

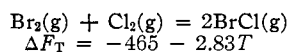
ΔS , and ΔH for the reaction under consideration. The necessary data for bromine were taken from the paper by Gordon and Barnes¹⁹ and for chlorine from Giauque and Overstreet.²⁰

TABLE IV
THERMODYNAMIC CONSTANTS FROM SPECTROSCOPIC AND
EQUILIBRIUM DATA

	Br ₂ (g) + Cl ₂ (g) = 2BrCl(g)	
<i>T</i> , °K.	301	462
ΔS° (spect.) cal./deg.	2.82	2.84
ΔH_0° cal.	-350 ^a -470 ^b	-434 ^c
ΔH cal.	-366 ^a -486 ^b	-443 ^c

^a $K_{\text{BrCl}} = 0.126$. ^b $K_{\text{BrCl}} = 0.107$. ^c $K_{\text{BrCl}} = 0.148$.

It is evident that ΔH_0° is more nearly constant when Vesper and Rollefson's room temperature value of K_{BrCl} is assumed. Accordingly the free energy equation 11 is more acceptable than 10. Inasmuch as the ΔS calculated from spectroscopic data is probably more reliable than that derived from equilibrium data alone, the following free energy equation can be regarded as best representing the data



(19) Gordon and Barnes, *J. Chem. Phys.*, **1**, 692 (1933).

(20) Giauque and Overstreet, *This Journal*, **54**, 1731 (1932).

We are indebted to Dr. D. P. Stevenson for making some of the calculations in this section.

Summary

Careful measurements on the gas phase equilibrium between nitric oxide, bromine, chlorine, nitrosyl chloride and bromide, and bromine chloride have been made in the temperature range 372 to 492°K. From the results, after an approximate correction for gas imperfections, the values of $K = P_{\text{Br}_2} P_{\text{Cl}_2} / P_{\text{BrCl}}^2$ were calculated. The mean value of K at 462°K. is 0.148 ± 0.011 .

This value of K was combined with the values obtained at room temperature by other investigators to calculate the heat content change ΔH attending the formation of two moles of bromine chloride. Three possible values were obtained, zero, -270 and -560 cal., depending on the room temperature value of K_{BrCl} selected. Spectroscopic data were employed to show that the probable value of ΔH is -465 cal. The most acceptable free energy equation for the reaction $\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{BrCl}$, is $\Delta F_T = -465 - 2.83T$.

PASADENA, CALIF.

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A Theory of Liquid Structure¹

BY ERNEST P. IRANY

That gases consist of free atoms or molecules in random motion and with a minimum of mutual interference, is elementary knowledge; that the truly solid, *i. e.*, the crystalline, state is distinguished by the geometrically regular arrangement of atoms, ions and electrons, has been established by X-ray analysis. The liquid state is transitory between these two forms of material constitution, but beyond this our knowledge is very vague.

The classical concepts do not provide an explanation for the obvious difference in physical appearance and the definite discontinuity between liquids and gases; we mostly think of a liquid in terms indistinguishable from those applied to a compressed gas. In crystals the molecular motion, due to the almost fixed positions of the molecules, is mainly vibratory, while in gases, on the contrary, translatory motion pre-

dominates. This classical distinction does not provide an explanation of the mobility and cohesion characteristic of the liquid state.

More recently, quantum theoretical considerations have been made the base of an approach to the problem. Formal solutions of some interest have been developed by statistical treatment but it hardly can be claimed that these solutions convey full comprehension of the liquid state.²

The problem can be solved only by assuming—no matter on what grounds—a definite concept of structure or molecular distribution, and by formulating it mathematically as an equation of the liquid state; the validity of the latter may then be proved by its ability to interpret and to repre-

(2) The question must be posed whether contemporary theory on liquid constitution rests on premises from which no conceivable molecular configuration is *a priori* excluded. If the primary concepts do not allow for, *e. g.*, the structure proposed in the present thesis—at least with some formal probability—no conclusions derived from them can claim uniqueness.

(1) Original manuscript received July 12, 1938.

sent quantitatively the observable "macroscopic" properties of liquids.

Modern theory tends toward the very important conclusion that liquids possess structure characteristic of their state and distinct from that of gases,³ but we are still free to conceive of such structure in mental pictures of our own choice. In this sense, a model of liquid structure is developed and evaluated in what follows. Whether physically real or merely symbolic, this model is evidently in very good accord with facts known about liquids and correct with respect to all inferences about their constitution.

What, fundamentally, distinguishes liquids from gases is the capacity to form a surface—a two-dimensional configuration of molecules. The intermolecular forces responsible for this preferred orientation must exist also, with the same or similar effects, in the interior of liquids but, supposedly, they would maintain a somewhat different balance as in the surface film. Thus, the relation between the molecules in a liquid may be essentially that found in its surface formation, resulting in a typical cohesion which is neither that of gases nor that of solids.

