad (\text{Eq. 21})$$

where  $\gamma$  is Euler's constant. Provided  $r'^2/4K_m t$  is sufficiently small in the range  $t_1$  to  $t_2$  then

$$T_{\infty}(r',t_2) - T_{\infty}(r',t_1) \simeq \frac{q/l}{4\pi\lambda} \ln \frac{t_2}{t_1} \quad (\text{Eq. 22})$$

so that a plot of temperature against log time enables the thermal conductivity to be obtained. In an actual hot wire cell, the heating wire has a finite diameter and length and in addition the medium is bounded so that an examination of the limitation of Eq. 21 when applied to an experimental cell is necessary. This has been done in detail by Van der Held and Van Drunen (132) and by Horrocks and McLaughlin (56) who show that under suitable conditions the only necessary correction is a small one due to the finite wire diameter. An advantage of this method is that it can be used to check for the absence of convection by departures from linear-

ity of the  $T$ -log  $t$  plots, and in addition the time dependence of the temperature can be readily obtained by using the electrical heating circuit. Suitable forms of this type of apparatus have been described by Van der Held and Van Drunen (132), Gillam and Lamm (44), and Horrocks and McLaughlin (56).

Numerous other types of apparatus have been described, especially those involving comparative techniques, but the above methods are those most commonly used in precise work. On comparative techniques it should, however, be remembered that the majority of viscosity results have been obtained in this manner, and that they are useful in exploring a wide variety of systems. A sophisticated comparative apparatus has been described in papers by Grassmann and Straumann (46) and Jobst (61).

## D. RADIATION

In Eq. 17-19 and 22, the quantity  $q$  is the heat lost by conduction alone. In an experimental apparatus, however, due to the temperature gradient, heat is also lost by radiation. The precise evaluation of this loss is a complex problem (7), but it is, nevertheless, possible to give an upper limit to its magnitude.

The radiant energy  $q_r^e$  emitted from the surface of a nonblack body, of emissivity  $\epsilon$ , at a temperature  $T_2$ , into a surrounding enclosure is given by the relationship

$$q_r^e = A\epsilon\delta T_2^4 \quad (\text{Eq. 23})$$

where  $\delta$  ( $5.67 \times 10^{-12}$  joule sec. $^{-1}$  cm. $^{-2}$  °K. $^{-4}$ ) is the Stefan-Boltzmann constant. The rate of energy absorption by the emitting surface of absorptivity  $\alpha$  from the surroundings at a temperature  $T_1$  is given by

$$q_r^a = A\alpha\delta T_1^4 \quad (\text{Eq. 24})$$

where it is assumed that the radiation reaching the surface is black body radiation corresponding to temperature  $T_1$ . The net rate of loss is therefore

$$q_r = A\delta(\epsilon T_2^4 - \alpha T_1^4) \quad (\text{Eq. 25})$$

where  $A$  is the effective emitting area. Although  $\epsilon$  and  $\alpha$  are less than unity (for example, for platinum  $\epsilon \simeq \alpha \simeq 0.1$  and for glass 0.8), the maximum heat loss can be obtained by assuming that the emitting surface is a black body. For small temperature differences, therefore (as is necessary to avoid convection),  $T_2 - T_1 = \Delta T$ , and hence

$$q_r \simeq 4A\delta T^3 \Delta T \quad (\text{Eq. 26})$$

where  $T = (T_2 + T_1)/2$ .

The ratio of the rate of heat loss due to radiation to that due to pure conduction follows from Eq. 17 to 19 for the steady-state systems as

$$\frac{q_r}{q} = \Omega \frac{1}{2} \quad (\text{parallel plates}) \quad (\text{Eq. 27})$$

$$\frac{q_r}{q} = \Omega a \ln \left( \frac{b}{a} \right) \quad (\text{concentric cylinders}) \quad (\text{Eq. 28})$$

$$\frac{q_r}{q} = \Omega \frac{a}{b} (b - a) \quad (\text{concentric spheres}) \quad (\text{Eq. 29})$$

and from Eq. 21 for the treatment hot wire cell as

$$\frac{q_r}{q} = \Omega \frac{a}{2} \ln \left( \frac{4K_m t}{a^2 \gamma} \right) \quad (\text{Eq. 30})$$

where

$$\Omega = \frac{4\delta T^3}{\lambda} \quad (\text{Eq. 31})$$

While both the absorption of the medium and the emissivity of the surfaces reduce the error calculated by the equations above, it is preferable to ensure that the correction so calculated is less than 1%.

#### E. CONVECTION

If a temperature gradient is applied to a fluid initially at rest, the resulting density gradient produces a buoyancy force which, although opposed by the viscous resistance in the state of mechanical equilibrium, eventually causes instability. This instability is manifested in bulk convective motion, which is the bodily motion of whole portions of the fluid. The problem was first studied experimentally by Bénard (5) but is still far from being completely understood. For the present work it is only necessary to consider free convection, by which is meant, flow where the motion is caused by the effect of gravity on the heated fluid of variable density.

From thermodynamics the change in density of a liquid due to pressure and temperature is

$$-d\rho = \rho\beta_T dp + \rho\alpha dT \quad (\text{Eq. 32})$$

where  $\beta_T$  is the isothermal compressibility. From this equation it follows that changes in density due to changes in pressure can be neglected, compared with changes in density due to temperature, provided

$$dp \ll \frac{\alpha}{\beta_T} dT \quad (\text{Eq. 33})$$

As  $dp \simeq \rho g d$  where  $d$  is the thickness of the liquid layer in a cell and  $\alpha/\beta_T \simeq 10 \text{ atm. deg.}^{-1}$  for common liquids (116) at atmospheric pressure when the density is approximately unity, then  $(\rho g)^{-1} \alpha/\beta_T \simeq 10^4 \text{ cm. deg.}^{-1}$  so that the effect of pressure on the density change is negligible for small thickness of fluid, and the equation of state reduces to

$$d\rho = -\alpha\rho dT \quad (\text{Eq. 34})$$

As the effect of pressure on the density change is negligible, the fluid can first be treated as incompressible in the equation of motion to eliminate the bulk viscosity and written

$$\frac{Dv}{Dt} = -\frac{1}{\rho} \text{grad } p + \frac{\eta}{\rho} \nabla^2 v + g \quad (\text{Eq. 35})$$

where  $g$  is the gravitational force per unit mass of fluid. This equation has now only to be modified to allow for the effect of the density change due to temperature.

It can be shown (70) that if the thermodynamic quantities  $\rho$ ,  $T$ , and  $p$  are written for small gradients in the form  $\rho = \rho_0 + \rho'$ ,  $T = T_0 + T'$ , and  $p = p_0 + p'$  where  $\rho_0$  and  $T_0$  are constants and  $p_0 = \rho_0 g r + \text{constant}$ , then

$$\frac{\text{grad } p}{\rho} \simeq g + \frac{\text{grad } p'}{\rho_0} + gT'\alpha \quad (\text{Eq. 36})$$

which on substituting in Eq. 35 gives for steady-state convection ( $\partial/\partial t = 0$ )

$$(v \cdot \text{grad})v = -(1/\rho) \text{grad } p' + (\eta/\rho) \nabla^2 v - \alpha T' g \quad (\text{Eq. 37})$$

and

$$\text{div } v = 0 \quad (\text{Eq. 38})$$

as the fluid is taken to be incompressible. Turning to the energy balance equation, Eq. 13, if the pressure is constant the  $Dp/Dt$  term vanishes, and as for the steady state with motion in one direction alone for a linear gradient (*cf.* 122)

$$\frac{\Phi}{\rho C_p v} \frac{\partial T}{\partial x} \simeq \frac{2\eta(\Delta v)^2}{\rho C_p v \Delta T d} \quad (\text{Eq. 39})$$

Then, as  $2\eta/\rho C_p \simeq 10^{-9}$  c.g.s. unit for a typical liquid like water at room temperature,  $\Phi$ , the viscous energy dissipation, can be neglected compared with the convective transport of thermal energy, reducing Eq. 13 finally to the form for the steady state

$$v \cdot \text{grad } T' = \frac{\lambda}{\rho C_p} \nabla^2 T' \quad (\text{Eq. 40})$$

Equations 34, 37, 38, and 40 applicable to convection phenomena therefore are seen to contain three parameters,  $\eta/\rho$ ,  $\lambda/\rho C_p$ , and  $\alpha g$ , which together with the temperature difference  $\Delta T$  and fluid thickness  $d$  serve to characterize the phenomena of convection. From these parameters two independent dimensionless quantities can be formed, the Prandtl number and the Grashof number given by  $Pr = \eta C_p/\lambda$ ,  $G = g\alpha\rho^2\Delta T d^3/\eta^2$ ,  $R = PrGr$ . The Grashof number is a measure of the relative importance of the buoyancy and viscous forces acting on a liquid, and the Prandtl number is a measure of the ratio of the molecular diffusivity of momentum to the molecular diffusivity of energy.

When Eq. 34, 37, 38, and 40 are applied to solve specific convection problems of fixed geometry, it is found that the onset of convection is determined by critical values of the product of the Prandtl and Grashof numbers known as the Rayleigh number. For example, for concentric cylinders the value of  $R$  is 1000. This means that provided the Rayleigh number in a fluid under investigation is less than the critical value for a given geometry, no convection would be expected. It follows, therefore, that measurements should be made

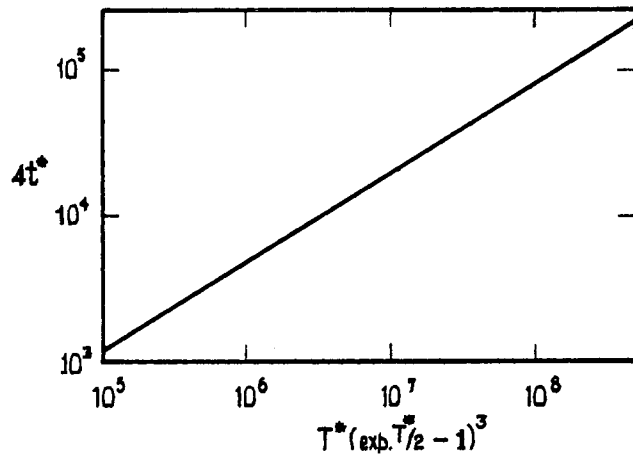


Fig. 1.—Reduced time–reduced temperature plot for the determination of the time of onset of convection in a hot wire cell.

at low Rayleigh numbers. As mentioned previously, however, while experimental conditions may be arranged to give low  $R$  values, “end effects” are a common source of initiation of convection and some additional check is therefore desirable.

While nonsteady-state methods have the particular disadvantage of requiring time-dependent temperature measurements, they can be used to determine experimentally the time of onset of convection and hence check the Rayleigh criterion. As pointed out previously, in the steady state heat transfer by convection between horizontal coaxial cylinders is negligible below a Rayleigh number of 1000, and as a hot wire cell is of this geometry, this criterion is applicable. To apply it to hot wire cells for nonsteady-state measurements requires reformulation. Van der Held and Van Drunen (132) suggested that to the instantaneous temperature field in the nonsteady state, there may be found a pseudo-steady-state situation. Convection may be expected to occur when this corresponding pseudo-steady-state situation reaches the critical value of  $R = 1000$ . In this situation, however, the distance  $b$  in the characteristic dimension  $d = b - a$  (see Eq. 18) corresponds to the radius of the expanding high temperature fluid which surrounds the axial heating wire and has to be determined. The slightly modified procedure used below is discussed in ref. 56.

The temperature differential in the nonsteady state is given by Eq. 21 which may be equated in the approximation outlined above with the temperature differential of a pseudo-steady state given by Eq. 18, *i.e.*

$$T_{\infty}(a,t) = \Delta T = \frac{q/l}{2\pi\lambda} \ln \frac{b}{a} \quad (\text{Eq. 41})$$

which yields  $b$  and hence

$$d = b - a = a \left\{ \exp \frac{2\pi\lambda T_{\infty}}{q/l} - 1 \right\} \quad (\text{Eq. 42})$$

Substituting Eq. 42 for  $d$  and the major terms of Eq. 21

TABLE II  
COMPARISON OF CALCULATED AND EXPERIMENTAL TIMES OF ONSET OF CONVECTION

Liquid	$t$ (measured)	$t$ (calcd.)
Water	16	16.4
Pentanol	50	55.3
Methanol	20	19.6
Aniline	50	59.9
Carbon tetrachloride	18	17.6
Benzene	18	18.2
Acetone	16	15.0
Chloroform	16	17.2
Toluene	15	14
Benzene	8.5	10

into the Rayleigh expression, with  $T^* = 4\pi\lambda T_{\infty}/(q/l)$  and  $t^* = 4\lambda t/\rho C_p a^2$ , yields the criterion for the onset of convection in the nonsteady-state case as

$$1000 = \frac{g\alpha\rho^2 q a^3 C_p}{\eta\lambda^2 4\pi l} \left[ T^* \left( \exp \frac{1}{2} T^* - 1 \right)^3 \right] \quad (\text{Eq. 43})$$

From Eq. 43, the onset of convection may be related to a value of  $T^*$  and hence by Eq. 21 in terms of the reduced variables to  $t^*$  and  $t$ . This is most readily done from a plot of  $4t^*$  against  $T^*(\exp^{1/2} T^* - 1)^3$  illustrated in Fig. 1, so that with the experimental values of  $\alpha$ ,  $\rho$ ,  $\lambda$ ,  $\eta$ , and  $q/l$  at any temperature for a wire radius  $a$ ,  $t^*$  can be obtained and hence  $t$ , the time of onset of convection.

Table II compares calculated and experimental values of the time of onset of convection for given experimental apparatus and conditions for a range of liquids. The calculated values are obtained using the Rayleigh criterion, and the experimental values from departures from linearity of the temperature–log time plots. The results are those of Van der Held and Van Drunen (132) with the exception of the last two values which are from Horrocks and McLaughlin (56) using the modified procedure discussed above. The results, on average, are in agreement well within about 10%, thus substantiating the Rayleigh criterion for the time of onset of convection.

For the steady-state situation, an analysis can also be made of the convection problem. This has been done by Michels and Sengers for a parallel plate apparatus (86), which was used to study  $\text{CO}_2$  in the critical region. Finally, with regard to convection, it can be said that although far from being completely understood, criteria in use at present do serve to indicate the onset of convection, provided spurious end effects are eliminated. No absolute guarantee can, however, be given unless direct experimental confirmation is obtained. The existence of convection during measurements is the most likely cause of the large discrepancies between thermal conductivity values for liquids reported by different experimenters. This is further discussed in the following section.

## F. THERMAL CONDUCTIVITY STANDARDS

To check the reliability of a thermal conductivity apparatus, it is essential to make measurements on standard materials of known thermal conductivity. As the liquid state covers a wide temperature range from the liquified common gases at about 80°K. to molten metals at about 1500°K., a number of standards are required. These materials should be thermally stable, one-component species, and obtainable in a high state of purity, which has been specified. In addition they should not be highly viscous, otherwise convection effects inherent in the apparatus may be obscured and spurious values result when the apparatus is used to make measurements on less viscous materials. Finally, reliability of recommended values of the thermal conductivity of standard materials can only be ensured if measurements, which must be absolute, have been checked in different types of apparatus.

To date, only two groups of experimental workers have endeavored to make systematic measurements of thermal conductivity, of the same liquids, in different types of apparatus, over comparable temperature ranges. Riedel (113) has compared a variety of liquids over a range of temperatures in three types of apparatus, parallel plates, concentric cylinders, and concentric spheres. His results are given in Table III.

TABLE III

 THERMAL CONDUCTIVITIES,  $\lambda \times 10^4$ ,<sup>a</sup> OF LIQUIDS FOR THREE DIFFERENT TYPES OF APPARATUS (RIEDEL)

Liquid	Temp., °C.	Type of apparatus			Average deviation from mean, %
		Parallel plates	Concentric cylinders	Concentric spheres	
Water	20	60.0	59.9	59.5	±0.3
	80	67.0	66.4	...	±0.5
Acetone	20	16.05	16.15	15.95	±0.4
	80	15.35	15.35	15.25	±0.2
<i>n</i> -Butyl alcohol	20	14.05	14.3	...	±0.8
	80	14.75	14.75	14.55	±0.6
Benzene	20	14.75	14.75	14.55	±0.6
	80	15.95	15.95	...	0
Toluene	20	13.5	13.6	13.5	±0.3
	80	11.75	11.85	...	±0.4
Carbon tetrachloride	20	10.35	10.35	10.25	±0.4

<sup>a</sup> In joules cm.<sup>-1</sup> sec.<sup>-1</sup> °C.<sup>-1</sup>.

Agreement between results obtained by the different experimental methods is excellent, lying on average within about ±0.4%.

Challoner, Gundry, and Powell (16) have also carried out an extensive series of measurements in two types of apparatus, *viz.* parallel plates and concentric cylinders. Their results are given in Table IV. Again good agreement is obtained, the average of the deviations from the mean being about ±0.6%.

It is unfortunate that, in both sets of data, no positive information is given that the measurements were made on samples of the same degree of purity as evidenced, for example, by the physical constants such as boiling

TABLE IV

 THERMAL CONDUCTIVITIES OF LIQUIDS,  $\lambda \times 10^4$ ,<sup>a</sup> FOR TWO DIFFERENT TYPES OF APPARATUS (CHALLONER, GRUNDY, AND POWELL)

Liquid	Temp., °C.	Type of apparatus		Average deviation from mean, %
		Parallel plates	Concentric cylinders	
Toluene	25.5	13.6	14.0	±1.5
	25.5	13.6	14.0	±1.5
	52.8	12.8	12.6	±0.8
	70.1	12.2	12.3	±0.4
	70.1	12.2	12.2	0
	24.1	13.7	14.0	±1.1
	24.1	13.7	13.7	0
	24.3	10.7	10.8	±0.5
Carbon tetrachloride	24.5	10.7	10.6	±0.5
	56.1	10.2	9.9	±1.5
	56.1	10.2	10.0	±0.5
	24.9	10.7	10.5	±1.0
	24.9	16.8	17.0	±0.6
Ethyl alcohol	51.1	16.0	15.8	±0.6
	51.2	16.0	16.0	0
	24.8	16.8	17.0	±0.6
	27.0	28.8	28.8	0
Glycerine	48.0	29.1	29.0	±0.2
	26.0	61.2	60.5	±0.6
Water	51.5	64.6	64.3	±0.2
	26.5	61.3	60.1	±1.0
	43.0	63.6	61.6	±1.6
Trifluorotrichloroethane	22.0	7.9	7.8	±0.6
	36.0	7.45	7.5	±0.3

<sup>a</sup> In joules cm.<sup>-1</sup> sec.<sup>-1</sup> °C.<sup>-1</sup>.

point and refractive index. However, the substantial agreement obtained using the different experimental techniques, is a strong indication of the reliability of the measurements, especially as these are over both a range of temperatures for particular substances and a range of values of thermal conductivities between substances. This is important in checking for the absence of convection. Two of the liquids used in these comparative studies, toluene and water, have been proposed as thermal conductivity standards.

To make a proper statistical analysis of the various results on the thermal conductivity of any particular substance, it is necessary to have available the actual experimental values obtained at the exact temperature of measurement, as well as the number of determinations made at this temperature. While this information is available in some papers, in others only smoothed values at regular temperature intervals are reported. In view of this, "recommended" or "best" values, in what follows, cannot be strictly defined, statistically speaking, due to this lack of information. On the other hand, to discard results where full information is not available is not justified.

## 1. Toluene

The use of toluene as a standard has been proposed by Riedel (113) and by Ziebland and Burton (148)

TABLE V  
THE THERMAL CONDUCTIVITY OF TOLUENE

Investigator	A	B	Range of measurements, °C.	No. of points	$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	
					25°	60°
Riedel	14.06	0.0272	-80-80	3	13.38	12.43
Schmidt and Leidenfrost	14.06	0.0259	20-80	7	13.41	12.51
Challoner and Powell	14.39	0.0314	0-80	8	13.60	12.51
Vargaftik	14.14	0.0238	25-85	6	13.54	12.71
Ziebland and Burton	14.02	0.0285	-15-112	29	13.31	12.31
Ziebland and Burton recommended values	14.06	0.0280	-20-120		13.36	12.38
Horrocks and McLaughlin	14.03	0.0292	25-60	4	13.30	12.28
Bridgman	15.94	0.0234	30-75	2	15.35	14.54

because of the temperature range of its liquid life, -94 to 110°. The latter authors have proposed a linear equation,  $10^4\lambda = A - BT$ , for the thermal conductivity as a function of temperature, in the range -20 to 120°, from a statistical analysis of the results of Riedel (113) (concentric cylinders, parallel plates, and concentric spheres), Schmidt and Leidenfrost (119) (concentric cylinders), Challoner and Powell (17) (parallel plates), Vargaftik (134) (steady-state hot wire cell), and their own results (concentric cylinders). The coefficients of this equation are given in Table V together with the coefficients from the corresponding equations of the individual sets determined by a least-squares analysis. Also included are the results of Horrocks and McLaughlin (56) (nonsteady-state hot wire cell) reported since Ziebland and Burton's analysis.

From Table V it can be seen that, leaving aside Bridgman's results (12), the average deviation from the mean of the other six investigations, in the overlapping temperature range 25-60°, is within 0.75% at 25° and just within 1% at 60°. It should be noted that the lowest values at these temperatures reported by Ziebland and Burton and Horrocks and McLaughlin are virtually identical, and that the highest values are given by Vargaftik and by Challoner and Powell. Over-all, Ziebland and Burton find that their equation is applicable within 1% for values between -20 and 110°

and probably within 2% between -80 and -20°. It is likely that if higher precision is required in the fixing of this standard, the lower values should be taken as these would be expected in the complete absence of convection. The results of Bridgman included in Table V indicate that his measurements are too high by about 10%. This is important to note as his measurements as a function of pressure are virtually the only ones available, for liquids as opposed to dense gases, in the high pressure range.

## 2. Water

Numerous measurements have been made of the thermal conductivity of water by different workers. The temperature range between 0 and 80° has been covered most extensively, and in this range the available data over the period from about 1900 to 1958 have been summarized and discussed by Powell (93) who has also proposed a "best" set of values. These are derived from the results of Vater (141) (parallel plates), Riedel (108, 113, 114) (parallel plates, concentric cylinders, concentric spheres), Schmidt and Sellschopp (121) and Schmidt and Leidenfrost (120) (concentric cylinders), and his own measurements with Challoner (17) (parallel plates). Values obtained by these authors interpolated at 10° intervals are given in Table VI together with the more recent measurements of Vargaftik and Oleshchuk (135) (steady-state hot wire cell) and Leneindre, Johanin, and Vodar (72) (concentric cylinders). Recent values reported by Lawson, Lowell, and Jain (71) at atmospheric pressure have not been included as these have been obtained by extrapolation procedures, and in addition the results of Vater are excluded as his technique is rather unorthodox. Those of Schmidt and Sellschopp are superseded by the more recent work of Schmidt and Leidenfrost.

