

The Properties of Pure Liquids

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By a semiempirical approach, a method is found to calculate the specific heat of a normal pure liquid at constant pressure from the specific heat of the gaseous state at the same temperature. It is also found that the coefficient of thermal expansion, the compressibility, and the velocity of sound of the liquid can be calculated accurately if the density, the molecular weight, and the normal boiling temperature of the liquid at atmospheric pressure are known. Finally, a method of computing the thermal conductivity of all liquids, except liquid metals, from compressibility and density is developed. For normal liquids, the thermal conductivity can again be determined if only the normal boiling temperature, the density, and the molecular weight are known.

IN ROCKET and jet propulsion engineering, because of the necessity of considering a very wide range of possible fuels and propellants, one often meets the situation that the physical properties, such as heat capacity and thermal conductivity, of liquid of interest are not listed in the handbooks. Naturally the question to ask is whether such physical properties can be estimated from known simple quantities such as the boiling point, the molecular weight, and the density of the liquid. It is clear that such a correlation of liquid properties must come from the theory of the liquid state. Although there was no lack of work by physicists and physical chemists in this field, the agreement in the numerical values of theoretical prediction and of experimental observation is usually very poor. Therefore it may be justified to say that there are only very few useful results in the engineering sense. The difficulty here is evidently due to the rather indefinite structure of the liquid state in comparison to other states of matter: For the gaseous state, the interaction between the molecules can be almost neglected, and the predominating feature of the state is the translational and internal motions of the individual molecules. For the solid state, the reverse is true. The predominating feature is the interaction between the molecules or the atoms. For the liquid state of matter, the molecular interaction and the molecular motion are of equal importance. This fact leads to great complexities, and any theory of liquids, necessarily based upon a simplified model, is incomplete and is predicated upon many assumptions. The divergences between the theoretical predictions and the experimental observations are thus to be expected.

In this paper a somewhat new approach to the subject will be attempted. The theory will not be used to predict the physical properties from the molecular and the atomic characteristics, but rather used as a framework to fit the experimental data. In other words, the theory only gives the parameters that will enter into a relation, while the exact form of the functional relation is to be determined by the experimental data. Thus the approach here is that of "dimensional analysis" so successful in the older fields of engineering science, such as fluid mechanics and solid mechanics (1).² The two specific useful results of this investigation are a method to calculate the specific heats and a method to calcu-

late the thermal conductivity of liquids. These methods are generally applicable to the so-called normal liquids, but a more general form for the thermal conductivity is available to include all liquids, normal or otherwise.

Lennard-Jones and Devonshire Theory of Liquids

One of the fairly successful theories of normal liquids is that given by Lennard-Jones and Devonshire (2). It is a theory of the "free volume" type in that the liquid molecule is assumed to move within a cage formed by the neighboring molecules. In this theory, the properties of the cage are determined by smoothing the bimolecular interactions of a face-centered cubic lattice where the nearest distance between molecules is a . The bimolecular interaction potential ϵ is taken from the theory of gaseous states and is expressed as

$$\epsilon(r) = \epsilon_m \left[\left(\frac{r^*}{r}\right)^{12} - 2 \left(\frac{r^*}{r}\right)^6 \right] \dots \dots \dots [1]$$

where r is the distance between the molecules, r^* the equilibrium distance, and ϵ_m is the magnitude of the potential at $r = r^*$.

The free energy F for an assembly of N molecules is found in this way to be

$$\frac{F}{N} = -kT \log \frac{(2\pi mkT)^{3/2}}{h^3} - kT \log j(T) - kT - \Lambda^* \left\{ 1.2 \left(\frac{V^*}{V}\right)^2 - 0.5 \left(\frac{V^*}{V}\right)^4 \right\} - kT \log (2\pi\gamma gV) \dots [2]$$

In this equation, k is the Boltzmann constant, T the absolute temperature, $j(T)$ the internal partition function of the molecule. And furthermore

$$\Lambda^* = z\epsilon_m \dots \dots \dots [3]$$

where z is the coordination number and is 12 for face-centered cubic lattice, V is the volume per molecule, and V^* is the characteristic volume. They are related to a and r^* as follows

$$V = \frac{1}{\gamma} a^3, V^* = \frac{1}{\gamma} r^{*3}, \gamma = \frac{1}{\sqrt{2}} \dots \dots \dots [4]$$

g is the following complicated integral

$$g = \int_0^{1/4} y^{1/2} \exp \left\{ -\frac{\Lambda^*}{kT} \left(\frac{V^*}{V}\right)^4 l(y) + 2 \frac{\Lambda^*}{kT} \left(\frac{V^*}{V}\right)^2 m(y) \right\} dy \dots \dots \dots [5]$$

where

$$l(y) = \frac{1 + 12y + 25.2y^2 + 12y^3 + y^4}{(1-y)^{10}} - 1, l(0) = 0 \dots \dots [6]$$

$$m(y) = \frac{1+y}{(1-y)^4} - 1, m(0) = 0 \dots \dots \dots [7]$$

Once the free energy is calculated, the thermodynamic properties of the liquid can be obtained by simple differentiations. For instance, the energy per molecule E/N is

$$\frac{E}{N} = -T^2 \frac{\partial}{\partial T} \left(\frac{F/N}{T} \right) \dots \dots \dots [8]$$

The pressure P is

$$P = -\frac{\partial}{\partial V} \left(\frac{F}{N} \right) \dots \dots \dots [9]$$

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² Numbers in parentheses refer to the References on page 24.

Mathematically then, the most difficult task of the theory is the evaluation of the integral g in Equation [5]. Recently, R. H. Wentorf, R. J. Buehler, J. O. Hirschfelder, and C. F. Curtiss (3) have carried out this tedious integration by numerical method, together with some inconsequential improvements in its formulation. Unfortunately, their extensive numerical tables are quite unsuitable for the present purpose of discovering the analytical functional relationships between the different quantities. However, for liquid states at low or atmospheric pressures, the ratio V/V^* is very nearly unity, while the ratio Λ^*/kT is of the order of 20. It is thus appropriate to seek the asymptotic expansion of the function g for large values of Λ^*/kT . This can be done as follows:

Let

$$s = \frac{\Lambda^*}{kT} \left(\frac{V^*}{V}\right)^4 \dots\dots\dots [10]$$

Then by expanding the functions $l(y)$ and $m(y)$ in power series of y , one has

$$-\frac{\Lambda^*}{kT} \left(\frac{V^*}{V}\right)^4 l(y) + 2 \frac{\Lambda^*}{kT} \left(\frac{V^*}{V}\right)^2 m(y) = -s\eta = -s \left[\left\{ 24 - 10 \left(\frac{V}{V^*}\right)^2 \right\} y + \left\{ 200.2 - 28 \left(\frac{V}{V^*}\right)^2 \right\} y^2 + \left\{ 1144 - 60 \left(\frac{V}{V^*}\right)^2 \right\} y^3 + \dots \right] \dots [11]$$