Considering the great magnitude of these cohesive forces and the estimated proximity of the molecules in liquids, it is most remarkable that dissolved substances observe laws which, if not actually identical with the gas laws, suggest that the mobility of their molecules is such as if the liquid medium possessed the permeability of empty space. It is necessary, therefore, to assume some form of molecular distribution in liquids so that, at least locally, the molecules of the liquid leave voids through which the molecules of the solute may perform their gas-like motions.

If such a structure exists in liquids it remains to be explained why it should not collapse under the strong cohesive pressure. This may be understood readily if the voids are not considered empty but occupied by molecules in a truly gaseous condition whose gas pressure balances the cohesion.

The other molecules of the liquid outside the voids must be crowded together in a more dense configuration, and the clue about their arrangement is given by the surface of liquids. This is certainly a two-dimensional "lattice" of mole-

cules capable of withstanding considerable tension, but in which the relative fixation still allows free deformation into space; comparable, *e. g.*, to a sheet of woven textile fabric. It may be assumed that the whole interior of the liquid is constituted in the same or in analogous form—that the whole liquid body is built up of such freely flowing but tightly knitted "lattice sheets" which, between one another, leave part of the substance in truly gaseous form, the whole being enclosed within a continuous sheet of the same description—the surface of the liquid (see Fig. 1).

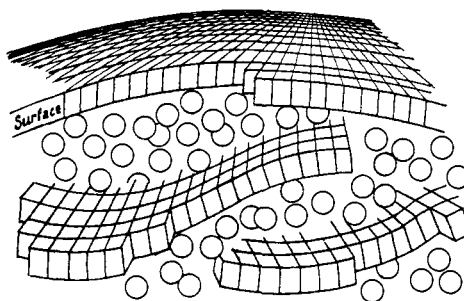


Fig. 1.

Supporting Evidence.—The tendency toward two-dimensional structure in liquids is well in accord with Langmuir's discoveries and theories on monomolecular layers. Evidence of orientation of polar molecules on planes of shearing motion, *i. e.*, two-dimensional configuration, appears in the viscosity-temperature relationships of homologous substances under high pressures.⁴ According to Brillouin⁵ light diffraction in solids results from interference between light and thermic waves which are orientated due to the coupled motions of the atoms. He thus explains certain doublet lines in the optical spectra of solids. Liquids show analogous doublets plus the original line. The present theory would ascribe the former to the lattice sheets and the latter to the gas phase.

Limits of the Liquid State.—If a crystal is heated to the melting point, one set of its spatially oriented force components, the weakest, will yield and release molecules in two-dimensional formations which then would reconstitute themselves as the "lattice sheets" of the liquid.⁶ At the melting point the inter-lattice voids are already in evidence: substances can be dissolved in the liquid and they reveal their gas-like mobility. Hence, the discontinuity of melting is not the theoretical origin of the liquid state but marks a condition under which the three-dimensional crystal lattice equals the liquid structure in sta-

(3) Andrade, *Phil. Mag.*, **17**, 497, 698 (1934); Kirkwood, *J. Chem. Phys.*, **3**, 300 (1935); Eyring, *ibid.*, **4**, 283 (1936); Eyring and Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937); Mayer and Harrison, *J. Chem. Phys.*, **6**, 101 (1938); Stewart, *Chem. Rev.*, **6**, 483 (1929); Barnes, *ibid.*, **23**, 29 (1938); Maass, *ibid.*, **23**, 27 (1938); Debye, *Z. Elektrochem.*, **45**, 174 (1939).

(4) Irany, *THIS JOURNAL*, **60**, 2106 (1938).

(5) Brillouin, *Ann. Phys.*, **17**, 88 (1922).

(6) In "crystalline liquids" this seems to occur in observable steps.

bility. The liquid state is conceivable below the melting point, possibly down to zero temperature, where the gas voids would necessarily disappear (for *evidence* from viscosity data, see ref. 4).

Under critical or higher pressure the liquid condition can be realized up to the critical temperature which is the definite limit of its existence. It must be assumed that over this range the two-dimensional molecule lattices or "sheets" gradually disintegrate into the growing voids, causing the liquid to expand. At any given temperature, the condition of the liquid is represented by a certain ratio between lattice and gas structure which becomes zero at the critical temperature.

Solubility, Vapor Pressure.—It is reasonable to assume that solutes at low concentrations remain entirely in the gas voids, *i. e.*, that their osmotic pressure represents their partial pressure in the internal gas phase. The growth of the latter with rising temperature also increases solubility. If a definite equilibrium exists between lattice and gas phase of the liquid, a solute entering the latter must force gas molecules into lattice formation or be expelled from the system; in other words, solutes must reduce the partial pressure of the solvent molecules in the gas voids. If, as most likely, there is a close relationship between the pressure within the voids and the external vapor pressure of the liquid, a solute at low concentration should reduce the vapor pressure of the solvent in proportion to the number of its molecules—which is a well-known fact.