Water exhibits exceptional behavior in that the thermal conductivity increases with temperature, rather than decreases, and in addition is not linear in  $T$ . The values in Table VI were therefore fitted to the equation

TABLE VI  
THE THERMAL CONDUCTIVITY,  $\lambda \times 10^4$ ,<sup>a</sup> OF WATER AT ATMOSPHERIC PRESSURE

Temp., °C.	Riedel		Challoner and Powell		Leneindre, Johanin, and Vodar		Schmidt and Leidenfrost		Vargaftik and Oleshchuk		Recommended
	Exptl.	Deviation	Exptl.	Deviation	Exptl.	Deviation	Exptl.	Deviation	Exptl.	Deviation	
0	56.5	0.30	56.1	-0.10					55.95	-0.25	56.20
10	58.25	0.11	58.35	0.21					57.9	-0.24	58.14
20	59.9	-0.01	60.4	0.49			59.6	-0.31	59.8	-0.11	59.91
30	61.4	-0.12	61.95	0.43			61.3	-0.22	61.3	-0.22	61.52
40	62.8	-0.17	63.2	0.23	63.55	0.58	62.7	-0.27	62.7	-0.27	62.97
50	64.1	-0.15	64.5	0.25	64.7	0.45	64.0	-0.25	64.0	-0.28	64.25
60	65.25	-0.12	65.7	0.33	65.7	0.33	65.1	-0.27	65.0	-0.37	65.37
70	66.3	-0.02	66.5	0.18	66.5	0.18	66.15	-0.17	66.05	-0.27	66.32
80	67.0	-0.11	67.3	0.19	67.2	0.09	67.15	0.04	66.9	-0.21	67.11
90	67.6	-0.13			67.7	-0.03	68.1	0.37	67.7	-0.03	67.73
100	68.05	-0.14			68.1	-0.09			68.3	0.11	68.19

<sup>a</sup> In joules cm.<sup>-1</sup> sec.<sup>-1</sup> °C.<sup>-1</sup>.



$$10^4\lambda = A + BT + CT^2$$

The coefficients are given by  $A = 56.200$ ,  $B = 2.022 \times 10^{-1}$ , and  $C = -8.230 \times 10^{-4}$  with  $T$  in  $^{\circ}\text{C}$ . The coefficient of variation of this regression is 0.4% and the maximum deviation 0.8%. Both figures are well within the experimental error and show that a quadratic is sufficient for adequate representation of the results. Table VI gives the recommended values and the deviations of the various sets of results. It should be noted that with the exception of the 0–20° range Challoner and Powell's values are consistently higher than those of Schmidt and Leidenfrost, Vargaftik and Oleshchuk, and Riedel. Slightly higher values were also reported by these authors for toluene. Riedel's value at 0° is, however, higher than Challoner and Powell's value, which is closer to the average at this temperature, and in addition the Schmidt and Leidenfrost values are higher than the average in the top end of the temperature range. The results of Leneindre, Johanin, and Vodar are highest in the 40–70° range.

### 3. Biphenyl

Above 100° reliable thermal conductivity data on liquids become increasingly scarce and are confined, principally to a few measurements on aromatic hydrocarbons, molten salts, and metals. Ziebland and Burton (149) (coaxial cylinders) and Horrocks and McLaughlin (56) (nonsteady-state hot wire cell) have reported measurements on biphenyl, the former for the range 90–310° at 60 atm. with an estimated accuracy of  $\pm 1.5\%$ , and the latter from 80 to 130° with an estimated accuracy of  $\pm 0.25\%$ . In the overlapping temperature range, agreement between both sets of results is within about 0.3% as shown in Table VII. In addition,

TABLE VII  
COMPARISONS OF DATA ON TOLUENE AND BIPHENYL

Biphenyl		Toluene	
$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>		$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	
Temp., °C.	Horrocks and McLaughlin	Temp., °C.	Ziebland and Burton
81.0	13.62	25	13.30
89.7	13.50	37.4	12.94
103.2	13.31	51.2	12.53
115.6	13.14	61.0	12.25
132.2	12.90		12.28

tion, the agreement between both sets of workers for the data on toluene (Table VII) strengthens the agreement on biphenyl and suggests that the influence of the small pressure used by Ziebland and Burton can be neglected. Cecil, Koerner, and Munch (15) have also measured the thermal conductivity of biphenyl, but, as their data exhibit no temperature dependence between 98 and 217°, it has not been included.

### 4. Lead and Sodium Nitrate

Above 300°, if resort is not made to high pressure

techniques, thermal stability requires a choice of standards based on molten salts or metals. This introduces complications in apparatus design because of the particular properties of these materials, and, as measurements above this temperature are more difficult, the discrepancy between different results will be correspondingly larger than when compared with the lower temperature range.

Four investigations have been made of the thermal conductivity of lead. The results of Bidwell (6) are about 40 to 50% higher than those of the other three authors and so have been discarded. In addition, while the values of Konno (67) are in close agreement at the melting point with those of Powell and Tye (94), they decrease with increase of temperature in contrast to the general behavior of other heavy metals (see section VIIIA) and so are also discarded. The results of Powell and Tye and Rosenthal (115) have the same slope and only differ by about 10%. In view of the fact that Powell and Tye cover the larger temperature range, and Powell's agreement with accepted results on other materials at lower temperatures, his smoothed values can be recommended for lead. These results are given in Table VIII.

TABLE VIII

THE THERMAL CONDUCTIVITY OF LEAD BETWEEN 350 AND 600°  
Temp., °C.

350	400	450	500	550	600
$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	1600	1690	1760	1810	1840

For sodium nitrate the situation is no more satisfactory than for lead. Three sets of data are available. The results of Turnbull (129) (nonsteady-state hot wire cell) are about 25% smaller than those of the other two investigators. The values of Bloom, Tricklebank, and Doroszkowski (8) (concentric cylinders) agree within better than 2% up to 370° and then differ by about 10% from those of McLaughlin, Merz, and Ubbelohde (83) (nonsteady-state hot wire cell) between 370 and 420°. As the values of the latter authors are linear throughout the range from 300 to 460°, they are provisionally recommended. The unsmoothed values are given in Table IX and have an extremely small coefficient. It must be added that greater discrepancies occur between the measurements (8, 83) for molten salts, other than those quoted above for sodium nitrate, and so the values in Table IX require further confirmation.

TABLE IX

THE THERMAL CONDUCTIVITY OF SODIUM NITRATE

Temp., °C.	313.2	318.1	325.2	336.2	343.3	348.8	370.9
$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	54.1	54.4	54.2	54.8	54.7	54.6	54.9
Temp., °C.	388.9	401.2	417.8	427.2	451.6	464.8	
$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	54.5	54.5	55.5	54.8	55.4	55.7	

## III. THEORIES OF THERMAL CONDUCTIVITY

In order to set up a theory and use it to calculate the thermal conductivity of a liquid or dense gas, it is necessary to have a supply of basic information about such things as the structure of the liquid, the molecular shape, the intermolecular forces between molecules, and the molecular mechanisms of thermal conduction. In practice, little of this information is available and resort has to be made to calculating the coefficient for an idealized system. This system is generally taken to be one composed of spherically symmetric molecules where the intermolecular potential can be approximated to, in successive degree of sophistication, by a rigid sphere, square well, or continuous spherically symmetric interaction potential such as the Lennard-Jones 12:6 potential. Rigid sphere and square well theories have the advantage of relative simplicity for analytic evaluation due to the discontinuous nature of the intermolecular potential.

In the discussion of the various theories that exist, it is convenient to divide them up on the basis of the form of the intermolecular potential that is assumed. Before discussing these theories, however, the relationship of the coefficient of thermal conductivity to other transport coefficients requires consideration as well as the structure of the liquid state and the molecular mechanism of thermal conduction.

In addition, while viscosity *per se* is not the topic of this review, it is necessary to consider it at times, particularly in discussing the mechanisms of transport and also in considering various statistical theories, as these can sometimes be checked more readily on the basis of the results they give for the dimensionless ratio  $m\lambda/k\eta$  than for the individual transport coefficients.

## A. RELATIONSHIP OF THERMAL CONDUCTIVITY TO OTHER TRANSPORT COEFFICIENTS (81)

In general, as with thermal conductivity, the other transport coefficients are defined as the proportionality constants between the flux and the corresponding driving force. The flux of mass  $J_m$  down a concentration gradient  $\partial c/\partial x$  gives rise to the phenomenon of diffusion (Fick's law), the flux of momentum  $J_{mv}$  down a velocity gradient  $\partial v/\partial z$  to viscosity (Newton's law), and the flux of charge  $J_e$  down a potential gradient  $\partial U/\partial x$  to electrical conductivity  $\sigma_e$  (Ohm's law). These laws and the dimensions of the transport coefficients derived from them are given by the equations

$$\begin{array}{llll} \text{Fourier's law} & J_q = -\lambda \partial T/\partial x & \lambda = mlt^{-2}T^{-1} & \\ \text{Fick's law} & J_m = -D \partial c/\partial x & D = l^2t^{-1} & \\ \text{Newton's law} & J_{mv} = -\eta \partial v/\partial z & \eta = ml^{-1}t^{-1} & \\ \text{Ohm's law} & J_e = -\sigma_e \partial U/\partial x & \sigma_e = Q^2 l^{-2} m^{-1} & \end{array} \quad (\text{Eq. 44})$$

where the fundamental quantities that have been chosen are mass  $m$ , length  $l$ , time  $t$ , charge  $Q$ , and temperature  $T$ .

The dimensions given above are not in a useful form for examining possible relationships between the transport coefficients because of the time dimension. This can however be eliminated (73) using the definition of absolute temperature ( $\frac{1}{2}mv^2 = 3kT/2$ ) to give

$$t = m^{1/2} l k^{-1/2} T^{-1/2}$$

and the transport coefficients rewritten

$$\begin{array}{ll} D = m^{-1/2} l k^{1/2} T^{1/2} & \eta = m^{1/2} l^{-2} k^{1/2} T^{1/2} \\ \lambda = m^{1/2} l^{-2} k^{1/2} T^{1/2} & \sigma_e = Q^2 m^{-1/2} l^{-2} k^{-1/2} T^{-1/2} \end{array} \quad (\text{Eq. 45})$$

where  $k$  is Boltzmann's constant.

Various possible relationships between the thermal conductivity and the other transport coefficients can now be deduced from Eq. 45 depending on whether or not the system contains charged particles.

## 1. Systems Containing Uncharged Particles

Of the other possible combinations that exist, the ratio of  $\lambda$  to  $\eta$  given from Eq. 45 by the dimensionless quantity  $m\lambda/k\eta$  is the one of most interest. This ratio is generally discussed in the form of the Prandtl number where  $k$  (Boltzmann's constant) is replaced by the specific heat. As  $m\lambda/k\eta$  is the basic dimensionless relationship, it is better to examine this ratio initially.

Table X (82) gives the ratio  $m\lambda/k\eta$  for a series of simple liquids, and it can be seen that this ratio is constant within about 10% of 2.48 for the series.

TABLE X  
RATIO OF  $m\lambda/k\eta$  FOR SIMPLE LIQUIDS

Liquid	Temp., °K.	$m\lambda/k\eta$
Argon	84.2	2.16
	87.3	2.31
Nitrogen	69.1	2.20
	71.4	2.39
	77.3	2.98
Carbon monoxide	72.0	2.19
	77.7	2.64
	80.8	2.80
Methane	93.2	2.21
	103.2	2.75
	108.2	2.98
Benzene	288.2	2.02
	298.2	2.28
	308.2	2.55
	318.2	2.83
Carbon tetrachloride	298.2	2.19
	308.2	2.42
	318.2	2.78

Certain important conclusions can therefore be drawn from these results. In the first case, as the specific heat of the liquids in the series varies considerably from argon to carbon tetrachloride, due to the excitation of internal modes in the polyatomic molecules, then no corresponding regularity in the Prandtl number would be observed since this involves  $C_p$ . Conversely if the thermal conductivity involved  $C_p$ , as distinct from some specific heat which is only translational and configurational,

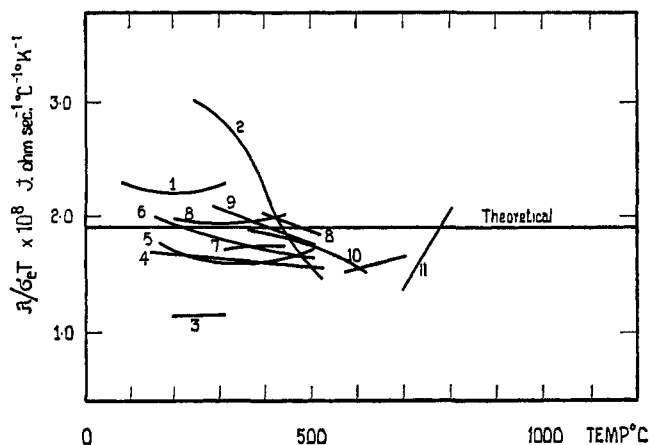


Fig. 2.—The Wiedemann-Franz-Lorentz ratio of the thermal to the electrical conductivity of a metal: 1, Hg; 2, Zn; 3, K; 4, Na-K 77 wt. % K; 5, Na; 6, Pb-Bi 55.5 wt. % Bi; 7, Cd; 8, Na-K 56.5 wt. % K; 9, Bi; 10, Pb; 11, Al (copied substantially from (82)).

then again no corresponding regularity in  $m\lambda/k\eta$  would be expected. Finally, examination of the temperature dependence of the ratio shows that in all cases it increases with increase in temperature, so that the temperature dependence of  $\lambda$  and  $\eta$  are not the same,  $\eta$  decreasing faster with increase of temperature than  $\lambda$ —a fact that must be accounted for in any statistical theory.

Of the possible relationships of the thermal conductivity coefficient to other transport coefficients in systems containing uncharged particles, the only points of interest to note are that the ratio  $\lambda/D$  and the product  $\lambda\eta$  are both independent of the mass, and such relationships are of interest in dealing with the transport properties of mixtures (see section IVD).

### 2. Systems Containing Charged Particles

Again only one well-known relationship is discussed in detail. From Eq. 45 it follows that

$$\frac{\lambda}{\sigma_e} = \frac{k^2 T}{Q^2 \xi} \quad (\text{Eq. 46})$$

where  $\xi$  is a dimensionless quantity and  $Q$  is the charge on the electron. The ratio  $\lambda/\sigma_e T$  for a series of metals and eutectics is given in Fig. 2 where it is seen to be substantially constant with respect to temperature variations. This is the well-known Wiedemann-Franz law (144) for the relationship of the electrical to the thermal conductivities of a metal. The results of Fig. 2 mean that the thermal conductivity of molten metal systems can therefore be obtained with reasonable accuracy from measurements of the electrical resistance alone.

As it is only meaningful to combine transport coefficients when the carrier species is the same, the relationship of the thermal and electrical conductivities obtained above must imply that the main carrier species

in the thermal conductivity of molten metals are the free electrons which determine the electrical conductivity. This conclusion which was put forward by Lorentz (77) to account for the anomalously large thermal conductivity does not mean that lattice terms are not operative. The role of lattice terms in such systems is discussed in section VIIIA.

### B. INTERMOLECULAR FORCES AND THE STRUCTURE OF THE LIQUID STATE

Intermolecular forces and the structure of liquids are discussed extensively in a number of books. For the present review the most appropriate references are 29, 51, and 116. The intermolecular potentials used in the present work are the rigid sphere, square well, and  $n,m$  spherically symmetric potentials given, respectively, by

$$\phi(R) = \begin{cases} \infty, & R < \sigma \\ 0, & R > \sigma \end{cases} \quad \text{rigid-sphere potential} \quad (\text{Eq. 47})$$

$$\phi(R) = \begin{cases} \infty, & R < \sigma_1 \\ -\epsilon, & \sigma_1 < R < \sigma_2 \end{cases} \quad \text{square-well potential} \quad (\text{Eq. 48})$$

$$\begin{aligned} \phi(R) &= AR^{-n} - BR^{-m} \quad (n > m) \quad \text{n,m potential} \\ \phi(R) &= 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right] \quad \text{Lennard-Jones 12:6 potential} \end{aligned} \quad (\text{Eq. 49})$$

For the case of an  $n,m$  potential, the Lennard-Jones 12:6 form is used in calculations as this has yielded adequate representation of the equilibrium and transport properties of dilute gases (51).

With regard to liquid structure most direct information has been provided by the scattering of X-rays (29). This technique gives the equilibrium radial distribution function  $g_0^{(2)}(R)$  which describes the radial distribution of neighbors about a particular molecule in the liquid; *i.e.*, in essence it gives the geometry of the liquid. It is however a time averaged geometry.

Various useful relationships between thermodynamic properties and integrals involving the radial distribution function and the intermolecular potential are well known. The principal ones of these are

$$U' = \frac{N^2}{2V} \int \phi(R) g_0^{(2)}(R) d^3R \quad (\text{Eq. 50})$$

$$\frac{pV}{NkT} = 1 - \frac{N}{6VkT} \int R \frac{d\phi(R)}{dR} g_0^{(2)}(R) d^3R \quad (\text{Eq. 51})$$

and for an  $n,m$  potential (see III F3)

$$\begin{aligned} \frac{6NkT}{V} \left[ -\frac{nm}{3} \frac{U'}{NkT} + (n+m-1) \left( \frac{pV}{NkT} - 1 \right) \right] = \\ \left( \frac{N}{V} \right)^2 \int R^{2\gamma} \phi(R) g_0^{(2)}(R) d^3R \end{aligned} \quad (\text{Eq. 52})$$

where  $U'$  is the configurational energy of the liquid and the other symbols have their usual significance. Equations 50, 51, and 52 show that provided  $\phi(R)$  and  $g_0^{(2)}(R)$  are known, various thermodynamic properties can be evaluated. Alternatively, if in statistical equations for transport coefficients the liquid structure and intermolecular force terms occur in integrals identical

with Eq. 50, 51, or 52, then the transcription to thermodynamic properties is straightforward.

Integration of the experimental radial distribution function for liquid argon at its melting point shows that the number of nearest neighbors has decreased from 12 in the solid to about 10.8 in the liquid, and this type of evidence provides some support for lattice theories of the liquid state, which are simplified models for the evaluation of the configuration partition function. In the simplest of these theories, molecules are assumed to be confined to cells created by the potential energy barrier of the nearest neighbors. If the assembly is a dense system of hard spheres, then the change in potential energy of a molecule displaced a distance  $R$  from the center of its cell due to its neighbors located at the centers of their own cells, is given by

$$\begin{aligned}\psi(R) - \psi(0) &= 0, \quad 0 < R < (a - \sigma) \\ \psi(R) - \psi(0) &= \infty, \quad (a - \sigma) < R\end{aligned}\quad (\text{Eq. 53})$$

where  $a$  is the nearest neighbor distance. Alternatively, if the molecules, located on f.c.c. lattice, interact with a Lennard-Jones 12:6 potential  $\psi(R) - \psi(0)$  is, to terms in  $R^2$  (*i.e.*, harmonic approximation)

$$\psi(R) - \psi(0) = \frac{Z\epsilon}{a^2} [L_1 v^{*4} - M_1 v^{*2}] R^2 \quad (\text{Eq. 54})$$

$v^* = v_0/v = \sigma^3/v$ , where  $v = V/N$  and  $Z = 12$  is the coordination number of the lattice.  $L_1$  and  $M_1$  are lattice summation constants of values 22.11 and 10.56, respectively. Considered in terms of frequencies these  $\psi(R) - \psi(0)$  values correspond (57) to

$$\nu_{\text{H.S.}} = \sqrt{\frac{8kT}{\pi m}} \frac{1}{4(a - \sigma)} \quad (\text{Eq. 55})$$

and

$$\nu_{\text{H.O.}} = \frac{1}{2\pi\sqrt{m}} \left[ \frac{2Z\epsilon}{a^3} \{L_1 v^{*4} - M_1 v^{*2}\} \right]^{1/2} \quad (\text{Eq. 56})$$

These frequencies are the basic quantities required to calculate the thermal conductivity on the cell model to be discussed. The lattice theories can also be used to calculate the thermodynamic properties of liquids. In the present work the only result which is required is the free volume expression for the compressibility factor of a dense fluid of rigid spheres

$$\frac{pV}{NkT} - 1 = \left[ \frac{a}{\sigma} - 1 \right]^{-1} \quad (\text{Eq. 57})$$

which has substantially the same dependence on  $(a/\sigma)$ , although slightly higher values than the exact expression obtained from Eq. 51, *viz.*

$$\frac{pV}{NkT} - 1 = \frac{2}{3} \frac{\pi N \sigma^3}{V} g_0^{(2)}(\sigma) \quad (\text{Eq. 57a})$$

where  $g_0^{(2)}(\sigma)$  is the radial distribution function at contact.

### C. THE MECHANISM OF THERMAL CONDUCTION AND THE TRANSPORT PROPERTIES OF ISOTOPIC MOLECULES

In the gas phase the coefficients of diffusion, viscosity, and thermal conductivity all increase with increase of temperature. In this case it is well known that the principal mechanism of transport, for all three phenomena, is the same, namely the transport over the mean free path between collision of mass momentum and energy, respectively.

Nonsingularity of the transport mechanism in the liquid phase may be evidenced in the temperature dependence of the coefficients. While the diffusion coefficient increases with temperature as in the gas phase, the shear viscosity coefficient decreases with temperature, and the coefficient of thermal conductivity can either decrease or increase with increasing temperature. For most normal cases it generally decreases.

In addition, evidence of changing molecular mechanisms of transport in the dense fluid phase can be obtained by examining the change in magnitude of the transport coefficients on passing from gas to liquid. Values for benzene and argon are given in Table XI.

TABLE XI  
COMPARISON OF VALUES OF TRANSPORT COEFFICIENTS FOR GASES AND CORRESPONDING LIQUIDS

	Temp., °C.	Liquid	Temp., °C.	Gas
Benzene				
$D_1^0 \times 10^5$ , cm. <sup>2</sup> sec. <sup>-1</sup>	25	2.15	25	4000
$\eta \times 10^3$ , poise	25	6.01	25	0.075
$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	25	14.63	0	0.70
Argon				
$D_1^0 \times 10^5$ , cm. <sup>2</sup> sec. <sup>-1</sup>	-189	2.07	25	16,000
$\eta \times 10^3$ , poise	-189	2.80	0	0.21
$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	-189	12.60	0	1.64

These values show that on passing from gas to liquid, the self-diffusion coefficient decreases by a factor of about  $10^3$ , while the coefficients of shear viscosity and thermal conductivity increase by a factor of between 10 and  $10^2$ . The fall in the self-diffusion coefficient reflects directly the relative ease of stochastic migration of a molecule in a dilute, compared with a dense, assembly, and it is in this case, where a singular mechanism exists in any phase, that the coefficient always increases with increase of temperature. The increase in magnitude for the other coefficients indicates that as the density is increased, the transport of momentum and energy is facilitated, hence eliminating the gas-phase mechanism as being of prime importance for these coefficients in the dense fluid phase.

The problem of the difference in transport mechanisms in a dense gas or liquid compared with the dilute gas was first considered by Enskog (19) who differentiated, for rigid spheres, between collisional and convective mechanisms. Convective transport is transport over the distance separating the peripheries of rigid spheres

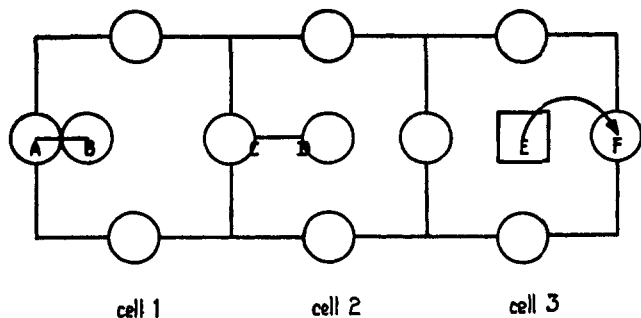


Fig. 3.—Transport mechanisms for a fluid of hard spheres: AB, collisional transport; CD, intracellular convective; and EF, intercellular convective transport.

between collisions, and collisional transport is transport between the centers of colliding rigid spheres at contact. In statistical theories both contributions can be described in terms of the Boltzmann equations.

If a lattice model of the liquid state for rigid spheres is assumed, it is possible (57) to factorize the convective contribution further. Figure 3 gives a schematic representation of three cells of a liquid quasi-lattice. In cell 1 the central rigid sphere has moved into contact with one on the boundary, collisional transport taking place across the centers between A and B on impact. In cell 2 the movement of the central sphere over the distance C-D constitutes the intracellular convective contribution. Such motions, while contributing to viscosity and thermal conductivity, do not lead to a net displacement of the central molecule with respect to the lattice sites and do not therefore lead to diffusion. In the third cell, motion of the central molecule from E to a vacant lattice site at F constitutes intercellular convective transport which does lead to a net displacement with respect to the lattice cells, and, while being the mechanism of diffusion, also contributes to viscosity and thermal conductivity under appropriate circumstances. As can be inferred from the small value of the self-diffusion coefficient in a liquid, the frequency of intercellular motion is small and, as the distance between molecular centers at contact A-B is generally greater than the distance between peripheries C-D in the dense phase, it follows that collisional transport is more important in this case than either of the convective contributions.

While the factorization of mechanisms given above is permissible in the case of rigid spheres, for real molecules, on the cell model due to the extension in space of the intermolecular forces, it is not readily possible to separate the intracellular and collisional contributions. If the central molecule in the cell is however imagined to oscillate about the lattice site, then in each quarter cycle of the period, intracellular convection and collisional transport occurs. These are lumped together and called the intermolecular force term. As for rigid spheres the intercellular convective contribution, which is the diffusive mechanism, also contributes to viscos-

ity and thermal conductivity. On the basis of the measured values of diffusion coefficients in liquids compared with gases as discussed above, indications are that for thermal conductivity and viscosity its role is likely to be unimportant. Confirmation is however required by a statistical calculation (see section III).

