THE LIQUID STATE PAPERS

DEWEY B. LARSON

THE LIQUID STATE PAPERS

DEWEY B. LARSON

I

General Theory

This is the first of a series of publications that will describe an entirely new theory of the liquid state of matter: a theory which not only provides a full qualitative explanation of the physical properties of liquids but also furnishes the means whereby accurate numerical values of these properties applicable to different liquids can be calculated from the chemical composition, temperature and pressure. The new theory is the result of an extension and elaboration of the consequences of two new postulates as to the nature of space and time which were formulated and discussed by the author in a recently published work. As explained in that publication, it follows directly from the fundamental postulates that there exists a progression of space-time (of which the observed progression of time is only one aspect) such that each location of space-time moves outward at a constant velocity from all other locations. It also follows from the postulates that the atoms of matter are rotating systems (the exact nature of which is immaterial for present purposes) and that this rotation is greater in magnitude than the space-time progression and opposite in direction. Because of this directional requirement the atomic rotation is translationally effective; that is, a rolling motion. By virtue of the same motion which gives them their atomic status, therefore, the atoms of matter are reversing the pattern of free space-time and are moving inward toward each other: a phenomenon which we call gravitation.

In the absence of any other type of motion gravitation will cause the atoms to approach each other until they are separated by only one unit of space, beyond which point the characteristics of both the gravitational motion and the space-time progression undergo some changes which are discussed at length in the work previously published. If thermal motion is introduced into the system it acts in the outward direction and adds to the motion of the space-time progression. At some particular value of this thermal motion (that is, at some particular limiting temperature) the sum of the outward motions may exceed the gravitational motion in one dimension and at some higher temperature it may exceed the gravitational motion in all three dimension simultaneously. When the direction of the net resultant motion is thus reversed either in one dimension or in all dimensions the characteristics of the motion are substantially modified and the corresponding properties of the substance are altered to such a degree that we regard the substance as being in a different physical state. We will identify the condition below the lower temperature limit as the *solid* state and the condition above the upper limit as the *gaseous* state.

Between these two temperature limits, which we identify as the melting point and the critical temperature respectively, there are two possibilities. An extension of the gaseous structure into the intermediate zone produces the *liquid* state: the subject of the present discussion. As can be seen from this description the relation between the liquid and vapor states is quite different from the solid-liquid and liquid-gas relationships. So far as the latter are concerned, the physical state of a molecule is uniquely determined by its temperature, but in the intermediate zone the choice between the two possible states is purely a matter of relative probability.

It should be recognized that on the foregoing basis physical state is essentially a property of the individual molecule and not a "state of aggregation" as commonly assumed. In a complex substance the cohesive forces between the atoms--the atomic bonds, as they are usually called--are stronger for same combinations than others, but as soon as the weakest bond is broken the molecule enters the new state and acquires all of the properties appertaining thereto. The properties of an aggregate are determined by the state or states of its constituent molecules, If all of the molecules of a liquid were at the same temperature (that is, if they all possessed the same amount of thermal energy) this distinction between the state of the molecule and that of the aggregate would have no particular significance in application to homogenous liquids, but because of the distribution of molecular velocities due to the operation of the probability principles the temperatures of the individual molecules are distributed through a range of values of which the temperature of the aggregate is merely the average. A liquid in the vicinity of the melting point therefore certain proportion of molecules with individual temperatures below the melting point and on the basis of the concept of physical state developed herein, these molecules are in the solid state. Similarly the solid aggregate just below the melting point contains a certain proportion of molecules which are individually at temperatures above the melting point and which are therefore in the liquid state.

Where a continuous property is involved the characteristics of a mixed solid and liquid aggregate are intermediate between those of a pure solid and those of a pure liquid. In the case of a discontinuous property such as the transition between physical states, the condition of the aggregate is basically determined by the condition of the majority of its liquid molecules. For the transition from solid to liquid nothing is required other than the necessary proportion of liquid molecules and the change of state therefore takes place automatically as soon as the melting temperature is reached. For this reason it is impossible to heat a solid above the melting point corresponding to the prevailing conditions. The reverse transition from liquid to solid is not automatic. Formation of a crystal lattice requires not only the presence of the required proportion of solid molecules but also the establishment of contact between these molecules and maintenance of this contact against the disruptive thermal forces for a long enough period to permit attachment of additions this proves may be hindered to a considerable degree and with appropriate precautions liquid can be subcooled to temperatures well below the freezing points normally applicable.

The ability of a liquid aggregate to incorporate solid or gaseous molecules into its structure is not confined to molecules of the same chemical composition. If the non-liquid molecules are of a different kind the aggregate is a *solution*. Such a solution is structurally identical with a liquid which contains solid or gas molecules of its own composition but the different physical properties of the solute introduce some additional variability. Where the solute has a high melting point, for example, the solid--liquid solution may persist through most or all of the liquid temperature range of the aggregate. An interesting point in this connection is that the properties of solutions furnish a positive verification of the existence of distinct solid and liquid molecules in the liquid aggregate. It has long been recognized that these properties are quite sensitive to the melting point of the solute; that is, the properties of a liquid-liquid solution often differ materially from those of the corresponding solid-liquid solution. Some of the less soluble substances, particularly, show a very marked change at the solute melting point, separating into the two-layer structures characteristic of many of the liquid-liquid solutions. In preparing a liquid-liquid solution of this kind it makes no difference whether we put the solid into the liquid and then raise the temperature of the solution beyond the solute melting point or whether we liquefy the solid independently and add the liquid solute to the solvent. In either case there is a very decided change in properties at a specific temperature and in both processes this is the same temperature: the solute melting point. The logical conclusion is that the solute is in the solid state below its melting point. The logical conclusion is that the solute is in the solid state below its melting point regardless of its environment and it makes the transition to the liquid state at its normal melting temperature in solution as well as out of solution.

The significance of these points in relation to the present subject lies in the fact the solute is known to exist in units of molecular or ionic size. If the solute is in the solid state below its melting temperature and in the liquid state above this point, this means that it exists in the form of *solid molecules (*or ions, which will be included in the term “molecules “in this discussion of solutions) and *liquid molecules* respectively. Obviously the existence of distinct solid and liquid molecules under *any* conditions precludes the possibility that the liquid and solid states are “states of aggregation” and establishes the fact that physical state is essentially a property of the individual molecule, as required by the principles developed in this work.

Each increment of thermal energy added to a molecule alters the behavior of the molecule to some extent; that is, it modifies the physical properties. Normally the incremental change is minor and a matter only of degree, but at the points where the unit levels are exceeded as previously described some properties undergo drastic modification and it is this transition to a new general type of behavior which we recognize as a change of state. The most distinctive feature of the solid state is that in this state the average positions of the molecules under any specific set of conditions maintain a constant relationship. In the crystalline form of the solid state the centers of thermal motion are fixed and maintain the same relative positions indefinitely. In the glassy or vitreous form the instantaneous positions of the centers of motion are variable but the average positions of these centers over any appreciable period of time are fixed. A solid aggregate of either kind therefore has a definite size and shape.

When the melting point is reached and the thermal motion becomes free in one dimension (that is, the inward-directed force is no longer able to reverse the direction of motion in this dimension), the fixed molecular positions are eliminated. Each molecule must still maintain the solid-state relationships in two dimensions but it has complete freedom in the third dimension, and since there is no requirement that this always has to be the same dimension, any liquid molecule has the ability to move about at random through the aggregate. A liquid thus has no permanent shape and is able to accommodate itself to any external forces which may be impressed upon it. In practice this normally means that it assumes the shape of the container.

The distinctive properties of liquids arise from this dual character of the dimensional relations. The property of fluidity and its reciprocal, viscosity, are obviously direct results of the freedom of motion in one dimension and the fluidity increases in magnitude as the temperature rises, since the energy in the free dimension then constitutes a larger proportion of the total thermal energy. Surface tension, on the other hand, is due to the solid-state forces exerted in the dimensions in which the outward forces are below the unit level and it decreases in magnitude as the temperature rises. Vapor pressure, another characteristic liquid property, is a result of the distribution of molecular velocities which brings a certain proportion of the liquid molecules up to the critical temperature and causes them to enter the gaseous state even though the average temperature of the aggregate is still within the liquid rage. These properties, density, specific heat, etc., will be covered in detail in the subsequent papers in this series.

In some instances the theoretical development in these papers is complete and specific numerical values are obtained directly from theory. In other cases the theory in its present state leads to several possible values rather than to one unique result and for the present the selection from among these possibilities is dependent on a study of series relationships or some similar expedient. It should be pointed on a out, however, that no arbitrary numerical constants are introduced anywhere in this development. Aside from the conversion constants required for expressing the results in conventional systems of units, all numerical constants which enter into the relationships are structural constants: integral or half-integral values which represent the actual numbers of the various types of physical units entering into the particular phenomenon under consideration.

No satisfactory theoretical system for the calculation of the numeral values of these liquid properties has ever been developed heretofore, although a vast amount of effort has been devoted to the task. Many ingenious and useful mathematical expression have been developed to facilitate interpolation and extrapolation of the experimental data but in most cases it has been impossible to attach any theoretical significance to these expressions. As one observer puts it, referring specifically to the property of volume, “The quantitative representation of the volumetric behavior of fluids over both gas and liquid regions has proven to be an unusually difficult problem.” The nature of the obstacle which has stood in the way of a solution to this problem is revealed by the discussion in the foregoing paragraphs. It has been taken for granted that a liquid is a complex structure requiring complex mathematical expressions for accurate representation of its properties. According to the theory developed herein this concept is erroneous; the liquid aggregate is not a complex structure but a composite in which relatively simple structures coexist in definite proportions. This theory eliminates the need for any complex mathematical treatment and the subsequent papers in this series will show that in each case accurate results can be obtained by very simple mathematics.

II

Volume - Relation to Temperature

This is the second of a series of publications, which will present a complete new theoretical treatment of the liquid state. As brought out in the first paper, the results reported herein have been derived entirely by extension and elaboration of the consequences of two new postulates as to the nature of space and time which were formulated and explained by the author in a previously published work.[1] The first paper gave a brief outline of the general theory of liquids thus derived. We now begin a detailed discussion of the application of this general theory to specific liquid properties. It will be convenient to start with the property of volume inasmuch as this is a relatively simple item which plays an important part in most of the more complex physical properties that will be discussed later. The volume presentation will be divided into three sections.' Since the available experimental values which will be used for comparison with the results calculated from theory include a temperature effect which varies widely from substance to substance the first section will establish the relation between volume and temperature so that the basic volumetric factors characteristic of each substance can be identified. The next section will show how these volumetric factors can be derived from the chemical composition and molecular structure, and the final section will develop the relation between volume and pressure.

Theoretically the initial point of the liquid state is at zero temperature; that is, when the thermal energy of a solid molecule reaches the limiting value the molecule undergoes a transition to the liquid state at zero temperature. Inasmuch as the surrounding molecules are at a higher temperature this zero temperature condition cannot persist and the molecule immediately absorbs enough heat from its environment to bring it into thermal equilibrium with the neighboring molecules. The theoretical initial point of the liquid is therefore a level that cannot be reached in practice but it does constitute a convenient reference point-for our calculations. From the basic theory of the liquid state as previously outlined it follows that the thermal motion beyond the initial point of the liquid is the one-dimensional equivalent of the thermal motion of a gas. It therefore conforms to the gas laws; in particular, the volume generated by this motion is directly proportional to the temperature. At the unit temperature level this volume should equal the initial liquid volume, V_0, the volume at zero temperature. The factors affecting the magnitude of the temperature unit will be analyzed in a subsequent publication and for present purposes we will merely note that the unit applicable to most organic liquids and a large number of common inorganic liquids has been evaluated as 510.2º K. The volume of a liquid molecule between absolute zero and the critical temperature can then be expressed as

$$V_L = (1 + T/510.2)\ V_0 \qquad (1)$$

In most cases the effective value of the initial volume applicable to the motion in the second dimension differs somewhat from that applicable to the initial dimension because of geometric factors which will be discussed later, and if we represent the two values of V_0 by V_1 and V_2 respectively, equation 1 becomes

$$V_L = V_1 + (T/510.2)\ V_2 \qquad (2)$$

The volume of a liquid aggregate deviates from the linear relation of equation 2 in two respects. At the lower end of the liquid temperature range the aggregate contains a certain proportion of solid molecules and the average volume per molecule is therefore either slightly above or slightly below the true liquid volume, depending on whether the volume of the solid is greater or less than that of the liquid. At the upper end of the liquid temperature range the aggregate contains a similar proportion of what we may call critical molecules; that is, molecules which have individually reached the critical temperature and have acquired freedom of movement of the liquid type in the third dimension but have not yet made the transition to the unidirectional translational motion characteristic of the gaseous state. On assuming the critical status each molecule acquires a volume component in the third dimension similar to the components in the other two dimensions and these additional volumes increase the average molecular volume of the liquid aggregate above the value given by equation 2.

In order to calculate the volume of the liquid-aggregate over the entire liquid temperature range it will thus be necessary to determine the proportion of solid molecules and the proportion of critical molecules existing in the aggregate at each temperature and then to apply these figures to the volume increments accompanying the change of state in the individual molecule. Since the existence of other-than-liquid molecules in the liquid aggregate is the result of the distribution of molecular velocities, the number of such molecules is a probability function of the temperature and its numerical evaluation is simply a question of using the appropriate probability expression.

Thus far in all of the applications of probability mathematics that have been encountered in the course of the investigation of which this liquid study forms a part, it has been found that sufficient accuracy for present purposes can be obtained by the use of one variation or another of the so-called "normal" probability function. Whether this mathematical expression is an exact representation of the true relationship or merely a very close approximation is a question that can be left for later treatment. Because of the extremely broad scope of this investigation it has been physically impossible to study the "fine structure" at every point and any question of this kind which is beyond the limits of accuracy of the work as a whole has been passed up for the time being. It should be noted, however, that eliminating consideration of these fine-structure factors has very little effect on the accuracy of the liquid volume calculations.

Ordinarily the only uncertain element entering into the application of the normal probability function is the size of the probability unit. Ultimately it will no doubt be possible to develop methods of determining this unit from, purely theoretical considerations but in the meantime it can be identified quite readily on an empirical basis since this present study has disclosed that the unit is a simple fraction of the appropriate reference temperature. For example, the reference temperature for the solid-liquid transition is the melting point and the unit applicable to this transition in the paraffin hydrocarbons is one-fourth of the melting temperature For the critical transition the reference temperature is not the critical temperature as might be expected but the critical temperature plus half of the 510º temperature unit. Furthermore, the change in the dimensions of motion at the critical point results in a corresponding change in-the probability unit and we find that the unit applicable to half of the molecules is only one-third as large as that applicable to the other half. If ire designate the larger unit, which we find is $(T_c + 255)/9$, as A, the smaller unit as B, and the corresponding probability functions as f_A and f_B, we may express the proportion of critical molecules in the saturated or orthobaric liquid aggregate as $½(f_A + f_B)$. The transition of the individual molecule from the liquid to the critical condition is necessarily instantaneous since it is simply the result of breaking the inter-molecular bond in the third dimension. The third-dimensional volume increase therefore takes place isothermally so far as the individual molecule is concerned and the added volume per critical molecule is V_0. Where the proportion of critical molecules $½(f_A + f_B)$ the average volume increase for the liquid aggregate as a whole is $½(f_A + f_B) V_0$. Here again the value of V_0 applicable to this particular dimension may differ somewhat from the values that apply to the other dimensions and we will therefore identify this effective initial volume in the third dimension as V_3. The complete volume equation for all three liquid components is then

$$V_L = V_1 + (T/510.2) V_2 + ½(\phi_A + \phi_B) V_3 \qquad (3)$$

As previously indicated, a small additional adjustment is required in the range just above the melting point to compensate for the effect of the solid molecules which are present in the aggregate at these temperatures. In computing this adjustment by means of the probability relations, one of the points which must be taken into consideration is the location of the equal division between solid and liquid molecules, On a temperature basis the end point of the solid and the initial point of the liquid are coincident. From an energy standpoint, however, there is a substantial difference between the two: a difference, which is represented by the heat of fusion. If we continue adding heat to liquid aggregate, which has just reached the melting point, we find that the first additions of this kind do not result in any increase in temperature but are absorbed in the change of state. According to the theoretical principles developed in this study the change of state or the individual molecule is completed instantaneously and an isothermal absorption of heat in an aggregate of this kind can only result from these complete changes of state on the part of the individual molecules. It is apparent; therefore, that the aggregate reaches the melting temperature when the proportion of liquid molecules contained therein arrives at some limiting value A, which is less than 50 percent. Further additions of heat then enable more solid molecules to make the transition into the liquid state until the proportion of liquid molecules reaches another limiting value B, above 50 percent, beyond which part of the added thermal energy goes into an increase of the temperature of the aggregate. It thus follows that the location of equal division between solid and liquid molecules is not at the end point of the solid nor at the initial point of the liquid but midway between the two; that is, it is offset from each of these points by half of the temperature equivalent of the heat of fusion. In order to calculate the volume deviation due to the presence of solid molecules in the liquid aggregate it will therefore be necessary to know the amount of this temperature offset as well as the difference between the pure solid and pure liquid volumes. For present purposes we may simplify the calculations by using average values applicable to entire classes of substances rather than computing these factors on an individual basis, as the volume deviations due to this cause are small in any event and the basic factors for substances of similar structure are almost identical. The theoretical aspects of this situation will be discussed-in detail in a subsequent publication, which will-examine the process of freezing liquids by the application of pressure.

In the Immediate vicinity of the critical temperature still another factor enters into the picture, as some of the gas molecules remain in solution in the liquid aggregate. It will be convenient, however, to terminate the present study at the lower limit of this zone, about 20 degrees below the critical temperature, and to defer the discussion of the gas adjustment to a later paper in which the results of a study of vapor volume will be published.