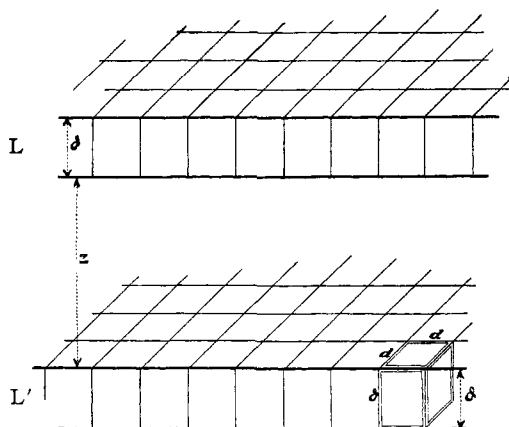


Fig. 2.

The Phase Rule.—It is important to ascertain how the proposed two-phase concept of liquid constitution agrees with the phase rule which must be considered fundamentally true. For a two-

phase system ($P = 2$), the term $F = N - P + 2$ becomes $F = N$, *i. e.*, the number F of variables required to specify the observable states must equal the number N of pure substances composing the system. For a liquid $F = 2$ because the choice of a given temperature does not at the same time fix the pressure which may be applied. Hence, N must be 2; the liquid must behave as if it were composed of two substances which cannot be converted into one another, at least in response to one of the variables of condition. As explained, the internal lattice and gas phase of the liquid are convertible into one another by changes of temperature. Supposing, however, that pressure be without effect upon their ratio; then they actually would behave as two individual substances in the sense of the phase rule and, with respect to pressure variation, $F = N = 2$. As shown later on, this assumption is confirmed fully by quantitative evidence.

Mathematical Solution

It is the purpose of this paper to present its conception of liquid structure in the most simple form—that of a static model, Fig. 2. The molecules in the lattice sheets L, L' are drawn as rectangular cells which are considered deformable, but incompressible. Two such lattice planes are separated by the distance z ; the space between them is a void occupied by detached gas molecules.

In the interior of the liquid no discontinuity of potential is likely to exist; hence, the lattices must be so constituted that they show the same polarity on both faces. This suggests that they contain two layers of molecules in reversed orientation, of the combined thickness δ . The free surface of the liquid is in equilibrium with the vapor space outside and the gas phase within the liquid; it must be a lattice structure of asymmetric polarity.

I. Mean Inter-lattice Distance z .—If N is the number of molecules per mole, and x the molar fraction engaged in the lattice structure while $1 - x$ mole remains in the gas voids, the fractions of the total liquid volume occupied by the

$$\text{lattices, } V_1 = Nx(d^2\delta) \quad (1)$$

$$\text{gas voids, } V_g = V - Nx(d^2\delta) = Nx d^2 z \quad (2)$$

The volume of the molecule, $(d^2\delta)$, is considered incompressible; the product $N(d^2\delta)$ represents the limiting volume of the liquid, b . Hence, from (2)

$$z = (V - bx)/Nd^2x \quad (3)$$

II. The Pressure Balance.—The gas phase in the voids is under a pressure P_0 , the "internal"

or "intrinsic" pressure of the liquid which has been estimated in various ways, *e. g.*, from van der Waals constant a , from the heat of vaporization, and graphically.⁴ P_0 , over the area of the surface sheet, is balanced by the surface tension, γ , over some equatorial length of the liquid body

$$P_0 V^{2/3} = K\gamma V^{1/3} \quad P_0 = \frac{K\gamma}{\sqrt[3]{V}} \quad (4)$$

where K is a constant.

Application of an external pressure P_e compresses the internal gas phase to $P_0 + P_e$, *i. e.*, the difference between external and internal pressure is always P_0 .

III. Lattice Cohesion (Surface Tension).—

The forces which hold the lattice molecules in formation are, by origin and nature, the same as those of surface tension. These intermolecular attractions vary with the distance d between the molecules; in the most general case of dipoles and at the close proximity within the lattice structure, they must be proportional to the inverse fourth power of d (Debye)

$$\gamma = g/d^4 \quad d = \sqrt[4]{g/\gamma} \quad (5)$$

where g is a material constant. Substituting (5) into (3)

$$z = [\sqrt{\gamma}(V - bx)]/N\sqrt{gx} \quad (6)$$

IV. Inter-lattice Forces (Viscosity).—

According to the model, viscosity may be defined as the shearing resistance per unit area, between two lattice sheets oriented in the direction of flow and moving at different velocity. The shearing resistance must be proportional to the oriented forces acting between the lattice sheets across the separating distance z . Assuming that z is much larger than d , quantized interference may be neglected; in this case the inverse square law becomes applicable. If f is a material factor, the viscosity