In some statistical theories based on the distribution function approach, the mechanisms of energy transport have been discussed in detail also. In the attempts due principally to Kirkwood (65) a molecule, because of its force field, is considered to experience a rapidly fluctuating force due to the random motion of its nearest neighbors. This motion can be described as a stochastic process. The contribution to energy and momentum transport during these encounters is called the intermolecular force contribution. Rice and Allnatt (101) have recently factorized this contribution into two terms. First the contribution arising in the region  $R > \sigma$  where  $\sigma = R$  at  $\phi(R) = 0$ , *i.e.*, the contribution due to the soft part of the intermolecular potential and the collisional contribution arising at  $R = \sigma$  when the hard cores of the molecules come into contact. This subdivision can also be made using the lattice model. The usual convective contribution arising from the motion between collisions leading to a net displacement has also to be included to yield the total thermal conductivity. Again the relative importance of the contributions has to be assessed on the basis of numerical calculations.

Some experimental information on possible molecular mechanisms of transport can be obtained from a study of isotopes (79). If a pair of molecules interact with a potential characterized by two parameters  $\epsilon/k$  and  $\sigma$  which are, respectively, a characteristic energy of interaction and a characteristic molecular diameter, then the transport coefficients can be rewritten from Eq. 45 in the dimensionless form

$$D^* = \frac{D\sqrt{m}}{\sigma\sqrt{\epsilon}} \quad \eta^* = \frac{\eta\sigma^3}{\sqrt{m\epsilon}} \quad \lambda^* = \frac{\lambda\sqrt{m}\sigma^2}{k\sqrt{\epsilon}} \quad (\text{Eq. 58})$$

where  $D^*$ ,  $\eta^*$ , and  $\lambda^*$  are functions of the dimensionless quantities  $kT/\epsilon$  and  $V/N\sigma^3$  only, where  $V$  is the molar volume of the liquid. For an isotopic pair of molecules like  $\text{CH}_4$  and  $\text{CD}_4$ ,  $\epsilon/k$  and  $\sigma$  are virtually identical and the mass alone is different so that from Eq. 58

$$\frac{D}{D_i} = \frac{\eta_i}{\eta} = \frac{\lambda}{\lambda_i} = \sqrt{\frac{m_i}{m}} \quad (\text{Eq. 59})$$

where  $i$  refers to the isotopically substituted species.

According to Eq. 59 the transport coefficient ratios for parent and isotopically substituted species should be proportional to the square roots of the masses, provided the force fields of the molecules are characterized by  $\epsilon/k$  and  $\sigma$  alone, or, alternatively, the force field is spherically symmetric and the equation of motion is of the form

$$F_\alpha = m \frac{dv_\alpha}{dt} \quad (\text{Eq. 60})$$

$F_\alpha$  is the force on a molecule due to the potential field of its neighbors and  $v_\alpha$  is its linear velocity. From the mechanistic point of view, agreement of Eq. 59 with experimental data on isotopic pairs will not differentiate between purely convective or purely vibrational motion, since both involve the same law of force (80).

If the intermolecular potential is noncentral (92), conservation of angular momentum given by the equation

$$G_\alpha = I_{\alpha\beta} \frac{d\omega_\beta}{dt} \quad (\text{Eq. 61})$$

must be considered as well.  $G_\alpha$  is the couple acting on the molecule from forces due to neighboring molecules,  $I_{\alpha\beta}$  is the inertia tensor, and  $\omega_\beta$  the angular velocity. Isotopic substitution does not alter  $F_\alpha$  and  $G_\alpha$  because the intermolecular potential is virtually unaffected. However, except for the special case when *all* atoms in the molecule are changed in the same ratio, isotopic substitution does alter  $m$  and  $I_{\alpha\beta}$  in different ratios so that the equations of motion of the two systems, isotopic and parent, are not altered by a simple scale factor and dimensional analysis is not applicable.

Table XII gives the measured values of the ratios of the viscosities and thermal conductivities of a series of molecules and their isotopically substituted counterparts, together with the square root of the mass and the square root of the mean moment of inertia ratios.

TABLE XII  
TRANSPORT COEFFICIENT RATIOS OF ISOTOPIC PAIRS OF MOLECULES

Pair	Temp., °K.	$\eta_1/\eta$	$\lambda/\lambda_1$	$(m_1/m)^{1/2}$	$(I_1/I)^{1/2}$
C <sub>6</sub> H <sub>12</sub> -C <sub>6</sub> D <sub>12</sub>	293.2	1.064	1.063	1.070	1.215
	311.0	1.062	1.061		
	333.2	1.060	1.059		
C <sub>6</sub> H <sub>6</sub> -C <sub>6</sub> D <sub>6</sub>	293.2	1.065	1.042	1.038	1.100
	311.0	1.062	1.039		
	332.2	1.058	1.036		
H <sub>2</sub> O-D <sub>2</sub> O	293.2	1.245	1.043	1.054	1.390
	313.2	1.202	1.053		
	333.2	1.178	1.060		
	353.2	1.164	1.050		

The viscosities of perdeuteriobenzene and perdeuterio-cyclohexane were measured by Schiessler and Dixon (118) and the thermal conductivities by Horrocks, McLaughlin, and Ubbelohde (53). The heavy water viscosities were measured by Hardy and Cottingham (49) and thermal conductivities by Challoner and Powell (17). Benzene and cyclohexane viscosities are taken from Circular C.461 of the National Bureau of Standards.

These results show that the means of the thermal conductivity ratios over the liquid range of the three pairs agree within an average of 0.5% with the corresponding square root of the mass ratios. This is a striking result in view of the diversity of structure and nature of the bonding in the three pairs, and contrasts sharply with the viscosity data where only for the

pseudo-spherically symmetric cyclohexane pair is the square root of the mass law obeyed.

This indicates that the thermal conductivity ratios are independent of the moments of inertia of the systems studied and hence possibly of rotational contributions to energy transport. Agreement with the square root of the mass law also substantiates the possibility of vibrational and convective mechanisms, provided no rotational terms enter the motion. Alternatively, if rotational motion accompanies diffusive motion, the mechanism must make a negligible contribution to the total heat conduction. For viscosity, on the other hand, the square root of the mass law is obeyed only by the cyclohexane system. For the nonspherical pairs the ratio lies between that of the square root of the masses and the square root of the mean moments of inertia, indicating that rotational motion is important in momentum transport.

The isotope data and the  $m\lambda/k\eta$  ratio therefore suggest that internal bond vibrations and molecular rotations are not important in thermal conduction in liquids. This contrasts with the gas phase where the Eucken correction factor, which takes account of internal modes, has been tacked on to the translational contribution to provide better agreement between calculated and experimental thermal conductivities. It might therefore be expected that statistical theories of thermal conductivity of liquids could be applied to simple pseudo-spherically symmetric molecules with internal degrees of freedom, without specifically having to take these factors into account in terms of energy transport mechanisms.

#### D. THEORIES FOR HARD-SPHERE MOLECULES

##### 1. The Theory of Enskog

The first real attempt to provide a proper theory of the thermal conductivity of a liquid was made by Enskog (19), who extended the dilute gas theory for hard spheres to take account of a change in density.

As a gas is compressed the ratio of the diameter of the molecules to the mean free path changes, from being virtually negligible, to the order of unity. During this process the collision frequency alters due to two causes: (i) it is increased due to the decrease in the mean free path, and (ii) it is decreased because molecules are close enough to shield each other from collisions with more distant neighbors. Enskog showed that the collision frequency in a dense gas of rigid spheres, differed from the value of the same dilute gas at the same temperature by a factor  $Y$  which depends only on the local thermodynamic state and molecular diameter  $\sigma$  as given by

$$Y = 1 + 0.6250 \left( \frac{b_0}{V} \right) + 0.2869 \left( \frac{b_0}{V} \right)^2 + 0.115 \left( \frac{b_0}{V} \right)^3 + \dots \quad (\text{Eq. 62})$$

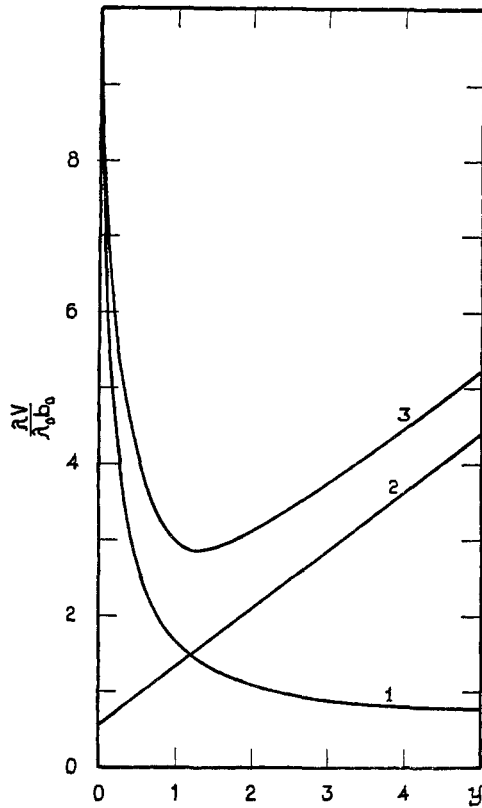


Fig. 4.—Convective, 1, collisional, 2, and total, 3, thermal conductivity contributions for a fluid of hard spheres on the Enskog model.

where  $b_0 = (\frac{2}{3}) \pi N \sigma^3$  is the rigid-sphere second virial coefficient.  $Y$  is actually the contact radial distribution function, *i.e.*,  $Y = g_0^{(2)}(\sigma)$ .

The second effect due to increasing compression is the growing importance of the collisional transfer of energy and momentum. With these assumptions, Enskog modified the Boltzmann equation for higher densities, solved it by the Chapman-Enskog method used in dilute gas theory, and derived equations for the transport coefficients in an analogous manner to the dilute gas treatment.

The derived heat flux vector  $J_q$  can be written as a sum of convective and collisional terms

$$J_{q, \text{conv}} = -\frac{1}{Y} \left(1 + \frac{2}{5} \pi n \sigma^3 Y\right) \lambda_0 \frac{\partial T}{\partial r} \quad (\text{Eq. 63})$$

$$J_{q, \text{coll}} = -\left[\frac{2}{5} \pi n \sigma^3 \left(1 + \frac{2}{5} \pi n \sigma^3 Y\right) \lambda_0 + \frac{3k}{2m} K\right] \frac{\partial T}{\partial r} \quad (\text{Eq. 64})$$

and the total subsequently as

$$J_q = -\left[\frac{1}{Y} \left(1 + \frac{2}{5} \pi n \sigma^3 Y\right) + \frac{2}{5} \pi n \sigma^3 \left(1 + \frac{2}{5} \pi n \sigma^3 Y\right) \lambda_0 + \frac{3k}{2m} K\right] \frac{\partial T}{\partial r} \quad (\text{Eq. 65})$$

where  $\lambda_0$  is the dilute gas coefficient given in the fourth approximation by

$$\lambda_0 = 1.02513 \frac{25}{32\sigma^2} \left(\frac{mkT}{\pi}\right)^{1/2} \frac{3k}{2m} \quad (\text{Eq. 66})$$

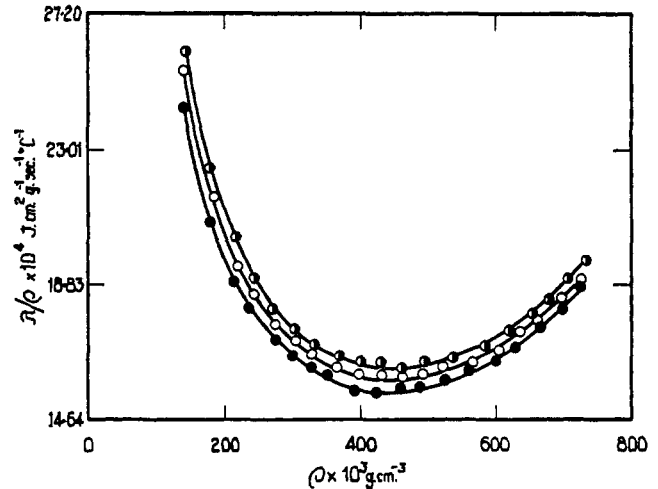


Fig. 5.—Plot of the ratio of the thermal conductivity to the density as a function of the density for nitrogen, illustrating the existence of the Enskog minimum: ● 25°, ○ 50°, ○ 75° (copied substantially from (84)).

and  $K$  the bulk viscosity coefficient is

$$K = \frac{4}{9} n^2 \sigma^4 Y (\pi m k T)^{1/2} \quad (\text{Eq. 67})$$

Substituting Eq. 66 and 67 into Eq. 65 and using  $(b_0/V)Y = y$  gives on comparing with Fourier's law

$$\frac{\lambda V}{\lambda_0 b_0} = \frac{1}{y} + 1.2 + 0.7574y \quad (\text{Eq. 68})$$

which has a minimum value 2.938 at  $y = 1.151$ . A correction factor of the form of Eq. 68 had previously been derived by Jäger (60). Factorizing Eq. 68 into its convective and collisional terms gives

$$\frac{\lambda_{\text{conv}} V}{\lambda_0 b_0} = \left(\frac{1}{y} + \frac{3}{5}\right) \quad (\text{Eq. 69})$$

and

$$\frac{\lambda_{\text{coll}} V}{\lambda_0 b_0} = \frac{3}{5} \left(1 + \frac{3}{5} y\right) + \frac{32y}{25(1.02513)\pi} \quad (\text{Eq. 70})$$

Equation 69 shows that the convective contribution to thermal conductivity decreases monotonically with increasing compression at constant temperature as would be expected. The collisional contribution, however, increases linearly with increasing compression becoming the dominant term in the dense phase. Both terms are plotted in Fig. 4 together with the sum as given by Eq. 68.

Relationship of Enskog's Theory to Experiment

If  $b_0$  in Eq. 68 is replaced by  $bM$  where  $M$  is the molecular weight it can be rewritten

$$\frac{\lambda}{\rho} = \lambda_0 b \left(\frac{1}{b\rho Y} + 1.2 + 0.7574b\rho Y\right) \quad (\text{Eq. 71})$$

where  $\rho$  is the density.  $\lambda/\rho$  plotted against the density therefore passes through a minimum on going from the dilute to the dense gas. This is illustrated in Fig. 5 for nitrogen (84) and shows that the general predictions of the theory are correctly given.

As the model is based on rigid spheres, it is not possible to use the theory directly to calculate the thermal conductivity without the injection of some empirical steps to correlate it with the properties of real molecules. This may be done as follows. As Eq. 17 has a minimum it can be rearranged (19) as

$$\frac{\lambda}{\rho} = \frac{1}{2.938} \left( \frac{\lambda}{\rho} \right)_{\min} \left( \frac{1}{b\rho Y} + 1.2 + 0.7574b\rho Y \right) \quad (\text{Eq. 72})$$

If  $b$  and  $Y$  are temperature independent then as

$$p = nkT(1 + b\rho Y) \quad (\text{Eq. 73})$$

on the model

$$\left( \frac{\partial p}{\partial T} \right)_{\rho} = nk(1 + b\rho Y) \quad (\text{Eq. 74})$$

Equation 74 suggests (85) that for real molecules  $b\rho Y$  should be obtained from experimental ( $pVT$ ) data using the relationship

$$y = b\rho Y = \frac{M}{R\rho} \left( \frac{\partial p}{\partial T} \right)_{\rho} - 1 \quad (\text{Eq. 75})$$

so that with Eq. 75 the value of  $\lambda$  can be calculated from Eq. 72.

A comparison (84) of calculated and experimental thermal conductivities for nitrogen as a function of pressure is given in Table XIII where it is seen that this procedure reproduces the experimental results satisfactorily.

TABLE XIII

CALCULATED AND EXPERIMENTAL THERMAL CONDUCTIVITIES OF NITROGEN AS A FUNCTION OF PRESSURE AT 50°

Pressure, atm.	$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>		Pressure, atm.	$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	
	Exptl.	Calcd.		Exptl.	Calcd.
1	2.77	2.94	521	6.36	6.28
12.2	2.83	3.01	603	6.91	6.83
33.8	2.92	3.06	688	7.37	7.37
62.6	3.07	3.22	783	7.91	7.91
93.1	3.26	3.42			
116.5	3.47	3.57	785	7.83	7.92
140.7	3.63	3.75	889	8.50	8.54
185.6	3.96	4.05	898	8.50	8.58
228.1	4.27	4.36	1080	9.30	9.55
258.7	4.52	4.56	1269	10.13	10.51
300.0	4.82	4.82	1450	11.01	11.39
343	5.19	5.15	1647	11.73	12.27
383	5.44	5.40	1931	12.86	13.44
453	5.95	5.86	2185	13.78	14.49

Alternatively Eq. 71 can be fitted at the low density end using the experimental value of  $\lambda_0$  and calculating  $b$  by substituting the virial expansion

$$pV = RT + B\rho \quad (\text{Eq. 76})$$

into Eq. 75 which gives  $b = dB/RdT$ . This method has been used by Michels, Sengers, and Van de Klundert (88).

A good check on the applicability of Eq. 75 can be obtained by examining the ratio  $m\lambda/k\eta$  on the Enskog theory. This is given by the expression (63)

$$\frac{m\lambda}{k\eta} = \frac{15}{4} \left[ \frac{1 + 1.2y + 0.7574y^2}{1 + 0.8y + 0.7614y^2} \right] \quad (\text{Eq. 77})$$

which shows that the dilute gas transport coefficients and the  $b$  factor are eliminated, the ratio being solely a function of  $y$ . This equation has a maximum of 4.333 at  $y = 1.126$  on the hard-sphere model. Table XIV gives experimental values (88) of this ratio and values calculated using  $y$  from Eq. 75 for argon. It also shows that the calculated maxima occur at a slightly higher density than that found experimentally, and, in addition, below the maximum the ratio decreases with increase of temperature contrary to experiment. Overall, however, the largest discrepancy between calculated and experimental values of the ratio is only about 5% so that Eq. 75 is a surprisingly good approximation for  $y$ .

TABLE XIV

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF THE RATIO  $m\lambda/k\eta$  FOR ARGON

$\rho$	Experimental				Calculated			
	0°	25°	50°	75°	0°	25°	50°	75°
1	3.733	3.753	3.773	3.795	3.753	3.753	3.753	3.753
10	3.801	3.807	3.815	3.840	3.781	3.780	3.779	3.778
25	3.854	3.878	3.884	3.898	3.825	3.822	3.820	3.819
40	3.930	3.946	3.952	3.962	3.866	3.866	3.861	3.858
60	4.002	4.029	4.031	4.035	3.920	3.917	3.911	3.910
80	4.081	4.095	4.099	4.109	3.972	3.965	3.959	3.955
100	4.171	4.159	4.161	4.167	4.016	4.009	4.004	3.999
120	4.230	4.226	4.221	4.234	4.060	4.053	4.046	4.040
160	4.340	4.336	4.330	4.340	4.135	4.128	4.121	4.116
200	4.425	4.425	4.431	4.447	4.197	4.191	4.186	4.181
240	4.503	4.493	4.501	4.519	4.247	4.242	4.238	4.235
280	4.551	4.535	4.549	4.569	4.285	4.282	4.279	4.276
320	4.563	4.557	4.569	4.593	4.312	4.310	4.308	4.306
360	4.555	4.561	4.573	4.601	4.328	4.327	4.326	4.325
400	4.551	4.545	4.571	4.597	4.333	4.343	4.346	4.340
440	4.539	4.533	4.561	4.593	4.328	4.329	4.330	4.331
480	4.519	4.513	4.543	4.571	4.314	4.317	4.319	4.321
520	4.477	4.485	4.521	4.549	4.295	4.299	4.302	4.305
560	4.435	4.449	4.489	4.512	4.271	4.276	4.281	4.285
600	4.374	4.402	4.447	4.459	4.244	4.250	4.256	4.262
640	4.288	4.328	4.347	4.419	4.218	4.224	4.229	4.235

It should be remembered that these values of  $m\lambda/k\eta$  are for the transition from the dilute to the dense fluid. As the density is further increased and the temperature lowered, the value becomes about 2.5 as given in Table X.

## 2. The Theory of Longuet-Higgins and Pople

Longuet-Higgins and Pople (74) have calculated the thermal conductivity and viscosity of a dense fluid of rigid spheres assuming the existence of a collisional mechanism alone. The two basic assumptions involved are: (i) that the spatial pair distribution function depends only on the temperature and density and not on the temperature gradient or rate of strain; (ii) that the velocity distribution function of a single particle is Maxwellian with a mean equal to the local hydrodynamic velocity and a spread determined by the local temperature. The resulting expression for the coefficient of thermal conductivity is

$$\lambda = \sigma k \left( \frac{kT}{\pi m} \right)^{1/2} \left( \frac{pV}{NkT} - 1 \right) \frac{N}{V} \quad (\text{Eq. 78})$$



Several features of this theory may be mentioned. First, combining Eq. 78 with the corresponding expression for the coefficient of viscosity derived by the same authors gives the ratio  $m\lambda/k\eta = 2.5$ . This is in substantial agreement with the experimental results of Table X, but as a rigid-sphere model is assumed no temperature dependence of the ratio is obtained. Secondly, Eq. 78 may be transformed into the reduced form as for Enskog's equations using values of  $\lambda_0$  for the corresponding infinitely dilute gas and the definition of  $y$  to give

$$\frac{\lambda V}{\lambda_0 b_0} = \frac{32}{25\pi} y \quad (\text{Eq. 79})$$

Comparison with Eq. 70 shows, as first pointed out by Dahler (28), that this result is identical with that portion of the Enskog equation which does not depend on the perturbed term of the distribution function. This can be expected from the assumption of i and ii. However, neglect of the contribution to thermal conductivity arising from the distortion of the distribution function neglects a substantial portion of the collisional transport as deduced by Enskog (19).

### 3. The Theory of Horrocks and McLaughlin

In this theory (57) a lattice structure for the liquid state is assumed. The change in potential energy of a molecule displaced from the center of its cell due to its neighbors located at the centers of their cells is given by Eq. 53. In such a system in which the unit is essentially that of a particle in a box, the intercellular convective contribution to thermal conductivity vanishes and  $C_v = 3k/2$  as the rigid sphere has only translational energy. The mean frequency of motion given by Eq. 55 then follows from the Maxwell-Boltzmann velocity distribution and the definition of the mean molecular velocity. Hence using Eq. 149 for the thermal conductivity in terms of the frequency and assuming a f.c.c. lattice geometry, the thermal conductivity expression is

$$\lambda = \frac{3}{2} k \left( \frac{kT}{\pi m} \right)^{1/2} \frac{1}{a(a - \sigma)} \quad (\text{Eq. 80})$$

Equation 80 includes both the intracellular and collisional contributions. In terms of the compressibility factor for a dense fluid of rigid spheres on the free volume theory, Eq. 80 becomes

$$\lambda = \sigma k \left( \frac{kT}{\pi m} \right)^{1/2} \left( \frac{pV}{RT} - 1 \right) \left( \frac{3}{2a\sigma^2} \right) \quad (\text{Eq. 81})$$

This result may be compared with that of Longuet-Higgins and Pople (78) which on assuming a f.c.c. lattice is

$$\lambda = \sigma k \left( \frac{kT}{\pi m} \right)^{1/2} \left( \frac{pV}{RT} - 1 \right) \left( \frac{\sqrt{2}}{a^3} \right) \quad (\text{Eq. 82})$$

Identity between the two expressions would not be expected. This arises as the present theory includes

both the intracellular convective term as well as the collisional contribution as can be seen from the expression for  $\nu$  derived from the mean molecular velocity  $\sqrt{8kT/\pi m}$ , whereas the Longuet-Higgins and Pople equation is for the collisional contribution alone.