As an example of the method of calculation of the solid-state volume increments shown in the columns headed D_s in the tabulations Included here with, let us look at the figures for hexane at -50º C. First we divide the melting temperature, 178º K, by 4 to obtain the probability unit 44.5º. Next we divide the 45 degrees difference between -50º C and the melting point by the unit value 44.5º, obtaining 1.01 as the number of probability units above the melting point. For present purposes the offset of the melting point from the location of equal division between solid and liquid molecules will be taken as .40 units, which is an average value that can be applied in all of the calculations of this kind that will be made in this paper. Adding the .40 units to 1.01 units we arrive at a total of 1.41 units. The corresponding value of the integral of the normal probability function, which we will designate f, is .158. This probability function is 1.00 at the point of equal division between the two states and the value .158 therefore indicates that 7.9 percent of the total number of molecules in the liquid hexane aggregate at -50º C are in the solid state. We then need only to multiply the difference in volume between solid and liquid molecules by .079 to obtain the average Increment for the aggregate as a whole. Again we will use average values to simplify the calculations, and for the lower paraffin hydrocarbons (C_{14} and below) we will take the molecular increment as +.080. The slightly higher value +.084 will be applied to the paraffins above C_{14}, including hexadecane, one of the compounds covered by the tabulations. The product .079 x .80 gives us .006 as the amount to be added to the true liquid volume calculated from equation 3 to obtain the volume of the actual liquid aggregate.

Calculation of the critical volume increment, V_3, is carried out in a similar manner.

Again the first step is to determine the probability unit. As indicated in the preceding discussion, this unit is 1/9 of (T_c + 255), and for hexane amounts to 84.8º. In the computation for +50º C, for examples, we next subtract 50º from the critical temperature, 235º C, obtaining a difference of 185º. Dividing 185 by 84.8, we find that the number of probability units below the critical temperature is 2.18. The corresponding value of ½(f_A + f_B) is .015. Here the 1.00 probability factor indicates the situation in which 100 percent of the molecules have reached the critical temperature and the result of our calculation therefore means that 1.5 percent of the total number of molecules at +50º C are in the critical condition. We then multiply .015 by .9778, the critical volume increment per molecule, which gives us .0147 as the critical increment (V_3) for the aggregate.

The quantity used in the foregoing multiplication, the critical volume increment per molecule or third dimensional value of the initial volume, V_0, and the corresponding initial volumes for the first and second dimensions can be derived from the molecular composition and structure by methods which will be discussed in the next paper in this series. For the present it will merely be noted that in most cases the basic value of the initial volume remains constant in all dimensions and the differences between the initial values of V_1, V_2, and V_3 are due to the modification of the basic value V_0 by a geometric factor which varies from .8909 to 1.00. In the base of hexane, or example, V_0 is .9778 and the geometric factors for the three dimensions of motion are .9864, .9727, and 1.000 respectively.

Volumetric data for a number of representative liquids are given in Table 11-1. In this table the D_s and V_3 volumes calculated in the manner described are added to the constant V_1 volume and the value Of V_2 obtained from the linear relation of equation 2 to arrive at the total volume of the liquid aggregate for comparison with the experimental volumes.[12] In those cases where the solid-state volume incremental, D_s negligible except for a few of the lowest temperatures of observation, calculation of this volume component has been omitted. All volumes are expressed in cm^3/g.

The extent of agreement between the calculated and experimental values in these tables is typical of the results obtained in the study of several hundred substances. In the most accurate experimental temperature range, in the neighborhood of room temperature, the deviations for the compounds which have been studied most thoroughly are within the general range of accuracy of the mathematical treatment, about 0.1 percent. At higher or lower temperatures and with less reliable experimental values the deviations are greater, as would be expected, but in most cases remain below one percent. The next paper in this series will present additional comparisons of the same kind for a wide variety of liquids at a few selected temperatures.

In this initial presentation of the liquid volume relations the discussion has been confined to liquids of the simplest type. It may be mentioned, however, that the modifications required in equation 3 to make it applicable to the more complex liquids are quite simple and usually amount to nothing more than replacing the temperature unit 510.2 degrees by 510.2 n degrees. In such liquids as water, the glycols and many condensed aromatic compounds the value of n is 2.

TABLE II - 1

LIQUID VOLUME

Hexane

$T_c = 508$			f unit = 84.8		
V_0= .9645 - .9512 - .9778 cm³/g					$V_S - V_L = .080$
T	V2	V3	D_s	V(calc.)	V(obs)
-100	.3229		.031	1.318	1.313
-90	.3415		.024	1.330	1.327
-80	.3601		.018	1.343	1.342
-70	.3788		.014	1.357	1.357
-60	.3974		.010	1.372	1.373
-50	.4361		.006	1.387	1.389
-40	.4347		.004	1.403	1.405
-30	.4534	.0010	.003	1.422	1.422
-20	.4720	.0010	.002	1.440	1.440
-10	.4907	.0020	.001	1.457	1.458
0	.5093	.0029		1.477	1.477
10	.5280	.0039		1.496	1.496
20	.5466	.0059		1.517	1.516
30	.5652	.0078		1.538	1.537
40	.5839	.0108		1.559	1.560
50	.6025	.0147		1.582	1.583
60	.6212	.0196		1.605	1.607
70	.6398	.0254		1.630	1.633
80	.6585	.0332		1.656	1.661
90	.6771	.0430		1.685	1.690
100	.6958	.0548		1.715	1.720
110	.7144	.0694		1.748	1.753

120	.7330	.0851		1.783	1.790
130	.7517	.1056		1,822	1.829
140	.7703	.1293		1.864	1.872
150	.7890	.1564		1.910	1.920
160	.8076	.1877		1.960	1.975
170	.8263	.2278		2.019	2.035
180	.8449	.2767		2.086	2.105
190	.8636	.3461		2.174	2.188
200	.8822	.4351		2.282	2.291
210	.9009	.5593		2.425	2.425

TABLE II - 1					
LIQUID VOLUME					
Hexadecane					
T_c = 728			f unit = 109.2		
V_0 = .8195 - .7764 - .8373 cm³/g					$V_S - V_L$ = .084
T	V2	V3	D_s	V(calc.)	V(obs)
20	.4461		.028	1.294	1.293
30	.4613		.024	1.305	1.305
40	.4766		.020	1.316	1.316
50	.4918		.017	1.328	1.328
60	.5070		.014	1.341	1.341
70	.5222		.011	1.353	1.353
80	.5374		.009	1.366	1.366
90	.5527		.007	1.379	1.379
100	.5679		.005	1.392	1.392
110	.5831	.0008	.004	1.407	1.407
120	.5983	.0008	.003	1.422	1.421
130	.6135	.0008	.002	1.436	1.436
140	.6287	.0017	.002	1.452	1.451

150	.6440	.0025	.001	1.467	1.466
160	.6592	.0033	.001	1.483	1.483
170	.6744	.0042		1.498	1.499
180	.6896	.0050		1.514	1.516
190	.7048	.0067		1.531	1.533
200	.7201	.0084		1.548	1.551
210	.7353	.0109		1.566	1.570
220	.7505	.0134		1.583	1.590
230	.7657	.0167		1.602	1.611
240	.7809	.0201		1.621	1.633
250	.7961	.0251		1.641	1.655
260	.8114	.0310		1.662	1.679
270	.8266	.0385		1.685	1.704
280	.8418	.0461		1.707	1.730
290	.8570	.0553		1.732	1.759

<table>
<tr><td colspan="6">TABLE II - 1</td></tr>
<tr><td colspan="6">LIQUID VOLUME</td></tr>
<tr><td colspan="6">Benzene</td></tr>
<tr><td colspan="4">$T_c = 564$</td><td colspan="2">f unit = 91.0</td></tr>
<tr><td colspan="4">V_0 =.7208 - .7208 - .8091 cm^3/g</td><td colspan="2">$V_S - V_L = 0$</td></tr>
<tr><td>T</td><td>V2</td><td>V3</td><td>D_s</td><td>V(calc.)</td><td>V(obs)</td></tr>
<tr><td>0</td><td>.3859</td><td>.0000</td><td></td><td>1.107</td><td>1.111</td></tr>
<tr><td>10</td><td>.4000</td><td>.0008</td><td></td><td>1.121</td><td>1.124</td></tr>
<tr><td>20</td><td>.4142</td><td>.0008</td><td></td><td>1.136</td><td>1.138</td></tr>
<tr><td>30</td><td>.4283</td><td>.0016</td><td></td><td>1.151</td><td>1.151</td></tr>
<tr><td>40</td><td>.4424</td><td>.0024</td><td></td><td>1.166</td><td>1.166</td></tr>
<tr><td>50</td><td>.4566</td><td>.0032</td><td></td><td>1.181</td><td>1.181</td></tr>
<tr><td>60</td><td>.4707</td><td>.0049</td><td></td><td>1.196</td><td>1.197</td></tr>
<tr><td>70</td><td>.4848</td><td>.0065</td><td></td><td>1.212</td><td>1.212</td></tr>
</table>

80	.4989	.0081		1.228	1.228
90	.5131	.0113		1.245	1.244
100	.5272	.0146		1.263	1.262
110	.5413	.0186		1.281	1.281
120	.5555	.0243		1.301	1.300
130	.5696	.0307		1.321	1.321
140	.5837	.0388		1.343	1.344
150	.5978	.0494		1.368	1.368
160	.6120	.0607		1.394	1.392
170	.6261	.0744		1.421	1.420
180	.6402	.0898		1.451	1.448
190	.6544	.1084		1.484	1.480
200	.6685	.1295		1.519	1.514
210	.6826	.1545		1.558	1.555
220	.6967	.1837		1.601	1.599
230	.7109	.2217		1.653	1.649
240	.7250	.2702		1.716	1.709
250	.7391	.3358		1.796	1.783
260	.7532	.4215		1.896	1.877
270	.7674	.5292		2.017	2.006

<table>
<tr><td colspan="6">TABLE II - 1</td></tr>
<tr><td colspan="6">LIQUID VOLUME</td></tr>
<tr><td colspan="6">Acetic Acid</td></tr>
<tr><td colspan="2">T_c = 596</td><td colspan="4">f unit a 94.55</td></tr>
<tr><td colspan="6">V_0 =.6346 - .5469 - .7016 cm^3/g</td></tr>
<tr><td>T</td><td>V2</td><td>V3</td><td>D_s</td><td>V(calc.)</td><td>V(obs)</td></tr>
<tr><td>20</td><td>.3143</td><td>.0000</td><td></td><td>.949</td><td>.953</td></tr>
<tr><td>30</td><td>.3250</td><td>.0007</td><td></td><td>.960</td><td>.962</td></tr>
<tr><td>40</td><td>.3357</td><td>.0007</td><td></td><td>.971</td><td>.972</td></tr>
</table>

50	.3464	.0014		.982	.983
60	.3571	.0021		.994	.994
70	.3679	.0028		1.005	1.005
80	.3786	.0035		1.017	1.017
90	.3893	.0049		1,029	1.029
100	.4000	.0063		1.041	1.042
110	.4107	.0084		1.054	1.055
120	.4215	.0112		1.067	1.068
130	.4322	.0147		1.082	1.083
140	.4429	.0182		1.096	1.100
150	.4536	.0239		1.112	1.116
160	.4643	.0302		1.129	1.133
170	.4751	.0372		1.147	1.150
180	.4858	.0463		1.167	1.169
190	.4965	.0554		1.187	1.189
200	.5072	.0681		1.210	1.210
210	.5179	.0807		1.233	1.233
220	.5287	.0968		1.260	1.259
230	.5394	.1151		1.289	1.288
240	.5501	.1361		1.321	1.321
250	.5608	.1621		1.358	1.358
260	.5715	.1936		1.400	1.401
270	.5823	.2343		1.451	1.449
280	.5930	.2884		1.516	1.509
290	.6037	.3578		1.596	1.579
300	.6144	.4448		1.694	1.681

TABLE II - 1

LIQUID VOLUME

Ethyl Acetate

T_c = 522		f unit = 86.35			
V_0 = .7043 - .7043 - .7771 cm^3/g					
T	V2	V3	D_s	V(calc.)	V(obs)
0	.3771	.0016		1.083	1.082
10	.3909	.0023		1.098	1.096
20	.4047	.0031		1.112	1.110
30	.4185	.0047		1.128	1.135
40	.4323	.0062		1.143	1.141
50	.4461	.0078		1.158	1.158
60	.4599	.0109		1.175	1.175
70	.4737	.0148		1.193	1.194
80	.4875	.0194		1.211	1.213
90	.5013	.0256		1.231	1.233
100	.5151	.0326		1.252	1.254
110	.5290	.0420		1.275	1.277
120	.5428	.0528		1.300	1.302
130	.5566	.0653		1.326	1.327
140	.5704	.0808		1.356	1.355
150	.5842	.0971		1.386	1.387
160	.5980	.1181		1.420	1.422
170	.6118	.1422		1.458	1.460
180	.6256	.1710		1.501	1.503
190	.6394	.2067		1.550	1.553
200	.6532	.2549		1.612	1.610
210	.6670	.3225		1.694	1.682
220	.6808	.4088		1.794	1.771

TABLE II - 1

LIQUID VOLUME

Ethyl Choride

T_c = 461 f unit = 79.55

V_0 = .7346 - .6545 - .7346 cm^3/g

T	V2	V3	D_s	V(calc.)	V(obs)
20	.3761	.0125		1.123	1.119
30	.3889	.0169		1.140	1.138
40	.4018	.0228		1.159	1.159
50	.4146	.0309		1.180	1.181
60	.4274	.0397		1.202	1.204
70	.4402	.0507		1.226	1.229
80	.4531	.0639		1.252	1.256
90	.4659	.0801		1.281	1.287
100	.4787	.0984		1.312	1.320
110	.4916	.1212		1.347	1.357
120	.5044	.1477		1.387	1.399
130	.5172	.1814		1.433	1.447
140	.5300	.2255		1.490	1.504
150	.5429	.2872		1.565	1.572
160	.5557	.3746		1.665	1.661
170	.5685	.4856		1.789	1.789

TABLE II - 1

LIQUID VOLUME

Ethanethiol

T_c= 498 f unit = 83.65

V_0 = 7552 - .7552 - .7629 cm^3/g

T	V2	V3	D_s	V(calc.)	V(obs)
0	.4044	.0031		1.163	1.160
10	.4192	.0038		1.178	1.183
20	.4340	.0053		1.195	1.196
30	.4488	.0076		1.212	

40	.4636	.0107		1.230	1.227
50	.4784	.0137		1.247	1.245
60	.4932	.0183		1.267	1.266
70	.5080	.0244		1.288	1.287
80	.5228	.0320		1.310	1.312
90	.5376	.0412		1.334	1.335
100	.5524	.0519		1.360	1.361
110	.5672	.0648		1.387	1.387
120	.5820	.0809		1.108	1.416
130	.5968	.0969		1.449	1.451
140	.6116	.1182		1.485	1.488
150	.6264	.1442		1.526	1.531
160	.6412	.1747		1.571	1.577
170	.6560	.2144		1.626	1.631
180	.6708	.2647		1.691	1.695
190	.6856	.3364		1.777	1.773
200	.6904	.4318		1.887	1.873

Supplement

This supplement to the original paper II in the liquid series has been prepared as a means of answering some questions that have been raised concerning the application of equation (3), the volume-temperature relationship, to liquids other than those of the simple organic type.

The particular advantage of a mathematical relation of this kind derived entirely from sound theoretical premises by logical and mathematical processes is that such a relation has no limitations. In its most general form this volume relationship is universally applicable throughout the entire range of the liquid state. The original paper showed that it is valid at all liquid temperatures and stated that it is applicable to all types of liquids, although the tabulated examples were limited to simple organic Compounds. The present supplement amplifies this statement by adding examples of other liquid types., including inorganic liquids., liquid metals and other elements, and fused salts. In the next paper in the series it will be shown that the same mathematical expressions can be applied to the calculation of liquid volumes under pressure, thus completing the coverage of the entire area in which the liquid state exists. The opening statement of this paragraph can then be applied in reverse; that is,, the demonstration that there are no limitations on the applicability of the mathematical relationship is strong evidence of the validity of the theoretical premises and of the processes by which the relationship was derived from those premises.

In equation (3) the term T in its general significance refers to the effective temperature rather than to the measured temperature. As long as the application of the equation is limited to simple organic compounds of the type covered in Tables II - 1 and III - 2 this distinction can be ignored as the effective temperature for these compounds is equal to the measured temperature. In general., however., the effective temperature is T/n, where n is an integral value ranging from 1 to 16. For general application the expression T/510.2 in equation (3) must therefore be modified to T/510.2 n as indicated in the last paragraph of paper II. The volume calculations for any liquid can then be carried out in the manner previously described.

In order to distinguish between this temperature factor n and the number of volumetric groups in the liquid molecule the symbols set and n_v will be used in the following discussion. Most of the cam, inorganic compounds which are liquid at room temperature have the same unit value of n_t as the organic compounds of the previous tabulations. Table II - 2 gives the volumetric data for CCl_4, which can quality either as organic or inorganic., depending on the definition that-is used, and for SO_2 and HCl, which are definitely inorganic. Also included in this table are similar data for hydrogen and fluorine, two elements with $n_t = 1$.

One of the influences which may increase the temperature factor n_t is a greater degree of molecular complexity such as that which characterizes the-condensed aromatic compounds, for example. Most of the complex aromatic liquids have $n_t = 2$. Table II - 3 gives the volumetric data for water ($n_t = 2$), an inorganic liquid with a similarly complex molecular structure. Because of the relatively large solid state increments the quantity $V_S - V_L$ has been determined individually for each temperature in this table using $V_S = 1.085$. Otherwise the calculations involved in the determination of these volumes are identical with those previously described.