$$\eta = f/z^2$$

High external pressure places the liquid structure under elastic strain which will add proportionally to the existing shearing forces and thus, to viscosity

$$\eta = \frac{f}{z^2} + CP_e \quad (7)$$

C is a constant which, due to the disparity in magnitude between intermolecular forces and practically applicable external pressures, has a very small value. For one atmosphere the term CP_e can be neglected. Substituting (6) into (7)

$$\eta = \frac{N^2fgx^2}{\gamma(V - bx)^2} + CP_e \quad (8)$$

$a = N\sqrt{fg}$, as a product of material factors, is constant.

V. The Gas Phase.—The internal gas phase is under the pressure $P_0 + P_e$ (see II), and its effective volume is the total liquid volume minus the constant displacement of all molecules; the quantity involved is $(1 - x)$ mole (see I). Hence

$$(P_0 + P_e)(V - b) = RT(1 - x)$$

and, after substituting P_0 from (4)

$$\left(\frac{K\gamma}{\sqrt[3]{V}} + P_e\right) \frac{V - b}{1 - x} = RT \quad (9)$$

Combination of Relationships I-V (Equation of State).—The term (8) represents, according to the assumed model, the behavior of the lattice phase; the term (9) that of the gas phase. If now the ratio x is eliminated between (8) and (9), the resulting function applies to the liquid as a whole; it is an equation of the liquid state

$$\left(\frac{K\gamma}{\sqrt[3]{V}} + P_e\right) \left[\frac{V}{1 - \frac{V-b}{a} \sqrt{\gamma(\eta - CP_e)}} - b \right] = RT \quad (10)$$

which contains

the constants (individual) $a, b, C,$

(general) K, R

the variables (independent) $P_e, V, T,$

(dependent) η, γ

The constant a has the dimensions of momentum, b is a volume, C a numerical factor; they represent constitutive elements of the substance. Surface tension, γ , and viscosity, η , express the two-dimensional orientation of structural forces.

In order to test the validity of equation (10), it is convenient to state it in parameter form—*i. e.*, as a set of three functions of two independent variables while the respective third one is constant. If these functions are made explicit for η , they appear as the three "viscosity functions," that of temperature, that of pressure and that of volume or ideal dilution. The viscosity functions, as derived in the following, are in accurate agreement with observed fact; they are valid over a variety of substances and conditions sufficient to prove the essential correctness—if not uniqueness—of the assumed two-dimensional, two-phase concept of liquid structure.

The Viscosity Functions

The Temperature Function.—Neglecting P_e for atmospheric pressure in equation (10), and making explicit for η

$$\eta = \frac{1}{\gamma} \left[\frac{a}{V-b} \frac{RTV^{1/3} - K(V-b)\gamma}{RTV^{1/3} + Kb\gamma} \right]^2 \quad (11)$$

In order to express the two variables V and γ in terms of temperature, two empirical relations of good general validity may be used

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_{cr}} \right)^{8/5} \quad (12)$$

$$\gamma = C \left(\frac{1}{V} - \frac{1}{W} \right)^4 \quad (13)$$

T_{cr} is the absolute critical temperature; γ_0 , nominally the surface tension at absolute zero, is a material constant. C is "McLeod's constant." Eliminating γ from (12) and (13)

$$\frac{1}{V} = \frac{1}{W} + \left(\frac{\gamma_0}{C} \right)^{1/4} \left(1 - \frac{T}{T_{cr}} \right)^{1/5}$$

where W , the molar volume of the vapor at the temperature T , is large against V under conditions well below the critical, so that $1/W$ can be neglected. For $T=0$, V would equal b

$$V = b\theta^{-2/10} \quad \theta = 1 - \frac{T}{T_{cr}} \quad (14)$$

Substituting terms (12) and (14) into (11)

$$\eta = A \left[\frac{T - B\theta(1 - \theta^{2/10})}{\theta^{2/10}(1 - \theta^{2/10})(T + B\theta^{2/10})} \right]^2 \quad (15)$$

where

$$A = \frac{a^2}{b^2\gamma_0} \quad B = \frac{Kb^{2/5}\gamma_0}{R}$$

This temperature function of viscosity contains three material constants, A , B , T_{cr} . The critical temperature is known through direct measurement but A and B must be calculated from two viscosity measurements at different temperatures. The formula can be simplified conveniently by development into a series

$$\eta = A \left[\theta^{2/10} f \left(\frac{1}{T} \right) \right]^{-2}$$

$$f \left(\frac{1}{T} \right) = (1 - \theta^{2/10}) + B \frac{\theta}{T} (1 - \theta^{2/10}) + \dots$$

The higher members may be neglected. After transformation

$$\eta = \frac{A}{\left[\theta^{2/10} (1 - \theta^{2/10}) \left(1 + B \frac{\theta}{T} \right) \right]^2} \quad (16)$$

Values of A and B appear in Table I. It is evident that A is a serial constant common for related substances. In Table II the calculated viscosities are compared with those observed by Thorpe and Rodger,⁹ showing remarkable agreement.