### 4. The Theory of Rice, Kirkwood, Ross, and Zwanzig

The modified Boltzmann equation for dense fluids used by Enskog is basically derived by intuitive arguments. Rice, Kirkwood, Ross, and Zwanzig (106) have suggested that the corresponding equation derived from the Kirkwood theory (see section IIIF1) for rigid spheres, considered as the limiting case of a spherically symmetric potential, is different from Enskog's equation. The final expression for the thermal conductivity given in terms of the kinetic and collisional contributions, in the notation of this paper, is

$$\frac{\lambda_{\text{conv}} V}{\lambda_0 b_0} = \left( \frac{1}{y} + \frac{3}{5} \right) \quad (\text{Eq. 83})$$

$$\frac{\lambda_{\text{coll}} V}{\lambda_0 b_0} = \frac{4}{5} \left( 1 + \frac{3}{5} y \right) + \frac{32}{25\pi} y \quad (\text{Eq. 84})$$

The sole difference lies therefore in the pre-bracket factor of the collisional contribution, *viz.*,  $4/5$  instead of the Enskog value of  $3/5$ .

Sengers and Cohen (124) have recently reconsidered the statistical mechanical derivation of the modified Boltzmann equation from the  $(N - 1)$  times integrated Liouville equation. The expression derived by Enskog was obtained and, in addition, eventually confirmed from a different derivation using the theory of Bogolubov. Curtiss and Snider (27) have also obtained an expression for the thermal conductivity of a dense fluid of rigid spheres which differs from the Enskog result. Their equation was subsequently reported to be in error (104).

## E. THEORIES FOR MOLECULES INTERACTING WITH A SQUARE-WELL POTENTIAL

### 1. Theory of Longuet-Higgins and Valleau

The equations for the coefficient of thermal conductivity of a dense gas of rigid spheres, while bringing out several features of interest, cannot be considered appropriate to real molecules where attractive forces exist. Certain of the simplifying features of the rigid-sphere model, due to the discontinuous nature of the intermolecular potential, can, however, be retained by considering that the molecules interact with a square-well potential (Eq. 48). The consideration of such molecules which have both attractive and repulsive forces should therefore give a zero-order approximation to the behavior of real molecules. This model has already been used with some success in studying the equilibrium and transport properties of gases (51).

The first attempt to calculate the transport properties of a dense fluid of molecules interacting with a

square-well potential is due to Longuet-Higgins and Valleau (76). They considered the four possible types of bimolecular collision between two "square-well" molecules and using methods similar to those in the rigid-sphere theory of Longuet-Higgins and Pople derived the equation

$$\lambda_{\text{coll}} = \frac{2}{3} k \left( \frac{\pi k T}{m} \right)^{1/2} \left( \frac{N}{V} \right)^2 \{ \sigma_1^4 g_0^{(2)}(\sigma_1) + \sigma_2^4 g_0^{(2)}(\sigma_2) e^{-s^2 \Xi(s^2)} \} \quad (\text{Eq. 85})$$

for the collisional contribution to thermal conductivity.

$$\Xi = e^{s^2} - \frac{1}{2} s^2 \left[ 1 - e^{s^2/2} K_1 \left( \frac{s^2}{2} \right) \right] \quad (\text{Eq. 86})$$

where  $s^2 = \epsilon/kT = 1/T^*$  and  $K_1(s^2/2)$  is a modified Bessel function of the second kind. Values of  $\Xi$  for various values of  $1/T^*$  are given in Table XV (123).  $g_0^{(2)}(\sigma_1)$  and  $g_0^{(2)}(\sigma_2)$  are the equilibrium pair correlation functions at  $\sigma_1$  and  $\sigma_2$ , respectively. When  $\epsilon = 0$ ,  $\Xi = 0$  and Eq. 85 reduces to the corresponding hard-sphere result (Eq. 79).

Equation 85 cannot be compared with experimental values without a knowledge of  $\sigma_1$ ,  $\sigma_2$ ,  $\epsilon$ ,  $g_0^{(2)}(\sigma_1)$ , and  $g_0^{(2)}(\sigma_2)$ . To overcome this difficulty Longuet-Higgins and Valleau suggested combining experimental compressibility and self-diffusion data with the corresponding equations on the theory

$$\frac{pV}{NkT} - 1 = \frac{2}{3} \pi \frac{V}{N} \{ \sigma_1^3 g_0^{(2)}(\sigma_1) - \sigma_2^3 g_0^{(2)}(\sigma_2) (1 - e^{-s^2}) \}$$

$$D_1^0 = \frac{3}{128} \frac{N}{V} \left( \frac{kT}{\pi m} \right)^{1/2} \{ \sigma_1^2 g_0^{(2)}(\sigma_1) + \sigma_2^2 g_0^{(2)}(\sigma_2) e^{-s^2 \Xi} \}^{-1}$$

which together with  $\epsilon$ ,  $\sigma_1$ , and  $\sigma_2$  from gas phase viscosity results yields  $g_0^{(2)}(\sigma_1)$  and  $g_0^{(2)}(\sigma_2)$ .

For argon at 84°K. using the compressibility data of Baly and Donnan (1) and Rice (96) together with the square-well parameters deduced by Holleran and Hulbert (52) and the self-diffusion coefficient of Corbett and Wang (26) gives a calculated collisional thermal conductivity of  $10.39 \times 10^{-4}$  joule cm.<sup>-1</sup> sec.<sup>-1</sup> °C.<sup>-1</sup> which compares with the experimental value of Uhler (131) of  $12.60 \times 10^{-4}$  joule cm.<sup>-1</sup> sec.<sup>-1</sup> °C.<sup>-1</sup>. The agreement is good. However, since the same terms are excluded in this theory as in the hard-sphere model the contribution calculated is probably low.  $m\lambda/k\eta$  on the theory is again found to be 2.5 in agreement with the rigid-sphere result of Longuet-Higgins and Pople and with the mean value of Table X. The temperature dependence of the ratio is not, however, brought out.

### 2. The Theory of Davis, Rice, and Sengers

Davis, Rice, and Sengers (30) have carried out a more elaborate treatment of the transport properties of a square-well fluid, computing both the convective and collisional contribution on the basis of a modified Boltzmann equation. As in Longuet-Higgins and

Valleau's treatment the four types of bimolecular collision are used, contributions due to the rigid core diameter,  $\sigma_1$ , and the attractive portion being factorized. The resulting equation for the coefficient of thermal conductivity is complicated, but reduces to Eq. 85 on setting derived nonequilibrium perturbation parameters to zero. The most interesting feature of the treatment is a prediction of the increase with temperature of the ratio  $m\lambda/k\eta$ . This has its origin in the perturbation terms neglected by Longuet-Higgins and Valleau. Evaluation of the equilibrium pair correlation functions is avoided in comparing the theory with experiment by similar methods used in IIEE1. These were obtained from viscosity and equation of state data and yield a calculated thermal conductivity for argon at 84°K. of  $13.3 \times 10^{-4}$  joule cm.<sup>-1</sup> sec.<sup>-1</sup> deg.<sup>-1</sup> compared with the experimental value of  $12.6 \times 10^{-4}$  joule cm.<sup>-1</sup> sec.<sup>-1</sup> deg.<sup>-1</sup>. No factorization in the final comparison was given between the convective and collisional terms.

### 3. The Theory of Sengers

Sengers has recently reconsidered the square-well model (123). His treatment includes the effect of the perturbation of the distribution function from the local equilibrium value which was omitted by Longuet-Higgins and Valleau. The result which is applicable at high densities only is substantially simpler than that of Davis, Rice, and Sengers and is

$$\lambda = \lambda_0 \left[ \frac{\left\{ 1 + \frac{3}{5} b\rho \left( g_0^{(2)}(\sigma_1) + g_0^{(2)}(\sigma_2) R^3 \Psi \right) \right\}^2}{g_0^{(2)}(\sigma_1) + g_0^{(2)}(\sigma_2) R^2 \left( \Xi + \frac{11}{16} s^2 \right)} + \frac{32}{25\pi} \left( g_0^{(2)}(\sigma_1) + g_0^{(2)}(\sigma_2) R^4 \Xi \right) \right] \quad (\text{Eq. 87})$$

where  $b\rho = 2\pi N\sigma_1^3/3V$ ,  $R = \sigma_2/\sigma_1$ , and  $\Psi$  given in Table XV is

$$\Psi = 1 - e^{-s^2} + \frac{1}{2} s^2 \left[ 1 + \frac{4}{\sqrt{\pi}} e^{s^2} \int_s^\infty e^{-x^2} x^2 dx \right]$$

In the limit as  $\epsilon \rightarrow 0$ ,  $s = 0$ ,  $\Xi = 0$ ,  $\Psi = 0$ , and Eq. 87 reduces to the Enskog result (68).

Square-well models, while bringing out some features of thermal conductivity not obtained on the hard-sphere model, are not very useful for predicting the thermal conductivity of simple systems due to the lack of knowledge of  $g_0^{(2)}(\sigma_1)$  and  $g_0^{(2)}(\sigma_2)$ . In fact, it is more useful to use the empirically modified hard-sphere theory of Enskog.

## F. THEORIES FOR MOLECULES INTERACTING WITH SPHERICALLY SYMMETRIC INTERMOLECULAR POTENTIALS

### 1. The Theory of Zwanzig, Kirkwood, Oppenheim, and Alder (150)

This theory is a development of the work of Kirkwood and his school which attempts to derive expres-

TABLE XV  
 PARAMETERS FOR THE SQUARE-WELL MODEL

$1/T^*$	$\Xi$	$\Psi$
0	0.0000	0.0000
0.1	0.0086	-0.0012
0.2	0.0324	-0.0066
0.3	0.0710	-0.0184
0.4	0.1252	-0.0387
0.5	0.1959	-0.0685
0.6	0.2846	-0.1105
0.7	0.3927	-0.1665
0.8	0.5221	-0.2385
0.9	0.6747	-0.3290
1.0	0.8528	-0.4403
1.1	1.0589	-0.5752
1.2	1.2958	-0.7368
1.3	1.5666	-0.9282
1.4	1.8747	-1.1530
1.5	2.2239	-1.4153
1.6	2.6196	-1.7194
1.7	3.0635	-2.0700
1.8	3.5635	-2.4726
1.9	4.1245	-2.9262
2.0	4.7529	-3.4570

sions for the transport properties of liquids using non-equilibrium statistical mechanics. The theory has been reviewed (23, 24, 37, 39, 73, and 103), and only an outline development of the theory for thermal conductivity is given here.

The probability that the coordinates  $r_i$  and momenta  $p_i$  of a system of  $N$  particles of mass  $m$  with no internal degrees of freedom have specified values at a given moment is given by the distribution function  $f^{(N)}$  which satisfies the normalizing condition

$$\int \cdots \int f^{(N)}(r_1, r_2, \cdots, r_N; p_1, p_2, \cdots, p_N) = 1 \quad (\text{Eq. 88})$$

The distribution  $f$  essentially determines ensemble averages of the form

$$\langle x \rangle = \int x f(x) dx \quad (\text{Eq. 89})$$

where  $\langle x \rangle$  is called the expectation value of  $x$ . The time dependence of the distribution function  $f^{(N)}$  satisfies a continuity equation in phase space which corresponds to the hydrodynamic equation of continuity for an incompressible fluid. This is known as Liouville's equation and can be written as

$$\partial f^{(N)} / \partial t + \sum_{i=1}^N \left[ (1/m) p_i \cdot \nabla_{r_i} f^{(N)} + F_i \cdot \nabla_{p_i} f^{(N)} \right] = 0 \quad (\text{Eq. 90})$$

or, using the substantial derivative in phase space, as

$$Df^{(N)} / Dt = 0 \quad (\text{Eq. 91})$$

$F_i$  is the force acting on the  $i$ th molecule due to the sum of the gradients of the separate pair potentials of its  $N - 1$  neighbors which on assuming spherical symmetry is

$$-F_i = \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \partial \phi_{ij} / \partial r_i = \frac{\partial \Phi}{\partial r_i} \quad (\text{Eq. 92})$$

$\phi_{ij}$  is not an explicit function of time but can depend on  $t$  through the change in  $r$  with  $t$ . The form of the Liouville equation was shown by Gibbs to be reversible to changes in time, whereas transport processes are irreversible. Kirkwood has shown (65) that when lower order distribution functions  $f^{(h)}$  ( $h < N$ ) are dealt with and these are averaged over a certain time  $\tau$  (coarse graining, see (103) for a discussion), this procedure leads to irreversible behavior. The small time  $\tau$ , determined on the basis of analogies with Brownian motion, is assumed by Kirkwood to be greater than the time interval  $t - t'$  such that the force on a given molecule at time  $t$  is statistically independent of the force at a previous time  $t'$ . This time is small compared with a transport relaxation time, but is long compared with the fluctuation of force on a molecule due to microscopic Brownian motion. This assumption plays a similar role to the molecular chaos assumption in the kinetic theory of gases.

The lower order distributions  $f^{(h)}$  can be derived from  $f^{(N)}$  by averaging with respect to the positions and momenta of the remaining  $(N - h)$  molecules so that

$$f^{(h)}(r_1, r_2, \cdots, r_h; p_1, p_2, \cdots, p_h; t) = \int \cdots \int f^{(N)}(r_1, r_2, \cdots, r_N; p_1, p_2, \cdots, p_N; t) \prod_{i=h+1}^N dr_i dp_i \quad (\text{Eq. 93})$$

which on coarse graining becomes

$$\tilde{f}^{(h)}(r_1, r_2, \cdots, r_h; p_1, p_2, \cdots, p_h; t) = \frac{1}{\tau} \int_0^\tau f^{(h)}(r_1, r_2, \cdots, r_h; p_1, p_2, \cdots, p_h; t + s) ds \quad (\text{Eq. 94})$$

*i.e.*, we are not interested in events occurring in time intervals less than  $\tau$ . When  $h = 1$  and 2 given by

$$f^{(1)}(r_1, p_1, t) = \int \cdots \int f^{(N)}(r_1, r_2, \cdots, r_N; p_1, p_2, \cdots, p_N; t) \prod_{i=2}^N dr_i dp_i \quad (\text{Eq. 95})$$

and

$$f^{(2)}(r_1, r_2, p_1, p_2; t) = \int \cdots \int f^{(N)}(r_1, r_2, \cdots, r_N; p_1, p_2, \cdots, p_N; t) \prod_{i=3}^N dr_i dp_i \quad (\text{Eq. 96})$$

these are known, respectively, as the singlet and doublet distributions in (momentum configuration) phase space. Integration of  $\tilde{f}^{(1)}$  and  $\tilde{f}^{(2)}$  over the momenta alone gives

$$n^{(1)}(r_1, t) = \frac{N!}{(N-1)!} \int \tilde{f}^{(1)}(p_1, r_1; t) dp_1 \quad (\text{Eq. 97})$$

and

$$n^{(2)}(r_1, r_2, t) = \frac{N!}{(N-2)!} \iint \tilde{f}^{(2)}(p_1, p_2, r_1, r_2; t) dp_1 dp_2 \quad (\text{Eq. 98})$$

which are the singlet and pair densities in configuration space. The singlet density is simply the number

density  $n^{(1)} = n = N/V$  and  $n^{(2)}$ , the probability that one molecule is at  $r_1$  and another at  $r_2$ , is related to the nonequilibrium radial distribution function  $g^{(2)}$  by the equation

$$n^{(2)}(r, r + \mathbf{R}; t) = n(r, t)n(r + \mathbf{R}; t)g^{(2)}(r, \mathbf{R}; t) \quad (\text{Eq. 99})$$

where  $r_2 - r_1 = \mathbf{R}$ , which has the same form as the equilibrium relation

$$n^{(2)}(r, r + \mathbf{R}) = n(r)n(r + \mathbf{R})g_0^{(2)}(r, \mathbf{R}) \quad (\text{Eq. 100})$$

or

$$n^{(2)}(R) = n^2 g_0^{(2)}(R)$$

when the fluid is isotropic.  $g_0^{(2)}(R)$  is the equilibrium radial distribution function.

Expressions for the momentum and energy fluxes in terms of nonequilibrium distribution functions have been derived from the equations of classical hydrodynamics (Eq. 2-4) and the nonequilibrium distribution functions by several authors (11, 38, 59). For the heat flux vector  $J_q$ , Irving and Kirkwood (59) derive an expression composed of two terms

$$J_q = J_q^K + J_q^\phi \quad (\text{Eq. 101})$$

where the first  $J_q^K$  corresponds to the heat current due to transport of thermal kinetic energy (convective contribution) and the second  $J_q^\phi$ , the heat current density due to molecular interaction arising from the imperceptible Brownian motion. These are given by the equations

$$J_q^K = \frac{Nm}{2} \int \left| \frac{\mathbf{p}}{m} - \mathbf{u} \right|^2 \left( \frac{\mathbf{p}}{m} - \mathbf{u} \right) f^{(1)}(\mathbf{p}, r, t) d\mathbf{p} \quad (\text{Eq. 102})$$

$$J_q^\phi = \frac{1}{2} \int \left[ \phi(R) \mathbf{I} + \frac{\mathbf{R}\mathbf{R}}{R} \frac{d\phi(R)}{dR} \right] \cdot \left[ j_1^{(2)}(r, r + \mathbf{R}) - \mathbf{u}(r, t)n^{(2)}(r, r + \mathbf{R}; t) \right] d\mathbf{R} \quad (\text{Eq. 103})$$

where  $\mathbf{I}$  is the unit dyad and

$$j_1^{(2)}(r_1, r_2; t) = N^2 \iint \frac{\mathbf{p}_1}{m} f^{(2)}(\mathbf{p}_1, \mathbf{p}_2, r_1, r_2; t) d\mathbf{p}_1 d\mathbf{p}_2 \quad (\text{Eq. 104})$$

where  $\mathbf{u}$  is the center of mass or hydrodynamic velocity (compare (23) and (38) for a discussion of the differences between the corresponding expressions derived by Born and Green and by Eisenschitz). In Eq. 103 the term containing  $\phi(R)$  represents the transport of potential energy due to macroscopically imperceptible Brownian motion, while the term  $\phi'(R)$  represents the work dissipated by this random motion.

It can be seen that Eq. 102 and 103 involve the lower order distribution functions  $f^{(1)}$ ,  $f^{(2)}$ , and  $n^{(2)}$  which have to be determined. This was done by Kirkwood using analogies with the theory of Brownian motion on the molecular scale to represent collision events in the liquid (see section IIIC). On this basis reduced Liouville equations were derived which express the development in time of the coarse grained

distribution. These equations take the form of the Fokker-Planck equation illustrated for  $f^{(1)}$  as

$$\frac{\partial \bar{f}^{(1)}}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{r_1} \bar{f}^{(1)} + \nabla_{p_1} \cdot \mathbf{F}^{(1)} \bar{f}^{(1)} = \zeta_p \nabla_{p_1} \cdot \left[ \left( \frac{\mathbf{p}_1}{m} - \mathbf{u} \right) \bar{f}^{(1)} + kT \nabla_{p_1} \bar{f}^{(1)} \right] \quad (\text{Eq. 105})$$

with a similar type for  $f^{(2)}$ .  $\zeta$  is the Brownian motion friction constant. It is the right-hand side of Eq. 105 which represents the change in  $f^{(1)}$  due to the collision processes.

This equation, which occurs in the theory of random processes, is called the Chandrasekhar equation. That it does represent a description of the irreversible evolution of  $f$  toward equilibrium, and hence describes a transport process, can be seen where the equation reduces to the Smoluchowski form for  $t \gg m/\zeta$

$$\frac{\partial \bar{f}^{(1)}}{\partial t} = \frac{1}{\zeta} \nabla_{r_1} \cdot (\mathbf{F}^{(1)} \bar{f}^{(1)}) + kT \nabla_{p_1}^2 \bar{f}^{(1)} \quad (\text{Eq. 106})$$

(see ref. 18, p. 40) which has the form of the "diffusion" equation

$$\frac{\partial \bar{f}^{(1)}}{\partial t} = \frac{kT}{\zeta} \nabla_{r_1}^2 \bar{f}^{(1)} \quad (\text{Eq. 107})$$

with

$$D_1^0 = kT/\zeta \quad (\text{Eq. 108})$$

when the intermolecular force term is discarded. Equation 108 is the Einstein equation.

Using the expressions for  $f^{(1)}$ ,  $f^{(2)}$ , and  $n^{(2)}$ , Zwanzig, Kirkwood, Oppenheim, and Alder have obtained expressions for  $J_q^K$  and  $J_q^\phi$  in terms of the temperature gradient. For example, the kinetic contribution to the heat flux vector is obtained as

$$J_q^K = \frac{k^2 T}{2\zeta} n \nabla T + \frac{k^2 T^2}{6} \left( \frac{\partial n}{\partial T} \right)_p \nabla T \quad (\text{Eq. 109})$$

where  $n$  is the number density. Identification of Eq. 109 with Fourier's law gives the convective contribution to thermal conductivity as

$$\lambda_{\text{conv}} = \frac{nk^2 T}{2\zeta} - \frac{k^2 T^2}{6\zeta} \left( \frac{\partial n}{\partial T} \right)_p \quad (\text{Eq. 110})$$

The more complicated expression for  $J_q^\phi$  gives the intermolecular force term as

$$\lambda_\phi = \frac{n^2 \pi k T}{3\zeta} \int R^3 \left( R \frac{d\phi}{dR} - \phi \right) g_0^{(2)}(R) \frac{d}{dR} \left( \frac{\partial}{\partial T} \ln g_0^{(2)}(R) \right) dR + \frac{n^2 \pi k T}{\zeta} \int R^2 \left[ \left( \phi - \frac{R d\phi}{3 dR} \right) \left( \frac{\partial}{\partial T} g_0^{(2)}(R) \right) \right] dR \quad (\text{Eq. 111})$$

and hence the total thermal conductivity is  $\lambda = \lambda_{\text{conv}} + \lambda_\phi$ .

The most obvious difference between Eq. 110 and 111 is that the convective term is dependent on  $n$  as expected from the single molecule contribution mechanism, whereas the term arising from the intermolecular interaction between molecular pairs depends on  $n^2$ . It would therefore be anticipated that the  $n^2$  term would

make a dominant contribution to thermal conduction compared with the term depending on  $n$ ; *i.e.*, the intermolecular force contribution would be more important than the convective.

The remaining central problem in evaluating Eq. 110 and 111 is the relationship of the friction constant to the intermolecular forces. This is discussed below.

### The Molecular Friction Constant

A number of attempts have been made to derive an expression for the friction constant in terms of the intermolecular potential  $\phi(R)$  and the structure of the liquid, which is usually contained in the equilibrium pair correlation function  $g_0^{(2)}(R)$ . These investigations all suggest that the basic form of the friction constant is given by the equation

$$\zeta = \xi \zeta_0 \quad (\text{Eq. 112})$$

where

$$\zeta_0^2 = \frac{Nm}{3V} \int \nabla^2 \phi(R) g_0^{(2)}(R) d^3R \quad (\text{Eq. 113})$$

$V$  is the volume of the fluid and  $m$  the molecular mass.  $\xi$  has been given different values by different authors. Kirkwood, Buff, and Green (66), Rice and Kirkwood (105), Collins and Raffel (24), and Naghizadeh and Rice (90) have obtained values of  $\xi$  of unity; Douglass, McCall, and Anderson (31)  $(1/\pi)^{1/2}$ , and Rice (97) the value  $(2/\pi)^{1/2}$ . Recently Rice (98) has used an acoustic continuum model to derive a further expression for  $\xi$

$$\xi = (4\pi m^2 C^3 \rho)^{-1} \zeta_0^3 \quad (\text{Eq. 114})$$

where  $C$  is the velocity of sound and  $\rho$  the density of the medium. In this work it was suggested that

$$\zeta_0 < \zeta (\text{real system}) < \zeta (\text{acoustic}) \quad (\text{Eq. 115})$$

but subsequently, on the basis of measured self-diffusion coefficients (90),  $\zeta$  (acoustic) was recommended as the best estimate of the molecular friction constant.

The basic difficulty in deciding which expression to use for  $\xi$  arises because of a lack of knowledge of  $g_0^{(2)}(R)$  and its temperature dependence. As the recommendation of Naghizadeh and Rice is based partly on a theoretical pair correlation function, and an approximate treatment of its temperature dependence, the problem still requires further investigation.

Provided the integral in Eq. 113 can be evaluated for an  $n, m$  potential of the form of Eq. 49 in terms of experimentally available quantities, then the various proposed values of  $\xi$  can be checked against experimental values from Eq. 108. This is now possible due to a development by Rowlinson (117).