η is thus the power series within the square bracket of Equation [11]. By inverting this power series, it is found that

$$y = a_1\eta + a_2\eta^2 + a_3\eta^3 + \dots\dots\dots [12]$$

where

$$a_1 = \frac{1}{24 - 10 \left(\frac{V}{V^*}\right)^2}$$

$$a_2 = -\frac{200.2 - 28 \left(\frac{V}{V^*}\right)^2}{\left[24 - 10 \left(\frac{V}{V^*}\right)^2\right]^2}$$

and

$$a_3 = \frac{2 \left[200.2 - 28 \left(\frac{V}{V^*}\right)^2 \right]^2 - \left[1144 - 60 \left(\frac{V}{V^*}\right)^2 \right] \left[24 - 10 \left(\frac{V}{V^*}\right)^2 \right]}{\left[24 - 10 \left(\frac{V}{V^*}\right)^2 \right]^3} \dots\dots\dots [13]$$

At the lower limit of integration for g , $y = 0$, so $\eta = 0$. At the upper limit of integration, $y = 1/4$, so $\eta = l(1/4) - 2(V/V^*)^2 m(1/4)$. $l(1/4)$ is, however, approximately 90, $m(1/4)$ is 2.95, and s is very large. Therefore it is correct to set the upper limit of integration in η as ∞ . Then

$$g \sim a_1^{3/2} \int_0^\infty e^{-s\eta} \left[\eta^{1/2} + \frac{5}{2} \frac{a_2}{a_1} \eta^{3/2} + \frac{7}{2} \left\{ \frac{a_3}{a_1} + \frac{1}{4} \left(\frac{a_2}{a_1}\right)^2 \right\} \eta^{5/2} + \dots \right] d\eta = \frac{\sqrt{\pi}}{2} \left(\frac{a_1}{s}\right)^{3/2} \times \left[1 + \frac{3.5}{2.2} \frac{a_2}{a_1} \frac{1}{s} + \frac{3.5 \cdot 7}{2 \cdot 2 \cdot 2} \left\{ \frac{a_3}{a_1} + \frac{1}{4} \left(\frac{a_2}{a_1}\right)^2 \right\} \frac{1}{s^2} + \dots \right] \dots\dots [14]$$

By substituting the value of s from Equation [10], and the value of a 's from Equation [13], the following expression for $\log g$ is obtained

$$\log g \sim \log \frac{\sqrt{\pi}}{2} + \frac{3}{2} \log \frac{kT \left(\frac{V}{V^*}\right)^4}{\Lambda^* \left[24 - 10 \left(\frac{V}{V^*}\right)^2 \right]} - \frac{3.5}{2.2} \left(\frac{V}{V^*}\right)^2 \frac{kT}{\Lambda^*} \frac{200.2 - 28 \left(\frac{V}{V^*}\right)^2}{\left[24 - 10 \left(\frac{V}{V^*}\right)^2 \right]} + \frac{3.5 \cdot 7}{2 \cdot 2 \cdot 2} \left(\frac{V}{V^*}\right)^4 \frac{(kT)^2}{(\Lambda^*)^2} \times \frac{12 \left[200.2 - 28 \left(\frac{V}{V^*}\right)^2 \right]^2 - 7 \left[1144 - 60 \left(\frac{V}{V^*}\right)^2 \right] \left[24 - 10 \left(\frac{V}{V^*}\right)^2 \right]}{7 \left[24 - 10 \left(\frac{V}{V^*}\right)^2 \right]^4} \dots [15]$$

It is evident that the expansion of Equation [15] is the appropriate one for large values of Λ^*/kT . By combining Equation [15] with Equation [2], the free energy of the liquid state can be obtained. Differentiation according to Equations [8] and [9] then gives the other thermodynamic quantities.

Specific Heat at Constant Volume

If $\frac{E^{int}}{N}$ is the internal energy per molecule, i.e.,

$$\frac{E^{int}}{N} = kT^2 \frac{\partial}{\partial T} \{ \log j(T) \} \dots\dots\dots [16]$$

then Equation [8] gives

$$\frac{E}{N} = \frac{E^{int}}{N} + 3kT - \Lambda^* \left\{ 1.2 \left(\frac{V^*}{V}\right)^2 - 0.5 \left(\frac{V^*}{V}\right)^4 \right\} - \frac{3.5}{2.2} \frac{200.2 - 28 \left(\frac{V}{V^*}\right)^2}{\left\{ 24 - 10 \left(\frac{V}{V^*}\right)^2 \right\}^2} \left(\frac{V}{V^*}\right)^4 \frac{kT}{\Lambda^*} \dots [17]$$

where terms of third power in T and higher are dropped. By differentiating Equation [17] once more with respect to T , the specific heat at constant volume can be determined. Let C_v^l be the molar specific heat of the liquid state at constant volume, and C^{int} be the molar specific heat of the internal energy alone, i.e., by taking N to be Avogadro's number

$$C^{int} = \frac{\partial}{\partial T} E^{int} \dots\dots\dots [18]$$

Then

$$C_v^l = C^{int} + 3R - \frac{3.5}{2.2} \frac{200.2 - 28 \left(\frac{V}{V^*}\right)^2}{\left\{ 24 - 10 \left(\frac{V}{V^*}\right)^2 \right\}^2} \left(\frac{V}{V^*}\right)^4 \frac{kT}{\Lambda^*} R \dots [19]$$

where R is the universal gas constant or $R = Nk$.

Equation [19] demonstrates the gratifying result that aside from the small correction of the third term, the specific heats at constant volume for the liquid state and the solid state are the same. This is in agreement with the concept that for pressures and temperatures below the critical pressure and the critical temperature, there are more points of similarity between the liquid state and the solid state than there are between the liquid state and the gaseous state. The full classical value of $3R$ means the absence of quantal effects. This is of course generally true, as will be discussed in more detail in the appendix.

The molar specific heat at constant pressure C_p^g for the gaseous state can be calculated as

$$C_p^g = C^{int} + \frac{5}{2}R \dots\dots\dots [20]$$

For molecules that are not excessively elongated as to restrict their rotational freedom in the liquid state, the molecular energy of the internal degrees of freedom must be the same in the liquid state as in the gaseous state. Therefore the values of C^{int} in Equations [19] and [20] must be the same. Then Equation [19] can be also written as

$$C_v^l = C_p^g + R \left[0.5 - \frac{15}{2} \frac{200.2 - 28 \left(\frac{V}{V^*}\right)^2}{\left\{ 24 - 10 \left(\frac{V}{V^*}\right)^2 \right\}^2} \left(\frac{V}{V^*}\right)^4 \frac{kT}{\Lambda^*} \right] \dots [21]$$

Now since the third term to the right of Equation [21] is a small correction term, it would be all right to use the following approximations, true for liquid state at low or atmospheric pressures, i.e., at pressures much lower than the critical pressure. Furthermore

$$\left. \begin{aligned} V/V^* &\sim 1 \\ \frac{kT_b}{\Lambda^*} &\sim 16.5 \end{aligned} \right\} \dots\dots\dots [22]$$

where T_b is the normal boiling temperature of the liquid at atmospheric pressure. Then Equation [21] becomes

$$C_v^l = C_p^g + R \left[0.5 - 0.4 \frac{T}{T_b} \right] \dots\dots\dots [23]$$

Therefore the specific heat of liquids at constant volume can be easily calculated once the specific heat of the gaseous state and the boiling point are known.