(7) Sugden, *J. Chem. Soc.*, **125**, 32 (1924).

(8) McLeod, *Trans. Faraday Soc.*, **19**, 38 (1923).

(9) Thorpe and Rodger, *Phil. Trans.*, **A185**, 397 (1894); *Proc. Roy. Soc. (London)*, **A60**, 152 (1896).

TABLE I
CONSTANTS OF THE VISCOSITY-TEMPERATURE FUNCTION (16)

	A	B	T_{cr} (°K.)
Hydrocarbons			
<i>n</i> -Pentane	0.00677	- 88.4	470
<i>n</i> -Hexane	.00706	-112.3	508
<i>n</i> -Heptane	.00718	-132.5	540
<i>n</i> -Octane	.00713	-164.4	569
Diallyl	.00631	-103.9	507.4
Diisopropyl	.00709	-168	500.5
Benzene	.00704	-215.5 ^a	561.5
Toluene	.00725	-152.4	593.6
<i>p</i> -Xylene	.00700	-154.8	622
Ethers			
Ethyl ether	0.00684	- 94.7	467
Methyl propyl ether	.00659	- 94.3	487
Ethyl propyl ether	.00686	-121.6	506.4
Ketones			
Acetone	0.00765	- 92.5	508
Esters			
Methyl formate	0.00882	-103.9	487
Methyl acetate	.00803	-125.3	506.7
Methyl propionate	.00794	-144.3	530.4
Ethyl acetate	.00787	-153.8	523
Ethyl formate	.00856	-129.4	487
Propyl formate	.00812	-160.5	538
Halogen Compounds			
Fluorobenzene	0.00774	-165.2	559.7
Ethyl bromide	.00978	- 80.4	499
Methyl iodide	.01106	- 81.1	528
Ethyl iodide	.01106	- 96.9	554
Methylene chloride	.00967	- 98.1	518
Chloroform	.01101	-113.1	532
Carbon tetrachloride	.01083	-215.8	556.2
Bromine	.01365	-173.8	810 ^a
Sulfur Compounds			
Ethyl sulfide	0.00743	-122.8	558
Carbon disulfide	.01555	- 16.9	550
Thiophene	.00771	-170.3	590

^a "Ultimate" critical temperature, estimated by graphical extrapolation.⁴ A has the dimension of viscosity, B that of temperature.

TABLE II
THE VISCOSITY-TEMPERATURE FUNCTION (EQUATION 16)
EXAMPLES

Temp., °C.	<i>n</i> -Hexane		Bromine	
	Calcd.	Obsd.	Calcd.	Obsd.
0	0.4012	0.4012	1.2668	1.2668
10	.3606	.3602	1.1246	1.1195
20	.3260	.3258	1.0087	1.0050
30	.2963	.2963	0.9119	0.9110
40	.2706	.2708	.8302	.8305
50	.2483	.2483	.7607	.7607
60	.2288	.2288		

TABLE II (Concluded)

Substance	Temp. range, °C.	No. of readings	Viscosity range centipoises	Average deviation	
				Cp.	% ^a
<i>n</i> -Pentane	0-30	4	0.2894-0.2200	0.0001	0.04
<i>n</i> -Hexane	0-60	7	.4012-.2288	.0001	.01
<i>n</i> -Heptane	0-90	10	.5236-.2239	.0005	.12
<i>n</i> -Octane	0-120	13	.7060-.2160	.0009	.2
Diallyl	0-50	6	.3450-.2164	.0004	.12
Diisopropyl	0-40	5	.495-.342	.000	.0
Benzene	0-70	8	.9060-.3591	.0030	.7
Toluene	0-110	12	.7719-.2588	.0013	.18
<i>p</i> -Xylene	10-130	13	.7358-.2424	.004	.9
Ethyl ether	0-30	4	.2950-.2230	.0004	.2
Methyl propyl ether	0-30	4	.3139-.2367	.0002	.08
Ethyl propyl ether	0-60	7	.4019-.2254	.0001	.03
Methyl formate	0-30	4	.4355-.3253	.0004	.02
Methyl acetate	0-50	6	.4837-.2929	.0005	.12
Methyl propionate	0-70	8	.5866-.2861	.0013	.29
Ethyl formate	0-50	6	.5103-.3077	.0009	.23
Ethyl acetate	0-70	8	.5825-.2786	.0009	.21
Propyl formate	0-80	9	.6720-.2883	.0011	.20
Acetone	0-50	6	.4013-.2561	.0001	.04
Methyl iodide	0-40	5	.6055-.4240	.0010	.18
Ethyl bromide	0-30	4	.4866-.3678	.0000	.00
Ethyl iodide	0-70	8	.7269-.3914	.0017	.3
Methylene chloride	0-40	5	.5431-.3727	.0010	.22
Chloroform	0-60	7	.7060-.3997	.0001	.02
Carbon tetrachloride	0-70	8	1.3509-.5342	.0055	.6
Fluorobenzene	10-80	8	0.647-.305	.002	.2
Bromine	0-50	6	1.2668-.7607	.0016	.15
Ethyl sulfide	0-90	10	0.5634-.2457	.0012	.3
Carbon disulfide	0-40	5	.4377-.3295	.0043	.7
Thiophene	0-80	9	.8746-.3580	.0005	.14