The intermolecular virial  $v(R)$ , its derivative  $w(R)$ , and the associated macroscopic functions  $\mathfrak{U}$  and  $\mathfrak{W}$  are given for an arbitrary molecular configuration by the equations

$$v(R) = R \frac{d\phi(R)}{dR} \quad \mathfrak{U} = -\frac{1}{3} \sum_i \sum_j v(R_{ij}) \quad (\text{Eq. 116})$$

and

$$w(R) = R \frac{dw(R)}{dR} \quad \mathfrak{W} = \frac{1}{9} \sum_i \sum_j w(R_{ij}) \quad (\text{Eq. 117})$$

hence

$$R^2 \nabla^2 \phi(R) = v(R) + w(R) \quad (\text{Eq. 118})$$

as

$$\nabla^2 \phi(R) = d^2 \phi(R)/dR^2 + 2d\phi(R)/RdR$$

The integral in Eq. 113 can therefore be rewritten in the form

$$\zeta_0^2 = \frac{Nm}{3V} R_*^{-2} \int g_0^{(2)}(R) [v(R) + w(R)] d^3R \quad (\text{Eq. 119})$$

where  $R_*$ , a function of  $V$  and  $T$ , is given by

$$R_*^2 = \frac{\int g_0^{(2)}(R) [v(R) + w(R)] d^3R}{\int R^{-2} g_0^{(2)}(R) [v(R) + w(R)] d^3R} \quad (\text{Eq. 120})$$

Rowlinson has shown that to a close approximation  $R_* = \sigma$ , where  $\sigma$  is the value of  $R$  at  $\phi(R) = 0$ , hence Eq. 119 transforms to

$$\zeta_0^2 = \frac{2m}{N\sigma^2} (3\overline{\mathfrak{W}} - \overline{\mathfrak{U}}) \quad (\text{Eq. 121})$$

where  $\overline{\mathfrak{W}}$  and  $\overline{\mathfrak{U}}$  are the mean values in a canonical ensemble given by

$$\overline{\mathfrak{U}} = pV - NkT \quad (\text{Eq. 122})$$

and

$$\overline{\mathfrak{W}} = -\frac{nm}{9} U' + \left( \frac{n+m}{3} \right) (pV - NkT) \quad (\text{Eq. 123})$$

with  $U'$  the average configurational energy. The friction coefficient is therefore

$$\zeta_0^2 = \frac{2mkT}{\sigma^2} \left[ -\frac{nm}{3} \frac{U'}{NkT} + (n+m-1) \left( \frac{pV}{NkT} - 1 \right) \right] \quad (\text{Eq. 124})$$

As experimental values of  $U'$  and  $pV/NkT$  are available for a number of simple molecules, Eq. 124 can be evaluated solely from the thermodynamic properties of the liquid, no knowledge of  $g_0^{(2)}(R)$  being necessary.

The most usual form of Eq. 49 has  $n, m$  values of 12 and 6, respectively; therefore

$$\zeta_0^2 = \frac{2mkT}{\sigma^2} \left[ -24 \frac{U'}{NkT} + 17 \left( \frac{pV}{NkT} - 1 \right) \right] \quad (\text{Eq. 125})$$

and so  $\zeta$  can be calculated for the various  $\xi$ . Comparison between calculated and experimental friction constants is done in more familiar terms by comparing calculated and experimental self-diffusion coefficients as the two quantities are connected by the Einstein equation (Eq.

TABLE XVI  
COMPARISON OF CALCULATED AND EXPERIMENTAL SELF-DIFFUSION COEFFICIENTS OF LIQUID ARGON

Temp., °K.	Pressure, (atm).	$C \times 10^{-4}$ , cm. sec. <sup>-1</sup>	$D_1^0 \times 10^6$ cm. <sup>2</sup> sec. <sup>-1</sup>			Exptl. (90)
			$\xi = 1$	$\xi = (2/\pi)^{1/2}$	$\xi = (4\pi m^2 C^2 \rho)^{-1} \times 10^3$	
84.3	0.722	8.636	2.35	2.95	0.97	1.77 <sup>a</sup>
87.3	1.000	8.304	2.45	3.07	0.91	2.10
90.0	1.319	7.969	2.55	3.20	0.85	2.43
100	3.20	7.001	2.95	3.70	0.72	3.54
110	6.58	6.405	3.40	4.26	0.69	4.80
120	11.98	5.664	3.88	4.86	0.61	6.06
130	20.00	4.607	4.53	5.68	0.42	7.45

<sup>a</sup> Additional values are 1.53 (21) and 2.07 (26).

108). Table XVI compares the experimental and theoretical values of  $D_1^0$  for liquid argon along the liquid-vapor coexistence curve. Similar results have been obtained by Boata, Casanova, and Levi (9).

The theoretical velocity of sound has been calculated from the thermodynamic data listed in ref. 116 and is used throughout for consistency, as experimental values are available (133) only between 83.8°K. ( $8.70 \times 10^4$  cm. sec.<sup>-1</sup>) and 87.3°K. ( $8.41 \times 10^4$  cm. sec.<sup>-1</sup>).

Table XVI shows in all cases only moderate agreement with experimental results. For 90°K. (the value  $2.60 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup> obtained by Kirkwood and Rice (105) for  $\xi = 1$  is in close agreement with the present calculations. The main drawback is that the calculated diffusion coefficient does not increase fast enough with increasing temperature and no constant value of  $\xi$  can remedy this defect. The self-diffusion coefficient calculated from the acoustic friction constant where a variable  $\xi$  is included, actually decreases with increasing temperature. This result is in sharp disagreement with the conclusions of Naghizadeh and Rice (90) who recommend  $\xi$  obtained by this method in preference to the other two values.

These results mean that transport theories which involve a friction coefficient given by Eq. 112 and 113 are, generally speaking, going to prove inadequate for calculating the thermal conductivity of a liquid. However, it is still useful to consider such theories, particularly in combinations which are independent of the friction coefficient, so that if a realistic expression for the friction coefficient is derived, a further assessment of the theory can be made.

In passing, it may be useful to point out that an equation of the form of Eq. 113 cannot be reduced to the hard-sphere friction constant obtained by Enskog and by Longuet-Higgins and Pople, *viz.*

$$\zeta_{\text{H.S.}} = \left(\frac{mkT}{\pi}\right)^{1/2} \frac{4}{\sigma} \left(\frac{pV}{NkT} - 1\right) \quad (\text{Eq. 126})$$

This would seem to be an essential feature of any realistic expression, as Eq. 126 reduces to the first approximation of the Chapman-Enskog equation for the self-

diffusion coefficient of an infinitely dilute gas of hard spheres on using Eq. 108

$$D_1^0 = \frac{3}{8n\sigma^2} \left(\frac{kT}{\pi m}\right)^{1/2} \quad (\text{Eq. 127})$$

where  $\left(\frac{pV}{NkT} - 1\right)$  is replaced by  $b_0/V$ .

To return to the comparison of Eq. 110 and 111 with experiment, it is seen that while the convective contribution can be transformed by the methods described above to purely thermodynamic quantities, numerical integration is required for the intermolecular force contribution. In view of this, only the comparison based on that of the original investigators is made.

Using the 12:6 potential with  $\epsilon/k = 120$  and  $\sigma = 3.405$  Å., for liquid argon at its boiling point, evaluation of Eq. 110 and 111 in c.g.s. units gives

$$\lambda_{\text{conv}} \zeta = 2.02 \times 10^{-8} \quad \lambda_{\phi} \zeta = 489.48 \times 10^{-8} \quad (\text{Eq. 128})$$

when  $g_0^{(2)}$  is evaluated with an *ad hoc* factor inserted to give the experimental pressure of argon at its boiling point. It is possible to evaluate these contributions using calculated or experimental friction coefficients. The results are given in Table XVII. The experi-

TABLE XVII  
CALCULATED AND EXPERIMENTAL THERMAL CONDUCTIVITIES OF Ar AT 87.3°K. AND 1 ATM.

$\zeta \times 10^{10}$ g. sec. <sup>-1</sup>	$\lambda_{\text{conv}}^a$	$\lambda_{\phi}^a$	$\lambda_{\text{exptl}}^a$
5.69 (exptl.)	0.035	8.45	12.16
2.85 (calcd.)	0.071	17.17	12.16

<sup>a</sup> Value  $\times 10^4$  in joules cm.<sup>-1</sup> sec.<sup>-1</sup> deg.<sup>-1</sup>.

mental friction coefficient is calculated from the self-diffusion data of Naghizadeh and Rice (90) (87.3°K.,  $D_1^0 = 2.10 \times 10^{-5}$  cm.<sup>2</sup> sec.<sup>-1</sup>). The experimental thermal conductivity is from Uhlir (131).

The calculated thermal conductivities differ substantially from the experimental values using either the calculated or experimental friction coefficients. The results do, however, show that the convective contribution to thermal conductivity is negligible (<1%) compared with the intermolecular force contribution in agreement with the conclusions arrived at in section IIIC, on the basis of heuristic arguments.

The convective and intermolecular force contributions to shear viscosity have also been calculated by Zwanzig, Kirkwood, Stripp, and Oppenheim (151) giving

$$\eta_{\text{conv}} = \frac{8.40 \times 10^{-15}}{\zeta} \quad \eta_{\phi} = 2.56 \times 10^6 \zeta \quad (\text{Eq. 129})$$

so that again the convective contribution to shear viscosity can be discarded. From Eq. 128 and 129 it follows that if the convective contribution is neglected,  $\eta \lambda \simeq \eta_{\phi} \lambda_{\phi}$  which is independent of the friction constant. Calculated and experimental values are

given, respectively, by 12.53 and 30.64 poise erg cm.<sup>-1</sup> sec.<sup>-1</sup> deg.<sup>-1</sup>, so that leaving aside the friction coefficient problem, the agreement of calculated and experimental quantities is still poor. No final assessment can be made of the theory until the form of the friction coefficient in terms of the intermolecular forces is firmly established and, in addition, until the assumptions involved in the Fokker-Planck-Chandrasekhar equation are proven valid when applied to small molecules. The latter problem is essentially similar to proving the validity of the Stokes-Einstein equation  $D = kT/3\pi\sigma\eta$  for a diffusing colloidal particle when applied to diffusing molecules of the same size as the viscous medium they move in.

### 2. The Theories of Born and Green and of Eisenschitz

In the same year as Kirkwood's first paper on transport processes by the methods described in section III F1, Born and Green (10) introduced a similar type of approach. This theory is also based on the Liouville equation giving results which can only be evaluated with further assumptions due to the lack of irreversibility in the Liouville equations. Similar statistical expressions for the pressure tensor and heat flux vectors were derived by both sets of authors, and, in addition, the equations for the transport coefficients are closely similar. The theory has not, however, been developed to the stage at which numerical calculations can be made.

The problem of determining the nonequilibrium distribution functions from the Chandrasekhar equation is simplified if  $\tau \gg m/\zeta$  as was first shown by the development due to Kramers (68). In this case the momenta essentially reach an equilibrium distribution in the time  $\tau$  whereas the configurational distribution does not. The singlet distribution is then Maxwellian, and as the doublet distribution in configuration space alone is given from  $f^{(2)}$  by Eq. 98, this is the only distribution to be determined.

Under these conditions, *i.e.*,  $\tau \gg m/\zeta$ , the Chandrasekhar equation reduces to the Smoluchowski equation (see Eq. 106). Eisenschitz in his theory (36) assumed that  $g^{(2)}(r_1, r_2; t)$  is given by

$$g^{(2)}(r_1, r_2; t) = g_0^{(2)}(R)(1 + w)$$

where  $w$  is a small distortion term due to nonequilibrium. For a linear temperature gradient  $T = T_0(1 + bz)$ ,  $w$  is determined from the Smoluchowski equation, and finally use of the Kirkwood expression for  $J_q^\phi$  gives an expression for the coefficient of thermal conductivity due to the intermolecular forces. This involves  $\zeta$  which has to be determined. The corresponding intermolecular force viscosity term is, however, a function of  $\zeta$  and not  $1/\zeta$  as for thermal conductivity so that the product can be evaluated independently of the friction coefficient. This has been

done by Orton (91) and a representative result given for argon at 84.4°K. and 0.8 atm. is  $\eta_0\lambda_\phi = 10.3$ , which compares with the experimental value of 36.4 poise erg cm.<sup>-1</sup> sec.<sup>-1</sup> deg.<sup>-1</sup>. On the basis of the same comparison, therefore, as the theory of Zwanzig, Kirkwood, Oppenheim, and Alder, the discrepancy between calculated and experimental values is roughly the same.

One of the interesting features of the Eisenschitz treatment is that by choosing different boundary conditions from those used by Kirkwood, Buff, and Green and Zwanzig, Kirkwood, Oppenheim, and Alder, he finds that his viscosity expression, unlike his thermal conductivity expression, has a term  $\exp(\epsilon/kT)$  thus establishing a different temperature dependence for the two coefficients. Hence qualitatively one expects an increasing value of  $m\lambda/k\eta$  with increase of temperature. This has not, however, been conclusively demonstrated.

### 3. The Theory of Rice and Kirkwood

In view of the complexities of the complete theory of Zwanzig, Kirkwood, Oppenheim, and Alder (150), Rice and Kirkwood (105) have given a much simpler approximate formulation for the intermolecular force contribution starting with Eq. 102 and 103. This theory involves three basic assumptions. (i) First, the gradient of the pair potential  $\phi(r)$  between molecules at time  $(t + s)$  can be expanded in a Taylor series about the gradient at time  $t$ , and higher terms than the second can be neglected. This is possible as  $\phi(R)$  is not an explicit function of time but depends on  $t$  only through the change in intermolecular separation with time. This expansion is, however, rigorously valid only if the molecular displacement follows Hooke's law. (ii) The distribution function in a pair space  $f^{(2)}$  is approximated as the product of the local equilibrium radial distribution function in configuration space and the zeroth order distribution function in momentum space, which is Maxwellian with a first-order perturbation due to the mean velocity. (iii) Thirdly, the friction tensor in pair space may be approximated as the direct sum of the friction tensors in singlet space, which implies that the molecules move independently of each other, an assumption which is true at large pair separation but the limitations of which are unknown at small separations.

The resulting expression for  $\lambda_\phi$  is

$$\lambda_\phi = -\frac{kT}{12\zeta} \frac{\partial}{\partial T} \left[ \left( \frac{N}{V} \right)^2 \int R^2 \nabla^2 \phi(R) g_0^{(2)}(R) d^3R \right] \quad (\text{Eq. 130})$$

which can be transformed to thermodynamic quantities for an  $\mathbf{n}, \mathbf{m}$  potential using Eq. 52, rewritten as

$$\lambda_\phi = \frac{kT}{2\zeta V} \left[ \frac{\mathbf{nm}}{3} C'_p - \frac{\mathbf{nm}}{3} pV\alpha - \frac{\mathbf{nm}}{3} U'\alpha - (\mathbf{n} + \mathbf{m} - 1)NkT\alpha + (\mathbf{n} + \mathbf{m} - 1)Nk \right] \quad (\text{Eq. 131})$$

TABLE XVIII

COMPARISON OF CALCULATED AND EXPERIMENTAL VISCOSITIES AND THERMAL CONDUCTIVITIES OF ARGON ON THE THEORY OF RICE AND KIRKWOOD

Temp., °K.	Pressure, atm.	$\eta \times 10^3, \text{ g. sec.}^{-1}$			$\lambda \times 10^4, \text{ joules cm.}^{-1} \text{ sec.}^{-1} \text{ } ^\circ\text{C.}^{-1}$			$m\lambda/k\eta$	
		Exptl.	Calcn. I	Calcn. II	Exptl.	Calcn. I	Calcn. II	Exptl.	Calcn. I
84.3	0.722	2.80	1.26	0.95	12.60	5.93	4.47	2.16	2.26
87.3	1.000	2.52	1.24	1.06	12.16	6.15	5.27	2.32	2.38
90.0	1.319	2.32	1.21	1.15	11.98	6.34	6.04	2.48	3.52
100.0	3.20	1.70	1.12	1.34	10.93	7.16	8.59	3.09	2.07
110.0	6.58	1.40	1.02	1.44	9.80	8.41	11.87	3.36	3.96
120.0	11.98	1.14	0.91	1.42	8.50	10.54	16.46	3.58	5.56
130.0	20.00	0.90	0.79	1.30	7.37	13.91	22.88	3.94	8.46

Equation 52 for a 12:6 potential has already been derived by Rice and Kirkwood. Rather than use a rigid-sphere value for  $\lambda_{\text{conv}}$  as did Rice and Kirkwood, this term can be taken from the theory of Zwanzig, Kirkwood, Oppenheim, and Alder (Eq. 110) and rewritten as

$$\lambda_{\text{conv}} = \frac{kT}{2\zeta V} \left[ \frac{NkT\alpha}{3} + Nk \right] \quad (\text{Eq. 132})$$

The total thermal conductivity resulting from Eq. 131 and 132 is, therefore, for a 12:6 potential

$$\lambda = \lambda_{\text{conv}} + \lambda_\phi = \Lambda \left[ \left( 1 + \frac{T\alpha}{3} \right) + \left\{ 24 \frac{C_p'}{Nk} - 24 \frac{U'}{Nk} - 24 \frac{pV}{Nk} \alpha - 17T\alpha + 17 \right\} \right] \quad (\text{Eq. 133})$$

where

$$\Lambda = k \frac{\sigma}{2} \left( \frac{kT}{2m} \right)^{1/2} \frac{N}{V} \left[ -24 \frac{U'}{NkT} + 17 \left( \frac{pV}{NkT} - 1 \right) \right]^{-1/2}$$

as  $\zeta = \zeta_0$  on the theory and Eq. 125 is applicable.

A direct comparison of the convective and collisional contributions can now be made by comparing the ratios of the first and second terms of Eq. 133 which at 84.3 and 130°K. for argon along the saturation curve are approximately 1.1:171 and 1.5:274, respectively. The per cent convective contribution in the case of thermal conductivity is therefore negligible and much less than the 10% contribution attributed by Rice and Kirkwood from the hard-sphere model.

Table XVIII compares thermal conductivities calculated from Eq. 133 (calcn. I) and experimental (131) values for argon. The results show that although the correct order of magnitude is obtained the calculated coefficient, contrary to experiment, actually increases with increasing temperature.

Using the experimental self-diffusion coefficient Eq. 133 can be rewritten

$$\lambda = D_{1,0,\text{exptl}} \frac{Nk}{2V} \left[ \left( 1 + \frac{T\alpha}{3} \right) + 24 \frac{C_p'}{Nk} - 24 \frac{pV}{Nk} \alpha - 24 \frac{U'}{Nk} - 17T\alpha + 17 \right] \quad (\text{Eq. 134})$$

The associated thermal conductivity values  $\lambda$  calcn. II are included in Table XVIII and show greater disagreement with experiment compared with  $\lambda$  calcn. I. The value calculated by numerical methods by Rice

and Kirkwood at 90°K. for the collisional contribution  $5.94 \times 10^{-4} \text{ joule cm.}^{-1} \text{ sec.}^{-1} \text{ } ^\circ\text{C.}^{-1}$  is in close agreement with the value from Eq. 134 which includes the small convective term.

On the theory the collisional or intermolecular force contribution to viscosity  $\eta_\phi$  is

$$\eta_\phi = \frac{m}{30\zeta} \left( \frac{N}{V} \right)^2 \int R^2 \left[ \nabla^2 \phi(R) + \frac{2}{R} \frac{d\phi(R)}{dR} \right] g_0^{(2)}(R) d^3R \quad (\text{Eq. 135})$$

so that using Eq. 51 and 52

$$\eta_\phi = \frac{N\sigma}{5V} \left( \frac{mkT}{2} \right)^{1/2} \frac{\left[ -\frac{nm}{3} \frac{U'}{NkT} + (n+m-3) \left( \frac{pV}{NkT} - 1 \right) \right]}{\left[ -\frac{nm}{3} \frac{U'}{NkT} + (n+m-1) \left( \frac{pV}{NkT} - 1 \right) \right]^{1/2}} \quad (\text{Eq. 136})$$

as  $\zeta = \zeta_0$  on the theory.

The kinetic or convective contribution  $\eta_{\text{conv}}$  has also to be included to give the total thermal conductivity. This can be taken from the theory of Kirkwood, Buff, and Green (66) again rather than from the rigid-sphere model used by Rice and Kirkwood. This expression is

$$\eta_{\text{conv}} = \frac{NmkT}{2\zeta V} \quad (\text{Eq. 137})$$

hence using  $\zeta = \zeta_0$ , the total viscosity is

$$\eta = \eta_{\text{conv}} + \eta_\phi = E \left[ \frac{1}{2} + \frac{1}{5} \left\{ -\frac{nm}{3} \frac{U'}{NkT} + (n+m-3) \left( \frac{pV}{NkT} - 1 \right) \right\} \right] \quad (\text{Eq. 138})$$

where

$$E = \frac{N\sigma}{V} \left( \frac{mkT}{2} \right)^{1/2} \left[ -\frac{nm}{3} \frac{U'}{NkT} + (n+m-1) \left( \frac{pV}{NkT} - 1 \right) \right]^{-1/2} \quad (\text{Eq. 139})$$

Calculated viscosities for argon for the 12:6 potential are given in Table XVIII.

A further check on the theory can now be obtained by examining the ratio  $m\lambda/k\eta$ . This is given for 12:6 molecules by the equation

$$\frac{m\lambda}{k\eta} = \frac{1}{2} \frac{\left[ \left( 1 + \frac{T\alpha}{3} \right) + \left\{ 24 \frac{C_p'}{Nk} - 24 \frac{U'}{Nk} - 24 \frac{pV}{Nk} \alpha - 17T\alpha + 17 \right\} \right]}{\left[ \frac{1}{2} - \frac{24}{5} \frac{U'}{NkT} + 3 \left( \frac{pV}{NkT} - 1 \right) \right]} \quad (\text{Eq. 140})$$



which is independent of the friction coefficient. Calculated and experimental values are compared in Table XVIII where the ratios are in close agreement except at the highest temperatures. This discrepancy is due to the rapid increase in  $C_p'/Nk$  and  $U'\alpha/Nk$ .

Where overlap between the calculations of this paper and those of Rice and Kirkwood occur good agreement is obtained. This confirms the essential correctness of the present method of calculation of  $\zeta_0$ . The transport properties of argon along the saturation curve as evaluated, however, indicate substantial discrepancies between the theory of Rice and Kirkwood with regard to either or both the sign and magnitude of the temperature dependence of the transport properties. This occurs for viscosity and thermal conductivity even when the experimental friction coefficient obtained from the self-diffusion coefficient is used. The agreement for the  $m\lambda/k\eta$  ratio does, however, suggest that the friction constant applicable to self-diffusion is not the friction constant which is applicable to thermal conductivity and viscosity. This may be so as the self-diffusion coefficient is really a property of an equilibrium system.

#### 4. The Theory of Collins and Raffel

Collins and Raffel (25) have introduced a different formalism for the thermal conductivity of liquids in which the primary step is the expression of the time derivative of the heat flux vector in terms of the gradient of the energy. This time derivative introduces irreversibility into the corresponding statistical mechanical ensemble without requiring time smoothing and is expressed in terms of an expansion of the molecular velocity distribution instead of the expansion of the configurational distribution. The latter would be required if the heat flux and not its time derivative was required.

The details of the theory will not be dealt with here. However, it is of interest to point out that the authors derive the same expression as obtained by Kirkwood, Buff, and Green for the friction coefficient, *i.e.*,  $\zeta = \zeta_0$ . Their results for thermal conductivity are of a form similar to those given by Kirkwood and Rice, except that they involve the square of the transport coefficient, but  $\zeta$  does not occur in the expressions. For thermal conductivity, the convective and intermolecular force contributions are

$$\lambda_{\text{conv}}^2 = \frac{0.694\pi k C_v}{3v^{7/2}M} \int 3R^2 \frac{d\phi}{dR} g_0^{(2)} dR \quad (\text{Eq. 141})$$

$$\lambda_\phi^2 = \frac{0.694\pi k C_v}{3v^{7/2}M} \int \left[ R^2 \frac{d\phi}{dR} + 4\alpha T \left( R^2 \frac{d^2\phi}{dR^2} + 3R^2 \frac{d\phi}{dR} \right) \right] g_0^{(2)} dR \quad (\text{Eq. 142})$$

which when combined and the integrals eliminated in

TABLE XIX

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY AND  $m\lambda/k\eta$  ON THE THEORY OF COLLINS AND RAFFEL

Temp., °K.	84.73	87.3	90	100	110	120	130
Pressure, atm.	0.722	1.000	1.319	3.20	6.58	11.98	20.00
$\lambda$ , calcd.	21.22	21.50	21.90	22.73	23.01	25.35	27.02
$\lambda$ , exptl.	12.60	12.16	11.98	10.93	9.80	8.50	7.37
$m\lambda/k\eta$ , calcd.	8.25	8.51	8.81	9.75	10.68	12.42	15.48
$m\lambda/k\eta$ , exptl.	2.16	2.32	2.48	3.09	3.36	3.58	3.94

terms of thermodynamic properties for a 12:6 potential gives

$$\lambda^2 = \frac{1.388k^2 T C_v}{v^{7/2} M} \left[ -24 \frac{U'}{NkT} \alpha T + \left( \frac{pV}{NkT} - 1 \right) (16\alpha T - 1) \right] \quad (\text{Eq. 143})$$

where  $C_v$  is the molar specific heat at constant volume,  $\alpha$  the coefficient of thermal expansion, and  $M = Nm$  the molecular weight and  $v = V/N$ .