The liquids thus far discussed are composed entirely of electronegative elements (for this purpose carbon and hydrogen which are on the borderline between electropositive and electronegative, are included in the electronegative class), and principally of those elements in this class which either (1) have atomic weights below 11 or (2) have unit valence. If both the mass and the valence of the principal constituent or constituents exceed these limits the temperature factor n_t is greater than unity. Thus sulfur and phosphorus have n_t values of 4 and 3 respectively. We may sum up the foregoing by saying that the extreme electronegative liquids ordinarily take the minimum n_t value, unity, and n_t increases as the liquid components move toward the electropositive side., either by increase of valence or by increase in the atomic mass. Conversely, the extreme electropositive liquids, the heavy liquid metals, ordinarily take the maximum n_t value, 16.

Table II - 4 shows the volumes of several liquids with temperature factors above 2. In calculating these volumes it has been assumed that the first and second dimension values of V_0 are equal. This appears to be the general rule in this class of compounds and in any event it would not be possible to verify the existence of any small difference as the experimental volumes of these liquids are subject to considerable uncertainty because of the unfavorable temperature conditions under which the measurements must be made. There is no appreciable third dimension component in the temperature range of Table II - 4 and only one V_0 value is therefore shown.

The n_t values for compounds of electropositive and electronegative elements are intermediate between the two extremes, as would be expected. Table II - 5 shows the pattern of values for the simplest compounds of this type, the alkali halides. Here we find some half-integral values: evidently averages of integral values for each of the positive and negative components. In Table II - 6 which follows, the number of volumetric units per formula molecule, n_v, is indicated for each of these same compounds. Table II - 7 then gives the calculated and experimental volumes at two different temperatures within the liquid range. The previous comments with respect to Table II - 4 also apply to Table II - 7.

TABLE II - 2

LIQUID VOLUME ($n_t = 1$)

Hydrogen $V_0 = 9.318 - 9.318 - 10.459$ cm^3/g

T	V_2	V_3	V calc.	V obs.
-257	.298	3.598	13.21	13.35
-253	.363	4.466	14.15	14.03
-250	.419	5.449	15.19	14.87
-246	.503	7.269	17.09	16.53
-243	.550	8.409	18.28	18.52

TABLE II - 2

LIQUID VOLUME ($n_t = 1$)

Fluorine $V_0 = .5241 - .4939 - .5543$ cm^3/g

T	V_2	V_3	V calc.	V obs.
-208	.0632	.0233	.610	.610
-203	.0677	.0268	.621	.620

-198	.0731	.0366	.634	.634
-193	.0775	.0438	.645	.646
-190	.0810	.05l0	.656	.657
-188	.0825	.0543	.661	.662

TABLE II - 2

LIQUID VOLUME ($n_t = 1$)

Hydrochloric Acid $V_0 = .6104 - .6025 - .6498 \ cm^3/g$

T	V_2	V_3	V calc.	V obs.
-80	.2283	.0l36	.852	.849
-70	.2398	.0l95	.870	.869
-60	.2518	.0273	.890	.891
-50	.2639	.0377	.912	.915
-40	.2753	.0513	.937	.940
-30	.2874	.0676	.965	.970
-20	.2988	.0884	.998	1.003
-10	.3109	.1124	1.034	1.040
0	.3229	.1443	1.078	1.082
10	.3344	.1891	1.134	1.135
20	.3464	.2541	1.211	1.203

TABLE II - 2

LIQUID VOLUME ($n_t = 1$)

Sulfur Dioxode $V_0 = .4394 - .4663 - .4932 \ cm^3/g$

T	V_2	V_3	V calc.	V obs.
-50	.2042	.0015	.645	.642
-40	.2131	.0025	.655	.652
-30	.2224	.0035	.665	.663
-20	.2313	.0049	.676	.674

-10	.2406	.0069	.687	.686
0	.2499	.0094	.699	.697
10	.2588	.0128	.711	.710
20	.2681	.0173	.725	.723
30	.2770	.0232	.740	.738
40	.2863	.0301	.756	.754
50	.2956	.0385	.774	.772
60	.3045	.0483	.792	.792
70	.3138	.0617	.815	.814
80	.3227	.0764	.839	.838
90	.3320	.0942	.866	.866
100	.3413	.1159	.897	.898
110	.3502	.1450	.935	.936
120	.3595	.1850	.984	.982
130	.3684	.2436	1.051	1.045
140	.3777	.3191	1.136	1.136

TABLE II - 2

LIQUID VOLUME ($n_t = 1$)

Carbon Tetrachloride $V_0 = .4108 - .3772 - .4108$ cm^3/g

T	V_2	V_3	V calc.	V obs.
0	.2019	.0004	.613	.612
10	.2093	.0004	.691	.620
20	.2167	.0008	.628	.627
30	.2241	.0012	.636	.635
40	.2315	.0016	.644	.643
50	.2388	.0021	.652	.651
60	.2462	.0029	.660	.660
70	.2536	.0037	.668	.668

80	.2610	.0053	.677	.677
90	.2684	.0070	.686	.687
100	.2758	.0090	.696	.697
110	.2832	.0115	.706	.708
120	.2906	.0148	.716	.719
130	.2980	.0189	.728	.731
140	.3054	.0234	.740	.744
150	.3128	.0292	.753	.757
160	.3201	.0357	.767	.770
170	.3275	.4444	.783	.785
180	.3349	.0534	.799	.802
190	.3423	.0637	.817	.820
200	.3497	.0760	.837	.841
210	.3571	.0g04	.858	.864
220	.3645	.1126	.888	.891
230	.3719	.1323	.915	.921
240	.3793	.1651	.955	.958
250	.3867	.2070	1.005	1.002
260	.3941	.2604	1.065	1.063

<table>
<tr><th colspan="6">TABLE II - 3</th></tr>
<tr><th colspan="6">LIQUID VOLUME (n_t)</th></tr>
<tr><th colspan="2">Water n_t = 4</th><th colspan="4">V_0 = .7640 - .7640 - .8769 cm^3/g</th></tr>
<tr><th>T</th><th>V_2</th><th>V_3</th><th>Ds</th><th>V(calc.)</th><th>V(obs.)</th></tr>
<tr><td>0</td><td>.2048</td><td></td><td>.0312</td><td>1.0000</td><td>1.0002</td></tr>
<tr><td>10</td><td>.2124</td><td></td><td>.0242</td><td>1.0006</td><td>1.0004</td></tr>
<tr><td>20</td><td>.2193</td><td></td><td>.0185</td><td>1.0018</td><td>1.0018</td></tr>
<tr><td>30</td><td>.2269</td><td></td><td>.0137</td><td>1.0046</td><td>1.0044</td></tr>
<tr><td>40</td><td>.2345</td><td></td><td>.0099</td><td>1.0084</td><td>1.0079</td></tr>
<tr><td>50</td><td>.2422</td><td>.0009</td><td>.0068</td><td>1.0139</td><td>1.0121</td></tr>
</table>

60	.2493	.0009	.0048	1.0188	1.0171
70	.2567	.0009	.0032	1.0248	1.0228
80	.2643	.0018	.0020	1.0321	1.0290
90	.2720	.0038	.0012	1.0390	1.0359
100	.2796	.0026	.0007	1.0469	1.0435
110	.2865	.0035	.0004	1.0544	1.0515
120	.2941	.0053	.0002	1.0636	1.0603
130	.3018	.0061		1.0719	1.0697
140	.3094	.0079		1.0813	1.0798
150	.3171	.0114		1.0925	1.0906
160	.3239	.0140		1.1019	1.1021
170	.3316	.0184		1.1140	1.1144
180	.3392	.0228		1.1260	1.1275
190	.3469	.0289		1.1398	1.1275
200	.3545	.0360		1.1545	1.1565
210	.3614	.0447		1.1703	1.1726
220	.3690	.0544		1.1874	1.1900
230	.3767	.0658		1.2065	1.2087
240	.3842	.0789		1.2272	1,2291
250	.3919	.0947		1.2506	1.2512
260	.3988	.1114		1.2742	1.2755
270	.4064	.1315		1.3019	1.3023
280	.4141	.1543		1.3324	1.3321
290	.4217	.1806		1.3663	1.3655
300	.4294	.2131		1.4065	1.4036

<table>
<tr><td colspan="2">TABLE II - 4</td></tr>
<tr><td colspan="2">LIQUID VOLUME</td></tr>
<tr><td colspan="2">Sulfur</td></tr>
<tr><td>$n_t = 4$</td><td>$V_0 = .4578$</td></tr>
</table>

T	V_2	V(calc.)	V(obs.)
115	.0869	.545	.552
134	.0911	.549	.557
158	.0966	.555	.563
178	.1012	.559	.565
210	.1085	.567	.570
239	.1149	.573	.576
278	.1236	.582	.584
357	.1415	.600	.602

TABLE II - 4

LIQUID VOLUME

Lithium

$n_t = 9$ $V_0 = 1.7729$

T	V_2	V(calc.)	V(obs.)
200	.1826	1.96	1.97
400	.2606	2.03	2.04
600	.3369	2.31	2.11
800	.4149	2.19	2.19
1000	.4911	2.26	2.27

TABLE II - 4

LIQUID VOLUME

Silver

$n_t = 16$ $V_0 = .0923$

T	V_2	V(calc.)	V(obs.)
960	.0139	.106	.105
1092	.0154	.108	.109
1195	.0166	.109	.110
1300	.0178	.110	.111

TABLE II - 4

LIQUID VOLUME

Tin

$n_t = 16$		$V_0 = .1331$	
T	V_2	V(calc.)	V(obs.)
300	.0093	.142	.145
450	.0118	.145	.147
600	.0142	.147	.149
700	.0158	.149	.150
800	.0174	.150	.151
900	.0192	.152	.153
1000	.0208	.154	.154
1100	.0224	.155	.156
1200	.0241	.157	.156

TABLE II - 5

TEMPERTURE FACTORS

	Li	Na	K	Rb	Cs
F	4	4	3½	3½	3
Cl	4	3½	3½	3	3
Br	3½	3½	3	3	3
I	3½	3	3	3	2½

TABLE II - 6

VOLUMETRIC UNITS

	Li(½)	Na(1)	)K(1½)	Rb(2)	Cs(2½)
F(½)	1	1½	2	2½	3½
Cl(1½)	2	2½	3	3½	4
Br(2)	2½	3	3½	4	4½

I(2½)	3	3½	4	4½	5

TABLE II - 7

LIQUID VOLUME

	T	V_0	V_2	V calc.	V obs.
LiF	887	.3617	.2058	.568	.558
	1058		.2358	.598	.587
LiCl	626	.4697	.2071	.677	.668
	900		.2701	.740	.727
LiBr	547	.2701	.1240	.394	.392
	700		.1472	.417	.410
NaF	1017	.3351	.2118	.547	.517
	1214		.2443	.579	.549
NaCi	809	.4013	.2432	.645	.650
	1010		.2885	.690	.697
NaBr	785	.2735	.1625	.436	.433
	954		.1882	.462	.460
NaI	675	.2267	.1406	.367	.367
	724		.1478	.375	.374
KF	913	.3230	.2145	.538	.534
	1054		.2400	.563	.563
KCl	785	.4161	.2467	.663	.658
	958		.2871	.703	.706
KBr	751	.2856	.1911	.477	.473
	945		.2273	.513	.512
KI	700	.2538	.1614	.415	.411
	751		.1698	.424	.420
RbF	820	.2245	.1374	.362	.347
	1006		.1610	.386	.372

RbCl	734	.2858	.1881	.474	.476
	822		.2046	.490	.493
RbBr	697	.2269	.1439	.371	.372
	780		.1561	.383	.384
RbI	700	.2177	.1385	.356	.357
	800		.1526	.370	.372
CsF	720	.2238	.1452	.369	.368
	824		.1605	.384	.386
CsCl	661	.2229	.1360	.359	.360
	741		.1478	.371	.372
CsBr	662	.1984	.1212	.320	.321
	743		.1317	.330	.333
CsI	639	.1806	.1291	.310	.315
	701		.1380	.319	.323

III

Volume - Relation to Composition

This is the third of a series of papers describing a complete new theory of the liquid state. The two previous publications have outlined the new theoretical structure and have established the mathematical relationship between volume and temperature. We now continue the volume study by examining the relation of this property to chemical composition and molecular structure.

From the fundamental postulates on which this entire work is based it follows directly that volume exists only in discrete units. In the book previously published the factors affecting the size of these units were examined and it was shown that the unit in the solid state is relatively small in comparison with the cube of the inter-atomic distance so that the succession of possible values of the specific volume under the-temperature and pressure conditions normally prevailing during our observations is essentially continuous.3 The unit of volume applicable to the liquid and gaseous states, on the other hand is of the same general order of magnitude as the cube of the inter-atomic distance. At the initial point of the liquid state, which coincides with the end point of the solid state, the solid and liquid volumes would be expected to be identical, aside from minor variations due to differences in the geometric packing, just as the liquid volume at the critical temperature is identical with the vapor volume. Because of the relatively large size of the liquid unit, however, the liquid volume includes an increment Δ, which is necessary to bring the solid volume up to the next complete liquid unit. We may therefore express the initial liquid volumes, V_0, as

$$V_0 = V_s + \Delta \qquad (4)$$

Since the range of values of the inter-atomic distance is relatively narrow the number of units of volume occupied by each independent volumetric group in the liquid is also restricted to a narrow range of values. For reasons which Win be discussed in a subsequent publication it will be convenient to designate the smallest liquid volume as a half unit rather than a full unit and on this basis the initial liquid volumes corresponding to the different solid-state inter-atomic ½ unit to 2½ units. The great majority of the structural distances range from 2 groups and independent atoms which enter into the composition of the substances that are liquid under the temperature and pressure conditions normally prevailing on the surface of the earth occupy one volumetric unit each. For present purposes there is no need to distinguish between n one-unit groups of this kind and a single group occupying n units, and when the number of volumetric group's corresponding to any particular structural complex is identified in the subsequent discussion it should be understood that any multi-unit group which may be included is being treated as if it were an equivalent number of one-unit groups.

With this understanding as to the meaning of the term "volumetric group" we may now observe that the volume of a liquid, aside from a small correction factor due to the geometric orientation in the solid state dimensions which will be discussed shortly, is determined entirely by the number of volumetric groups which it contains, irrespective of the chemical composition of those groups, just as the volume of a gas is determined by the number of molecules irrespective of their composition. Replacing the heavy atoms in metal-organic compounds can produce same very striking illustrations of this fact by light organic groups. For instance, if we replace the one-unit metallic atom in diethyl mercury by the one unit CO group, producing diethyl ketone, we do not change the molecular volume in the least even though we have taken out two hundred units of mass and put back only twenty-eight. Similarly diethyl amine (molecular weight 73.14) has practically the same molecular volume as diethyl cadmium (molecular weight 170.53) and so on,

Because of the flexibility introduced by the freedom of movement in one dimension the liquid groups are able to arrange themselves in the closest possible geometric pattern and the geometric space occupied by these groups is therefore reduced by the factor .707 which expresses the effect of the close-packed arrangement. A further reduction in the size of the volumetric unit itself is possible where-conditions are such that close-packing can also be achieved In the one dimension that retains the solid-state characteristics throughout the liquid temperature range. Where this geometric arrangement prevails the size of the volumetric unit is reduced by the cube root of .707, or .891, but since this arrangement is a property of the individual liquid group rather than of the molecule as a-whole the average value applicable to the molecule varies with the composition. Representing this average value by its and the number of liquid groups by n, we have the relation

$$V_0 = .707\ nk_s \text{ natural units of volume} \qquad (5)$$

In order to convert equation 5 to conventional units so that comparisons can be made between theoretical and observed volumes it is necessary to multiply the expression .707 nks by the cgs value of the natural unit of liquid volume. It will also be convenient to deal With the specific volume rather than the molecular volume and for this purpose we divide by the cgs value of the natural unit of mass, Applying the previously published values of these conversion factors, 4 equation 5 becomes

$$V_0 = 10.5326\ nk_s/m \text{ cm}^3/\text{g} \qquad (6)$$

Where the inter-atomic bonds are all alike the value of n can be calculated from the solid-state interatomic distance. In complex substances a purely theoretical calculation of this kind encounters some difficulties which have not been resolved as yet, but for the most part the values applicable to the organic structural groups can be recognized without calculation. Each of the common interior groups such as CH_2, CH, and CO. constitutes one volumetric unit. Each CH_3 substitution (addition of CH_2) adds one unit. Thus there are two volumetric units in $CHCH_3$, three in $C(CH_3)_2$, and so on. The CH_3 groups in the end positions of the aliphatic chains occupy two units each. The corresponding CH group in the olefins and alkadienes acts as 1½ units and the lone carbon atom in the acetylenes is a single unit. Similar values can be assigned to each of the elements and structural groups, which are capable of replacing hydrogen in the compounds of the organic division.

Since the inter-atomic bonds have directional characteristics the strength of these bonds can-be altered by changes in orientation within the molecule and in some cases variations of this kind alter the number of effective volumetric groups. The acid radical CO·OH, for example, can act either as a combination of independent CO and OH groups, each occupying one volumetric unit, or as a more strongly bound COOH structure occupying 1½ volumetric units. Close associations of this kind are quite common in simple molecules composed of no more than two or three structural groups.

Inasmuch as the motion in each of the liquid dimensions is independent of that in the other two, it is possible for differences of this kind to exist between the separate dimensions of motion in the same molecule as well as between molecules, and some of the common organic families-the normal alcohols and the aliphatic acids, for example-follow such a pattern. More commonly the value of n remains constant and to simplify this initial presentation the tabular comparisons with experimental values will be limited to liquids of this type.