Thermal Expansion and Compressibility

The equation of state for the liquid can be determined by using Equation [9]. By using only two terms of the expansion for g as given by Equation [15], one has

$$P = \frac{\Lambda^*}{V} \left\{ 2 \left(\frac{V^*}{V} \right)^4 - 2.4 \left(\frac{V^*}{V} \right)^2 \right\} + \frac{kT}{V} \frac{84 - 20 \left(\frac{V}{V^*} \right)^2}{12 - 5 \left(\frac{V}{V^*} \right)^2} \dots [24]$$

Now the coefficient of thermal expansion α is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \dots\dots\dots [25]$$

Then by differentiating Equation [24] with respect to T , keeping the pressure P constant, one has

$$\alpha \left[\frac{\Lambda^*}{V} \left\{ 10 \left(\frac{V^*}{V} \right)^4 - 7.2 \left(\frac{V^*}{V} \right)^2 \right\} + \frac{kT}{V} \left\{ \frac{84 - 20 \left(\frac{V}{V^*} \right)^2}{12 - 5 \left(\frac{V}{V^*} \right)^2} - \frac{360 \left(\frac{V}{V^*} \right)^2}{\left[12 - 5 \left(\frac{V}{V^*} \right)^2 \right]^2} \right\} \right] = \frac{k}{V} \frac{84 - 20 \left(\frac{V}{V^*} \right)^2}{12 - 5 \left(\frac{V}{V^*} \right)^2}$$

However, the pressure P is very small in comparison with the size of both terms in the right of Equation [24], i.e.,

$$\frac{\Lambda^*}{V} \left\{ 2 \left(\frac{V^*}{V} \right)^4 - 2.4 \left(\frac{V^*}{V} \right)^2 \right\} + \frac{kT}{V} \frac{84 - 20 \left(\frac{V}{V^*} \right)^2}{12 - 5 \left(\frac{V}{V^*} \right)^2} \cong 0$$

Therefore the equation for the thermal expansion can be simplified to

$$\alpha \left[\Lambda^* \left\{ 8 \left(\frac{V^*}{V} \right)^4 - 4.8 \left(\frac{V^*}{V} \right)^2 \right\} - \frac{kT}{\left\{ 12 - 5 \left(\frac{V}{V^*} \right)^2 \right\}^2} \right] = k \frac{84 - 20 \left(\frac{V}{V^*} \right)^2}{12 - 5 \left(\frac{V}{V^*} \right)^2}$$

By again using the approximations of Equation [22], one has finally

$$\alpha T_b = \frac{0.554}{3.2 - 0.445 \frac{T}{T_b}} \dots\dots\dots [26]$$

The compressibility β of the liquid is defined as

$$\beta = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \dots\dots\dots [27]$$

By following a similar procedure as outlined in the preceding paragraph for α , the compressibility is found to be

$$\beta \frac{RT_b}{V_l} = \frac{1}{52.8 - 7.35 \left(\frac{T}{T_b} \right)} \dots\dots\dots [28]$$

where R is again the universal gas constant, V_l is the volume per mole of the liquid.

Equations [26] and [28] give the coefficient of thermal expansion α and the compressibility β according to the Lennard-Jones and Devonshire theory of liquids. Other theories of liquids give different formulas. For instance, the free volume theory of H. Eyring and J. O. Hirschfelder (4) gives

$$\alpha T_b = \frac{3}{9.4 - 4 \left(\frac{T}{T_b} \right)} \dots\dots\dots [29]$$

and

$$\beta \frac{RT_b}{V_l} = \frac{1}{3.13 \left(9.4 \frac{T_b}{T} - 4 \right)} \dots\dots\dots [30]$$

Such discrepancies between the theories probably indicate

TABLE I COEFFICIENT OF THERMAL EXPANSION OF LIQUIDS

Liquid	Formula	T_b , °K	T , °K	$\alpha \times 10^3$, °K ⁻¹	T/T_b	αT_b
Acetone	(CH ₃) ₂ CO	329.7	293.2	1.071	0.890	0.353
Aniline	C ₆ H ₅ NH ₂	457.6	293.2	0.855	0.641	0.382
Arsenic trichloride	AsCl ₃	403.4	293.2	1.029	0.728	0.415
Benzene	C ₆ H ₆	353.2	293.2	1.237	0.830	0.437
Bromine	Br ₂	332.0	293.2	1.132	0.883	0.376
Carbon disulfide	CS ₂	319.5	293.2	1.218	0.918	0.390
Carbon tetrachloride	CCl ₄	350.0	293.2	1.236	0.838	0.433
Chloroform	CHCl ₃	334.5	293.2	1.273	0.877	0.426
Ethyl ether	(C ₂ H ₅) ₂ O	307.8	293.2	1.656	0.953	0.510
Ethyl iodide	C ₂ H ₅ I	345.4	293.2	1.179	0.848	0.407
Trimethyl ethane	C ₃ H ₁₂	301.2	293.2	1.598	0.973	0.481
Phosphorus tribromide	PBr ₃	446.1	293.2	0.868	0.657	0.387
Phosphorus trichloride	PCl ₃	348.7	293.2	1.154	0.841	0.402
				1.211		0.422
Phosphorus oxychloride	POCl ₃	378.5	293.2	1.116	0.775	0.423
Pentane	C ₅ H ₁₂	309.4	293.2	1.608	0.948	0.498
<i>i</i> -Propyl chloride	C ₃ H ₇ Cl	308.6	293.2	1.591	0.950	0.491
Isoprene	C ₅ H ₈	307.2	293.2	1.567	0.955	0.481
Silicon bromide	SiBr ₄	426.2	293.2	0.983	0.688	0.419
Silicon chloride	SiCl ₄	330.8	293.2	1.430	0.886	0.473
Stannic chloride	SnCl ₄	387.3	293.2	1.178	0.757	0.456
Titanium tetrachloride	TiCl ₄	409.6	293.2	0.998	0.715	0.409
<i>o</i> -Toluidine	C ₇ H ₇ NH ₂	473.0	293.2	0.847	0.620	0.401

that neither theory is really accurate enough for calculations of α and β . But both theories give αT_b and $\beta RT_b/V_l$ as functions of the temperature ratio T/T_b . Therefore it seems justified to consider such functions as unknown theoretically, but to be determined by experimental data. Once determined, these functions are then universal and applicable to all normal liquids.

Table 1 lists the values of the coefficient of thermal expansion at 20°C taken from the Landolt-Börnstein Tabellen for various normal liquids at atmospheric pressure. The non-dimensional quantity αT_b is then plotted against T/T_b in Fig. 1, where the relations specified by Equations [26] and [29] are also plotted. Although the theories do predict the increasing thermal expansion with temperature, a behavior contrary to that of the gaseous state, the experimental data lie between the theoretical curves and are grouped definitely around a different curve. This empirical curve is drawn as a heavy line in Fig. 1. Therefore the surmise that αT_b is a function of T/T_b is now justified. By using this empirical curve, the thermal expansion of normal liquids can be calculated to 10 per cent accuracy once the boiling point T_b is known.