Table XIX compares calculated and experimental thermal conductivities for liquid argon along the saturation curve and also gives the ratio  $m\lambda/k\eta$  which on the theory is

$$\frac{m\lambda}{k\eta} = \left[ 7.977 \frac{C_v}{Nk} \frac{\left\{ -24\alpha T \frac{U'}{NkT} + \left( \frac{pV}{NkT} - 1 \right) (16\alpha T - 1) \right\}^{1/2}}{\left\{ -24 \frac{U'}{NkT} + 10 \left( \frac{pV}{NkT} - 1 \right) \right\}} \right]^{1/2} \quad (\text{Eq. 144})$$

as the corresponding viscosity expression is

$$\eta^2 = \frac{0.174mkT}{10v^{7/2}} \left[ -24 \frac{U'}{NkT} + 10 \left( \frac{pV}{NkT} - 1 \right) \right] \quad (\text{Eq. 145})$$

Agreement between theory and experiment is seen to be poor. Like the theory of Rice and Kirkwood, the wrong temperature dependence is obtained. In addition, however, the values are out by a factor of about two, and agreement between calculated and experimental values of the ratio  $m\lambda/k\eta$  is poor compared with the results from Rice and Kirkwood's expression.

#### 5. The Theory of Rice and Allnatt

Rice and Allnatt (101, 102) have recently derived expressions for the thermal conductivity of a dense fluid based on a model in which the intermolecular forces are factorized into hard and soft terms. For example, the 12:6 potential can be used to represent the soft portion up to  $R = \sigma$ , after which it is replaced by an infinite repulsion as for hard spheres. On this model three contributions to thermal conduction are separated. The first is the usual convective or kinetic term, the second is the collisional hard core term, and the third is due to the soft part of the potential.

The convective term is

$$\frac{\lambda_{\text{conv}} V}{\lambda_0 b_0} = \left( \frac{1}{y} + \frac{3}{5} \right) A^{-1} \quad (\text{Eq. 146})$$

where  $A = 1 + (45\zeta V/N + 16mY)/(4\pi kT/m)^{1/2}\sigma^2$  and reduces to the Enskog result (69) when  $A$  is unity, *i.e.*, when  $\zeta = 0$ .  $\zeta$  in this case is given by

$$\zeta = \zeta_0 - \zeta_{\text{H.S.}}$$

where  $\zeta_0$  is the Kirkwood expression (Eq. 113) and  $\zeta_{\text{H.S.}}$  the hard-sphere value given by Eq. 126. The collisional term which arises at  $R = \sigma$  when the cores of the molecules collide is

$$\frac{\lambda_{\text{coll}}V}{\lambda_0 b_0} = \left[ \frac{3}{5} \left( 1 + \frac{3}{5} y \right) + \frac{32}{25\pi} y \right] C \quad (\text{Eq. 147})$$

where  $C$  is a perturbation parameter making Eq. 147 different from the corresponding Enskog result (Eq. 70). This is due to the different nature of the intermolecular potential as well as the deviation of the triplet distribution function from equilibrium. Finally the contribution arising from the soft part of the intermolecular forces at  $R > \sigma$ , *i.e.*,  $\lambda_{\phi, \text{S}}$  is identical with the intermolecular force term given by Eq. 111 of Zwanzig, Kirkwood, Oppenheim, and Alder except that the integration limits run from  $\sigma$  to  $\infty$  rather than from 0 to  $\infty$ .

Using experimental friction constants for  $\zeta_0$ , *i.e.*, replacing  $\zeta_0$  by  $kT/D_1^0$ , and using a theoretical  $g_0^{(2)}(R)$ , Ikenberry and Rice (58) have calculated the separate contributions for argon as given in Table XX.

TABLE XX  
THE THERMAL CONDUCTIVITY OF LIQUID ARGON ON THE THEORY  
OF RICE AND ALLNATT

Temp., °K.	90	128	133.5	185.5
Pressure, atm.	1	50	100	500
$\lambda_{\text{conv}}$	0.08	0.21	0.29	0.46
$\lambda_{\text{coll}}$	0.34	0.17	0.34	0.75
$\lambda_{\phi, \text{S}}$	11.42	7.36	6.78	6.49
$\lambda_{\text{total}}$	11.84	7.74	7.41	7.70
$\lambda_{\text{exptl}}$	12.38	7.91	7.78	7.82

This shows that as in all other theories, the convective contribution while increasing with falling density as expected, makes a negligible contribution to the total conduction. It is surprising, however, that the core term is also small with the majority contribution arising from the soft part of the potential. Over-all the agreement with experiment is surprisingly good. It is, however, unfortunate that the result depends on a theoretical  $g_0^{(2)}$ , as when this was previously used by Naghizadeh and Rice (90) to calculate the temperature dependence of the self-diffusion coefficient, the good agreement found by these authors is not reproduced when the methods used in section IIIF1a are used. This is seen from Table XVI where the wrong temperature dependence results for the acoustic calculation in column 6.

#### 6. Fluctuation-Dissipation Theory

Since the problem of constructing a satisfactory non-equilibrium distribution function is not yet fully re-

solved, as the results of the previous sections show, a more recent approach has attempted to avoid this problem by considering irreversible phenomena in terms of equilibrium ensembles whose properties are known. This type of approach was originally considered by Einstein (35) in the problem of Brownian particle diffusion, and more recent work is due to Kubo (69), Green (47), and Mori (89). A particularly simple presentation of the method of this approach has been given by Helfand (50).

In essence, the idea behind the method is, that in an equilibrium ensemble, there occur macroscopic fluctuations in the various properties of the system. The decay of these fluctuations is accompanied by transport phenomena. The theory is not concerned with how the fluctuation arises. In the case of thermal conductivity, for example, at a point in the liquid, if the total energy of a particle has a value  $E$  at time zero, which is in excess of the average energy  $\langle E \rangle$ , then the decay to the average value is accompanied by thermal conduction. The theory gives the thermal conductivity coefficient in terms of an integral over time of an autocorrelation function which has to be evaluated.

To date little has been done to enable the theory to be used to calculate the thermal conductivity of a liquid, but recently Cohen and Ernst (22) have suggested that the theory, for the case of hard spheres, omits a term which, if correspondingly discarded in the theory of Enskog (first term of Eq. 70) would give poor agreement with experiment. At present little can be said about the possibilities of this type of approach being successful for calculating transport properties. However, the particular inadequacies of the friction constant as formulated in the Kirkwood-type treatment must provide a stimulus to alternative considerations of irreversibility. Fluctuation-dissipation theory and the master equation approach, which is a further alternative method of tackling the problem of irreversibility due principally to Brout, Prigogine, and Van Hove, have been extensively discussed by Chester (20) and by Rice and Frisch (103).

#### 7. The Theory of Horrocks and McLaughlin

In this theory (54), a f.c.c. lattice-type structure is assumed for the liquid, and the excess energy due to the temperature gradient is assumed to be transferred down the gradient with a frequency  $\nu$  which is determined by the molecular mass and the intermolecular forces. The expression obtained for the thermal conductivity again can be written as two terms: the first due to motion of molecules between cells,  $\lambda_{\text{conv}}$ , and the second  $\lambda_{\phi}$ , due to the intracellular term arising from the intermolecular forces, transfer taking place by the vibrational mechanism. The resulting equations are

$$\lambda_{\text{conv}} = \sqrt{2} k_0 C_{\nu} / a \quad (\text{Eq. 148})$$

$$\lambda_{\phi} = \sqrt{2} \nu C_{\nu} / a \quad (\text{Eq. 149})$$

where  $a = (\sqrt{2}V/N)^{1/3}$  is the nearest neighbor distance,  $\nu$  is the lattice frequency, and  $k_0$  the frequency of diffusive displacement. Using the theory of self-diffusion of McLaughlin (78) to calculate  $k_0$ , it is shown that the convective term (Eq. 148) is negligible, amounting, for example, for argon at its normal boiling point to less than 1% of the total conduction.

The intermolecular force contribution given by Eq. 149 is evaluated in the harmonic approximation by taking  $\nu$  from Eq. 56, so that  $\lambda_{\phi}$  becomes

$$\lambda_{\phi} = \frac{\sqrt{2} C_{\nu}}{2\pi\sqrt{m}a^3} [2Z\epsilon\{L_1\nu^{*4} - M_1\nu^{*2}\}]^{1/2} \quad (\text{Eq. 150})$$

As  $C_{\nu} = 3k$  on the model, then Eq. 150 can be evaluated solely from the density of the liquid which gives  $a$ , provided  $\epsilon/k$  and  $\sigma$  are known. These parameters of the intermolecular potential are known from studies of the infinitely dilute gas (51). The results for a series of simple liquids are given in Table XXI.

TABLE XXI

CALCULATED AND EXPERIMENTAL THERMAL CONDUCTIVITIES OF SIMPLE LIQUIDS ON THE THEORY OF HORROCKS AND McLAUGHLIN

Liquid	Temp., °K.	$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	
		Calcd.	Exptl.
Argon	84.2	9.92	12.60
	87.3	9.28	12.16
Nitrogen	69.1	10.28	15.11
	71.4	9.77	14.80
	77.3	8.49	13.96
Carbon monoxide	72.0	7.70	15.89
	77.7	6.59	15.05
	80.8	5.96	14.21
Methane	93.2	17.24	21.53
	103.2	15.27	20.27
	108.2	14.36	19.64
	108.2	12.26	14.94
Benzene	298.2	11.71	14.63
	308.2	11.24	14.24
	318.2	10.78	13.89
	298.2	10.18	10.64
	318.2	9.42	10.39

Agreement with experiment is surprisingly good. In all cases the correct temperature dependence is obtained and the calculated values are in substantial agreement with experimental values. Recent preliminary work on this model extending it to the case of anharmonic frequencies improves this agreement. In addition, as discussed later, the theory has proved useful in studying the factors which control the pressure and temperature dependence of thermal conductivity. The theory cannot however be extended beyond the high density end of the liquid range, *i.e.*, beyond the normal boiling point, because the concept of a lattice beyond this temperature is unrealistic.

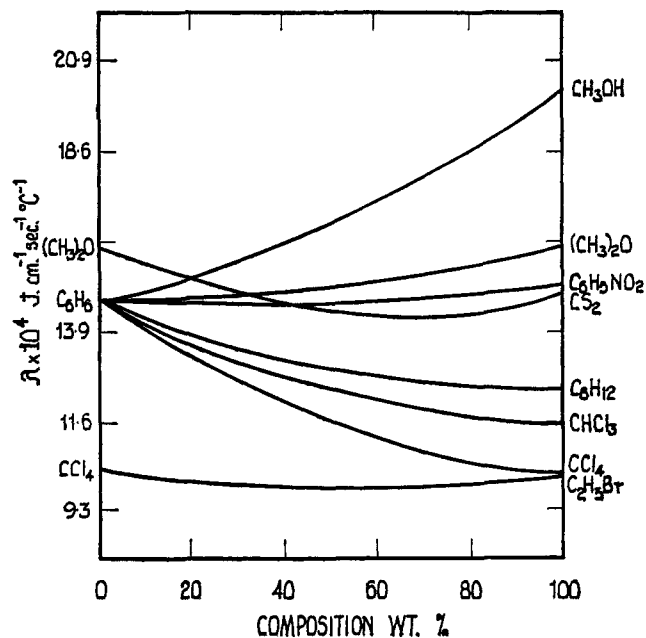


Fig. 6.—The thermal conductivity of simple binary mixtures at 20° (copied substantially from (109)).

In conclusion to this section, it can be said that so far as existing statistical theories go, substantial progress has been made in getting a better understanding of the problem of thermal conductivity. Now that the friction constant as given by Eq. 113 has been shown to be clearly inadequate, this may stimulate fresh thinking on the problem. The reduction of the statistical equations to thermodynamic terms has simplified the checking procedure for statistical expressions, and the inadequacies of some of these expressions are now more clearly evident. All this constitutes a distinct advance but clearly leaves the impression that the problem of calculating the thermal conductivity, of even a simple liquid, is still not satisfactorily solved.

#### IV. THE THERMAL CONDUCTIVITY OF MIXTURES

##### A. HEURISTIC CONSIDERATIONS

In this section attention is restricted to binary mixtures where most of the available experimental results have been obtained by Riedel (109) and by Filippov and Novoselova (41). Figure 6 illustrates the concentration dependence of the thermal conductivity of a series of binary mixtures of liquids at 20°. In all cases, even where polar molecules are involved, the thermal conductivity of the mixture  $\lambda_{\text{mix}}$  is a smooth function of the concentration. This suggests a quadratic mixing law of the form

$$\lambda_{\text{mix}} = x^2\lambda_1 + 2x(1-x)\lambda_{12} + (1-x)^2\lambda_2 \quad (\text{Eq. 151})$$

where  $\lambda_1$  and  $\lambda_2$  are the values for the pure components of corresponding mole fractions  $x$  and  $(1-x)$ .  $\lambda_{12}$ , the cross-terms coefficient, can be taken as approximately constant at a fixed temperature. This can be

TABLE XXII

VALUES OF THE CROSS-TERM COEFFICIENT OF THERMAL CONDUCTIVITY FOR THE SYSTEM CCl <sub>4</sub> -C <sub>6</sub> H <sub>6</sub> AT 20°				
x <sub>1</sub> , mole fraction of C <sub>6</sub> H <sub>6</sub>	0.8551	0.5716	0.3742	0.1359
λ <sub>12</sub> × 10 <sup>4</sup> , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	8.11	9.51	9.56	9.97

seen from Table XXII (82) for the case of carbon tetrachloride-benzene mixtures where a constant value of  $9.29 \pm 0.6$  fits the results. It would be expected that  $\lambda_{12}$  is in some way associated with the heteromolecular interaction just as in the case of the corresponding formula for the second virial coefficient of a binary mixture. It would therefore be of interest to explore the relationship between theoretical expressions and Eq. 151.

## B. THE THEORY OF THORNE

Thorne (127) has generalized the Enskog theory for the thermal conductivity of a dense fluid of hard spheres to the case of a binary mixture. The expression is complex and no simplification or application of it has been made to date. This may be due to the fact that experimental results are not available on the behavior of the thermal conductivity of mixed simple gases as a function of pressure covering the region from the dilute to the dense gas.

## C. THE THEORY OF LONGUET-HIGGINS, POPE, AND VALLEAU

Longuet-Higgins, Pople, and Valleau (75) have extended the hard-sphere theory of Longuet-Higgins and Pople to cover the case of thermal conductivity for a binary mixture of hard-sphere molecules of the same molecular diameter. The expression obtained is

$$\lambda_{\text{mix}} = \frac{2\sigma k}{n} \left( \frac{pV}{NkT} - 1 \right) \sum_{i=1}^2 \frac{n_i n_2}{m_1 + m_2} \left( \frac{2\mu_{12} kT}{\pi} \right)^{1/2} \quad (\text{Eq. 152})$$

where  $\mu_{12} = m_1 m_2 / (m_1 + m_2)$  is the reduced mass and  $n_i$  is the number density of the individual species,  $i$ , with  $n_1 + n_2 = n$ . Equation 152 reduces to Eq. 78 for  $n = n_1$ ,  $n_2 = 0$  and can be rewritten in the form of Eq. 151 with

$$\lambda_{12} = 2\sigma k \left( \frac{pV}{NkT} - 1 \right) \frac{N}{V} \left[ \frac{2\mu_{12} kT}{\pi(m_1 + m_2)^2} \right]^{1/2} \quad (\text{Eq. 153})$$

No attempt has been made to apply this result to systems of real molecules to calculate  $\lambda_{12}$  using the procedures discussed in section IIID1a on the Enskog theory. This is due again principally to the lack of suitable data, but it is also unlikely to be a fruitful line of approach for the same reasons as mentioned previously when comparing the Enskog and Longuet-Higgins and Pople theories.

## D. THE THEORY OF BEARMAN

Bearman and Kirkwood (3) have extended the Kirkwood theory of section IIIF1 to mixtures, and

TABLE XXIII

PRODUCT $\lambda_{\text{mix}} \eta_{\text{mix}}$ FOR CCl <sub>4</sub> -C <sub>6</sub> H <sub>6</sub> MIXTURES AT 30°			
Mole fraction $x$ of C <sub>6</sub> H <sub>6</sub>	$\eta$ , cp.	$\lambda \times 10^4$ , joules cm. <sup>-1</sup> sec. <sup>-1</sup> °C. <sup>-1</sup>	$\lambda_{\text{mix}} \eta_{\text{mix}}$
0.0	0.84	10.16	8.534
0.2	0.79	10.41	8.224
0.4	0.73	10.87	7.935
0.8	0.62	12.59	7.806
0.9	0.59	13.49	7.959
1.0	0.56	14.35	8.036

this has subsequently been developed in detail in a series of papers by Bearman. For the thermal conductivity of a binary mixture (2), the resulting expression undergoes substantial simplification to the form

$$\lambda_{\text{mix}} = x^2 \lambda_1 \left( \frac{v_1^2 D_1}{v^2 D_1^0} \right) + x(1-x) B_{12} \left( \frac{D_1}{v^2} \right) + (1-x)^2 \lambda_2 \left( \frac{v_2^2 D_1}{v^2 D_1^0} \right) \quad (\text{Eq. 154})$$

when it is assumed that no volume change on mixing occurs, the solution is regular with a composition-independent radial distribution function, and  $\alpha/\beta_T$  is independent of composition.  $\alpha$  and  $\beta_T$  are, respectively, the coefficients of thermal expansion and isothermal compressibility.  $D_1^0$  is the self-diffusion coefficient of pure species one, and  $D_1^\infty$ , the self-diffusion coefficient of species one infinitely diluted in species two. Both are constants at constant temperature.  $D_1$  is the self-diffusion coefficient of species one in the mixture and varies with composition.  $B_{12}$  is a composition independent quantity,  $v_1$  and  $v_2$  the molecular volumes and  $v = x_1 v_1 + x_2 v_2$ .

Bearman and Vaidhyanathan (4) have shown that in this approximation  $\eta_{\text{mix}} \lambda_{\text{mix}}$  should be constant and that this is substantially true for the system CCl<sub>4</sub>-C<sub>6</sub>H<sub>6</sub> can be seen from Table XXIII. This result is not so surprising when it is remembered (see section IIIA1) that  $\eta\lambda$  is independent of the mass.

Horrocks and McLaughlin (55) have reduced Bearman's equations still further and given the expressions

$$B_{12} = 2v_1 v_2 \lambda_2 / D_1^\infty = 2v_1 v_2 \lambda_1 / D_1^0 \quad (\text{Eq. 155})$$

$$\lambda / D_1 = \lambda_1 / D_1^0 = \lambda_2 / D_1^\infty \quad (\text{Eq. 156})$$

and

$$\lambda / D_2 = \lambda_2 / D_2^0 = \lambda_1 / D_2^\infty \quad (\text{Eq. 157})$$

which when coupled with the corresponding viscosity equations

$$\eta D_1 = \eta_1 D_1^0 = \eta_2 D_1^\infty \quad (\text{Eq. 158})$$

$$\eta D_2 = \eta_2 D_2^0 = \eta_1 D_2^\infty \quad (\text{Eq. 159})$$

enables the thermal conductivity of a mixture to be expressed in terms of other transport coefficients. The main obstacle in checking Bearman's theory is the lack of experimental data on simple systems and, in particular, of the various diffusion coefficients.

## E. THE THEORY OF RICE AND ALLNATT

Rice and Allnatt (100) have extended the theory of Rice and Kirkwood (IIIF3) to cover the case of mixtures. As in the original theory, only the intermolecular force term is given. The expression again is complicated and no attempt to use the theory to calculate the thermal conductivity of a mixture has been made. In view of the results of the Rice-Kirkwood theory discussed in section IIIF3, it is unlikely that the theory for mixtures will be any better than for the pure components. This was seen to give poor agreement with experiment.

In conclusion it can be said that very little attention has been devoted to the study of the thermal conductivity of mixtures. There is a definite need for experimental information on simple binary mixtures so that theories can be tested and progress made.

## V. THE TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITY

Where as the coefficient of viscosity of a simple liquid usually decreases exponentially with increasing temperature according to the law

$$\eta = \eta_0 \exp(A/T) \quad (\text{Eq. 160})$$

the coefficient of thermal conductivity  $\lambda$  usually decreases linearly with increasing temperature.

$$\lambda = \lambda_0 - BT \quad (\text{Eq. 161})$$

$\eta_0$ ,  $\lambda_0$ ,  $A$ , and  $B$  are constants characteristic of the liquid

considered. Correlations proposed by Eyring (45) have shown that  $A$  is related to the energy of vaporization of the liquid, and hence the temperature dependence of viscosity is substantially controlled by an energy parameter. The question then arises as to what factors control the temperature dependence of thermal conductivity.

Figure 7 gives the thermal conductivities (56) of a series of aromatic hydrocarbons of increasing complexity. Two features immediately distinguish the behavior shown here from the corresponding viscosity behavior. In the first case, all the thermal conductivities are within about 10% of the mean value for the temperature range covered. This contrasts sharply with the case of viscosity where, for example, for *o*-terphenyl and *p*-terphenyl, viscosities at the melting points are about 350 and 8 m.p., respectively. Secondly, the steepest temperature dependence is obtained for the simplest molecule of the series, benzene, and decreases with increasing molecular complexity which is opposite to what occurs for viscosity. The contrast in sensitivities to structure of viscosity and thermal conductivity also applies when the effect of pressure is examined. For example,  $\eta_p/\eta_1$  values for methyl and isoamyl alcohol are 9.95 and 895, respectively ( $\eta_p$  is the value of viscosity at 11,000 atm., and  $\eta_1$  the value at 1 atm.) which contrasts with the close similarity of the corresponding  $\lambda_p/\lambda_1$  values of 2.10 and 2.07.

These problems have been dealt with by Horrocks and McLaughlin (57). From Eq. 145 as  $C_v$  is con-

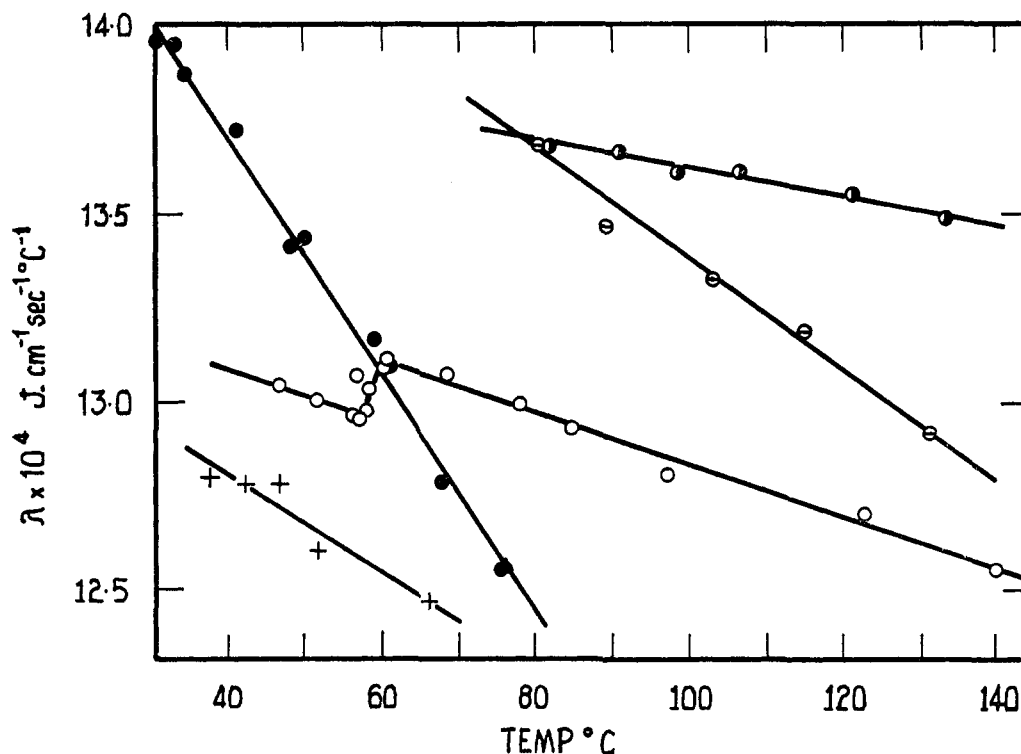


Fig. 7.—The thermal conductivities of a series of aromatic hydrocarbons: ● benzene, ⊖ diphenyl, ○ *o*-terphenyl, ⊙ *m*-terphenyl, + *p*-terphenyl (for the temperature scale for *p*-terphenyl, add 180°) (copied substantially from (56)).