^a Presumable error of measurement 0.1-0.3%.

The Pressure Function.—From (8) and (4)

$$\eta = \frac{Ka^2x^2}{P_0 \sqrt{V}(V-bx)^2} + CP_0$$

Since, in accord with the phase rule (see above), x does not vary with external pressure

$$\eta = \frac{A}{\sqrt{V}(V-B)^2} + CP_0 \quad (17)$$

TABLE III

THE VISCOSITY-PRESSURE FUNCTION (EQUATION 17) CONSTANTS

	Temp., °C.	A	B	C
<i>n</i> -Pentane	30	0.0337	0.6625	-0.000030
<i>n</i> -Pentane	75	.0362	.6480	-.000041
Isopentane	75	.0308	.6640	-.000030
Hexane	75	.0349	.6980	.000013
Ethyl bromide	30	.0500	.6765	-.000032
Ethyl bromide	75	.0519	.6599	-.000034
Ethyl iodide	30	.0607	.6993	-.000008
Ethyl iodide	75	.0639	.6829	-.000055
Ethyl ether	30	.0346	.6585	-.000030
Ethyl ether	75	.0437	.6323	-.000030
Acetone	30	.0448	.6613	-.000011
Acetone	75	.0598	.6150	-.000036
Carbon di-sulfide	30	.0503	.6604	-.000027
Carbon di-sulfide	75	.0569	.6455	-.000051

$$A = \frac{Ka^2x^2}{P_0} \quad B = bx$$

where A , B , and C are constants.

Equation (17) represents the viscosity-pressure function of normally behaving liquids within the presumable error of measurements by Bridgman,¹⁰ see Tables III and IV.

The Volume (Ideal Dilution) Function.—An ideal mixture of liquids, *i. e.*, one where each component acts as an indifferent diluent toward the

TABLE IV

THE VISCOSITY-PRESSURE FUNCTION (EQUATION 17)

Pressure kg./cm. ²	EXAMPLES			
	<i>n</i> -Pentane		Ethyl iodide	
	Calcd.	Obsd.	Calcd.	Obsd.
1	0.142	0.142	0.375	0.375
1000	.346	.320	.621	..
2000	.527	.528	.900	.902
4000	1.010	1.043	1.60	1.60
6000	1.77	1.78	2.53	2.57
8000	2.91	2.89	3.90	3.90
10000	4.53	4.53	5.90	5.86
12000	8.65	8.66

(10) Bridgman, *Proc. Nat. Acad. Sci. U. S.*, **11**, 603 (1925).

TABLE IV (Concluded)
SUMMARIZED DATA ON OTHER PURE LIQUIDS

Substance	Temp., °C.	Max. pres. kg./cm. ²	Minimum volume ^a	No. of readings	Viscosity range, cp.	Average dev., % ^b
n-Pentane	30	10000	0.7266	7	0.220-9.07	1.3
n-Pentane	75	10000	.7381	7	.142-4.53	0.5
Isopentane	75	8000	.7660	6	.131-2.99	.0
n-Hexane	75	10000	.7680	6	.188-7.90	1.1
Ethyl bromide	30	12000	.7520	8	.368-9.24	0.4
Ethyl bromide	75	12000	.7638	7	.434-4.87	.1
Ethyl iodide	30	12000	.7582	8	.546-19.13	1.1
Ethyl iodide	75	12000	.7696	7	.375-8.66	0.1
Ethyl ether	30	12000	.7202	8	.223-10.43	3.3
Ethyl ether	75	12000	.7315	8	.170-4.57	1.4
Acetone	30	8000	.7900	6	.302-2.94	0.4
Acetone	75	12000	.7607	7	.392-3.05	.2
Carbon disulfide	30	12000	.7627	8	.352-5.44	.0
Carbon disulfide	75	12000	.7745	8	.265-3.11	.0

^a 0°, 1 kg./cm.² and $V = 1.0000$. Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 3 (1913); **61**, 55 (1926); **66**, 185 (1931).