Table 2 lists the values of the compressibility of normal liquids at approximately atmospheric pressure taken again from the Landolt-Börnstein Tabellen. The nondimensional quantity $\beta RT_b/V_l$ is then plotted against the temperature ratio T/T_b in Fig. 2. The theoretical curves specified by Equations [28] and [30] are also plotted. It is seen that a

similar situation as for α exists. In fact, the empirical curve can be very closely represented by

$$\beta \frac{RT_b}{V_l} = \frac{1}{101.6 - 82.4 \left(\frac{T}{T_b} \right)} \dots \dots \dots [31]$$

Therefore the compressibility of any normal liquid can be calculated with 10 per cent accuracy if the boiling point T_b , the liquid density, and the molecular weight are known.

Specific Heat at Constant Pressure

For many engineering calculations, what is desired is not the specific heat at constant volume C_v^l but rather the specific heat at constant pressure C_p^l . According to the general thermodynamic laws, the difference between C_p^l and C_v^l is given by

$$C_p^l - C_v^l = \frac{\alpha^2}{\beta} V_l T \dots \dots \dots [32]$$

where α and β are the thermal expansion and compressibility, respectively. By combining Equations [23] and [32], the molar specific heat at constant pressure for the liquid state is related to the molar specific heat at constant pressure for the gaseous state as follows

$$C_p^l - C_p^g = R \left\{ 0.5 - 0.4 \frac{T}{T_b} + \frac{(\alpha T_b)^2}{\beta \frac{RT_b}{V_l}} \frac{T}{T_b} \right\} \dots \dots [33]$$

The relation given by Equation [33] can be compared with

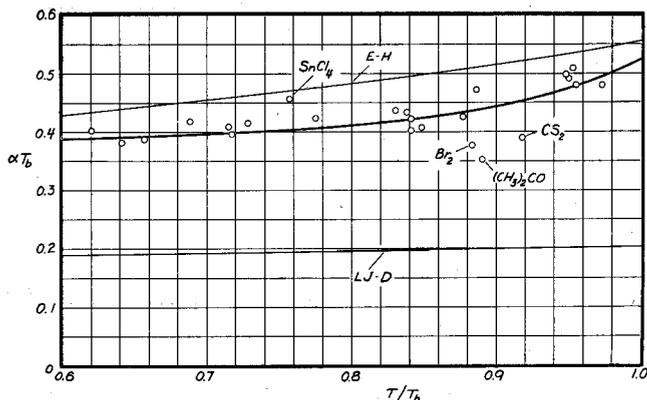


FIG. 1. α , COEFFICIENT OF THERMAL EXPANSION; T , TEMPERATURE; T_b , NORMAL BOILING TEMPERATURE. *E-H*, RELATION GIVEN BY EYRING AND HIRSCHFELDER (REF. 4), EQUATION [29]. *LJ-D*, RELATION DEDUCED FROM LENNARD-JONES AND DEVONSHIRE THEORY OF LIQUIDS, EQUATION [26]

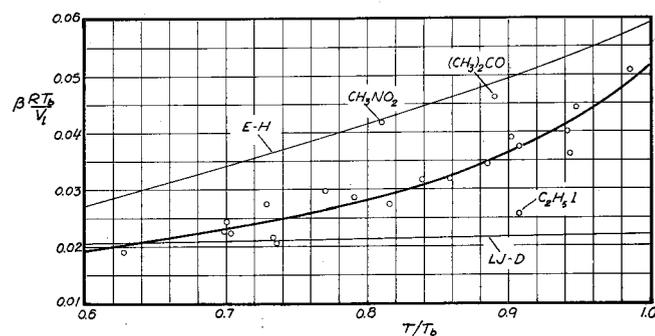


FIG. 2. β , COMPRESSIBILITY; T , TEMPERATURE; T_b , NORMAL BOILING TEMPERATURE; V_l , MOLAR VOLUME OF LIQUID; R , UNIVERSAL GAS CONSTANT. *E-H*, RELATION GIVEN BY EYRING AND HIRSCHFELDER (REF. 4), EQUATION [30]. *LJ-D*, RELATION DEDUCED FROM LENNARD-JONES AND DEVONSHIRE THEORY OF LIQUIDS, EQUATION [28]

TABLE 2 COMPRESSIBILITY OF LIQUIDS

Liquid	Formula	Molecular weight	T_b , °K	T , °K	Density, gr/cc	$\beta \times 10^6$, atm ⁻¹	T/T_b	$\frac{\beta RT_b}{V_l}$
Acetone	(CH ₃) ₂ CO	58.08	329.7	293.2	0.792	125.6	0.890	0.0464
Benzene	C ₆ H ₆	78.11	353.3	303.2	0.868	98.5	0.858	0.0318
				333.2	0.836	116.4	0.944	0.0362
Carbon disulfide	CS ₂	76.13	319.7	303.2	1.261	102.0	0.948	0.0444
Carbon tetrachloride	CCl ₄	153.84	350.0	293.2	1.595	105.8	0.838	0.0316
Chlorobenzene	C ₆ H ₅ Cl	112.56	405.2	283.2	1.107	72	0.698	0.0226
Chloroform	CHCl ₃	119.39	334.5	303.2	1.49	109.5	0.907	0.0375
Ethyl ether	(C ₂ H ₅) ₂ O	74.12	307.8	303.2	0.713	210	0.986	0.0510
Ethyl bromide	C ₂ H ₅ Br	108.98	311.2	293.2	1.430	120	0.942	0.0402
Ethyl iodide	C ₂ H ₅ I	155.98	345.4	313.2	1.91	74	0.907	0.0257
<i>n</i> -Heptane	C ₇ H ₁₆	100.20	371.7	303.2	0.684	134	0.815	0.0274
<i>n</i> -Hexane	C ₆ H ₁₄	86.17	342.2	303.2	0.66	159	0.885	0.0343
Nitrobenzene	C ₆ H ₅ NO ₂	123.11	484.1	303.2	1.1987	49	0.627	0.0190
Nitromethane	CH ₃ NO ₂	61.04	374.2	303.2	1.13	73.6	0.810	0.0419
<i>n</i> -Octane	C ₈ H ₁₈	114.23	399.0	293.2	0.704	101.6	0.735	0.0205
Paraldehyde	C ₆ H ₁₂ O ₃	132.16	397.6	291.2	0.994	88.2	0.733	0.0216
Silicon bromide	SiBr ₄	347.72	426.2	298.2	2.814	86.6	0.700	0.0245
Silicon chloride	SiCl ₄	169.89	330.8	298.2	1.483	165.2	0.902	0.0391
Titanium tetrachloride	TiCl ₄	189.73	409.6	298.2	1.726	89.8	0.728	0.0275
Stannic chloride	SnCl ₄	260.53	387.3	298.2	2.232	108.9	0.770	0.0296
Toluene	C ₆ H ₅ CH ₃	92.13	384.0	303.2	0.862	96.5	0.790	0.0285
<i>o</i> -Xylene	C ₆ H ₄ (CH ₃) ₂	106.16	417.2	293.2	0.875	79.7	0.703	0.0224

the equation given by S. W. Benson (5) for the difference of molar specific heats at constant pressure for the saturated liquid and saturated vapor. Benson's relation is

$$C_p^l - C_p^g = n\Delta E_{\text{vap}} \alpha + R$$

where n is approximately 5/3 for a large number of substances, ΔE_{vap} is the molar energy of evaporation, and α the thermal expansion coefficient defined by Equation [25]. However, this relation, which requires a knowledge of n and ΔE_{vap} , seems to be less convenient to use than Equation [33] together with the semi-empirical information on the thermal expansion α and the compressibility β .