Dimensional differences in the value of the solid-state structural factor k_s are normal. The initial dimension has considerable latitude for variation because of the close relationship to the solid state. Each volumetric group must conform to one of the two possible its values, .891 or 1.00, but in a multi-group molecule the number of groups taking each value may vary all the way form one extreme to the other. The same considerations apply to the second-dimension except that the greater freedom of movement in this dimension tends to favor the close-packed arrangement and the value of its is generally lower than in the initial dimension. The minimum value .891 is very common in the case of the larger molecules. No method has been developed thus far for calculating the average factor in these two dimensions on a purely theoretical basis and for the present it will be necessary to obtain it from the series relationships in the third dimension there are no solid-state characteristics remaining and there is no solid-state geometric effect. The k_s value in this dimension is therefore 1.00 in all cases.

Table III - 1 illustrates the nature of the progression of its factors that takes place in a homologous series of compounds and shows how the individual values of this factor can be derived from the series pattern. In this series the chlorine molecule occupies 1½ volumetric units. The hydrocarbon groups take their normal values: two units for CH_3 and one unit for CH_2. Lethal chloride thus occupies 3½ volumetric units and each added CH group increases the volume by one unit. Applying these values of n to equation 6 with k_s equal to 1.00 we arrive at the normal initial volume, V_0. Since k_s is always unity in the third dimension this value of V_0 also represents the initial V_3 volume and the latter quantity is not shown I of the separately in the tabulations. As indicated in the column headed n_s, 1½ of the

3½ volumetric units in methyl chloride have the .891 factor in the first dimension, but in the higher compounds of the series all groups take the full 1.00 factors. The second dimension factor is .891 in all-volumetric units of the first three members of the series. The next two added CH_2 groups take the 1.00 factor, after which all further additions revert to .891. By applying these its factors to the corresponding values of V_0 we obtain the V_1 and V_2 initial volumes shown in the table. With these values available we may then calculate the liquid volume at any specified temperature by the methods outlined in the preceding papers.

Table III - 2 presents a comparison of calculated and experimental volumes for a number of common organic families. In order to enable including a large number and variety of compounds the comparisons have been limited to a single temperature in each case and to further simplify the presentation this temperature has been selected from the range in which no solid-state adjustment is necessary. In a long series it is, of course, necessary to increase the reference temperature as the molecules became larger and the melting points move upward. As indicated in the preceding discussion only three items are needed for a complete definition of the volume pattern of a compound of the type under consideration: the effective number of volumetric groups, n, and the value of n_s, the number of volumetric groups with the solid-state close packing, separately for the first and second dimensions. The two columns headed n and n_s therefore furnish all of the basic information that is necessary for the calculation of the theoretical volumes of column 4.

REFERENCES

(Combined list for the first three papers)

1. Larson D. B., The Structure of the Physical Universe, published by the author, 755 N. E. Royal Court. Portland 121, Oregon., 1959.
2. Ibid., Page 40.
3. Ibid., Appendix A.
4. Ibid., Page 30.
10. For a discussion-of this point see Hildebrand and Scott, The Solubility of Non-Electrolytes, 3rd Edition., Reinhold., Now York, 1959.
11. Pfizer, K. S., Journal of the American Chemical Society. 77-3427.
12. The experimental values in the tables have been taken from Timmermans' "Physico-chemical Constants of Pure Organic Compounds" or from the publications of the American Petroleum Institute Research Project 44 if available from one of those sources. Most of the other values are either from the International Critical Tables or from the extensive work of Vogel and collaborators published in the Journal of the Chemical Society.

TABLE III - I

INITIAL VOLUMES - ALKYL CHLORIDES

	n	V_0 (and V_3)	n_s	Dimension 1 Av. k_s	V_1	n_s	Dimension 2 Av k_s	V_1
Methyl	3½	.7301	2½	.922	.6732	3½	.891	.6506
Ethyl	4½	.7346	0	1.000	.7346	4½	.891	.6545
Propyl	5½	.7376	0	1.000	.7376	5½	.891	.6571
Butyl	6½	.7396	0	1.000	.7396	5½	.908	.6713
Amyl	7½	.7410	0	1.000	.7410	5½	.920	.6817
Hexyl	8½	.7422	0	1.000	.7422	6½	.917	.6803
Heptyl	9½	.7431	0	1.000	.7431	7½	.914	.6791
0etyl	10½	.7439	0	1.000	.7439	8½	.912	.6782
Nonyl	13½	.7445	0	1.000	.7445	9½	.910	.6774
Decyl	12½	.7450	0	1.000	.7450	10½	.908	.6767
Undecyl	13½	.7454	0	1.000	.7454	11½	.907	.6761
Dodecyl	14½	.7458	0	1.000	.7458	12½	.906	.6756

TABLE III - 2

LIQUID VOLUME

Paraffins

	n	n_s	T	V(calc)	V(obs)
Propane	5	1-1	-50	1.697	1.695
Butane	6	1-1	-50	1.538	1.536
Pentane	7	1-1	0	1.552	1.550
Hecate	8	1-2	0	1.477	1.477
Heptane	9	1-3	50	1.519	1.519
Octane	10	1-4	50	1.474	1.474
Nonane	11	1-5	100	1.531	1.530
Decane	12	1½-6	100	1.496	1.497
Undecane	13	1½-7	150	1.562	1.563

Dodecane	14	2-8	150	1.534	1.536
Tridecane	15	2-9	150	1.515	1.514
Tetradecane	16	2½-10	150	1.496	1.496
Pentadecane	17	3-11	200	1.564	1.568
Hexadecane	18	3½-12	200	1.548	1.551
Heptadecane	19	4-13	200	1.534	1.536
Octadecane	20	4½-14	200	1.521	1.523
Nonadecane	21	5-15	200	1.510	1.511
Eicosane	22	5½-16	200	1.501	1.501

Olefins					
	n	n_s	T	V(calc)	V(obs)
Ethylene	3½	0-3½	-100	1.756	1.774
Propane	4½	0-0	0	1.830	1.834
Carotene	5½	0-0	0	1.611	1.616
1-Pentene	6½	0-0	0	1.507	1.512
1-Hexene	7½	0-0	50	1.549	1.551
1-Heptene	8½	0-1	50	1.490	1.491
Carotene	9½	0-2	50	1.447	1.449
1-Nonene	10½	0-3	50	1.416	1.417
1-Decene	11½	½-4	100	1.473	1.474
1-Undecene	12½	½-5	100	1.450	1.450
1-Dodecene	13½	1-6	100	1.428	1.429
1-Tridecene	14½	1-7	100	1.413	1.414
1-Tetradecene	15½	1½-8	120	1,429	1.429
1-Pentadecene	16½	2-9	120	1.416	1.416

Ketones					
	n	n_s	T	V(calc)	V(obs)
Diethyl	7	5-7	50	1.276	1.274

Ethyl Propyl	8	4½-8	50	1.267	1.269
Ethyl Butyl	9	4-9	50	1.260	1.259
Ethyl Amyl	10	3½-10	50	1.255	1.254
Ethyl Hexyl	11	3-11	61	1.265	1.263
Ethyl Heptyl	12	3-12	61	1.259	1.258

Amines

	n	n_s	T	V(calc)	V(obs)
Methyl	3	2-2½	20	1.511	1.511
Ethyl	4	½-1	20	1.461	1.464
Propyl	5	0-1½	20	1.394	1.390
Butyl	6	0-1½	20	1.351	1.351
Amur	7	0-1½	20	1.323	1.322
Hexyl	8	0-1½	40.5	1.336	1.335

Thiols

	n	n_s	T	V(calc)	V(obs)
1-Propanethiol	6	4½-6	41	1.222	1.222
1-Butanethiol	7	4-7	80	1.280	1.279
1-Pentanethiol	8	3½-8	100	1.306	1.305
1-Hexanethiol	9	3½-9	100	1.296	1.295
1-Heptanethiol	10	3½-10	100	1.288	1.289
1-Octanethiol	11	3½-11	100	1.283	1.284
1-Nonanethiol	12	3½-12	100	1.279	1.281

Chlorides

	n	n_s	T	V(calc)	V(obs)
Methyl	3½	2½-3½	30	1.107	1.114
Ethyl	4½	0-4½	30	1.140	1.138
Propyl	5½	0-5½	30	1.135	1.136

Beryl	6½	0-5½	30	1.141	1.142
Amyl	7½	0-5½	42	1.165	1.164
Hexyl	8½	0-6½	87	1.229	1.226
Heptyl	9½	0-7½	87	1.226	1.225
Octyl	10½	0-8½	87	1.225	1.221
Nonyl	11½	0-9½	87	1.223	1.221
Decyl	12½	0-10½	86	1.221	1.224
Undecyl	13½	0-11½	87	1.223	1.222
Dodecyl	14½	0-12½	87	1.223	1.223

Bromides					
	n	n_s	T	V(calc)	V(obs)
Ethyl	5	5-5	30	.690	.694
Propyl	6	5-5	62	.779	.783
Butyl	7	5-5	89	.855	.853
Amyl	8	4-8	67	.882	.883
Hexyl	9	4-9	86	.909	.916
Heptyl	10	4-10	86	.933	.934
Octyl	11	4-11	87	.954	.957
Nonyl	12	4-12	87	.972	.974

Sulfides					
	n	n_s	T	V(calc)	V(obs)
Lethal	4½	0-2½	90	1.310	1.309
Ethyl	7	3½-7	90	1.305	1.307
Propel	9	2½-9	87	1.285	1.284
Butyl	11	2-11	88	1.278	1.277
Amyl	13	2-13	87	1.266	1.267
Hexyl	15	2-15	89	1.262	1.263
Heptyl	17	2-17	88	1,256	1,256

C_7 Esters					
	n	n_s	T	V(calc)	V(obs)
Hexyl forbade	9½	3½-9½	60	1.187	1.185
Amyl acetate	9½	3-9½	62	1.194	1.193
Butyl propionate	9½	2½-9½	61	1.197	1.195
Propyl butyrate	9½	2-9½	61	1.202	1.202
Ethyl Lacerate	9½	2½-9½	64	1.201	1.200
Methyl caproate	9½	4½-9½	61	1.180	1.182

IV

Volume - Relation to Pressure

The preceding papers in this series have developed the general characteristics of the liquid state from new fundamental theory and have shown that on this new theoretical basis the volume of a liquid molecule consists of three separate components which respond to changes in temperature in the foil owing manner: the initial component remains constant, the second component varies in direct proportion to the effective temperature, and the third component is generated isothermally at the critical temperature. Because of the distribution of molecular velocities in the liquid aggregate the number of molecules which are individually at or above the critical temperature is a matter of probability and the third volume component of a liquid aggregate therefore followers a probability function which represents the proportion of critical molecules in the total.

This paper will extend the volume relationships to liquids under pressure and will show that in its general aspects the response to variations in pressure is identical with the response to variations in temperature; that is, the initial component remains constant, the second component varies in direct proportion to the reciprocal of the effective pressure, and the third volume component of the aggregate follows a probability function for the same reasons as in the case of temperature variations. Equation (3), the volume-temperature relation previously developed, can therefore be extended to apply to liquids under pressure.

In calculating the volume of a liquid at temperature T and pressure P, we first determine the three volume components at temperature T and saturation pressure in the manner described in paper II. We will call these components V_I, V_{II}, and V_{III}. The initial component, V_I, is not affected by either temperature or pressure. The second component, V_{II}, responds to an increase in effective pressure in the same manner as to a decrease in effective temperature. It should be noted, however, that this effective pressure includes the pressure equivalent of the cohesive force between the liquid molecules and an evaluation of this initial pressure, as we will call it, is the first step toward a determination of the second volume component at pressure P.

The unit of pressure corresponding to the 510.2 degree temperature unit is 415.84 atm. or 429.8 kg/cm^2, where the initial specific volume, V_0, is 1.00. In order to avoid an extended theoretical discussion at this point we will consider this as an empirically determined value for the present, as was done with the temperature unit. For any value of V_0 other than unity the pressure unit becomes 415.84./$V_0^{2/3}$ atm. This is the pressure exerted against each independent liquid unit within the liquid molecule. The external pressure is exerted against the molecule as a whole rather than against the individual units and where there arc n_v units in the liquid molecule, the pressure exerted against each unit is P/n_v. For purposes of calculation, however, it will be more convenient to use the external pressure as the reference value and on this basis the external pressure is P and the initial pressure is

$$P_0 = 415.84\ n_v / V_0^{2/3} \text{ atm.} \tag{7}$$

Since the application of pressure is not exactly equivalent to a decrease in thermal energy it is quite possible that the nature of the atomic association that participates in the pressure process may differ from that which participates in the temperature process. The values of n_v applicable to equation (7) are therefore not necessarily identical with those, which were arrived at in paper III in connection with the evaluation of V_0. Such equality is quite common but there is a tendency to split up into a larger number of units in the pressure process, particularly in the case of the smaller molecules. In the limiting condition each atom is acting independently.

It should also be remembered that the previous determination of n_v was concerned only with a ratio: the number of volumetric units corresponding to the mass represented by the formula molecule. The initial pressure calculation, on the other hand, requires a knowledge of the absolute number of individual liquid units in the actual molecule and where the liquid molecule comprises two or more formula molecules the value of n_v applicable to equation (7) is the corresponding multiple of the value previously found. The value of n_v used in calculating the Cs_2 volumes in Table II-3, for instance, is 3, where we now find that the value that must be used in equation (7) is 9. This does not conflict with the previous determination; it merely means that the true liquid molecule is $(CS_2)_3$.

Another factor, which enters into the calculation of VII, is that above 510.2° K part of the V_{II} component is subject to only one-sixteenth of the total initial pressure. A complete theoretical explanation of this situation which exists beyond the unit temperature level is not available as yet, but it has been found that the proportion of high temperature volume at any temperature of observation can be computed from the normal probability function using 510.2° K as the base and one-fourth of this value as the probability unit. Up to 2/3 of 510.2° the lower initial pressure is applicable to the full amount thus calculated, beyond 8/9 of 510.2° it is applicable to half of the calculated value, and in between these points the effective proportion decreases linearly.

Turning now to the third component, V_{III}, we first obtain from our previous calculations the figure representing the number of probability units between temperature T and the critical temperature. Since this quantity will play an important part in the volume determinations it will be desirable to give it a name for convenient reference and we will therefore call it the probability index. To this probability index at saturation pressure we now add the increment corresponding, to the applied pressure, taking the previously established value 415.84 atm. as the probability unit. If the index is above 1.15 at saturation pressure we can proceed directly to a determination of V_{III}, first obtaining from the probability tables the probability value corresponding to the probability index at each individual pressure and then multiplying each of these probabilities by V_3, the third dimensioned value of V_0, to obtain V_{III}.

If the probability index is below 1.15 at saturation pressure the B component of the probability expression $\frac{1}{2}(\phi_A + \phi_B)$ has an appreciable magnitude and this introduces an additional operation into the calculations. The nature of this B component was not indicated very clearly by the way in which it enters into the computation of the saturation volume but its behavior under pressure is more enlightening. We have previously found that the A probability represents the proportion of the total number of molecules which have individually reached the critical temperature and consequently have acquired a volume component in the third dimension. These molecules are still subject to the cohesive forces of the liquid; that is, to the liquid initial pressure. Now we find that as the average temperature of the aggregate approaches closer to the critical temperature and more thermal energy is available some of the molecules escape from the cohesive forces, doubling their volume in the process. The B component of the probability represents the proportion of molecules in this condition and the expression $\frac{1}{2}\phi_B V_3$ is the volume added by this process at saturation pressure. The total volume of these B molecules at saturation is then twice this amount, or $0_B V_3$, and the A portion of the V_{III} volume, the part still subject to the initial pressure, is $\frac{1}{2}(\phi_A + \phi_B) V_3$. Dividing $\frac{1}{2}(\phi_A + \phi_B)$ by $\frac{1}{2}\phi_A$ gives us the percentage reduction in the A volume due to molecules shifting to the B status.

We now calculate the total A volume at each pressure by means of the expression $\frac{1}{2} \phi V_3$ and apply the foregoing reduction factor to arrive at the portion of the volume still remaining in the A condition. The B volume is subject only to the externally applied pressure and it varies in in$_v$erse proportion to that pressure. The effective volume at each pressure P is therefore obtained by application of the factor P_S/P to $\phi_B V_3$, the B volume at saturation pressure P_S.

As can be seen from this description, the whole operation of calculating the liquid volumes under pressure is carried out entirely on the basis of values previously determined in the course of computing the volumes at saturation pressure, with the exception of those cases where n_v must be redetermined, either because of an actual difference in the internal behavior of the molecule or because the liquid molecule is composed of more than one formula molecule. There are no "adjustable constants" which can be manipulated to fit the observed values; the volumes under pressure must conform to a fixed pattern in each case, or if there is any element of uncertainty present, must conform to some one of two or three possible alternate patterns. These are very stringent requirements and the degree of correlation between the calculated and observed volumes as shown by the tabulations, which follow, is therefore highly significant as an indication of the validity of the new theoretical principles on which the work is based.

To illustrate the method of calculation let us consider heptane at 30° C. By the methods of paper III we determine that n_v for heptane is 9 and the three values of the geometric factor are .9878, .9636, and 1.000. From these figures we obtain V_1 =

.9346, V_2 = .9117, and V_3 = .9461. Entering equation (3) with these three values we then calculate the volume components at 30° C and saturation pressure, obtaining V_I = .9346, V_{II} = .5417, and V_{III} = .0038. From our probability tables we find that at 30° C the volume originating above 510.2° K is 5.3 percent of the total V_{II} component, and on this basis we separate V_{II} into two parts: $V_{II}(L)$ = .5130 and $V_{II}(H)$ = .0287. Applying the previously determined values $n_v = 9$ and V_0 = .9461 to equation (7) we find that the initial pressure, P_0, effective against V_{II} (L) is 3884 atm. The initial pressure effective against $V_{II}(H)$ is then 1/16 x 3884 = 243 atm. To find the V_{II} components at each pressure we now reduce the saturation values of $V_{II}(L)$ and $V_{II}(H)$ by the effective pressure ratios. $P_n/(P + P_0)$ and $P_0/(16P + P_0)$ respectively. The results are shown in columns 2 and 3 of Table IV-1.