^b Presumable error of measurement 1-3%.

other, does not involve energy transfer, the component volumes are strictly additive, and the constitutional condition of each substance is unaffected by the presence of others. If, for a binary

TABLE V
THE VISCOSITY-VOLUME (IDEAL MIXTURE) FUNCTION.
(EQUATION 18)

Volume % (II)	Examples			Volume % (II)	Obsd.		
	VM. naphtha (I) Paraffin oil (II) Calcd. Cp.	Obsd.	Ethyl ether (I) Phenyl ether (II) Calcd. Cp.		Obsd.	Obsd.	Obsd.
0	0.71	0.71	0	0.223	0.2233		
10	.95	0.93	13.26	.305	.3106		
20	1.31	1.26	29.84	.455	.4551		
30	1.85	1.80	38.61	.567	.5733		
40	2.70	2.63	49.72	.758	.7614		
50	4.17	4.10	59.50	.993	.9926		
60	6.74	6.88	67.49	1.253	1.258		
70	12.3	12.9	75.69	1.612	1.631		
80	26.5	26.5	84.50	2.157	2.153		
			90.91	2.711	2.737		
			95.29	3.199	3.158		
			100	3.864	3.864		

SUMMARIZED DATA ON OTHER IDEAL MIXTURES

Components	Obsd.	Temp. °C.	No. of readings	Viscosity range centipoises	k	Average deviation, %
VM. Naphtha-paraffin oil	(4)	20	9	0.71 - 26.5	4.37	0.8
Benzene-ethyl benzoate	(11)	25	8	.605 - 1.992	1.747	.12
Toluene-benzyl benzoate	(11)	25	7	.552 - 8.450	2.91	.5
Phenetole-aniline	(12)	20.2	10	1.24 - 4.26	2.77	.13
Ethyl ether-phenyl ether	(13)	25	12	0.2233-3.864	2.718	.10
Phenetole-phenyl ether	(13)	25	11	1.158 - 3.864	1.680	.4
Toluene-naphthalene	(14)	25	6	0.5526-2.65*	1.970	.11
Benzene-diphenyl	(14)	25	5	.6051-3.65*	2.097	.21

(11) Kendall and Monroe, *THIS JOURNAL*, **39**, 1787 (1917).

(12) Bramley, *J. Chem. Soc.*, **109**, 23 (1916).

(13) Kendall and Wright, *THIS JOURNAL*, **42**, 1776 (1920).

(14) Kendall and Monroe, *ibid.*, **39**, 1802 (1917).

mixture, the respective symbols are distinguished by the indices 1 and 2, the molar volumes of the lattices

$$v_1 = N_1(d_1^3\vartheta_1)x_1 + N_2(d_2^3\vartheta_2)x_2$$

combined gas voids

$$v_g = (v_1 + v_2) - v_1 = (N_1d_1^3x_1 + N_2d_2^3x_2)z$$

Considering no change in the condition of either component, the respective quantities, d , ϑ and x remain constant. N_1 and N_2 , the relative numbers of molecules present, are always proportional to the volumes of the components entering into and independently preserved within the mixture. Hence $N_1/v_1 = \text{const.}$ $N_2/v_2 = \text{const.}$

$$v_g = \alpha_1v_1 + \alpha_2v_2 = Z(\beta_1v_1 + \beta_2v_2) \dots Z = \frac{\alpha_1v_1 + \alpha_2v_2}{\beta_1v_1 + \beta_2v_2}$$

$$\eta = \frac{f}{z^2} = f \left(\frac{\beta_1v_1 + \beta_2v_2}{\alpha_1v_1 + \alpha_2v_2} \right)^2$$

For

$$v_1 = v, v_2 = 0 \dots \beta_1 \sqrt{f} = \alpha_1 \sqrt{\eta_1}$$

$$v_2 = v, v_1 = 0 \dots \beta_2 \sqrt{f} = \alpha_2 \sqrt{\eta_2}$$

$$\eta = \left[\frac{K \frac{v_1}{v_2} \sqrt{\eta_1} + \sqrt{\eta_2}}{K \frac{v_1}{v_2} + 1} \right]^2 \quad (18)$$

K is a constant characteristic of the system. It represents the ratio between the relative gas void volumes of the two component liquids.¹⁵ Table V shows the excellent agreement of equation (18) with measurements on liquid mixtures which are known to be ideal.

Summary

True solids, *i. e.*, crystals, are distinguished by the three-dimensional fixation of their constituents; in gases no fixation or orientation of any kind exists. The structure characteristic of the liquid state must be intermediate and transitory between these two types of material constitution, but our present knowledge does not provide a

unique interpretation. We are still free to con-

(15) The "free spaces" assumed by McLeod, *Trans. Faraday Soc.*, **19**, 17 (1923), are similar in concept.

struct such models of structure as may best explain the observable facts about liquids.