With the empirically determined relations for the coefficient of thermal expansion α and the compressibility β , the right side of Equation [33] can be calculated as a function of the temperature ratio T/T_b . This is carried out in Table 3. It

TABLE 3 DIFFERENCE OF SPECIFIC HEATS OF LIQUID AND GAS

T/T_b	αT_b	$\beta \frac{RT_b}{V_l}$	$\frac{(\alpha T_b)^2}{\left(\beta \frac{RT_b}{V_l}\right)} \frac{T}{T_b}$	$0.5-0.4 \frac{T}{T_b}$	$\frac{C_p^l - C_p^g}{R}$
0.6	0.392	0.0192	4.80	0.26	5.06
0.7	0.398	0.0232	4.78	0.22	5.00
0.8	0.410	0.0280	4.80	0.18	4.98
0.9	0.445	0.0365	4.88	0.14	5.02
1.0	0.525	0.0520	5.30	0.10	5.40

is seen that except possibly near the boiling point, the difference between the molar specific heats of liquid and gas at constant pressure is very nearly $5R$, or

$$C_p^l - C_p^g = 10 \text{ cal/}^\circ\text{C mole} \dots \dots \dots [34]$$

This is indeed a remarkably simple result.

The comparison of the calculated specific heat of liquid using Equation [34] with the experimental data is exhibited in Table 4. Since the theory is developed for normal liquids, molecules containing hydroxyl group or amino group, and molecules that are excessively elongated should be excluded. The experimental data are taken also from the Landolt-Börnstein Tabellen. For diatomic molecules, the theoretical value of C_p^g without vibrational heat is used. This value of 7 cal/°C is correct for the prevailing low temperature. For silver chloride, this value of C_p^g may be too low. The first half of the table shows excellent agreement between the calculated and the experimental molar specific heat of liquid at constant pressure, with differences well within the experimen-

tal error. The only exception is carbon disulfide. This success of the theory is notable for the very wide range of temperature covered, from 120° K for nitric oxide to 763° K for silver chloride.

The second half of Table 4 indicates, however, considerable discrepancy between the calculated specific heat and the experimental specific heat. The calculated values are too large by approximately 4 cal/°C. A similar discrepancy for Trouton's ratio, the ratio of heat of evaporation and the boiling temperature T_b , also occurs for this group of liquids (6). Such differences are well outside the probable experimental error. Furthermore, the temperatures concerned, although low, are not low enough for the occurrence of quantal effects (see appendix). Nor is there any likelihood of a different molecular interaction than the first group of liquids in the table. This is shown by their similar transport properties in the gaseous state. The only possible explanation seems to be the association effects. For instance, oxygen tends to associate to O_4 molecule in liquid state. If so, the molar specific heat of the liquid will be twice as large as listed in the table, or 25 cal/°C. The fictitious O_4 molecule in gaseous state then should have a C_p^g of 15 cal/°C. This is an entirely reasonable value.

From the foregoing discussion, it seems justified to use Equation [34] for normal liquids at room temperature or higher when association and dissociation are absent. For normal liquids, the accuracy of present method is very much higher than the method, suggested by R. R. Wenner (7), based upon counting individual atoms in the liquid molecule. Of course it may be argued that when it is necessary to predict the specific heat of liquid, the specific heat for the gaseous state is generally also not available, and then Equation [34] is of no practical utility. Fortunately, however, it is not necessary to depend on direct experimental determination of the specific heat of gaseous state. C_p^g can be very accurately calculated from the fundamental frequencies of the molecule determined by spectroscopy. Or C_p^g can be calculated with sufficient accuracy from the averaged frequencies for each type of chemical bonds, a method recently rendered more complete by R. V. Meghreblian (8). As an example of such a situation, one may consider the molecule CHCl_2Br , bromodichloromethane. This molecule is not even listed in the well-known Handbook of Chemistry and Physics. But Meghreblian has calculated its molar specific heat C_p^g at 27°C to be 16.2 cal/°C. Then according to Equation [34], the molar specific heat of the liquid C_p^l at the same temperature is 26.2 cal/°C. Since the molecular weight of this compound is 163.85, the specific

TABLE 4 SPECIFIC HEAT OF LIQUIDS AT CONSTANT PRESSURE

Liquid	Formula	Molecular weight	T_b , °K	T , °K	C_p^g , cal/°C, exp	C_p^l , cal/°C, calc'd	C_p^l , cal/°C, exp
Ammonia	NH_3	17.032	239.8	213.2	8.0	18.0	17.9
.....	273.2	8.7	18.7	18.7
Acetone	$(\text{CH}_3)_2\text{CO}$	58.08	329.7	313.2	20.1	30.1	30.8
Benzene	C_6H_6	78.11	353.3	293.2	21.8	31.8	32.5
.....	323.2	23.3	33.3	34.3
Bromine	Br_2	159.83	332.0	270.0	7.0 ^a	17.0	17.1
Carbon disulfide	CS_2	76.13	319.7	290.7	12.0	22.0	18.4
Carbon tetrachloride	CCl_4	153.84	350.0	273.2	21.5	31.5	30.9
.....	293.2	20.7	30.7	31.8
Chloroform	CHCl_3	119.39	334.5	313.2	17.2	27.2	27.9
Ethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$	74.12	307.8	303.2	31	41	40.5
Nitric oxide	NO	30.01	121.4	120	7.0 ^a	17.0	17.3
Silver chloride	AgCl	143.34	1823	763	<7.0, >9.0	<17.0, >19.0	18.5
Stannic chloride	SnCl_4	260.53	387.3	287-371	24.4	34.4	38.5
Sulphur dioxide	SO_2	64.06	263.2	273.2	9.9	19.9	20.4
Argon	A	39.944	87.4	85.0	5.0	15.0	10.5
Carbon monoxide	CO	28.01	81.1	69.4	7.0 ^a	17.0	14.27
Methane	CH_4	16.04	111.7	100	8.0	18.0	13.01
Nitrogen	N_2	28.016	77.3	64.7	7.0 ^a	17.0	13.15
.....	72.8	7.0 ^a	17.0	13.33
Oxygen	O_2	32.00	90.1	73.2	7.0 ^a	17.0	12.60

^a Theoretical value for diatomic molecules without vibrational heat.

heat at constant pressure of the liquid is 0.1598 cal/gr °C, or 0.1598 Btu/lb °F.