Next we evaluate the probability index at 30° C and saturation pressure by the methods of paper II, obtaining the value 2.68. To this we add the increment corresponding to each pressure, which we obtain by dividing the increase in pressure above the saturation level by 415.84 atm. The composite probability indexes thus derived are shown in column 4 of the table. Column 5 gives the values of ½ϕ corresponding to each index. Multiplying each of these values of ½ϕ by .9461 we arrive at the V_{III} component for each pressure as shown in column 6. Column 7 then indicates the total theoretical volume of the liquid aggregate, the sum of V_I (constant at .9346), $V_{II}(L)$ from column 2, $V_{II}(H)$ from column 3, and V_{III} from column 6. Column 8 shows the corresponding measured volumes for comparison.

In order to carry the comparisons into the pressure range above 351 atm., the highest pressure reached in the set of measurements listed in Table IV-1, we now turn to the work of Bridgman who gives us a set of values at 50° C, with the first observation at 1000 kg/cm^2 (approximately 1000 atm.) and increasing by steps of 1000 kg/cm^2 to a maximum of 10,000 kg/cm^2. Bridgman's results are reported as relative volumes based on the volume at 0° C and atmospheric pressure as the reference level. Our first requirement, therefore, is to compute from equation (3) the volume under these reference conditions, which we find to be 1.424 cm^3/g. m is value can then be used as a conversion factor to reduce the calculated volume components at 50° C and saturation pressure to Bridgman's relative basis. By this means we arrive at the following volumes: V_I = .656, $V_{II}(L)$ = .377, and $V_{II}(H)$ = .029. V_{III} is negligible in the pressure range of this work and can be disregarded. The volumes under pressure are then calculated in the manner described in the preceding paragraphs. Table IV-2 compares the results with Bridgman's values.

Table IV-3 summarizes the results of a number of similar calculations in the relatively low-pressure field. Since all of these calculations follow the regular pattern without exception, intermediate data such as the probability indexes have been omitted and the table shows only the separate volume components and the tot al calculated and measured volumes. The objective of the comparisons in this table is to show that there is a wide range of temperatures and substances in which the calculated and measured volumes agree within 0.5 percent at all experimental pressures. In some of the other sets of measurements, which have been examined during this investigation, the agreement is less satisfactory in certain portions of the pressure range but the general trend of the values follow the theoretical pattern in all cases.

The preceding papers have stressed the fact that the temperature term in equation (3) refers to the effective temperature: a quantity which is commonly identical with the measured temperature, but not necessarily so. The same is true of the pressure factors with which we are dealing in this paper. We have already seen that the pressure effective against the V_{II} volume component is substantially reduced beyond the unit temperature level (510.2° K). In some substances, chiefly outside the organic division, the pressure applicable to the V_{III} component is also subject to a reduction from P to P/n_p and two examples of this kind are included in Table IV-3: H_2S ($n_p = 2$) and NH_3 ($n_p = 3$).

Table IV-4 presents some further comparisons with Bridgman's measurements in the range up to 12,000 kg/cm^2. Some of his more recent work has extended to considerably higher pressures' reaching a level of 50,000 kg/cm^2 in a few instances. At these extreme pressures the transition to the solid state is well under way and the volumes of the liquid aggregates are modified quite substantially by the presence of solid molecules. Consideration of the volume situation in this pressure range will therefore be deferred to the next paper in this series, which will examine the characteristics of the liquid-solid transition. Some of the results at 12,000 kg/ cm^2 and below are also subject to this solid state effect and in these cases the tabular comparisons have not been carried beyond the point where the volume decrease due to solid molecules amounts to more than about .002. Double asterisks in the column of observed volumes indicate omissions due to this cause.

As mentioned in a previous paper, the scope of this investigation has been so broad that it has been physically impossible to study the "fine structure" of all of the relationships that have been covered, and it is quite possible that there may be factors of this kind which would alter the results slightly. Some additional uncertainty has been introduced by the use of the measured values of the vapor pressure at saturation. Since these uncertainties probably amount to something in the neighborhood of 0.1 percent there is no particular advantage in carrying the calculations to any higher degree of accuracy and it does not appear that such refinements as additional decimal places, fractional values of the probability indexes, etc., are justified at this stage of the project.

TABLE IV - 1								
LIQUID COMPRESSION - HEPTANE - 30° C								
P_0 = 3884 atm.		V_1 = .9346		V_2 = .9117			V_3 = .9461 cm^3/g	
P(atm.)	V_{II}(L)	V_{II}(H)	P.I.	½ϕ	V_{III}(A)	V_{III}(B)	V(calc)	V(obs)[13]
0	.5130	.0287	2.68	.004	.0038		1.480	1.480
7.12	.5121	.0279	2.70	.003	.0028		1.477	1.479

19.08	.5105	.0266	2.73	.003	.0028		1.475	1.476
31.04	.5089	.0254	2.75	.003	.0028		1.475	1.472
43.00	.5074	.0244	2.78	.003	.0028		1.469	1.470
52.31	.5062	.0236	2.81	.002	.0019		1.466	1.467
82.20	.5024	.0214	2.88	.002	.0019		1.460	1.761
112.10	.4986	.0196	2.95	.002	.0019		1.155	1.455
171.09	.4913	.0168	3.09	.001	.0009		1.444	1.444
231.68	.4841	.0147	3.24	-	-		1.433	1.433
291.46	.4772	.0130					1.425	1.423
351.25	.4705	.0117					1.417	1.413

TABLE IV - 2

LIQUID COMPRESSION - HEPTANE -50° C

P_0 = 4013 kg/cm^3		V_1 = .656			V_2 = .406 (relative)				
P	V_{II}(L)	V_{II}(H)	V(calc)	V(obs)[14]	P	V_{II}(L)	V_{II}(H)	V(calc)	V(obs)
1000	.302	.006	.964	.958	6000	.151	.001	.808	.815
2000	.252	.003	.911	.908	7000	.137	.001	.794	.800
3000	.261	.002	.874	.875	8000	.126	.001	.783	.7875
4000	.189	.002	.847	.851	9000	.116	.001	.773	.776
5000	.168	.001	.825	.831	10000	.108	.001	.765	.766

TABLE IV - 3

LIQUID COMPRESSION (LOW PRESSURES)

Basic Factors

	V_1	V_2	V_3	Units	P_0	
Propane	.8253	.8253	.8436	cu.ft./lb. mole	48860	psi
Butane	.017103	.017103	.017419	cu.ft./lb.	52014	psi
Pentane	.016116	.016116	.016371	cu.ft,/lb.	54218	psi
Hexane	1.3314	1.3131	1.3498	cu.ft./lb. mole	55839	psi

	83.11	81.97	84.26	cm^3/g mole	3800	atm.
Heptane	1.5002	1.4635	1.5187	cu.ft./lb. mole	57077	psi
	.9346	.9117	.9461	cm^3/g	3884	atm.
Octane	.9120	.8819	.9221	cm^3/g	4389	atm.
Nonane	1.8378	1.7640	1.8558	cu.ft./lb. mole	71940	psi
2-Methyl propane	.017416	.017416	.018867	cu.ft./lb.	46239	psi
3-Methyl pentane	.9512	.9512	.9778	cm^3/g	3800	atm.
2,2-Dimethyl butane	.9712	.9712	.9778	cm^3/g	4222	atm.
2,3-Dimethyl butane	.9578	.9512	.9778	cm^3/g	3800	atm.
2,2,4-Trimethyl pentane	.9221	.9019	.9221	cm^3/g	4389	atm.
Propene	.018045	.018045	.018045	cu.ft./lb.	50805	psi
1-Butene	.9278	.9278	1.0123	cu.ft./lb. mole	71798	psi
1-Pentene	.9762	.9762	1.0513	cm^3/g	5916	atm.
Benzene	.011547	.011547	.012962	cu.ft./lb.	84456	psi
Ammonia	.9642	1.0655	1.0823	cm^3/g	6312	atm.
Hydrogen Sulfide	.4033	.4033	.4217	cu.ft./lb. mole	87102	psi

In the second section of this table, which follows, the values of the individual volume components are given in the following units: cm^3/g x 10^4, cu.ft./lb. x 10^6, cm^3/g mole x 10^2, cu.ft./lb. mole x 10^4. Total volumes are exnpessed in the units listed above.

Specific Volumes

Propane 100° F (15)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	4660	235	1220	9	1.438	1. 441
2000	4568	186	921	5	1.393	1.394

3000	4479	155	697	3	1.359	1.358
4000	4394	132	514	2	1.330	1.329
5000	1312	115	365	2	1.305	1.307
6000	4234	102	257	2	1.285	1.287
7000	4157	92	174	1	1.268	1.269
8000	4084	83	116	1	1.254	1.254
9000	4013	76	75	1	1.242	1.240
10000	3945	71	50	1	1.232	1.227

Propane 190° F (15)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	5150	556	1172	2302	1.751	1.768
2000	5048	434	991	1191	1.592	1.606
3000	4949	355	819	794	1.517	1.525
4000	4855	301	667	595	1.467	1.471
5000	4764	261	526	476	1.428	1.431
6000	4676	230	411	397	1.397	1.396
7000	4592	206	341	340	1.371	1.371
8000	4510	187	230	298	1.348	1.348
9000	4431	170	169	265	1.329	1.327
10000	4355	157	118	238	1.312	1.308

Butane 100° F (16)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	9641	477	784		.02801	.02808
2000	9163	385	540		.02749	.02755
3000	9290	323	383		.02710	.02714
4000	9124	278	244		.02675	.02679

5000	8964	244	157		.02647	.02649
6000	8810	218	105		.02624	.02621
7000	8660	196	70		.02603	.02597
8000	8516	179	35		.02583	.02575
9000	8376	164	17		.02566	.02553
10000	8241	152	0		.02550	.02534

Butane 280° F (16)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	11591	1762	2519	3873	.03685	.03719
2000	11375	1396	2112	1937	.03392	.03414
3000	11167	1156	1739	1291	.03246	.03252
4000	10966	987	1399	968	.03142	.03146
5000	10772	860	1113	775	.03062	.03066
6000	10585	763	860	646	.02996	.03000
7000	10401	685	660	554	.02941	.02943
8000	10229	622	480	484	.02892	.02895
9000	10061	569	353	430	.02852	.02854
10000	9897	525	247	387	.02816	.02815

Heptane 200° C (13)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
52.6	6749	1389	1754	40	1.928	1.926
112.4	6648	1148	1403	19	1.856	1.846
172.1	6550	979	1125	12	1.801	1.793
231.9	6454	853	882	9	1.754	1.751
291.7	6362	756	675	7	1.715	1.718
351.5	6272	678	513	6	1.682	1.690

0ctane 100° C (27)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	5606	660	111		1.550	1.547
100	5544	571	83		1.532	1.530
150	5483	504	55		1.516	1.514
200	5423	451	46		1.504	1.501
250	5364	408	28		1.492	1.489
300	5307	372	18		1.482	1.477

0ctane 125° C (27)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	5855	818	221		1.601	1.602
100	5789	708	166		1.578	1.580
150	5726	624	129		1.560	1.560
200	5663	558	92		1.543	1.544
250	5602	505	65		1.529	1.529
300	5542	461	46		1.517	1.516

0ctane 150° C (27)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	6100	977	406		1.660	1.662
100	6032	846	314		1.631	1.634
150	5966	745	240		1.607	1.610
200	5901	666	175		1.586	1.589
250	5837	603	129		1.569	1.571
300	5775	550	92		1.554	1.554

Pendane 100° F (17)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	9086	449	262		.02591	.02598
2000	8924	366	180		.02559	.02564
3000	8768	308	115		.02531	.02534
4000	8618	267	65		.02507	.02505
5000	8472	235	49		.02487	.02481
6000	8331	210	33		.02468	.02460
7000	8195	189	16		.02452	.02442
8000	8064	173	0		.02435	.02424
9000	7936	159			.02421	.02407
10000	7812	147			.02408	.02394

Pentane 340° F (17)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	11605	1910	3058	1735	.03442	.03480
2000	11398	1532	2520	867	.03243	.03256
3000	11197	1280	2057	578	.03123	.03120
4000	11004	1098	1631	434	.03028	.03026
5000	10817	962	1279	147	.02952	.02950
6000	10636	856	964	289	.02886	.02886
7000	10462	771	723	248	.02832	.02831
8000	10293	701	519	217	.02785	.02786
9000	10129	643	371	193	.02745	.02750
10000	9971	594	259	174	.02711	.02721

Hexane 160° F (18)			
P	V_{II}	V_{III}	Total V

	(L)	(H)	(A)	(B)	calc.	obs.
1000	7862	657	243		2.210	2.219
2000	7746	537	162		2.176	2.187
3000	7614	454	112		2.149	2.159
4000	7487	393	70		2.126	2.133
5000	7364	347	42		2.107	2.110
6000	7245	310	28		2.090	2.089
7000	7129	281	14		2.074	2.071
8000	7018	256	0		2.059	2.054
9000	6909	236			2.046	2.039
10000	6804	218			2.034	2.025

Octane 175° C (27)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	6415	1078	719		1.733	1.732
100	6344	933	572		1.697	1.697
150	6274	822	443		1.666	1.664
200	6205	735	350		1.641	1.638
250	6139	664	258		1.618	1.616
300	6073	606	203		1.600	1.596

Octane 200° C (27)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	6533	1356	1145	2	1.816	1.808
100	6460	1172	934	1	1.769	1.760
150	6389	1033	751	1	1.729	1.721
200	6319	922	605	0	1.697	1.689
250	6251	834	476		1.668	1.663

300	6184	760	366		1.643	1.640

3-Methyl Pentane 150° C (28)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
49.0	6584	1058	1420	7	1.858	1.847
101.5	6496	891	1169	3	1.807	1.794
154.1	6409	769	937	2	1.763	1.755
206.7	6325	676	734	2	1.725	1.723
259.4	6243	603	589	1	1.695	1.696
311.8	6163	545	444	1	1.667	1.673

2,2-Dimettyl Butane 100° C (29)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	6182	731	655		1.728	1.730
100	6111	630	518		1.697	1.696
150	6041	553	401		1.671	1.670
200	5972	493	303		1.648	1.667
250	5906	445	235		1.630	1.627
300	5840	405	176		1.613	1.606

2,3-Dimethyl Butane 100° C (30)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
48.9	6040	706	508		1.683	1.686
101.5	5959	596	381		1.651	1.658
154.1	5879	515	293		1.627	1.635
206.7	5802	454	215		1.605	1.613
252.4	5737	411	166		1.589	1.595

311.8	5654	366	117		1.572	1.570

Hexane 400° F (18)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	9707	2037	2584	1073	2.072	2.886
2000	9539	1646	2136	537	2.717	2.705
3000	9376	1381	1728	358	2.616	2.596
4000	9219	1189	1361	268	2.535	2.519
5000	9066	1045	1052	215	2.469	2.458
6000	8919	931	807	179	2.415	2.408
7000	8776	840	567	153	2.367	2.368
8000	8630	765	432	134	2.328	2.333
9000	8505	702	310	119	2.295	2.301
10000	8375	649	212	107	2.266	2.272

Heptane 40° F (19)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	7558	212	15		2.278	2.284
2000	7430	174	0		2.261	2.266
3000	7306	147			2.246	2.250
4000	7186	128			2.232	2.234
5000	7071	113			2.219	2.220
6000	6959	101			2.206	2.207
7000	6850	91			2.194	2.195
8000	6745	84			2.183	2.184
9000	6643	77			2.172	2.172
10000	6544	71			2.162	2.160

Heptane 100° F (19)

P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	8256	412	46		2.372	2.373
2000	8116	338	30		2.349	2.352
3000	7981	286	15		2.328	2.333
4000	7850	248	0		2.310	2.315
5000	7724	219			2.295	2.298
6000	7601	197			2.280	2.282
7000	7483	178			2.266	2.267
8000	7368	163			2.253	2.252
9000	7256	150			2.241	2.236
10000	7148	139			2.229	2.222

Nonane 220° F (20)

P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	11281	1325	130		3.111	3.12
2000	11128	1321	23		3.072	3.08
3000	10960	972	56		3.039	3.04
4000	10835	857	37		3.011	3.01
5000	10694	767	19		2.986	2.980
6000	10557	694	0		2.963	2.956
7000	10423	633			2.943	2.935
8000	10293	583			2.925	2.916
9000	10166	540			2.908	2.895
10000	10042	502			2.892	2.872

2,3-Dimethyl Butane 125° C (30)

P	V_{II}	V_{III}	Total V

	(L)	(H)	(A)	(B)	calc.	obs.
48.9	6316	878	880		1.765	1.763
101.5	6231	740	704		1.725	1.726
154.1	6148	639	548		1.691	1.696
206.7	6067	563	430		1.664	1.666
259.4	5988	503	323		1.639	1.645
311.8	5912	454	235		1.618	1.623

2,2,4-Trimethyl Pentane 100° C (31)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	5739	678	184		1.582	1.582
100	5675	587	138		1.562	1.563
150	5612	518	101		1.545	1.545
200	5551	463	74		1.531	1.530
250	5491	419	55		1.519	1.515
300	5433	382	37		1.507	1.502

2,2,4-Trimethy1 Pentane 125° C (31)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
50	5993	839	360		1.641	1.639
100	5926	726	277		1.615	1.614
150	5860	640	212		1.593	1.593
200	5797	572	157		1.575	1.573
250	5734	518	120		1.559	1.556
300	5673	472	83		1.545	1.541