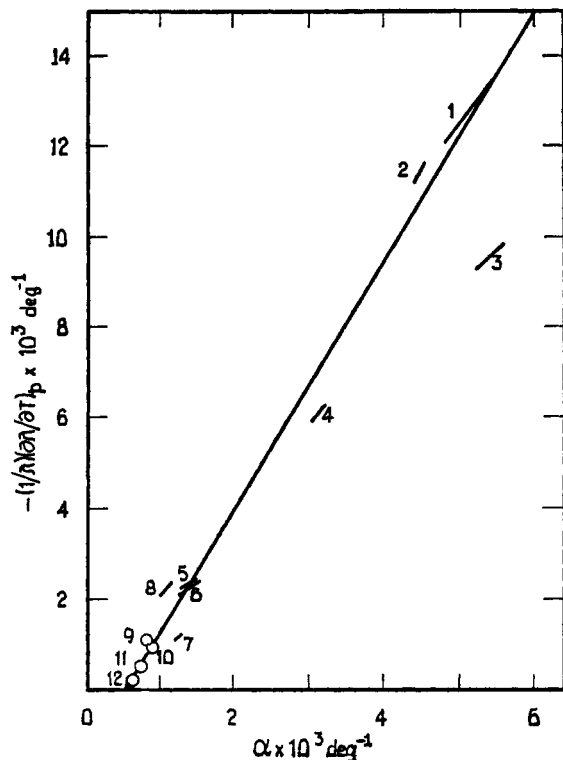


Fig. 8.—Plot of the temperature dependence of thermal conductivity against the coefficient thermal expansion for: 1, carbon monoxide; 2, argon; 3, nitrogen; 4, methane; 5, benzene; 6, cyclohexane; 7, carbon tetrachloride; 8, toluene; 9, biphenyl; 10, *p*-terphenyl; 11, *o*-terphenyl; 12, *m*-terphenyl (copied substantially from (57)).

stant, the temperature dependence of thermal conductivity follows on differentiating as

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial T} \right)_p = -\alpha \left[ \frac{1}{3} - \left( \frac{\partial \ln \nu}{\partial \ln v} \right)_p \right] \quad (\text{Eq. 162})$$

where  $(\partial \ln \nu / \partial \ln v)$  is called Gruneisen's constant. Equation 162 shows that the important factor in controlling the temperature dependence of thermal conductivity is the coefficient of thermal expansion  $\alpha$ . As  $\alpha$  is generally greatest for the simplest liquids and smallest for the complex, this then explains the decrease in the slopes of the lines on Fig. 7 on passing from benzene to the terphenyls. To put this observation onto a more quantitative basis, as Gruneisen's constant can, in the first approximation, be assumed constant, then Eq. 162 predicts that  $(1/\lambda)(\partial\lambda/\partial T)_p$  should be linear in  $\alpha$ . This is shown to be the case in Fig. 8 for a wide variety of liquids starting with those of the simple liquefied gases.

The curve does not, however, pass through the origin but intersects the  $\alpha$ -axis at a value of  $0.5 \times 10^{-3} \text{ deg.}^{-1}$ . This means that for a liquid with a value of  $\alpha$  lower than this, the sign of the temperature dependence of thermal conductivity should be reversed and the coefficient of thermal conductivity should increase with increasing temperature. This reversal has been

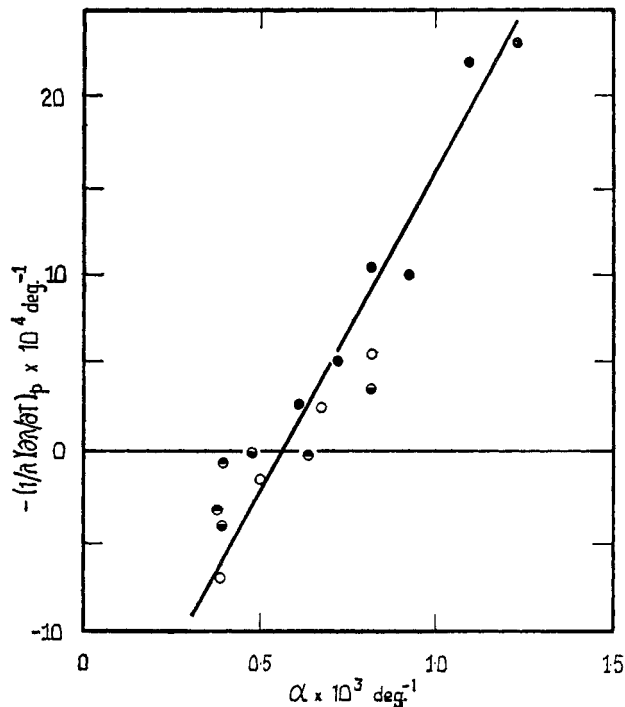


Fig. 9.—Plot of the temperature dependence of thermal conductivity against the coefficient of thermal expansion for: ● various aromatic hydrocarbons, ○ carbon disulfide, ● methanol, ● *n*-pentane; the straight line corresponds to that of Fig. 8 (copied substantially from (56)).

shown (56) to agree with some high pressure thermal conductivity measurements by Bridgman (13) because at high pressures, expansion coefficients which are much smaller even than those of complex liquids like *m*-terphenyl can be obtained. This is illustrated in Fig. 9 which shows that when the temperature dependence of thermal conductivity at various constant high pressures for methanol, *n*-pentane, and carbon disulfide are plotted the reversal is obtained. This was originally noted by Bridgman who pointed out that the sign of the temperature dependence for most common liquids was reversed beyond about 5000 atm., but the origin of the phenomenon as discussed above was not deduced.

The quantity  $(\partial \ln \nu / \partial \ln v)_p$  can be evaluated on the basis of the rectangular cell potential model (IIID3) or the harmonic oscillator model (IIIF7). In the former case, Eq. 162 reduces to

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial T} \right)_p = \alpha \left[ -\frac{1}{3} + \frac{1}{2T\alpha} - \frac{1}{3}(y + 1) \right] \quad (\text{Eq. 163})$$

which can be compared with the result from the Longuet-Higgins and Pople theory, Eq. 78, *viz.*

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial T} \right)_p = \alpha \left[ -1 + \frac{1}{2T\alpha} - \frac{1}{3}(y + 1) \right] \quad (\text{Eq. 164})$$

and the result from the corresponding Enskog collisional term (Eq. 70) which gives

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial T} \right)_p = \alpha \left[ -1 + \frac{1}{2T\alpha} - \frac{1}{3}(y + 1) \left\{ \frac{5y(0.7574)}{5y(0.7574) + 3} \right\} \right] \quad (\text{Eq. 165})$$

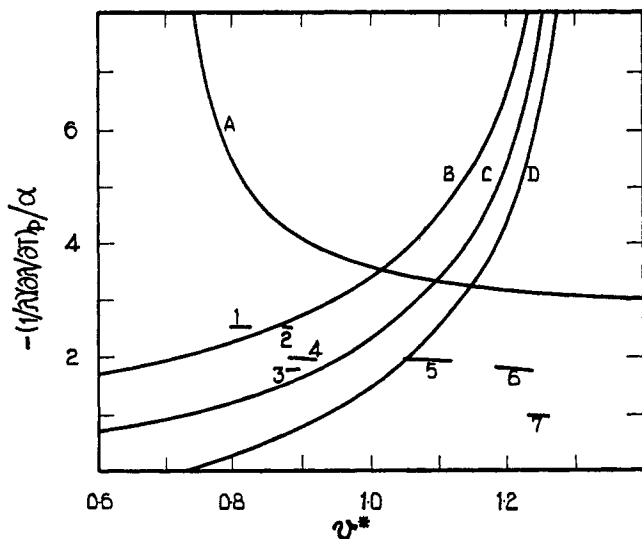


Fig. 10.—Plot of  $-(1/\lambda)(\partial\lambda/\partial T)_p/\alpha$  against  $v^*$  for: 1, carbon monoxide; 2, argon; 3, nitrogen; 4, methane; 5, benzene; 6, cyclohexane; 7, carbon tetrachloride; curve A, harmonic model; curves B, C, and D, rectangular cell potential model with  $2T\alpha$  values, respectively, of  $\infty$ , 1, and 0.5 (copied substantially from (57)).

Differences between the three results are only of a minor nature, and all three expressions tend to the same value in the limit of high densities. In addition the origin of these differences is already known from the discussions in section IIID.

On the harmonic oscillator model the corresponding result is

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial T} \right)_p = -\alpha \left[ \frac{1}{3} - \frac{1}{2} \left\{ \frac{103.18v^{*2} - 28.16}{Lv^{*2} - M_1} \right\} \right] \quad (\text{Eq. 166})$$

and the comparison between theory and experiment on both models (Eq. 163 and 166) is given in Fig. 10 for a series of simple liquids. This shows that the experimental values lie parallel to the high density end of the harmonic oscillator curve and secondly that, while overlap between the experimental and rectangular cell potential model occurs, the slopes in this case are in the wrong direction. This suggests that the quartic potential, which is the intermediate case, will give better agreement between theory and experiment and this investigation is still in progress.

The temperature dependence at constant volume follows from Eq. 149 as

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial T} \right)_v = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_v \quad (\text{Eq. 167})$$

and is 0 and  $1/2T$  on the harmonic oscillator and rectangular cell potential models, respectively. This means that as  $\lambda/2T$  is small the various isotherms for the thermal conductivity of a liquid plotted as a function of density should be either coincident or closely spaced together. This has been verified by Ziebland (146) and by Michels and co-workers (88) for a number of dense gases and liquids.

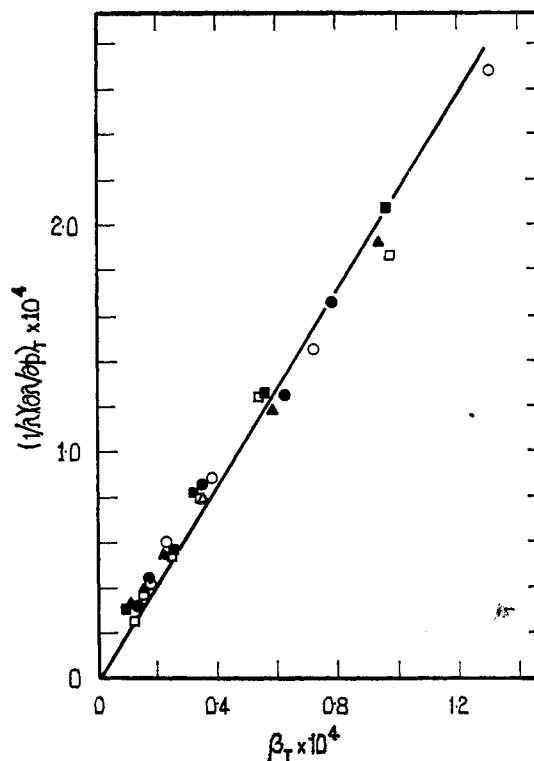


Fig. 11.—Plot of the pressure dependence of thermal conductivity against the isothermal compressibility for:  $\circ$  ether,  $\bullet$  acetone,  $\square$  carbon disulfide,  $\blacktriangle$  methanol,  $\blacksquare$  ethanol (units in  $\text{kg.}^{-1} \text{cm.}^2$ ) (copied substantially from (62)).

## VI. THE PRESSURE AND VOLUME DEPENDENCE OF THE THERMAL CONDUCTIVITY

This problem has been investigated by Kamal and McLaughlin (62) who showed that on doing the appropriate differentiation on Eq. 149 the two equations

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial p} \right)_T = \beta_T \left[ \frac{1}{3} - \left( \frac{\partial \ln v}{\partial \ln v} \right)_T \right] \quad (\text{Eq. 168})$$

and

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial v} \right)_T = -\frac{1}{v} \left[ \frac{1}{3} - \left( \frac{\partial \ln v}{\partial \ln v} \right)_T \right] \quad (\text{Eq. 169})$$

were obtained, where  $\beta_T$  is the isothermal compressibility. Figures 11 and 12 give the relevant plots for ether, acetone, carbon disulfide, methanol, and ethanol obtained from Bridgman's thermal conductivity measurements at  $30^\circ$  and pressures up to 10,000 atm. These do show that  $(1/\lambda)(\partial\lambda/\partial p)_T$  is linear in the isothermal compressibility and  $-(1/\lambda)(\partial\lambda/\partial v)_T$  is linear in the reciprocal of the molar volume. In addition, the slopes of the two graphs are equal as follows from the thermodynamic connecting equation

$$\frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial p} \right)_T = -\beta_T v \frac{1}{\lambda} \left( \frac{\partial \lambda}{\partial v} \right)_T \quad (\text{Eq. 170})$$

Figures 11 and 12 also show that both curves pass through the origin; hence the pressure and volume coefficients of thermal conductivity would always be expected to be positive, unlike the temperature de-

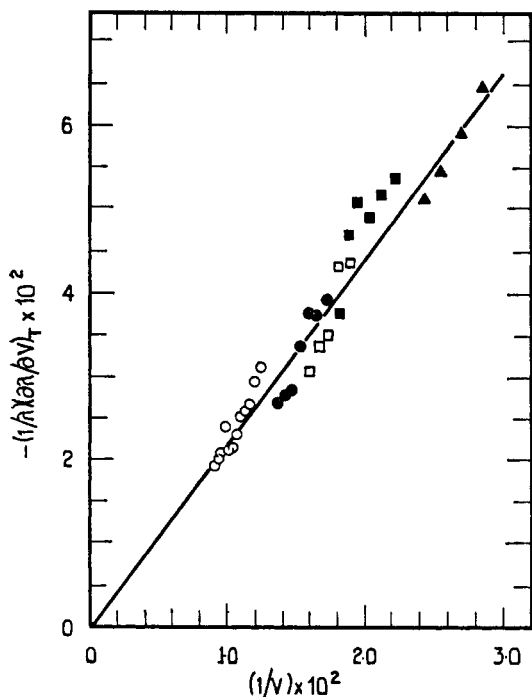


Fig. 12.—Plot of the volume dependence of thermal conductivity against the reciprocal molar volume for ○ ether, ● acetone, □ carbon disulfide, ▲ methanol, ■ ethanol (units in  $\text{cm.}^{-3}$  mole) (copied substantially from (62)).

pendence which can be negative. Again when Eq. 168 and 169 are evaluated on the hard-sphere rectangular cell potential model, the results are closely similar to the corresponding equations derived from the Longuet-Higgins and Pople and Enskog theories, just as discussed in section VI.

So far, none of the statistical theories which assume spherically symmetric intermolecular potentials have been shown to predict the general type of behavior of the pressure, volume, and temperature dependence of thermal conductivity that has been obtained from the lattice model. The ample confirmation of these predictions with experimental measurements, however, suggests that an additional criterion for checking statistical expressions is that they can be effectively reduced to a form which shows the importance of the various thermodynamic properties  $\alpha$ ,  $\beta_T$ , and  $1/V$  in controlling  $(1/\lambda)(\partial\lambda/\partial T)_p$ ,  $(1/\lambda)(\partial\lambda/\partial p)_T$ , and  $(1/\lambda)(\partial\lambda/\partial V)_T$ , respectively.

The substantial success of the lattice theory tends to suggest that the imposition of a temperature gradient on a liquid is a small perturbation of the structure compared with the imposition of a velocity gradient. This makes thermal conductivity comparatively structure insensitive, because to transport energy a molecule need only oscillate in its cell without breaking off the intermolecular forces with its nearest neighbors. For momentum transport, however, continual disruption of the intermolecular forces between molecules, moving

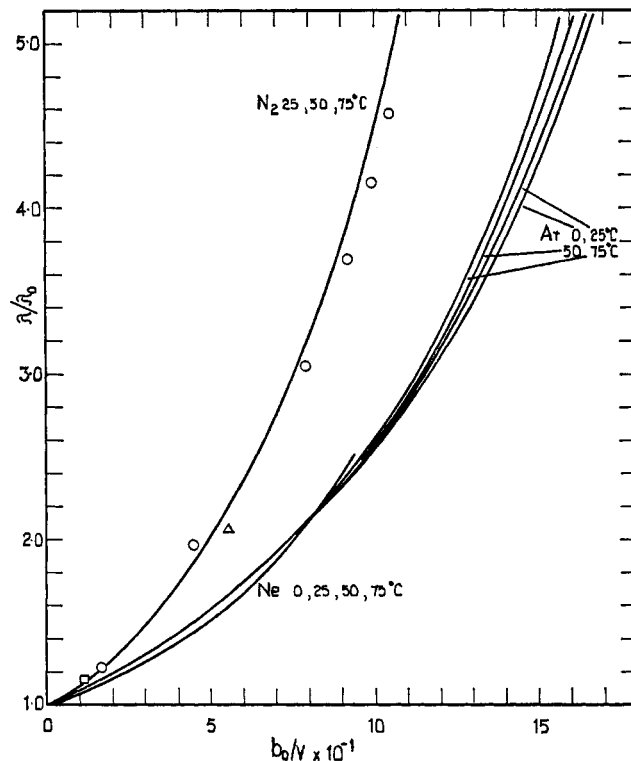


Fig. 13.—Corresponding states plot of reduced thermal conductivity against reduced number density: ○  $\text{CH}_4$  at  $-42.2^\circ$ , □  $\text{CH}_4$  at  $-73.2^\circ$ , Δ  $\text{O}_2$  at  $-114.2^\circ$ .

with different hydrodynamic velocities, is essential for the process to occur and leads to sensitivity to structure (79).

## VII. THE PRINCIPLE OF CORRESPONDING STATES

In the absence of complete experimental information on the equilibrium or transport properties of gases or liquids, prediction of the properties is generally made by correlations which have a basis in the principle of corresponding states. According to this principle, molecules obeying the same form of intermolecular potential have the same values of a particular reduced property in corresponding physical states. No real effort has yet been made to apply this principle to the thermal conductivity of dense gases and liquids due mainly to the lack of sufficient experimental data and a suitable guide from theory of the functional behavior to expect.

As seen from Eq. 58 the thermal conductivity of a liquid composed of simple molecules interacting with a spherically symmetric potential can be written in a reduced form  $\lambda^*$  which is a universal function of  $kT/\epsilon$  and  $V/N\sigma^3$  only. However, none of the existing statistical theories of thermal conductivity for real molecules, covering the dilute to dense gas and liquid region, have shown sufficient promise to be used as a basis for producing a corresponding states correlation. Attention is therefore restricted to the Enskog theory.

According to the ratio Eq. 68, of the thermal con-



ductivity of a dense gas  $\lambda$  to that of the corresponding infinitely dilute gas  $\lambda_0$ , at the same temperature, is a function of the compressibility only. This suggests that for a series of simple liquids  $\lambda/\lambda_0$ , which is a reduced thermal conductivity, should be plotted against  $b_0/V$  which is a reduced number density. As the theory is for rigid spheres, the appropriate diameter  $\sigma$  can be obtained (22) by equating the experimental thermal conductivity of the infinitely dilute gas to Eq. 63 and solving for  $\sigma$  which is then used to give  $b_0$  and hence  $b_0/V$  provided the density is available.

Figure 13 shows the behavior of  $\lambda/\lambda_0$  as a function of  $b_0/V$  for the limited amount of suitable data for which the compressibility and  $\lambda_0$  are also known. Data are given for argon (88), neon (125), nitrogen (84), methane (58), and oxygen (147). Due to the absence of low temperature values of  $\lambda_0$ , these results are confined principally to the dense gas region. The data falls clearly on two separate curves, one for the inert gases and the other for the simple diatomic molecules and methane. These curves can be used to estimate the thermal conductivity of a dense gas, but additional experimental results are necessary to confirm the behavior exhibited here.

#### VIII. THE THERMAL CONDUCTIVITY OF PARTICULAR MATERIALS

In this final section it is relevant to consider the thermal conductivities of materials which are of particular interest from the theoretical or technological point of view.

##### A. MOLTEN METALS

While the viscosities and diffusion coefficients of molten metals do not exhibit exceptional behavior, compared with ordinary liquids, the thermal conductivity does. Figure 14 gives the known thermal conductivities of a series of molten metals, which, as mentioned in section IA and IIIA2, are substantially larger than those of ordinary liquids. The problem of the anomalously high thermal conductivity of solid metals was largely solved by Lorentz who attributed it to the free electrons in the metal. These comprise most of the valency electrons. The treatment considered a metal as a mixture of light and heavy gas molecules corresponding to the free electrons and the metal cores, respectively. For such a mixture, the velocity distribution function is comparatively simple provided the influence of mutual collisions between the electrons in altering their motion is negligible compared with that of their collisions with the cores.

On this basis, expressions for the electrical and thermal conductivities can be derived which, although they cannot be readily evaluated explicitly, give the simple ratio (*cf.* Eq. 46)

$$\frac{\lambda}{\sigma_e T} = \frac{\pi^2 k^2}{3e^2} \quad (\text{Eq. 171})$$

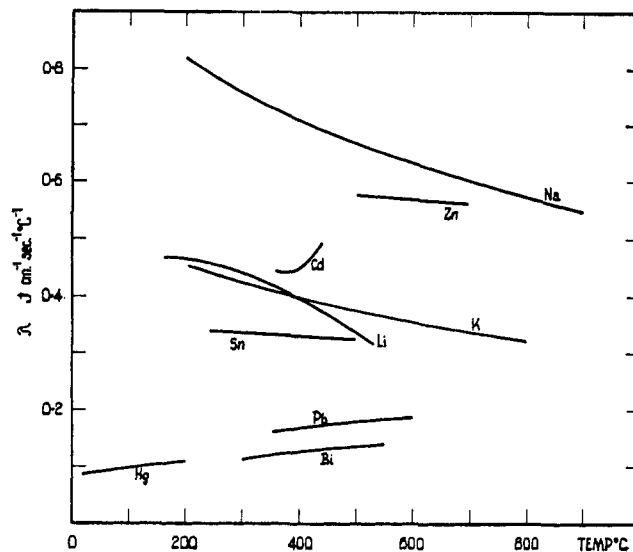


Fig. 14.—The thermal conductivities of molten metals.

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, as was first observed experimentally by Wiedemann and Franz (144). The quantity  $\lambda/\sigma_e T$  is called the Lorentz number  $L$  and has a value of  $2.45 \times 10^{-8}$  joule ohm sec.<sup>-1</sup> °C.<sup>-1</sup> °K.<sup>-1</sup>.

As the volume change on fusion of metals is only about 5% (130) and the conduction is due principally to the free electrons, then Eq. 171 should also be applicable to liquid metals, a fact which has already been shown in Fig. 2 for the Lorentz number as a function of temperature for a series of molten metals and some eutectic mixtures. While on average, the results lie slightly below the theoretical value, Eq. 171 can be used to estimate the thermal conductivity from a measurement of the electrical resistance alone using a value of the Lorentz number of  $2.4 \times 10^{-8}$ .

While the bulk of the thermal conductance in metals is due to free electrons, a lattice term also exists. It is of interest, therefore, to determine the magnitude of this term which can be estimated using Bridgman's theory (13). This has been done for a series of metals at the melting point and the results (79) are given in Table XXIV. This shows that the percentage contribution of lattice terms to the total thermal conductivity, while small, is greatest for the poorest electrical conductors and lowest for the best, as would be expected.