Liquid Metals

Pure metal atoms do not associate into molecules. Therefore the specific heat of pure liquid metals should be correlated on the basis of one gram atomic weight. When this is done, pure liquid metals give a specific heat at constant pressure from 6.4 cal/°C to 8 cal/°C. Therefore it is reasonable to take as a first approximation

$$C_p^l = 7 \text{ cal/}^\circ\text{C} \dots\dots\dots [35]$$

per gram atomic weight. Since the specific heat at constant volume should be close to $3R$ or 6 cal/°C, Equation [35] shows that the difference between C_p and C_v for liquid metals is only 1 cal/°C. This is very much less than the corresponding value found for normal liquids as discussed in the previous section. For the particular case of liquid mercury, a more detailed discussion has been given by J. F. Kincaid and H. Eyring (9). They have also pointed out that the difference in behavior of the liquid metals from that of normal liquids is due to the difference in the interaction potential of the constituent particles. Since the interaction in normal liquids is the interaction between molecules, the interaction in liquid metals is the interaction between the metallic atoms. This difference is certainly expected.

Velocity of Sound

The velocity of propagation of small disturbances is generally called the velocity of sound c and is a very important quantity in fluid dynamics. The general formula for computing this quantity is

$$c^2 = -\frac{v^2 dP}{dv} = -\frac{1}{\rho} \left(\frac{V dP}{dV} \right) \dots\dots\dots [36]$$

where v is the volume for unit mass of the liquid, ρ is the density or $1/v$, and the derivative is to be computed according to the adiabatic process.

If the frequency of the sound wave is sufficiently low, or if the characteristic time of the small disturbance is longer than the relaxation time for reaching thermodynamic equilibrium, then it can be easily shown that

$$c^2 = \frac{1}{\rho\beta} \frac{C_p^l}{C_v^l} \dots\dots\dots [37]$$

where β is the compressibility defined by Equation [27]. For normal liquids, β is given by Equation [31], and according to Table 3, the difference between C_p and C_v is approximately 9.6 cal/°C. Let M be the molecular weight. Then

$$c^2 = \frac{RT_b}{M} \left(101.6 - 82.4 \frac{T}{T_b} \right) \frac{C_p^l}{C_p^l - 9.6} \dots\dots\dots [38]$$

The comparison between the calculated and the experimental values of the velocity of sound is shown in Table 5. It is seen that with the exception of carbon disulfide, Equation [38] predicts the velocity of sound to within one per cent of the experimental value. This accuracy is perhaps expected, since Equation [38] already contains the empirically deduced relations for $C_p - C_v$ and β . Nevertheless, the agreement is satisfying in that it indicates the inner consistency of the theory. The case of CS₂ may be partially explained by the ex-

ceptionally low experimental value of C_p . Table 4 shows that the theoretical value for C_p^l of carbon disulfide is considerably higher. If so, the calculated velocity of sound for CS₂ will be lowered and the agreement with the experimental data will be better. Therefore it is justified to say that Equation [38] gives a satisfactory prediction of the velocity of sound for pure normal liquids. Since C_p^l increases with temperature, Equation [38] shows that the velocity of sound decreases with temperature. This behavior of normal liquid is contrary to that of gaseous state, for which the velocity of sound increases with temperature.

Transport Properties

The properties of liquids discussed in the preceding sections are all properties at thermodynamic equilibrium. Transport properties are properties of matter not at equilibrium, and the theory of transport properties is very much more complex than the theory of equilibrium properties. A "basic" approach to the theory of transport properties of liquids was made by J. G. Kirkwood and by M. Born and H. S. Green. However, no useful result has yet been obtained by their theories. Here the method of simple model followed by fitting the theoretical relation to empirical data will be used. An example of this method applied to the transport properties of liquids is Eyring's theory of viscosity of liquids (10).

According to Eyring's theory, the viscosity μ of a liquid at temperature T is related to the energy of vaporization ΔE_{vap} per mole of the liquid as follows.

$$\mu = \frac{hN}{V_l} \exp(\Delta E_{vap}/2.45RT) \dots\dots\dots [39]$$

where h is Planck's constant, N Avogadro's number, and V_l the molar volume of the liquid. For normal liquids, energy of vaporization is related to the normal boiling temperature T_b by Trouton's rule. That is

$$\Delta E_{vap} \cong 9.4RT_b \dots\dots\dots [40]$$

By combining Equations [39] and [40], the viscosity in centipoises is given by

$$\mu \cong \frac{0.3990}{V_l} \exp(3.83T_b/T) \dots\dots\dots [41]$$

where V_l is in cc per mole.

Thermal Conductivity

The elementary theory of heat conduction in gas gives (11) the thermal conductivity λ of a gas as

$$\lambda = \frac{1}{3} c c_v \dots\dots\dots [42]$$

where c is the velocity of sound, c_v the specific heat of the gas at constant volume per unit volume, and l is the mean free path of the molecules in the gas. In other words, l is the mean distance for which the molecules will maintain their individual velocities. I. Estermann and J. E. Zimmerman (12) noted that if l is interpreted as the distance, a lattice wave in a solid will travel before scattering, then the thermal conductivity of solid due to lattice oscillations calculated by R. E. B. Makinson (13) can be easily obtained from the relation of Equation [42]. This observation clearly shows the fundamental character of Equation [42]. It should then be true

TABLE 5 VELOCITY OF SOUND

Liquid	Formula	Molecular weight	T_b , °K	T , °K	C_p^l , cal/°C	$c_{calc} \times 10^{-5}$, cm/sec	$c_{exp}^a \times 10^{-5}$, cm/sec
Benzene	C ₆ H ₆	78.11	353.3	290.2	39.8	1.176	1.166
Carbon disulfide	CS ₂	76.13	319.7	288.2	18.2	1.350	1.161
Chloroform	CHCl ₃	119.39	334.5	288.2	27.9	0.967	0.983
Ethyl ether	(C ₂ H ₅) ₂ O	74.12	307.8	288.2	39.8	1.022	1.032

^a Taken from Smithsonian tables.

for all three states of matter, if the different quantities entering into it are properly identified. P. W. Bridgman (4), in fact, suggested such a correlation as early as 1931. However, the following theory differs from that of Bridgman in important details, as will be explained presently.

For liquids other than liquid metals, the heat must be conducted as oscillations of the molecules from its mean position, similar to the heat conduction in solid by "lattice waves." Therefore if Equation [42] will be used to calculate the thermal conductivity of a liquid, the c is the velocity of sound in the liquid. This is exactly what Bridgman proposed. It will not be correct, however, to compute c by Equation [37], because the frequencies of the lattice waves are generally so high as to not allow the thermodynamic equilibrium assumed for Equation [37]. Therefore there are some questions in determining c . For lack of better information, let c be tentatively taken simply as

$$c \sim 1/\sqrt{\rho\beta} \dots\dots\dots [43]$$

Thus the uncertain ratio of specific heats in Equation [37] is dropped.