It has been assumed that liquids are systems of two phases at equilibrium. The one, exemplified by the surface, consists of two-dimensional molecular lattice structures; the other occupies the spaces between the former in a truly gaseous condition. The equilibrium is supposed to depend on temperature but not on pressure imposed from outside.

On this basis an equation of the liquid state has

been formulated which contains, besides V , P and T , the dependent variables surface tension and viscosity. The three viscosity functions derived from this equation and representing it in parameter form, *viz.*, that of temperature, pressure and volume, respectively, are in very accurate agreement with measurements on a large number and variety of liquids, and thus confirm the validity of the proposed theory of liquid structure.

SHAWINIGAN FALLS
QUEBEC, CANADA

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMICAL LABORATORY OF LEHIGH UNIVERSITY]

Studies in Ester Hydrolysis Equilibria—Formic Acid Esters

BY RAYMOND F. SCHULTZ

In 1901 Euler¹ studied the hydrolysis equilibrium at 50° for simple formic, acetic and propionic esters, using hydrochloric acid as a catalyst. In 1928 Williams, *et al.*,² in attempting to correlate the hydrolysis equilibrium constants with the dissociation constants of the corresponding acids, investigated the same series of esters at 100° in the absence of a mineral acid catalyst.

The results of Williams agree fairly well with those of Euler and others^{1,3-7} for acetic and propionic esters, but his constants for formic esters are very much higher (see Table I). He believed Euler's results in error due to side reactions between the alcohol and the large amount of hydrochloric acid in his mixtures (0.25 *N* in hydrogen chloride). It is difficult to see why such errors should be confined to the formic esters and not affect the results for the other esters,

because all of Euler's mixtures contained the same high concentration of hydrochloric acid.

In another connection, we attempted to apply the above data to the analysis of various formic ester hydrolysis mixtures, and found inconsistencies. We, therefore, have determined carefully the hydrolysis equilibrium constants for formic esters under a variety of new conditions, and have found a change in the "constants" with varying mole fractions of water present. These effects have not been studied previously in the formic ester series, though they occur to about the same extent as in the acetic ester hydrolyses.³⁻⁷

We also have redetermined constants for ethyl formate in mixtures identical with those of Euler and of Williams.

Experimental

Purification of Materials. Methyl, ethyl and *n*-propyl formate (Eastman Kodak Co.) were purified carefully. Analyses indicated that the final products contained more than 99.5% ester and less than 0.02% formic acid.

Methyl and ethyl alcohols were of absolute c. p. reagent quality, with densities indicating a purity of 99.5% or more. *n*-Propyl alcohol, 99.7% pure by density measurements, was prepared by fractional distillation of an Eastman product.

Formic acid was purified by fractional distillation of a Baker and Adamson 90% product. Analysis by titration of weighed samples showed 99.34% formic acid. In our determinations, a correction was made for the remaining 0.66% as water.

Procedure.—Weighed samples of ester and of 0.005 *N* hydrochloric acid (total volume *ca.* 5 cc.) were sealed into clean Pyrex ampoules of 7-cc. capacity. The mixtures were kept at 100 ± 2° for forty-eight to sixty hours; shorter heating periods gave inconsistent results. Experi-

TABLE I

A COMPARISON OF HYDROLYSIS EQUILIBRIUM CONSTANTS FOR FORMIC ACID ESTERS OBTAINED BY EULER¹ AND WILLIAMS²

	Init. comp. in moles				$K = \frac{[\text{Acid}]^2}{[\text{Ester}][\text{H}_2\text{O}]}$	
	Acid	Alcohol	H ₂ O	HCl	Euler	Williams
Methyl	0.04	0.04	0.95	0.005	0.20	
Methyl	7.10	18.81	1.03
Ethyl	0.04	0.04	0.91	.005	.36	
Ethyl	9.95	9.95	4.00	1.45

(1) Euler, *Z. Physik. Chem.*, **36**, 408 (1901).

(2) Williams, *et al.*, THIS JOURNAL, **50**, 1267 (1928).

(3) Jones and Lapworth, *J. Chem. Soc.*, **99**, 1427 (1911).

(4) Schlesinger, *Ber.*, **59**, 1965 (1926); **60**, 1479 (1927); *Acta phys. chim.*, **5**, 93 (1936); **6**, 769 (1937).

(5) Dobrzynski, *Roczniki chemji*, **8**, 369 (1928).

(6) Poznanski, *ibid.*, **8**, 377 (1928); **9**, 369 (1929).

(7) Berthelot and Péan de Saint Gilles, *Ann. chim. phys.*, [3] **65**, 395 (1862); [3] **66**, 5 (1862); [3] **68**, 225 (1863).