1-Pentene 80° C (32)			
P	V_{II}	V_{III}	Total V

	(L)	(H)	(A)	(B)	calc.	obs.
49.0	6000	632	673		1.707	1.717
101.5	5948	561	536		1.681	1.687
154.1	5896	504	399		1.656	1.662
206.7	5846	458	305		1.637	1.640
259.4	5796	419	231		1.621	1.621
311.8	5747	387	168		1.606	1.605

1-Pentene 100° C (32)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
49.0	6237	776	1093		1.787	1.789
101.5	6182	689	862		1.750	1.749
154.1	6129	619	694		1.720	1.716
206.7	6076	562	536		1.694	1.689
259.4	6024	514	399		1.670	1.666
311.8	5973	474	305		1.651	1.647

Nonane 400° F (20)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	13033	2726	1559		3.570	3.56
2000	12857	2303	1151		3.469	3.46
3000	12685	1993	835		3.389	3.38
4000	12518	1757	575		3.323	3.32
5000	12355	1571	390		3.269	3.27
6000	12196	1421	260		3.226	3.22
7000	12042	1297	167		3.188	3.18
8000	11891	1193	111		3.157	3.15
9000	11744	1104	74		3.130	3.12

10000	11601	1027	37		3.104	3.09

2-Methyl Propane 160° F (21)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
500	10562	997	3003	24	.03200	.03215
1000	10449	866	2648	12	.03139	.03139
1500	10340	763	2331	8	.03086	.03079
2000	10232	683	1996	6	.03033	.03027
2500	10127	617	1734	5	.02990	.02986
3000	10024	563	1511	4	.02952	.02944

Propene 70° F (22)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	9778	369	2133	5	.03033	.03026
2000	9592	296	1613	3	.02955	.02943
3000	9413	247	1183	2	.02889	.02883
4000	9241	212	842	1	.02834	.02832
5000	9075	185	609	1	.02792	.02790
6000	8915	165	412	1	.02754	.02755
7000	8760	148	269	1	.02722	.02725
8000	8611	135	179	1	.02697	.02696
9000	8467	124	108	1	.02675	.02670
10000	8327	114	72	1	.02656	.02645

Ammonia 30° C (33)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
100	5911	273	747		1.657	1.658

200	5820	227	639		1.633	1.637
300	5732	193	552		1.612	1.608
400	5646	169	465		1.592	1.593
500	5563	150	390		1.575	1.577
600	5482	134	325		1.558	1.558
700	5404	122	271		1.544	1.543
800	5328	112	227		3.531	1.530
900	5254	103	184		1.518	1.519
1000	5182	96	152		1.507	1.511
1100	5112	89	119		1.496	1.503

Ammonia 110° C (33)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
100	6935	978	2198	2679	2.243	2.235
200	6827	790	2017	1340	2.062	2.080
300	6722	663	1848	893	1.977	1.903
400	6621	571	1680	670	1.918	1.918
500	6523	501	1523	536	1.873	1.868
600	6427	447	1373	447	1.834	1.830
700	6335	403	1228	383	1.799	1.793
800	6245	367	1096	335	1.769	1.763
900	6157	337	975	298	1.741	1.733
1000	6072	311	855	268	1.715	1.710
1100	5989	289	753	244	1.692	1.688

Hydrogen Sulfide 40° F (25)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	2099	65	304	.	650	.652

2000	2075	56	261		.643	.643
3000	2052	49	224		.636	.635
4000	2030	44	190		.630	.627
5000	2008	40	156		.624	.621
6000	1986	36	131		.619	.614
7000	1965	33	110		.614	.6085
8000	1944	31	89		.610	.604
9000	1924	29	72		.606	.600
10000	1904	27	59		.602	.598

1-Butene 160° F (23)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	5601	500	1237	3	1.662	1.676
2000	5525	421	935	1	1.616	1.625
3000	5451	364	684	1	1.578	1.585
4000	5379	320	503	1	1.548	1.555
5000	5309	286	342	1	1.522	1.530
6000	5240	258	241	0	1.502	1.509
7000	5174	235	161		1.485	1.490
8000	5109	216	101		1.470	1.473
9000	5046	200	70		1.459	1.458
10000	4984	186	40		1.449	1.444

1-Butene 220° F (23)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	5956	734	2102	246	1.832	1.852
2000	5875	615	1682	123	1.757	1.759
3000	5796	530	1321	82	1.701	1.695

4000	5719	465	1021	62	1.655	1.650
5000	5644	415	764	49	1,615	1.616
6000	5571	374	566	41	1.583	1.589
7000	5500	341	403	35	1.556	1.565
8000	5431	313	283	31	1.534	1.542
9000	5364	289	197	27	1.516	1.522
10000	5298	269	129	25	1.500	1.504

Benzene 100° F (24)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	6550	350	26		.01847	.01849
2000	6475	302	13		.01835	.01836
3000	6401	265	0		.01821	.01823
4000	6328	237			.01811	.01810
5000	6258	214			.01802	.01799
6000	6188	195			.01793	.01790
7000	6121	179			.01785	.01783
8000	6054	165			.01777	.01776
9000	5990	154			.01769	.01767
10000	5926	144			.01762	.01758

Benzene 220° F (24)						
P	V_{II}		V_{III}		Total V	
	(L)	(H)	(A)	(B)	calc.	obs.
1000	7400	895	181		.02002	.02003
2000	7314	772	117		.01975	.01981
3000	7231	678	78		.01953	.01961
4000	7149	605	39		.01934	.01942
5000	7069	546	26		.01919	.01923

6000	6991	497	13		.01905	.01907
7000	6914	457	0		.01892	.01895
8000	6839	422			.01881	.01882
9000	6766	393			.01871	.01869
10000	6695	367			.01861	.01856

<table>
<tr><td colspan="5">Table IV - 4</td></tr>
<tr><td colspan="5">LIQUID COMPRESSION
(HIGH PRESSURE)</td></tr>
<tr><td colspan="5">Octane 50° C</td></tr>
<tr><td colspan="2">$V_I = .656$</td><td colspan="3">$P_0 = 4535$ Kg/cm^2</td></tr>
<tr><td>P</td><td>$V_{II}(L)$</td><td>$V_{II}(H)$</td><td>calc.</td><td>obs.</td></tr>
<tr><td>0</td><td>.373</td><td>.029</td><td></td><td></td></tr>
<tr><td>1000</td><td>.306</td><td>.006</td><td>.968</td><td>.965</td></tr>
<tr><td>2000</td><td>.259</td><td>.004</td><td>.919</td><td>.920</td></tr>
<tr><td>3000</td><td>.224</td><td>.003</td><td>.883</td><td>.888</td></tr>
<tr><td>4000</td><td>.198</td><td>.002</td><td>.856</td><td>.864</td></tr>
<tr><td>5000</td><td>.177</td><td>.002</td><td>.837</td><td>.843</td></tr>
<tr><td>6000</td><td>.161</td><td>.001</td><td>.818</td><td>.825</td></tr>
<tr><td>7000</td><td>.147</td><td>.001</td><td>.804</td><td>.810</td></tr>
</table>

<table>
<tr><td colspan="5">Decane 95° C</td></tr>
<tr><td colspan="2">$V_I = .653$</td><td colspan="3">$P_0 = 5580$ Kg/cm^2</td></tr>
<tr><td>P</td><td>$V_{II}(L)$</td><td>$V_{II}(H)$</td><td>calc.</td><td>obs.</td></tr>
<tr><td>0</td><td>.399</td><td>.053</td><td></td><td></td></tr>
<tr><td>1000</td><td>.338</td><td>.014</td><td>1.005</td><td>.995</td></tr>
<tr><td>2000</td><td>.294</td><td>.008</td><td>.955</td><td>.946</td></tr>
<tr><td>3000</td><td>.259</td><td>.006</td><td>.918</td><td>.915</td></tr>
<tr><td>4000</td><td>.232</td><td>.004</td><td>.889</td><td>.888</td></tr>
<tr><td>5000</td><td>.210</td><td>.003</td><td>.866</td><td>.868</td></tr>
</table>

6000	.192	.003	.848	.848
7000	.177	.003	.033	.834
8000	.164	.002	.819	.822

Hexane 50° C				
V_I = .653		P_0 = 3926 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.379	0029		
1000	.302	.006	.961	.957
2000	.251	.003	.907	.905
3000	.215	.002	.870	.872
4000	.188	.002	.843	.847
5000	.167	.001	.821	.826
6000	.150	.001	.804	.809
7000	.136	.001	.790	.794
8000	.125	.001	.779	.782
9000	.115	.001	.769	.771
10000	.107	.001	.761	.7615
11000	.100	.001	.754	.754

2-Metlyl Butane 0° C				
V_I = .647		P_0 = 3388 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.336	.011		
1000	.259	.002	.908	.903
2000	.211	.001	.859	.857
3000	.178	.001	.826	.826
4000	.154	.001	.802	.8025
5000	.136		.783	.783
6000	.121		.768	.767

7000	.110		.757	.753

2,3-Dimethyl Butane 95° C				
V_I = .652		Po = 3926 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.412	.055		
1000	.328	.011	.991	.988
2000	.273	.006	.931	0920
3000	.234	.004	.890	.884
4000	.204	.003	.859	.856
5000	.181	.003	.036	.834
6000	.163	.002	.817	.816
7000	.148	.002	.802	.801
8000	.136	.002	.790	.787
9000	.125	.001	.778	.776
10000	.116	.001	.769	.76115
11000	.108	.001	.761	.755

Hexane 95° C				
V_I = .653		P_0 = 3926 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.141	.054		
1000	.328	.011	.992	
2000	.272	.006	.931	.930
3000	.233	.004	.890	.891
4000	.204	.003	.860	.863
5000	.181	.003	.837	.870
6000	.163	.002	.818	.8225
7000	.148	.002	.803	.807
8000	.135	.002	.790	.794

9000	.125	.001	.779	.782
10000	.116	.001	.770	.772
11000	.108	.001	.762	.763

2-14ethyl Butane 95° C				
V_I = .653		P_0 = 5580 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.412	.055		
1000	.318	.010	.975	.981
2000	.259	.005	.911	.912
3000	.219	.004	.870	.871
4000	.189	.003	.839	.840
5000	.166	.002	.815	.818
6000	.149	.002	.798	,800
7000	.134	.002	.783	.786
8000	.123	.001	.771	.771

2-Methyl Pentane 95° C				
V_I = .651		P_0 = 3926 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.42	.055		
1000	.328	.011	.990	.985
2000	.273	.006	.930	.923
3000	.234	.004	.889	.883
4000	.204	.003	.858	.855
5000	.181	.003	.835	.834
6000	.163	.002	.816	.818
7000	.148	.002	.801	.802
8000	.136	.002	.789	.787
9000	.125	.001	.777	.776

10000	.116	.001	.768	.766

2,3-Dimethyl Butane 0° C				
V_I = .652		P_0 = 3926 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.335	.011		
1000	.267	.002	.921	.915
2000	.222	.001	.875	.870
3000	.190	.001	.843	.8395
4000	.166	.001	.819	.818
5000	.147	.001	.800	.800
6000	.133		.785	.7855

Propyl Alcohol 60° C				
V_I = .720		P_0 = 4356 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.312	.028		
1000	.254	.006	.980	.978
2000	.214	.003	.937	.934
3000	.185	.002	.907	.906
4000	.163	.002	.885	.885
5000	.145	.001	.866	.867
6000	.131	.001	.852	.852
7000	.120	.001	.841	.839
8000	.110	.001	.831	.828
**				

Anyl Alcohol 80° C				
V_I = .699		P_0 = 4828 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.

0	.347	.041		
1000	.287	.009	.995	.914
2000	.245	.005	.949	.945
3000	.214	.004	.917	.914
4000	.190	.003	.892	.890
5000	.170	.002	.871	.871
6000	.155	.002	.856	.856
7000	.142	.002	.843	.842
8000	.131	.001	.831	.830
9000	.121	.001	.821	.819
10000	.113	.001	.813	.809
11000	.106	.001	.806	.800
12000	.103	.001	.800	.793

2-Methyl Pentane, 0° C				
V_I = .651		P_0 = 3926 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.335	.011		
1000	.267	.002	.920	.913
2000	.222	.001	.874	.871
3000	.190	.001	.842	.842
4000	.165	.001	.818	.819
5000	.147	.001	.799	.801
6000	.133		.784	.784

Butyl Alcohol 50° C				
V_I = .708		P_0 = 4857 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.320	.025		
1000	.265	.006	.979	.978

2000	.227	.003	.938	.937
3000	.198	.002	.908	.909
4000	.175	.002	.885	.887
5000	.158	.001	.867	.868
6000	.143	.001	.852	.853
7000	.131	.001	.840	.839
8000	.121	.001	.830	.827
				**

Acetone 60° C				
V_I = .647		P_0 = 5045 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.393	.035		
1000	.328	.008	.983	.992
2000	.281	.005	.933	.937
3000	.246	.003	.896	.900
4000	.220	.003	.870	.8725
5000	.197	.002	.846	.851
6000	.180	.002	.829	.834
7000	.165	.002	.814	.818
8003	.152	.001	.000	.804
9000	.141	.001	.789	.791
10000	.132	.001	.780	.780
11000	.124	.001	.772	.770
12000	.116	.001	.764	.761

Ethyl Chloride 20° C				
V_I = .653		P_0 = 3167 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.329	.015		

1000	.250	.003	.926	.928
2000	.202	.001	.876	.877
3000	.169	.001	.843	.844
4000	.145	.001	.819	.820
5000	.128	.001	.802	.799
				**

Ethyl Bromide 20° C				
$V_I = .650$		$P_0 = 4884$ kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.357	.017		
1000	.296	.004	.950	.948
2000	.253	.002	.905	.904
3000	.223	.002	.873	.878
4000	.196	.001	.847	.8505
5000	.176	.001	.827	.832
6000	.160	.001	.811	.816
7000	.147	.001	.798	.802
8000	.135	.001	.786	.790
9000	.126	.001	.777	.779
10000	.117	.001	.768	.769
11000	.110		.760	.760
12000	.103		.753	.752

Butyl Bromide 0° C				
$V_I = .651$		$P_0 = 5846$ kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.338	.011		
1000	.289	.003	.943	.938
2000	.252	.002	.905	.9025

3000	.223	.001	.875	.874
4000	.201	.001	.853	.853
5000	.182	.001	.834	.836
6000	.167	.001	.819	.821
7000	.154	.001	.806	.808
8000	.143		.794	.797
9000	.133		.784	.786
10000	.125		.776	.777
11000	.117		.768	.768
12000	.111		.762	.761

Propyl Chloride 0° C				
V_I = .675		P_0 = 3684 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.313	.010		
1000	.246	.002	. 923	.926
2000	.203	.001	.879	.888
3000	.173	.001	.849	.854
4000	.150	.001	.826	.832
5000	.133		.808	.814
6000	.119		.794	.799
7000	.108		.783	.785
8000	.099		.774	.773
9000	.091		.766	.7625
**				

Propyl Bromide 0° C				
V_I = .651		P_0 = 5358 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.338	.011		

1000	.285	.003	.939	.936
2000	.246	.002	.899	.897
3000	.217	.001	.869	.8695
4000	.194	.001	.846	.848
5000	.175	.001	.827	.829
6000	.159	.001	.811	.813
7000	.147	.001	.7/9	.800
8000	.136		.786	.789
9000	.126		.777	.778
10000	.118		.769	.769
11000	.111		.762	.7595
12000	.104		.755	.7515

Amyl Bromide 0° C				
V_I = .664		P_0 = 5708 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.326	.010		
1000	.277	.003	.944	.943
2000	.241	.002	.907	.907
3000	.214	.001	.879	.881
4000	.192	.001	.857	.860
5000	.174	.001	.839	.843
6000	.159	.001	.824	.828
7000	.146		.810	.815
8000	.136		.800	.804
9000	.127		.791	.793

Ethyl Ether 20° C				
V_I = .657		P_0 = 5738 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.

0	.333	.016		
1000	.261	.003	.934	.936
2000	.215	.002	.887	.887
3000	.182	.001	.853	.853
4000	.158	.001	.829	.8275
5000	.140	.001	.811	.807
6000	.125	.001	.796	.792
**				

Butal Iodide 50° C				
$V_I = .653$		$P_0 = 5580$ kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.368	.028		
1000	.312	.007	.984	.9785
2000	.270	.004	.939	.936
3000	.239	.003	.907	.907
4000	.214	.002	.881	.883
5000	.193	.002	.859	.864
6000	.177	.002	.844	.847
7000	.162	.001	.828	.833
8000	.150	.001	.816	.821
9000	.140	.001	.806	.810
10000	.131	.001	.798	.7995
11000	.123	.001	.789	.7905
12000	.116	.001	.782	.782

Phosphorus Trichloride 80° C				
$V_I = .651$		$P_0 = 6113$ kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.403	.047		

1000	.346	.013	1,010	1.0065
2000	.304	.008	.963	.956
3000	.270	.005	.926	.922
4000	.241	.004	.899	.896
5000	.222	.003	.876	.876
6000	.203	.003	.857	.860
7000	.188	.002	.841	.8115
8000	.115	.002	.828	.832
9000	.163	.002	.816	.821
10000	.153	.002	.806	.811
11000	.144	.002	.797	.801
12000	.136	.001	.788	.793

Benzene 95° C				
V_I = .649		P_0 = 5938 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.413	.055		
1000	.353	.015	1.017	1.020
1500	.330	.011	.990	.992
2000	.309	.009	.967	.968
2500	.291	.007	.947	.949
3000	.274	.006	.929	.932
3500	.260	.005	.914	.918

Carbon Disulfide 20° C				
V_I = .657		P_0 = 5738 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.350	.017		
1000	.298	.005	.960	.959
2000	.260	.003	.920	.917

3000	.230	.002	.888	.888
4000	.206	.001	.864	.865
5000	.187	.001	.845	.845
6000	.171	.001	.829	.8295
7000	.158	.001	.816	.815
8000	.146	.001	.804	.802
9000	.136	.001	.794	.792
10000	.128	.001	.786	.7805
11000	.120	.001	.778	.7715
12000	.113		.770	.766

Carbon Disulfide 80° C				
V_I = .657		P_0 = 5738 kg/cm^2		
P	V_{II}(L)	V_{II}(H)	calc.	obs.
0	.395	.046		
1000	.336	.012	1.005	1,008
2000	.293	.007	.957	.955
3000	.259	.005	.921	.9185
4000	.233	.004	.894	.890
5000	.211	.003	.871	.868
6000	.193	.003	.853	.850
7000	.178	.002	.837	.835
8000	.165	.002	.824	.822
9000	.154	.002	.813	.811
10000	.144	.002	.803	.900
11000	.135	.001	.793	.789
12000	.128	.001	.786	.7795

REFERENCES

13. Smith, L. Be, Beattie, J. A*, and Kay, W. C., J. Am. Chem. Soc., 59-1587.

14. For a bibliography of Bridgman's reports see his book “The Physics of High

Pressure.” G. Bell & Sons'. Ltd., London, 1958.