The appropriate mean free path l for the lattice waves in liquid must be the size of the local organization of the liquid molecules. This size of local organization is a few times the molecular spacing a . Therefore according to Equation [4]

$$l \sim V^{1/3} \dots\dots\dots [44]$$

where V is the liquid volume per molecule. l is thus of the order of a few ångströms.

Bridgman proposed to identify c_v as the total heat capacity including the internal degrees of freedom. However, with l only of the order of 10^{-7} cm, and with c as large as 10^5 cm per sec, the characteristic time for the lattice waves must be of the order of 10^{-12} sec. This is much shorter than the known relaxation time for the internal degrees of freedom of molecules. Then it is reasonable to suppose that the internal degrees of freedom of the molecule do not participate in the conduction

of heat. Therefore for computing the thermal conductivity of liquids, the specific heat should be that of external degrees of freedom of the molecules only. The specific heat per mole is then approximately $3R$. Or

$$c_v \sim \frac{3R}{V_l} \dots\dots\dots [45]$$

By combining Equations [43], [44], and [45], the thermal conduction of liquid can be written as

$$\lambda \sim \frac{1}{\sqrt{\rho\beta}} V^{1/3} \frac{3R}{V_l}$$

The factor of proportionality of the above relation remains undetermined. To determine it, one has to introduce the experimental data. This is done in Table 6 and Fig. 3. The compressibility data were taken from the Landolt-Börnstein Tabellen and the thermal conductivity from the Appendix of McAdam's book on heat transfer (15). These data include such "abnormal" liquids as water and alcohols. It thus seems that the great majority of experimental thermal conductivity falls within 20 per cent of the calculated value if one simply takes

$$\lambda = \frac{1}{\sqrt{\rho\beta}} V^{1/3} \frac{3R}{V_l} = \frac{1}{\sqrt{\rho\beta}} \left(\frac{M}{N\rho}\right)^{1/3} \frac{3R\rho}{M} \dots\dots\dots [46]$$

Therefore the factor of proportionality is just unity. By comparing Equations [42] and [44], it is seen that mean free path l of the lattice waves is approximately 3 times the intermolecular distance. The local structure of the liquid may be pictured as a cubic lattice having nearly 12 neighbors to the central molecule. This deduction is entirely in agreement with the adopted concept of the liquid state. Equation [46] shows that the thermal conductivity of all liquids, normal or otherwise, can be calculated satisfactorily if the molecular weight, the density, and the compressibility of the liquid are known.

TABLE 6 THERMAL CONDUCTIVITY

Liquid	Formula	Molecular weight	Temperature, °C	Density, gr/cc	$\beta \times 10^{-5}$, atm ⁻¹	$(\rho\beta)^{-1/2} \times 10^{-5}$, cm/sec	$V^{1/3} \times 10^8$, cm	$\frac{V^{1/3}}{\sqrt{\rho\beta}} \frac{3R}{V_l}$	$\frac{\lambda_{exp}}{cal/cm \cdot ^\circ C \cdot sec}$	$\frac{\lambda_{exp}}{V^{1/3} \frac{3R}{V_l}}$
Acetic acid	CH ₃ COOH	60.05	20	1.049	90.6	1.033	4.56	0.000491	0.000409	0.833
Acetone	(CH ₃) ₂ CO	58.08	20	0.792	125.6	1.010	4.96	0.000407	0.000430	1.056
Allyl alcohol	C ₂ H ₃ CH ₂ OH	58.08	20-30	0.855	75	1.257	4.83	0.000533	0.000430	0.807
Amyl alcohol	C ₅ H ₁₁ OH	88.15	17.7	0.814	90.5	1.172	5.65	0.000365	0.000392	1.075
Aniline	C ₆ H ₅ NH ₂	93.12	20	1.022	36.1	1.657	5.32	0.000577	0.000413	0.715
Benzene	C ₆ H ₆	78.11	30	0.868	98.5	1.089	5.30	0.000382	0.000380	0.995
	60	0.836	116.4	1.020	5.37	0.000350	0.000359	1.026
Carbon dioxide	CO ₂	44.01	13.3 ^a	0.960	624.4	0.412	4.23	0.000246	0.000245	0.995
Carbon disulfide	CS ₂	76.13	30	1.261	102.0	0.888	4.64	0.000407	0.000384	0.945
Carbon tetra-chloride	CCl ₄	153.84	20	1.595	105.8	0.775	5.43	0.000260	0.000392	1.510
Chlorobenzene	C ₆ H ₅ Cl	112.56	10	1.107	72	1.128	5.53	0.000336	0.000343	1.020
Chloroform	CHCl ₃	119.39	30	1.49	109.5	0.788	5.11	0.000299	0.000330	1.104
Ethyl alcohol	C ₂ H ₅ OH	46.07	20	0.789	112	1.071	4.59	0.000502	0.000434	0.865
Ethyl bromide	C ₂ H ₅ Br	108.98	20	1.430	120	0.769	5.01	0.000301	0.000289	0.962
Ethyl ether	(C ₂ H ₅) ₂ O	74.12	30	0.713	210	0.808	5.56	0.000258	0.000330	1.280
Ethyl iodide	C ₂ H ₅ I	155.98	40	1.91	74	0.847	5.15	0.000318	0.000264	0.830
Ethylene glycol	(CH ₂ OH) ₂	62.07	0	1.12	34	1.63	4.51	0.000790	0.000632	0.800
Glycerine	(CH ₂ OH) ₂ -CHOH	92.09	20	1.260	22	1.912	4.94	0.000773	0.000678	0.877
n-Heptane	C ₇ H ₁₆	100.20	30	0.684	134	1.051	6.25	0.000268	0.000334	1.246
n-Hexane	C ₆ H ₁₄	86.17	30	0.66	159	0.983	6.01	0.000270	0.000330	1.220
Hexyl alcohol	C ₆ H ₁₃ OH	102.17	30	0.818	60	1.437	5.91	0.000405	0.000384	0.948
Methyl alcohol	CH ₃ OH	32.04	20	0.7928	123.5	1.016	4.07	0.000609	0.000512	0.841
Nitrobenzene	C ₆ H ₅ NO ₂	123.11	30	1.199	49	1.313	5.54	0.000422	0.000393	0.930
Nitromethane	CH ₃ NO ₂	61.04	30	1.13	73.6	1.104	4.47	0.000544	0.000517	0.950
n-Octane	C ₈ H ₁₈	114.23	20	0.704	101.6	1.190	6.45	0.000282	0.000347	1.230
Paraldehyde	C ₃ H ₂ O ₃	132.16	18	0.994	88.2	1.075	6.04	0.000291	0.000355	1.220
Toluene	C ₆ H ₅ CH ₃	92.13	30	0.862	96.5	1.103	5.62	0.000347	0.000355	1.023
Water	H ₂ O	18.02	30	0.996	47.9	1.457	3.104	0.001490	0.001470	0.987
o-Xylene	C ₆ H ₄ (CH ₃) ₂	106.16	20	0.875	79.7	1.207	5.87	0.000347	0.000372	1.070

^a At 87 atm.