TABLE XXIV  
PERCENTAGE LATTICE CONTRIBUTION TO THE THERMAL CONDUCTIVITY OF MOLTEN METALS

	Metal				
	Na	Cd	Sn	Pb	Bi
$\lambda$ lattice/ $\lambda$ exptl., %	1.1	2.6	3.0	4.4	5.9
Electrical resistivity, ohm cm.	10	33	48	95	128

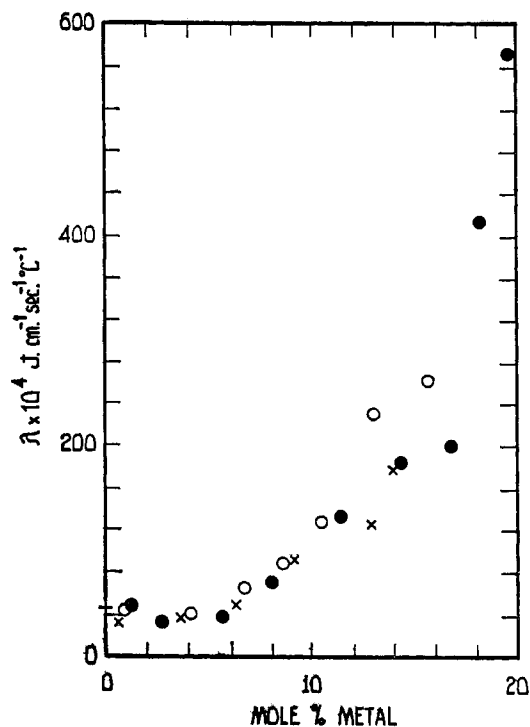


Fig. 15.—The thermal conductivity of various solutions of alkali metals in liquid ammonia at 235°K.: + pure ammonia, ● lithium solution, × sodium solution, ○ potassium solution (copied substantially from (140)).

One further feature of the thermal conductivity of metals can be seen from Fig. 14. For metals with the highest atomic volumes, the thermal conductivity decreases with increase in temperature while for those with the lower atomic volumes it increases with increasing temperature. This behavior is in all probability due to differences in the coefficients of expansion between the light and heavy systems as discussed in section V, but no full investigation of the problem has yet been made.

#### B. METAL SOLUTIONS IN LIQUID AMMONIA

Like water, liquid ammonia has an abnormally high thermal conductivity ( $50 \times 10^{-4}$  joule  $\text{cm}^{-1} \text{sec}^{-1} \text{°C}^{-1}$  at 235°K.) when compared with other liquids. In addition, it is of particular interest for its solvent power for alkali and alkaline earth metals as well as some salts. In fresh solutions, which have abnormally high electrical conduction, the metal can be recovered. If allowed to stand, however, the metal amide tends to form with the evolution of hydrogen.

The extremely high electrical conductivity of metal-ammonia solutions has been attributed to the presence of free electrons, and anomalously large thermal conductivities would, therefore, be expected on the basis of the Lorentz theory. The results (140) of thermal conductivity determinations on a series of freshly prepared solutions of lithium, sodium, and potassium in liquid ammonia are given in Fig. 15. Saturation solubility

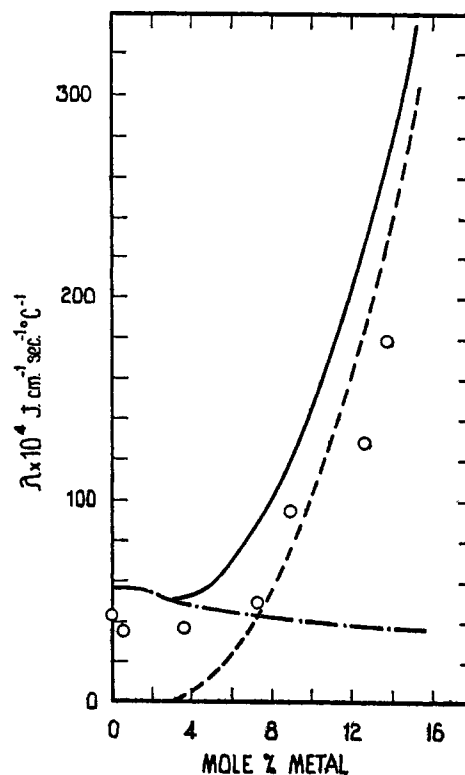


Fig. 16.—Electronic---, lattice— · —, and total—— thermal conductivity of sodium-ammonia solutions at 235°K.: ○ experimental values (copied substantially from (140)).

tends to be reached at about 15 mole % for Na and K and 20 mole % for Li, and at these concentrations the thermal conductivity does become extremely high.

Figure 16 compares the experimental results on sodium with the sum of the calculated values of the electronic contribution on the basis of Eq. 171 and a lattice contribution from Bridgman's theory. Agreement is satisfactory, and, if the lattice contribution were adjusted to agree with the experimental value on pure ammonia, the discrepancy between calculated and experimental values would be substantially reduced. From Fig. 15 it can be seen that the thermal conductivity is independent of the metal dissolved and from Table XXV that the experimentally determined

TABLE XXV  
LORENTZ NUMBER  $L$  FOR METAL-AMMONIA SOLUTIONS

Metal	Concn., mole %	Temp., °K.	$L \times 10^8$	Metal	Concn., mole %	Temp., °K.	$L \times 10^8$
Na	7.3	235	1.0	K	4.0	235	2.3
	9.1	235	2.0		6.6	235	2.8
	12.7	235	1.4		8.5	235	2.5
		223	1.3		10.4	235	2.5
		213	1.3		12.9	235	2.5
		203	1.3		15.5	235	3.2
		198	1.2			214	2.7
		235	1.6			194	2.6
		218	1.7			174	2.5
		205	1.7				
	192	1.7					

Lorentz number is virtually independent of temperature and concentration. These results tend to confirm the presence of free electrons in metal ammonia solutions.

Systems of alkali metals in liquid ammonia could be important in low temperature heat transfer problems where a heat transfer fluid of very high thermal conductivity is required.

### C. MOLTEN SALTS

With the exception of electrical conductivity and viscosity, little information is available on the transport properties of molten salts especially the simpler ones like the alkali halides where both ions are spherically symmetric. This is due principally to the experimental difficulties encountered in making measurements at temperatures of the order of 1000°. Such high temperatures are not necessary for a study of the properties of salts like the alkali nitrates with comparatively low melting points, and it is for such salts with complex anions that most information is available.

Molten salts differ from simple liquids like argon in properties where the long-range nature of the coulomb potential plays an important role such as the lattice energy. However, with regard to transport properties there is no evidence that either the viscosities (43), diffusion coefficients (32), or thermal conductivities (83) are substantially different from those of ordinary simple liquids. For example (143), for KCl which is isoelectronic with argon, viscosities at the melting point are, respectively,  $15.1 \times 10^{-3}$  and  $2.8 \times 10^{-3}$  poise.

The effect of the long-range coulomb potential on the transport properties of molten salts has recently been investigated by Rice (99) using as his basis the theoretical form, Eq. 113, of the friction coefficient  $\zeta_0$ . For the application of the theory, it is necessary to define an "ideal" ionic melt. This consists of one in which the ions are spherically symmetric, are of the same size, and have identical electronic properties except for the sign of the charge. This reduces the problem to that of a one-component system. Further simplification is ensured as, due to the preservation of electroneutrality, a positive ion is surrounded by negative ions and *vice versa* so that collisions most likely to occur are those between oppositely charged ions.

The pair potential assumed for the interaction is of the form

$$\begin{aligned} \phi_{\alpha\beta}(R) &= \left. \begin{aligned} &\infty, R < \sigma_{\alpha\beta} \\ &= 0, R > \sigma_{\alpha\beta} \end{aligned} \right\} \text{hard} \\ \phi_{\alpha\beta}(R) &= \left. \begin{aligned} &-\frac{C_{\alpha\beta}}{R^6} + \frac{z_{\alpha}^+ z_{\beta}^- e^2}{DR}, R > \sigma_{\alpha\beta} \\ &= 0, R < \sigma_{\alpha\beta} \end{aligned} \right\} \text{soft} \end{aligned} \quad (\text{Eq. 172})$$

in which the repulsive term has been replaced by a rigid core and the polarization term by the insertion of the dielectric constant  $D$  in the coulomb  $R^{-1}$  term.  $z_{\alpha}^+$

and  $z_{\beta}^-$  are the ion valencies and  $e$  the electronic charge.  $C_{\alpha\beta}$  in the van der Waals attractive  $R^{-6}$  term is a constant, and the core diameter  $\sigma_{\alpha\beta}$  is the contact distance between oppositely charged ions.

From section IIIF1a, the friction constant is of the form

$$\zeta_0 \propto \int \nabla^2 \phi(R) g_0^{(2)}(R) d^3R \quad (\text{Eq. 173})$$

so that as

$$\nabla^2 \phi(R) = \frac{\partial^2 \phi(R)}{\partial R^2} + \frac{2}{R} \frac{\partial \phi(R)}{\partial R} \quad (\text{Eq. 174})$$

this gives  $\zeta_0 = 0$  for a pure coulomb potential. By assuming the existence of a rigid core and a soft long-range attractive term, the ion collisions can be taken as consisting of a basic rigid core collision followed by a quasi-Brownian motion in the fluctuating force field of the neighboring ions. As the core collision is instantaneous, the separation of force fields into the various terms implies a separation in relaxation times which leads to transport equations for the separate contributions.

The core contribution which is the collisional contribution in the terminology of section III can be taken as given by Eq. 70 of the Enskog theory for hard spheres, and the contribution from the soft portion of the potential  $\lambda_{\phi}$  as a contribution to be evaluated on the Kirkwood type of treatment. The actual core contribution taken by Rice is slightly different from the Enskog equation and is given by Eq. 146, derived by Rice and Allnatt (101). For the soft part of the potential, the approximation of Rice and Kirkwood to  $\lambda_0$  (Eq. 130) was assumed. As  $\nabla^2 \phi(R)$  for the coulomb potential makes no contribution to the integral or  $\zeta_0$ , then the soft portion of the potential can be taken approximately as given by the evaluation of Eq. 130 for the 12:6 potential which, when  $T$  is large as is the case for a molten salt, is (99)

$$\lambda_{\phi} \simeq \frac{5kT\eta\phi\alpha}{m} \quad (\text{Eq. 175})$$

where  $\alpha$  is the coefficient of thermal expansion. Rough estimation (99) of these contributions for KCl at its melting point gives them as  $3.05 \times 10^{-4}$  and  $180 \times 10^{-4}$  joule cm.<sup>-1</sup> sec.<sup>-1</sup> deg.<sup>-1</sup> for the core and soft portions, respectively. Compared with values available for molten nitrates, the calculated value of the thermal conductivity seems high. In addition, the weakness of the expression for  $\zeta_0$  and the Kirkwood-Rice theory already discussed mean that little of this argument can be taken as quantitative. Nevertheless, the spirit of it must be substantially in order as the long-range coulomb potential does not seem to be important in thermal conductivity.

### D. WATER AND STEAM

In section IIF2 where water has been discussed as a thermal conductivity standard, it was pointed out that

TABLE XXVI  
MOLE FRACTION OF WATER POLYMERS

Temp., °C.	Mole fraction of various species				$\lambda_{\text{calcd}}$
	H <sub>2</sub> O	(H <sub>2</sub> O) <sub>2</sub>	(H <sub>2</sub> O) <sub>4</sub>	(H <sub>2</sub> O) <sub>8</sub>	
0	0.050	0.350	0.300	0.300	53.6
20	0.081	0.434	0.308	0.178	60.3
40	0.119	0.492	0.293	0.096	64.1
60	0.162	0.529	0.261	0.048	67.9

the thermal conductivity is comparatively high. The principal attempt to explain this is due to Eigen (33) who bases his theory on the Eucken model of water (40). On this model water is assumed to be a mixture of single molecules, dimers, tetramers, and octamers. Table XXVI gives the mole fractions of the various species as a function of temperature.

According to Eigen, the dissociation of the polymers under the influence of the temperature gradient gives rise to an excess thermal conductivity over the normal liquid value. This excess value coupled with the normal lattice term estimated by a formula due to Riedel yields (Table XXVI) surprisingly good agreement between experimental and calculated thermal conductivities and, in addition, correctly predicts the anomalous increase of thermal conductivity with temperature up to the boiling point (*cf.* Tables VI and XXVI). Obvious weaknesses in the theory are the Riedel formula and the Eucken model of water. However, the theory is of interest as a first attempt to calculate the transport properties of a liquid in which chemical reactions are taking place—in this particular case, dissociation.

No "best" set of values of the thermal conductivity of steam have yet been proposed although the problem is at present under investigation by the International Co-ordinating Committee for the Properties of Steam whose recommendations should be available shortly. Figure 17 gives smoothed isobars for steam up to 600 kg. cm.<sup>-2</sup> and temperatures up to 800°, as proposed by Vargaftik and Tarzimanov (138) who also give a table of closely spaced values for the same range. The smoothing was done on experimental values originally obtained by Vargaftik and Tarzimanov (136, 137) and Vargaftik and Timrot (139). Other investigations have been made by Leneindre, Johanin, and Vodar (72), Keyes and Vines (64), Lawson, Lowell, and Jain (71), and Vukalovich and Cherneeva (142).

#### E. AQUEOUS SALT SOLUTIONS

Unlike the case of melts of pure salts, extensive data are available on the thermal conductivities of aqueous salt solutions. These measurements have been made principally by Riedel (110–112). With respect to temperature dependence, the thermal conductivities of the salt solutions studied increase with increasing temperature following the anomalous behavior of water with a positive temperature coefficient not very different from pure water.

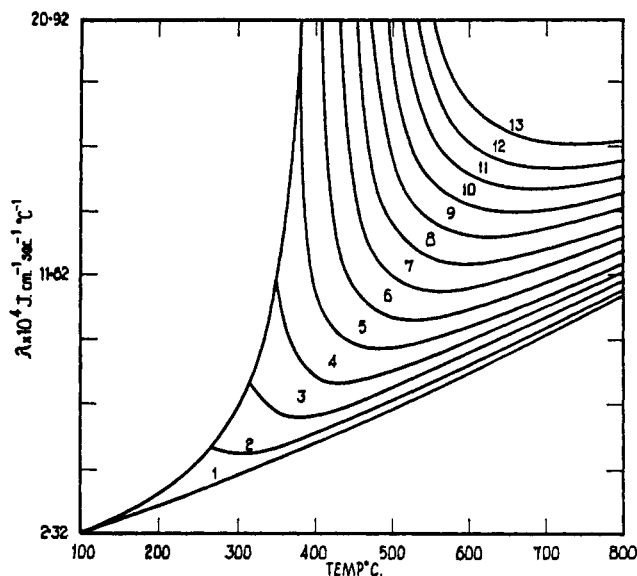


Fig. 17.—The thermal conductivity of steam; pressures in kg. cm.<sup>-2</sup>: 1, 1; 2, 50; 3, 100; 4, 150; 5, 200; 6, 250; 7, 300; 8, 350; 9, 400; 10, 450; 11, 500; 12, 550; 13, 600 (copied substantially from (138)).

At constant temperature, the thermal conductivities of most salt solutions, except the alkali hydroxides, are linear in the concentration over the ranges studied which are often up to several moles per liter. In the majority of cases the conductivity decreases with increasing concentration. Exceptions are solutions of Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, NaF, and Na<sub>3</sub>PO<sub>4</sub>, and it is of interest to note that where the corresponding potassium salts have been studied, *viz.*, K<sub>2</sub>SO<sub>4</sub>, KF, and K<sub>2</sub>CO<sub>3</sub>, the behavior conforms to the usual pattern with  $\lambda$  decreasing with increasing concentration.

Because of the linear behavior of thermal conductivity with concentration, Riedel has proposed the relationship

$$\lambda = \lambda_w + \sum \alpha_i C_i \quad (\text{Eq. 176})$$

to represent the thermal conductivity of salt solutions at 20° where  $\lambda_w$  is the value of the thermal conductivity of pure water at this temperature,  $\alpha_i$  a constant characteristic of the ion, and  $C_i$  its concentration in moles per liter. Values of  $\alpha_i$  for a series of ions based on a value of 0 for the Na<sup>+</sup> ion at 20° at a concentration of 1 mole l.<sup>-1</sup> are given in Table XXVII, *i.e.*, the  $\alpha_i$  of Cl<sup>-</sup> is taken as the magnitude of the difference of the thermal conductivity of pure water and a molar solution of NaCl. As Riedel reports thermal conductivities in kcal. m.<sup>-1</sup> hr.<sup>-1</sup> °C.<sup>-1</sup>, the equation for calculating the thermal conductivity of a salt solution at any temperature between -40 and 100°, where  $\lambda$  is in joule cm.<sup>-1</sup> sec.<sup>-1</sup> °C.<sup>-1</sup>, is

$$\lambda \times 10^4 = f(0.515 + \sum \alpha_i C_i)/86.042 \quad (\text{Eq. 177})$$

where  $f$ , which is the ratio of the thermal conductivity of water at a temperature  $T$  compared with the value

TABLE XXVII  
 $\alpha_1$  FOR COMMON CATIONS AND ANIONS

Cations	$\alpha_1 \times 10^4$	Anions	$\alpha_1 \times 10^4$
H <sup>+</sup>	-78	OH <sup>-</sup>	180
Li <sup>+</sup>	-30	F <sup>-</sup>	18
Na <sup>+</sup>	0	Cl <sup>-</sup>	-47
K <sup>+</sup>	-65	Br <sup>-</sup>	-150
NH <sub>4</sub> <sup>+</sup>	-100	I <sup>-</sup>	-236
Mg <sup>+2</sup>	-80	NO <sub>2</sub> <sup>-</sup>	-40
Ca <sup>+2</sup>	-5	NO <sub>3</sub> <sup>-</sup>	-60
Sr <sup>+2</sup>	-34	ClO <sub>3</sub> <sup>-</sup>	-122
Ba <sup>+2</sup>	-66	ClO <sub>4</sub> <sup>-</sup>	-150
Ag <sup>+</sup>	-90	BrO <sub>3</sub> <sup>-</sup>	-122
Cu <sup>+2</sup>	-140	CO <sub>3</sub> <sup>-2</sup>	-65
Zn <sup>+2</sup>	-140	SiO <sub>3</sub> <sup>-2</sup>	-80
Pb <sup>+2</sup>	-80	SO <sub>3</sub> <sup>-2</sup>	-20
Co <sup>+2</sup>	-100	SO <sub>4</sub> <sup>-2</sup>	10
Al <sup>+3</sup>	-280	S <sub>2</sub> O <sub>3</sub> <sup>-2</sup>	-70
Th <sup>+4</sup>	-375	CrO <sub>4</sub> <sup>-2</sup>	10
		Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	-137
		PO <sub>4</sub> <sup>-3</sup>	180
		Fe(CN) <sub>6</sub> <sup>-4</sup>	-160
		CH <sub>3</sub> COO <sup>-</sup>	-197
		(COO) <sub>2</sub> <sup>-</sup>	-30

at 20°, is given in Table XXVIII. It should be remembered that  $\alpha_1$  is for the single ion, so that for salts with several anions or cations  $\alpha_1$  must be multiplied by the appropriate factor.

TABLE XXVIII

FACTOR $f = \lambda_T/\lambda_{20}$ FOR WATER							
$T, ^\circ\text{C.}$	$f$	$T, ^\circ\text{C.}$	$f$	$T, ^\circ\text{C.}$	$f$	$T, ^\circ\text{C.}$	$f$
-40	0.838	0	0.946	40	1.048	80	1.119
-30	0.865	10	0.973	50	1.069	90	1.130
-20	0.892	20	1.000	60	1.088	100	1.137
-10	0.919	30	1.025	70	1.105		

Eigen (34) has interpreted the effect of the addition of salts on the thermal conductivity of water based on the model mentioned in section VIII, but the theory will not be discussed here.

#### F. CARBON DIOXIDE

The thermal conductivity of carbon dioxide is of particular interest because it is the only substance where extensive measurements have been made in the critical region (48). In the critical region the problem of convection is substantially magnified compared with the normal gas or the normal liquid away from the critical point. Michels and Sengers (86) have made a careful analysis of the convection problem for a steady-state parallel plate apparatus as mentioned in section IIE, and their results, obtained with Van der Gulik (Fig. 18) (87) in the critical region for CO<sub>2</sub>, are claimed to be free from convection. These exhibit a pronounced peak in the thermal conductivity-density plot which diminishes on raising the temperature from the critical temperature.

The form of these curves closely resemble those for  $C_v$  over the same range, and hence from Eq. 149 the peak in thermal conductivity is not unexpected. As dis-

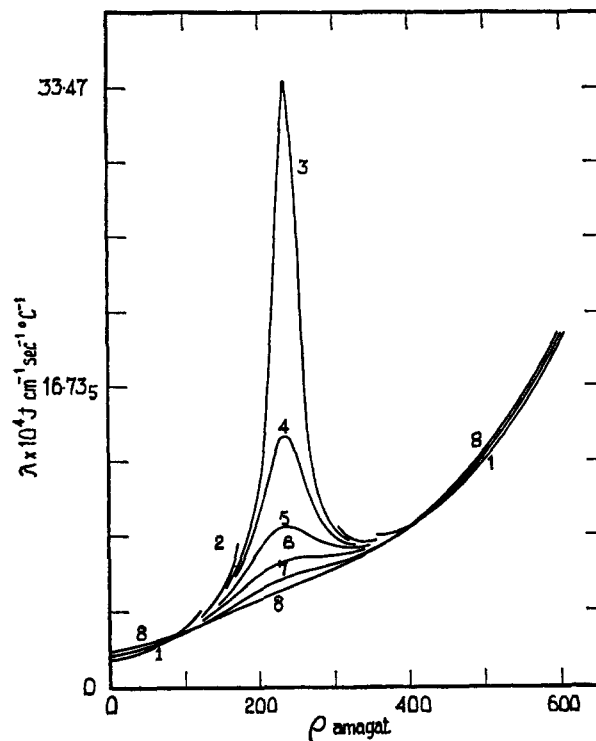


Fig. 18.—The thermal conductivity of carbon dioxide in the critical region; temperatures in °C.: 1, 25; 2, 30; 3, 31.2; 4, 32.1; 5, 34.8; 6, 40; 7, 50; 8, 75 (copied substantially from (87))

cussed in section IIIC, however, it is not yet fully established what contributions to the specific heat are operative in thermal conductivity, and in the critical region, as the gas phase convective mechanism is still important, the problem is more complex. However, as the peak in the  $C_v$  curve is known to be due to cluster formation, it must follow (122) that the energy variation involved in the association and dissociation of clusters contributes to thermal conductivity. This conclusion is also basically similar to Eigen's conclusions on the origin of the anomalous thermal conductivity of water. Finally, as the thermal conductivity curves like the  $C_v$  curves are continuous, whereas  $C_p$  is discontinuous at the critical point, this strongly supports the necessity for  $C_v$  as opposed to  $C_p$  terms in thermal conductivity equations.

#### IX. CONCLUSIONS

The present survey of thermal conductivity in dense gases and liquids indicates that over the course of the past 10 years considerable attention has been devoted to this subject. This has somewhat remedied the previous situation where, in the study of transport phenomena, viscosity and diffusion attracted most attention, particularly among chemists.

Obvious gaps in experimental knowledge require filling, principally in the establishment of the thermal conductivities of standard materials and the effects of temperature and pressure on the thermal conductivity

of liquids of simple molecules. Such results are necessary to check statistical theories.

With regard to theoretical work, significant progress has been made. The factors which control the pressure and temperature dependence of the coefficient have been largely established, and, in addition, transcription of the friction coefficient into a thermodynamic expression has enabled further checks to be made on existing statistical theories. While a better understanding of the problems of transport theory has been achieved, no statistical theory for dense fluids can be said to have attained a comparable degree of success to that of the Chapman-Enskog theory for the dilute gas phase. Development of such a theory for thermal conductivity is dependent, not only on the solution of transport problems *per se*, but on the emergence of a satisfactory equilibrium theory for liquids. It is hoped that the large amount of effort being devoted at present to a study of the liquid state will yield significant progress in the near future.

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