15. Reamer, H. H., Sage, B. H., and Lacey., W. N., Ind, Eng. Chem. 41-482.

16. Olds, R. H., Reamer, H. H., Sage B. H., and Lacey., W. M. Ibid., 36-282.

17. Sage, B. H., and Lacey., W. N., Ibid., 34-732.

18. Stewart, D. E., Sage, B. H., and Lacey., W. N. Ibid., 46-2529.

19. Nichols, W. B., Reamer, H. H., and Sage., B. H. Ibid., 47-2219.

20. Carmichael, L. T., and Sage, B. H., Ibid., 45-2697.

21. Sage., B. H., and Lacey., W. N., Ibid., 30-673.

22. Farrington., P. S., and Sage,, B. H., Ibid., 41-1734.

23. Olds., R. H., Sage. B. H., and Lacey., W. N., Ibid., 38-301

24. Glanville, J. W., and Sage, B. H., Ibid. 41-1272.

25. Reamer., H. H., Sage., B. H., and Lacey, W. N., Ibid., 42-140.

26. Kelso E. A., and Felsing, W. A.,, J. Am. Chem. Sec., 62-3132.

27. Felsing, W. A., and Watson., G. M., Ibid., 64-1822.

28. Day, H. 0., and Felsing, W. A., Ibid., 74-1952.

29, Felsing, W. A., and Watson., G. M., Ibid., 65-1889.

20. Kelso, E. A., and Felsing, W. A., Ind. Eng. Chem., 34-161.

31. Felsing, W. A., and Watson, G. M., J. Am. Chem. soc., 65-780.

32. Day, H. O., and Felsing, W. A., Ibid., 73-4839.

33. Keyes, Frederick G., Ibid., 53-967.

V

The Liquid-Solid Transition

As pointed out in paper I of this series, development of the consequences of the postulates on which this work is based indicates that physical state is a property of the individual molecules and not, as generally assumed, a "state of aggregation". Because of the distribution of molecular velocities due to the operation of the probability principles it follows that a liquid aggregate in the vicinity of the melting point is not a homogeneous structure but a composite which includes both solid and liquid molecules. The effect of the presence of solid molecules on the volume of the liquid aggregate was discussed briefly in paper II. Further consideration of this situation will now be required in order to permit extending the liquid compressibility calculations into the extreme high-pressure range.

The procedure is essentially simple. The proportion of solid molecules in the liquid aggregate at any specified pressure is determined by the same technique utilized in paper IV for the calculation of the critical volume component; that is, by the use of a composite probability index obtained by adding the equivalent of the applied pressure to the index corresponding to the prevailing temperature. The percentages thus determined are then multiplied by the difference between the pure solid and pure liquid volumes at each individual pressure to arrive at the increase (or decrease) in the volume of the aggregate due to the presence of the solid molecules.

Table V-1 shows how this procedure is applied to the calculation of the volumes of liquid methyl alcohol at 50° C and various pressures.

TABLE V - 1

LIQUID COMPRESSION - METHYL ALCOHOL 50° C

P M kg/cm²	V_L	V_S	Diff.	P.I.	P.I adj.	$½\phi$	Δ	V(calc.)	V(obs.)[14]
0				3.04					
1	.969	.746	.223	2.79		.003	.001	.968	.976
2	.925	.743	.182	2.54		.006	.001	.924	.927
3	.894	.740	.154	2.29		.011	.002	.892	.895
4	.869	.737	.132	2.03		.021	.003	.866	.869
5	.853	.734	.119	1.78		.038	.005	.848	.848
6	.839	.732	.107	1.53		.063	.007	.832	.831
7	.828	.729	.099	1.28		.100	.010	.818	.816

8	.818	.726	.092	1.03	1.08	.140	.013	.805	.804
9	.810	.724	.086	.78	.91	.181	.016	.794	.792
10	.803	.721	.082	.53	.75	.227	.019	.784	.782
11	.797	.718	.079	.27	.63	.264	.021	.776	.772
12	.791	.715	.076	.02	.53	.298	.023	.768	.765

The first step is to determine the pure liquid volume by the methods of paper IV. The values thus obtained for each of the pressures of column 1, relative to the volume at 0° C and atmospheric pressure, are given in column 2. Column 3 lists the corresponding volumes of the pure solid. Since the theoretical study of the volume of solid organic compounds is still incomplete, the solid volumes used in this paper have been derived from whatever measured volumes are available adjusted to the various pressures by the methods explained in a previous paper.[5] Column 4 is the difference between the pure liquid and pure solid volumes.

The next operation is the determination of the percentage of solid molecules in the aggregate at each pressure. Paper II has already indicated how the number of probability units corresponding to the difference between any specified temperature and the location of equal division between solid and liquid can be obtained. This number, the probability index, for methyl alcohol at 50° C is 3.04. The pressure probability unit applicable to the liquid side of the solid-liquid transition is the initial pressure P_0, and we now subtract the pressure equivalent P/P_0 for each of the pressures of column 1 from 3.04, entering the results in column 5.

A detailed study of the liquid-solid transition process has revealed that the probability unit of pressure, which is P_0 on the liquid side of the neutral point, is $2P_0$ on the solid side. The probability index increment due to a change in pressure therefore undergoes a decrease from P/P_0 to $P/2P_0$ in the middle of the transition zone.

This shift from one probability unit to the other is itself governed by probability and it has been found that the transition curve can be defined by taking 0.5 on the probability index scale as the probability unit. Since the value of ½ ϕ is very small beyond 2 units, this means that the effective probability index stays on the P_0 basis down to the vicinity of a 1.00 index, then follows a transition curve of the probability type to a point midway between P_0 and $2P_0$ at zero index, and continues on a reverse curve of the same kind to the vicinity of index -1.00, beyond which the $2P_0$ basis prevails. Column 6 gives the adjusted values of the probability index where adjustment for the change in the probability unit is required.

From the probability tables we now obtain the values of ½ϕ corresponding to the effective probability index for each pressure, entering them in column 7. These figure which represent percentage of solid molecules, are then multiplied by the values in column 4, giving the volume decrease due to the presence of the solid, which we show in column 8. Subtracting this amount from the volume of the pure liquid, column 2, we arrive at the volume of the aggregate, column 9. Bridgman's results are shown in column 10 for comparison.

Table V-2 gives similar data for a number of other liquids in the same pressure range. To conserve space some of the columns of Table V-1 have been omitted from these additional tabulations, but the calculations are identical.

TABLE V - 2

LIQUID COMPRESSION

Ethyl Alcohol 30° C

P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			3.23			
1	.952	.712	2.93	.002	.952	.957
2	.910	.709	2.63	.004	.909	.913
3	.882	.706	2.33	.010	.880	.883
4	.863	.704	2.02	.022	.859	.859
5	.847	.701	1.72	.043	.841	.838
6	.836	.699	1.42	.077	.825	.822
7	.825	.696	1.13	.129	.808	.807
8	.817	.693	.91	.181	.795	.795
9	.811	.691	.70	.242	.782	.784
10	.805	.688	.56	.288	.771	.773
11	.800	.685	.45	.330	.762	.763
12	.795	.683	.34	.367	.754	.755

TABLE V - 2

LIQUID COMPRESSION

Isopropyl Alcohol 50° C

P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			3.52			
1	.973	.757	3.29	.000	.973	.972
2	.930	.754	3.06	.001	.930	.930

3	.899	.751	2.83	.002	.899	.900
4	.877	.748	2.60	.005	.876	.876
5	.858	.745	2.37	.009	.857	.858
6	.844	.742	2.14	.016	.842	.841
7	.832	.739	1.91	.028	.829	.828
8	.822	.737	1.68	.046	.818	.816
9	.813	.734	1.45	.074	.807	.805
l0	.806	.731	1.24	.107	.798	.795
11	.800	.728	1.04	.149	.789	.786
12	.794	.726	.91	.181	.782	.778

TABLE V - 2

LIQUID COMPRESSION

Propyl Alcohol 20° C

P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			3.52			
1	.956	.773	3.29	.000	.956	.950
2	.918	.770	3.06	.001	.918	.914
3	.890	.767	2.83	.002	.890	.890
4	.870	.764	2.60	.005	.869	.870
5	.854	.761	2.37	.009	.853	.853
6	.841	.758	2.14	.016	.840	.839
7	.830	.755	1.91	.028	.828	.827
8	.821	.752	1.68	.046	.818	.816
9	.813	.750	1.45	.074	.808	.807
10	.807	.747	1.24	.107	.801	.798
11	.801	.744	1.06	.145	.793	.791
12	.796	.741	.92	.179	.786	.784

TABLE V - 2						
LIQUID COMPRESSION						
Isobutyl Alcohol 50° C						
P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			3.37			
1	.972	.757	3.14	.001	.972	.970
2	.928	.754	2.91	.002	.928	.925
3	.896	.751	2.68	.004	.895	.895
4	.873	.748	2.44	.007	.872	.871
5	.853	.745	2.21	.014	.851	.851
6	.839	.742	1.98	.024	.837	.837
7	.827	.739	1.75	.040	.823	.823
8	.816	.737	1.52	.064	.811	.812
9	.808	.734	1.30	.097	.801	.802
10	.800	.731	1.09	.138	.791	.792
11	.794	.728	.94	.174	.783	.783
12	.788	.726	.80	.212	.775	.775

TABLE V - 2						
LIQUID COMPRESSION						
Butyl Alcohol 50° C						
P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			3.56			
1	.979	.773	3.35	.000	.979	.978
2	.938	.770	3.15	.001	.938	.937
3	.908	.767	2.94	.002	.908	.909
4	.885	.764	2.74	.003	.885	.887
5	.867	.761	2.53	.006	.866	.868

6	.852	.758	2.32	.010	.851	.853
7	.840	.755	2.12	.017	.839	.839
8	.830	.752	1.91	.028	.828	.827
9	.821	.750	1.71	.044	.818	.815
10	.814	.747	1.50	.067	.809	.807

TABLE V - 2

LIQUID COMPRESSION

Propyl Chloride 50° C

P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			4.50			
5	.827	.677	3.14	.001	.827	.832
6	.811	.674	2.87	.002	.811	.816
7	.798	.671	2.60	.005	.797	.800
8	.788	.669	2.33	.010	.787	.788
9	.779	.667	2.06	.020	.777	.776
10	.772	.664	1.79	.037	.768	.766
11	.765	.661	1.51	.066	.758	.756
12	.759	.659	1.25	.106	.748	.748

TABLE V - 2

LIQUID COMPRESSION

Ethyl Bromide 50° C

P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			3.89			
5	.741	.724	2.87	.002	.841	.844
6	.623	.721	2.66	.004	.823	.827
7	.808	.718	2.46	.007	.807	.812
8	.796	.714	2.25	.012	.795	.800

9	.786	.711	2.05	.020	.785	.788
10	.777	.708	1.84	.033	.775	.778
11	.769	.705	1.64	.051	.766	.768
12	.762	.702	1.43	.076	.757	.760

TABLE V - 2

LIQUID COMPRESSION

Ethyl Chlorlde 20° C

P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			4.01			
1	.926	.687	3.70	.000	.926	.928
2	.876	.684	3.38	.000	.876	.877
3	.843	.682	3.06	.001	.843	.644
4	.819	.679	2.75	.003	.819	.820
5	.802	.677	2.43	.008	.801	.799
6	.787	.674	2.12	.017	.785	.782
7	.775	.671	1.80	.036	.771	.768
8	.766	.669	1.48	.069	.759	.756
9	.759	.667	1.18	.119	.748	.745
10	.752	.664	.93	.176	.736	.735
11	.747	.661	.72	.236	.727	.726
12	.742	.659	.57	.284	.718	.718

TABLE V - 2

LIQUID COMPRESSION

Propyl Bromide 50° C

P	V_L	V_S	P.I adj.	½ϕ	V (calc.)	V (obs.)
0			4.41			
5	.851	.728	3.48	.000	.851	.850

6	.834	.725	3.29	.000	.834	.833
7	.818	.722	3.10	.001	.818	.818
8	.806	.718	2.92	.002	.806	.806
9	.795	.715	2.73	.003	.795	.794
10	.786	.712	2.54	.006	.786	.784
11	.777	.709	2.36	.009	.776	.774
12	.769	.706	2.17	.015	.768	.765

TABLE V - 2

LIQUID COMPRESSION

m-Xglene 25° C
(250 base)

P	V_L	V_S	P.I adj.	$\frac{1}{2}\phi$	V (calc.)	V (obs.)
0			1.89			
1	.942	.768	1.71	.044	.941	.940
2	.906	.765	1.52	.064	.903	.903
3	.880	.762	1.36	.087	.876	.876
4	.859	.759	1.21	.113	.854	.855
5	.842	.756	1.07	.142	.836	.838

In Table V-3 the calculations are extended to the maximum pressure of Bridgman's liquid experiments, 50,000 kg/cm^2, taking ethyl acetate at 75° C and at 125° C as the example.

TABLE V - 3

LIQUID COMPRESSION - ETHYL ACETATE 75° C

P M kg/cm^2	V_L	V_S	Diff.	P.I.	P.I adj.	$\frac{1}{2}\phi$	Δ	V	V(calc.)	V(obs.)
0				3.04						
5	.837	.683	.154	2.10		.018	.003	.834		
10	.769	.671	.098	1.15	1.20	.115	.011	.758	.076	.066

15	.736	.659	.077	.21	.66	.255	.020	.716	.118	.105
20	.716	.647	.065	-.73	.37	.356	.025	.691	.143	.134
25	.701	.636	.065	-1.67	.17	.433	.028	.673	.161	.157
30	.692	.626	.066	-2.62	.00	.500	.033	.659	.175	.174
35	.684	.616	.068	-3.56	-.16	.564	.038	.646	.188	.189
40	.679	.606	.073	-4.50	-.33	.629	.046	.633	.201	.201
45	.674	.597	.077	-5.45	-.52	.698	.054	.620	.214	.211
50	.670	.589	.081	-6.39	-.77	.779	.063	.607	.227	.220

TABLE V - 3

LIQUID COMPRESSION - METHYL ALCOHOL 125° C

P M kg/cm^2	V_L	V_S	Diff.	P.I.	P.I adj.	½ϕ	Δ	V	V(calc.)	V(obs.)
0				3.84						
5	.856	.683	.173	2.90		.002	.000	.856		
10	.783	.671	.112	1.95		.026	.003	.780	.076	.069
15	.745	.659	.086	1.01	.108	.140	.012	.731	.123	.111
20	.723	.647	.076	.07	.61	.271	.021	.702	.154	.141
25	.709	.636	.073	-.87	.34	.367	.027	.682	.174	.165
30	.698	.626	.072	-1.82	.15	.440	.032	.666	.190	.184
35	.690	.616	.074	-2.76	-.03	.512	.038	.652	.204	.200
40	.684	.606	.078	-3.70	-.19	.575	.045	.639	.217	.214
45	.679	.597	.082	-4.65	-.36	.641	.053	.626	.230	.225

The procedure is exactly the same as that described in the explanation of Table V-1 except that the reference temperature is 20° C. When the volume of the liquid aggregate (column 9) is obtained, this value is subtracted from the volume at 5000 kg/cm^2 to obtain the volume decrease for comparison with the experimental results.

When we determine the probability index at the normal freezing point by the method explained in paper II we usually find it to lie within the range of .40 to .60, which means that the liquid normally freezes when the proportion of solid molecules reaches a level somewhere in the neighborhood of 30 percent. Under pressure, however, we find the ethyl acetate aggregate at 75° C still liquid when over 75 percent of the molecules are in the solid state. At first glance this may seem to be an impossibly high figure, but fortunately Bridgman has given us another set of observations, which enables us to put the situation into the proper perspective. He finds that under more favorable conditions ethyl acetate at 75° C will 1 freeze at 23,800 kg/cm^2 and at 125° it will freeze at 31,860 kg/cm^2. These pressures correspond to solid percentages of 41.4 and 46.7 respectively. At 25° freezing was experienced at a pressure of 12,100 kg/cm^2 (28 percent solid molecules) in this series of experiments, whereas in the other set of observations the liquid state persisted up to the pressure limit of 50,000 kg/cm^2.