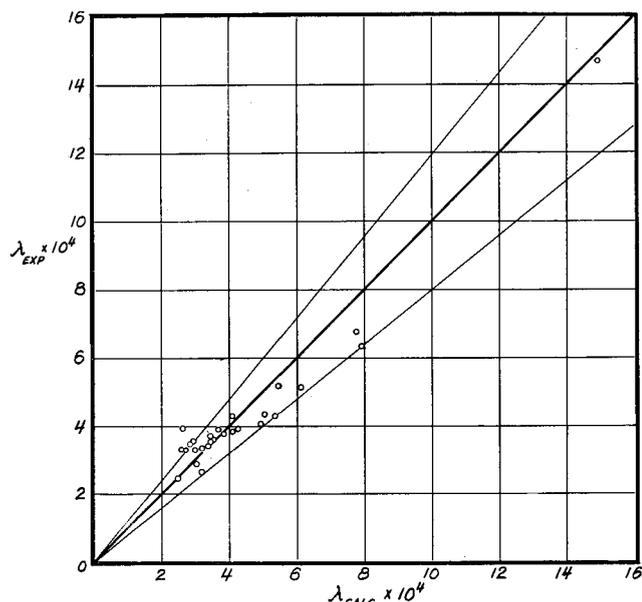


FIG. 3 COMPARISON OF CALCULATED, $\lambda_{\text{calc.}}$, AND EXPERIMENTAL, $\lambda_{\text{exp.}}$, VALUES OF THE THERMAL CONDUCTIVITY OF LIQUIDS. THE UNIT OF λ IS CAL/CM SEC $^{\circ}\text{C}$.

As a further check on Equation [46], the variation of the thermal conductivity of water with temperature is computed and compared with the experiments. Since the ratio of specific heats for liquid water is very nearly equal to one, the velocity $1/\sqrt{\rho\beta}$ for water is in fact the velocity of sound c . Thus for water, the ratio of thermal conductivity at two temperatures designated by subscripts 1 and 2, is given by

$$\frac{\lambda_2}{\lambda_1} = \frac{c_2}{c_1} \left(\frac{\rho_2}{\rho_1} \right)^{2/3}$$

This relation is compared with experimental data on λ in Table 7 where 13°C is taken as the lower comparison temperature. The ratios of conductivity at two higher temperatures of 19 and 31°C check closely with the test values. Therefore Equation [46] can also predict satisfactorily correct temperature variation of the thermal conductivity.

TABLE 7 THERMAL CONDUCTIVITY OF WATER

Temperature, $^{\circ}\text{C}$	$c \times 10^{-1}$ cm/sec ^a	ρ gr/cc	λ_{exp} , cal/sec $^{\circ}\text{C}$ cm	$\left(\frac{\lambda_2}{\lambda_1}\right)_{\text{calc}}$	$\left(\frac{\lambda_2}{\lambda_1}\right)_{\text{exp}}$
13	1.441	0.9994	0.001410	1.000	1.000
19	1.461	0.9984	0.001431	1.012	1.015
31	1.505	0.9954	0.001475	1.040	1.046

^a Taken from Smithsonian tables.

For normal liquids, the compressibility β is given by Equation [31]; then Equation [46] reduces to

$$\lambda = \frac{3R}{N^{1/3}} \left\{ \frac{RT_b}{M} \left(101.6 - 82.4 \frac{T}{T_b} \right) \right\}^{1/2} \left(\frac{\rho}{M} \right)^{2/3} \dots [47]$$

Therefore the thermal conductivity of normal liquid can be calculated once the molecular weight M , the boiling temperature T_b , and the density are known. Since density decreases with temperature, Equation [47] shows that the conductivity of normal liquids also decreases with temperature. The increasing conductivity of water with temperature shown in Table 7 indeed indicates the anomaly of water as a liquid.

Concluding Remarks

The properties of pure liquids studied in the preceding sections are properties at low pressures, i.e., at pressures below the critical pressure of the substance. Then the pressure of the liquid is not a parameter in the calculations. In fact, for normal liquids, the only essential parameter is the normal

boiling temperature of the liquid. This parameter, together with the density and the molecular weight of the liquid, then determines the coefficient of thermal expansion, the compressibility, the specific heats, the velocity of sound, the viscosity, and the thermal conductivity. The required information for calculating the properties is thus generally available in the handbook.

From the point of view of physical mechanics of predicting macroscopic behavior of matter in bulk from microscopic behavior of the molecules, the remaining task is then the determination of the liquid density and the normal boiling temperature from the knowledge of the molecular structure. Since both of these quantities are related to the bimolecular interaction, the missing link is then a method of calculating the molecular interaction from the structural formula of the liquid molecules. The well-known theory of molecular interaction due to F. London and W. Heitler and others has unfortunately not yet been developed into a form useful for this purpose. Here clearly is a field for future research.

APPENDIX

Quantal Effects at Low Temperatures

S. D. Hamann (16) has investigated the quantal correction to the Lennard-Jones and Devonshire theory of liquids by approximating the spherical cage of the theory by a cube with a square-well potential. The size of the cube is determined by the diameter of the sphere within which the Lennard-Jones-Devonshire potential is negative. Let the ratio of this size to the molecular distance a be x . When $V \cong V^*$, as is the case for liquid at low pressures, $x \cong 0.2$. Hamann showed that the temperature T for appreciable quantal effects is given by the equation

$$\frac{2\pi mkT}{h^2} \left(\frac{4\pi}{3} \sqrt{2} V \right)^{2/3} x^2 \cong 1$$

where m is the mass of a molecule, k the Boltzmann constant, h the Planck constant, and V the volume of liquid per molecule. For N_2 molecule, if the density of the liquid is taken to be 0.8, this temperature for appreciable quantal effects is only 5.5°K . Therefore it is certain that none of the anomalies in Table 5 can be due to quantum mechanical reasons.

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10 See, for instance, "The Transport Properties at High Densities," chapter in the book "The Properties of Gases," by J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, and E. L. Spatz, issued as report of the Naval Research Laboratory, Department of Chemistry, University of Wisconsin, 1951.

11 See, for instance, "Kinetic Theory of Gases," by L. Loeb, McGraw-Hill Book Co., Inc., New York, 1927, p. 240.

12 "Heat Conduction in Alloys at Low Temperatures," by I. Estermann and J. E. Zimmerman, *Journal of Applied Physics*, vol. 23, 1952, pp. 578-588.

13 "The Thermal Conductivity of Metals," by R. E. B. Makinson, *Proceedings of the Cambridge Philosophical Society*, vol. 34, 1938, pp. 474-477.

14 "Physics of High Pressures," by P. W. Bridgman, G. Bell and Sons, London, 1931. See also "On Heat Conductivity in Liquids," by A. W. Lawson, *Journal of Chemical Physics*, vol. 18, 1950, p. 1421.

15 "Heat Transmission," by W. H. McAdams, McGraw-Hill Book Co., Inc., New York, 2nd Ed., 1942, p. 389.

16 "A Quantum Correction to the Lennard-Jones and Devonshire Equation of States," by S. D. Hamann, *Transactions Faraday Society*, vol. 48 (2), 1952, pp. 303-307.