From these figures we may obtain a consistent pattern. Ethyl acetate at the lower temperatures and pressures freezes when the proportion of solid molecules reaches the normal limit at about 30 percent. As pointed out in paper I, however, the requisite proportion of solid molecules is not in itself sufficient to insure freezing. These solid molecules must not only be present in adequate numbers but they must be able to make contact and to maintain that contact against the disruptive forces long enough to establish the nucleus of a crystal lattice. Although pressure and temperature are opposed from many standpoints they are both in the category of disruptive forces and when higher pressures are applied at higher temperatures the formation of the crystal lattice-becomes progressively more difficult. Consequently we find (1) that even under the most favorable conditions an increasing margin above the normal 30 percent solid molecules is required for freezing and (2) where conditions are unfavorable (mechanical agitation, asymmetric molecules, etc.) the super-saturated liquid may persist to very high solid percentages.

Table V-4 gives some additional comparisons of calculated and experimental volumes in this extreme high-pressure range. As in Table V-2 some of the less significant columns of figures have been omitted for economy of space but the calculations have been carried out just as described previously.

TABLE V- 4

LIQUID COMPRESSION - Ethyl Alcohol 75° C

P	V_L	V_S	P.I	½ϕ	V	ΔV	V (obs.)
0			4.08				
5	.839	.687	2.57	.005	.839		
10	.795	.674	1.08	.140	.778	.061	.069
15	.774	.662	.32	.374	.732	.107	.109
20	.762	.651	-.09	.536	.703	.136	.137
25	.755	.640	-.40	.655	.680	.159	.159
28.7	.750	.632	-.71	.761	.660	.179	.174

TABLE V - 4

LIQUID COMPRESSION - Ethyl Bromide 75° C

P	V_L	V_S	P.I.	½ϕ	V	ΔV	V (obs.)
0			4.38				
5	.827	.708	3.36		.827		
10	.761	.693	2.33	.010	.760	.067	.066
15	.729	.677	1.33	.092	.724	.103	.104
20	.710	.665	.69	.245	.699	.128	.130
25	.697	.650	.35	.363	.680	.147	.152
28.5	.689	.643	.19	.425	.669	.158	.167

TABLE V - 4

LIQUID COMPRESSION - Buty1 A1coho1 25° C

P	V_L	V_S	P.I.	½ϕ	V	ΔV	V (obs.)
0			3.01				
5	.839	.741	1.98	.024	.837		
10	.789	.727	1.03	.151	.780	.057	.058
11.7	.779	.722	.82	.206	.767	.070	.072

TABLE V - 4

LIQUID COMPRESSION - Buty1 A1coho1 75° C

P	V_L	V_S	P.I.	½ϕ	V	ΔV	V (obs.)
0			4.11				
5	.856	.741	3.08	.001	.856		
10	.800	.727	2.05	.020	.799	.057	.063
15	.773	.714	1.08	.140	.765	.091	.100
19	.760	.704	.64	.261	.745	.111	.122

TABLE V - 4

LIQUID COMPRESSION - Ethy1 Bromide 175° C

P	V_L	V_S	P.I.	½ϕ	V	ΔV	V (obs.)
0			6.33				
5	.867	.707	5.31	.000	.867		
10	.788	.693	4.28	.000	.788	.079	.076
15	.748	.677	3.26	.000	.748	.119	.122
20	.724	.665	2.24	.013	.723	.144	.154
25	.709	.650	1.24	.107	.703	.164	.178
30	.698	.638	.65	.258	.683	.184	.198
35	.690	.627	.32	.374	.666	.201	.213
40	.684	.615	.11	.456	.653	.214	.226
45	.679	.605	-.09	.536	.639	.228	.237

TABLE V - 4

LIQUID COMPRESSION - Propy1 Brom1de 175° C

P	V_L	V_S	P.I.	½ϕ	V	ΔV	V (obs.)
0			7.47				
5	.881	.713	6.54	.000	.881		
10	.800	.699	5.60	.000	.800	.081	.077
15	.759	.684	4.67	.000	.759	.122	.119
20	.734	.670	3.74	.000	.734	.147	.149
25	.717	.658	2.80	.003	.717	.164	.173
30	.706	.646	1.87	.031	.704	.177	.193
35	.697	.635	1.03	.151	.688	.193	.208
40	.690	.623	.60	.274	.672	.209	.226
45	.685	.614	.33	.371	.659	.222	.234

TABLE V - 4

LIQUID COMPRESSION - Buty1 Bromide 75° C							
P	V_L	V_S	P.I.	½ϕ	V	ΔV	V (obs.)
0			5.13				
5	.849	.717	4.27	.000	.849		
10	.781	.702	3.42	.000	.781	.068	.067
15	.746	.689	2.56	.005	.746	.103	.105
20	.724	.675	1.71	.044	.722	.127	.133
25	.710	.662	1.00	.159	.702	.147	.155
30	.700	.650	.59	.278	.686	.163	.173
35	.691	.639	.37	.356	.672	.177	.189
40	.685	.628	.20	.421	.661	.188	.202
45	.680	.618	.05	.480	.651	.198	.214
50	.676	.608	-.09	.536	.640	.209	.224

The last three tables presented in this paper constitute an appropriate climax to the entire discussion of liquid volume as they confirm the validity of the volume calculation process developed herein by producing theoretical volumes for water which agree almost exactly with the volume pattern determined by experiment: a pattern so complicated that Bridgman was led to doubt that it could ever be reproduced by any mathematical expression.[34]

Actually all of this complexity originates from a simple causes the existence of distinct high temperature and low temperature forms of the water molecules both in the solid state and in the liquid state. Aside from the necessity of determining the proportionality between these two forms, the entire volume calculation for water is carried out in exactly the same manner as heretofore described and without introducing any additional numerical constants. The polymorphism of the solid is well established by the work of Bridgman and other investigators. Several low temperature forms have actually been identified but the densities are nearly the same and for present purposes it will be sufficiently accurate to make the low-pressure computations on the basis of the familiar ice of our everyday experience. The two forms of the liquid are difficult to distinguish and in this study it has been determined that the essential difference between the two is in the nature of the atomic association under pressure. These findings indicate that the high temperature water molecule is $(H_2O)_4$ and all atoms act as independent liquid units. The value of n_v for use in equation 7, the initial pressure equation, is therefore 12, and the resulting initial pressure is 5965 kg/cm^2. In the low temperature form the number of independent liquid units in the molecule drops to eight, which evidently means that OH associations have been formed and the molecule has become $(H.OH)_4$. Substitution of 8 for 12 in equation 7 gives us 3976 kg/cm^2 as the initial pressure.

The transition from the low temperature liquid form to the high temperature form begins at the normal melting point, 0° C, and continues linearly to completion at 59° C. This liquid, in whatever stage it may be at the temperature under consideration, with the appropriate proportion of ice molecules of the low temperature form, constitutes the low temperature water aggregate, which we will designate L_I. The high temperature water aggregate, L_{II}, consists of high temperature ice molecules dispersed in the high temperature form of the liquid.

Table V-5 shows the calculation of the volumes of the super-saturated liquid at -10° C, the highest temperature at which the pure low-pressure liquid (L_I) exists throughout the entire observed liquid range. Values of L_I at other temperatures are obtained in the same manner. It should be noted that the pressure increment applied to the probability index is positive in these calculations because the solid volume exceeds that of the liquid.

TABLE V - 5

LIQUID COMPRESS ION - WATER(LOW TEMPETATURE FORM) -10° C

P M kg/cm^2	V_L	V_S	Diff.	P.I.	½ϕ	Δ	V(calc.)	V(obs.)[14]
0.0				0.43				
0.5	.939	1.078	.139	0.56	.288	.040	.979	.9795
1.0	.921	1.076	.155	0.68	.248	.038	.959	.954
1.5	.907	1.074	.167	0.81	.209	.035	.942	.9415
2.0	.895	1.072	.177	0.93	.176	.031	.926	.924
2.5	.885	1.070	.185	1.06	.145	.027	.912	.9105
3.0	.876	1.068	.192	1.18	.119	.023	.899	.8985
3.5	.669	1.066	.197	1.31	.095	.019	.888	.8875
4.0	.862	1.064	.202	1.44	.075	.015	.877	.8775
4.5	.856	1.061	.205	1.56	.059	.012	.868	.8685
5.0	.851	1.059	.208	1.69	.045	.009	.860	.860

Table V-6 is a similar presentation of the volumes at 250° C where only the high temperature form of the liquid (L_{II}) is present. Here there are no solid molecules in the aggregate but the V_3 volume component has an appreciable magnitude and the critical volume calculation is necessary as in Table IV-3.

TABLE V - 6

LIQUID COMPRESSION - WATER (HIGH TEMPERATURE FOPN) 250° C

P bars	V_{II}(L)	V_{II}(H)	P.I.	½ϕ	V_{III}(A)	V(calc.)	V(obs.)[35]
200	.3715	.0071	1.30	.097	.0851	1.228	1.225
400	.3595	.0051	1.38	.084	.0737	1.202	1.198
600	.3483	.0040	1.45	.074	.0649	1.181	1.175
800	.3377	.0033	1.53	.063	.0552	1.160	1.156
1000	.3278	.0028	1.61	.054	.0574	1.142	1.139
1200	.3184	.0024	1.68	.046	.0403	1.125	1.123
1400	.3096	.0022	1.76	.039	.0342	1.110	1.110
1600	.3012	.0019	1.84	.033	.0289	1.096	1.094
1800	.2933	.0017	1.91	.028	.0246	1.084	1.085
2000	.2858	.0016	1.99	.023	.0202	1.072	1.073
2250	.2769	.0014	2.09	.018	.0158	1.058	1.059
2500	.2686	.0013	2.18	.015	.0132	1.047	1.046

Table V-7 summarizes the complete calculation for water at 30° C, an intermediate temperature at which the normal liquid aggregate is a mixture of L_I and L_{II}. The first section of the table shows the computation of L_I, following the pattern of Table V-5.

TABLE V - 7

LIQUID COMPRESSION - WATER (INTERMEDIATE TEMPERATURES) L_I 30° C

P M kg/cm^2	V_L	V_S	P.I adj.	½ϕ	V
0.0			1.02		
0.5	.969	1.078	1.12	.131	.983
1.0	.952	1.076	1.22	.111	.966
1.5	.938	1.074	1.32	.093	.951

2.0	.925	1.072	1.42	.177	.936
2.5	.915	1.070	1.52	.064	.925
3.0	.905	1.068	1.62	.053	.914
3.5	.897	1.066	1.72	.043	.904
4.0	.889	1.064	1.82	.034	.895
4.5	.883	1.061	1.92	.027	.888
5.0	.877	1.059	2.02	.022	.881
5.5	.871	1.057	2.12	.017	.874
6.0	.867	1.055	2.22	.013	.869
6.5	.862	1.053	2.32	.010	.864
7.0	.858	1.051	2.42	.008	.860
7.5	.854	1.049	2.52	.006	.855
8.0	.851	1.018	2.62	.004	.852
8.5	.848	1.046	2.72	.003	.849
9.0	.845	1.044	2.82	.002	.845
9.5	.842	1.042	2.92	.002	.842
10.0	.839	1.040	3.03	.001	.839
10.5	.837	1.038	3.13	.001	.637

In the next section L_{II} is calculated by the same methods, with these differences in the basic numerical values: (1) the solid phase is the high temperature form of ice with a specific volume of .734 at zero pressure, rather than the low temperature form which, as it exists in the liquid aggregate, has a specific volume of 1.0805 in the absence of external pressure, (2) the probability index at zero pressure is .42 units higher than the L_I value, because of the heat of transition, (3) the pressure increment applicable to the probability index is negative rather than positive as the volume of the high temperature solid is less than that of the liquid, (4) the L_{II} initial pressure is the full high temperature value, 5965 kg/cm^2, whereas the L_I value at 30° C is 4987 kg/cm^2, the linear transition from 3976 kg/cm^2 to 5965 kg/cm^2 being 50.8 percent complete at this temperature, and (5) there is a similar difference in the probability unit of pressure since this unit is equal to the initial pressure. The difference in the initial pressure accounts for the difference in the pure liquid volumes, column 2 of each table.

TABLE V - 7

LIQUID COMPRESSION - WATER (INTERMEDIATE TEMPERATURES) L_{II} 30° C

P M kg/cm^2	V_L	V_S	P.I adj.	½ϕ	V
0.0			1.44		
2.5	.923	.727	1.10	.136	.896
3.0	.914	.725	1.04	.149	.886
3.5	.906	.724	.99	.161	.877
4.0	.099	.723	.94	.174	.868
4.5	.593	.721	.89	.187	.861
5.0	.867	.720	.84	.200	.854
5.5	.882	.718	.79	.215	.647
6.0	.877	.717	.75	.227	.841
6.5	.872	.715	.72	.236	.835
7.0	.868	.714	.69	.245	.830
7.5	.864	.713	.65	.258	.825
8.0	.861	.712	.63	.264	.122
8.5	.857	.710	.60	.274	.817
9.0	.854	.709	.57	.284	.813
9.5	.853	.707	.55	.291	.809
10.0	.848	.706	.52	.302	.805
10.5	.846	.705	.50	.309	.802

TABLE V - 7

LIQUID AGGREGATE 30° C

P	V_I	V_{II}	P.I.	ϕ	V calc	V obs
0.0			-.43			
0.5	.983		-.34		.983	.984
1.0	.966		-.26		.966	.966
1.5	.951		-.18		.951	.9505

2.0	.936		-.10		.036	.9365
2.5	.925		-.01		.925	.922
3.0	.914	.886	.07	.944	.912	.9105
3.5	.904	.877	.16	.873	.901	.900
4.0	.895	.868	.24	.810	.890	.890
4.5	.888	.861	.32	.749	.081	.8805
5.0	.881	.854	.41	.682	.872	.872
5.5	.874	.847	.49	.624	.864	.864
6.0	.869	.841	.58	.562	.857	.8565
6.5	.864	.835	.66	.509	.850	.849
7.0	.860	.830	.74	.459	.844	.8425
7.5	.855	.825	.83	.407	.837	.836
8.0	.852	.822	.91	.363	.833	.830
8.5	.849	.817	.99	.322	.827	.826
9.0	.845	.813	1.08	.280	.822	.821
9.5	.042	.809	1.16	.246	.817	.8155
10.0	.839	.805	1.25	.211	.812	.811
10.5	.837	.802	1.33	.184	.808	.806

TABLE V - 7				
LIQUID AGGREGATE 30° C				
&nbps;	V_1	V_2 cm^3	V_3	P_0 kg/cm^2
Methyl alcohol	.8786	.6575	.8218	3978
Ethyl alcohol	.9145	.6110	.9145	3315
Propyl alcohol	.8764	.6341	.8764	4356
Butyl alcohol	.8526	.6562	.8526	4857
Isopropyl alcohol	.8764	.6724	.8764	4356
Isobutyl alcohol	.8526	.6795	.8526	4317
m-Xylene	.7937	.6296	.7937	5479

Ethyl chloride	.7346	.6545	.7346	3167
Propyl chloride	.7376	.6571	.7376	3684
Ethyl bromide	.4305	.4305	.4832	4884
Propyl bromide	.4671	.4671	.5138	5358
Butyl bromide	.4961	.4961	.5380	5846
Ethyl acetate	.7043	.7043	.7771	5303
Water 1	.7640	.7640	.8769	3976
Water II	.7640	.7640	.8769	5965

A study of the transition from L_I to L_{II} indicates that this change begins at the upper transition point of the pure liquid, 59° C, and follows a probability curve with the same probability units as the liquid-solid transition curve; that is, 40 degrees and 5965 kg/cm^2. The probability increment is positive for both temperature and pressure as an increase in either of these quantities favors L_{II}. The third section of Table V-7 is set up in the same manner as the two preceding sections but deals with the relative proportions of the two types of liquid aggregate rather than with the proportions of liquid and solid molecules. The transition from L_I to L_{II} is asymmetrical; that is, the liquid is 100 percent L_I at all negative probability indexes and the probability value corresponding to each index is therefore ϕ rather than the ½ ϕ value which prevails in the symmetrical transitions where the condition at the probability base is an equal division between the two alternates. The quantity ϕ represents the proportion of L_I in the aggregate and is applied in the usual manner to compute the volume increment due to the presence of the less dense component.

Table V-8 lists the basic volume and pressure factors used in the calculations in this paper. These are; of course, the same factors that are utilized in computing the volume components at atmospheric pressure, which constitute the starting point for the compression calculations.

References

5. Larson. D. B., Compressibility of Solids. privately circulated paper available from the author on request.

14. All experimental values are from Bridgman unless otherwise specified. For a bibliography of Bridgmants reports see his book “The Physics of High Pressure.” G. Bell Sons, Ltd., London. 1958.

34. Bridgman. P. W., Ibid., Page 153.

35. Kennedy. George C., American Journal of Science. 248-540.

VI

Critical Constants

Having completed the coverage of the property of liquid volume we now turn to another important liquid characteristic: the critical temperature, As brought out in the first paper of this series, development of the consequences of the fundamental postulates on which the entire work is based indicates that physical state is a property of the individual molecule determined by its thermal energy level. In the solid state the inward-directed cohesive forces exceed the outward-directed thermal forces in all dimensions. At the lower transition temperature, the melting point, the thermal forces attain equality with the cohesive forces in one dimension and the molecule acquires freedom of movement in this dimension. At the location of the upper transition, the critical temperature, the thermal forces are equal to the cohesive forces in all three dimensions and the molecule is therefore able to escape from all ties with its neighbors.

A complete explanation of the derivation of this and the other theoretical conclusions that will be utilized in setting up the mathematical relations presented in this paper is beyond the scope of the present work, The general theoretical background is described in a preliminary edition of the authors book "The Structure of the Physical Universe' and further details will be added in a more complete edition to follow. This paper, like those which preceded it' will be devoted to demonstrating that the mathematical expressions developed from this new theoretical system are capable of reproducing the experimental results within the probable error of the latter.

It is apparent merely from inspection that the critical temperature is related to the molecular mass and from the basic theory we can obtain the additional information that enables expressing this relation in specific mathematical form. Three items are involved: (1) the direct relationship is not with the critical temperature itself but with a quantity that we will call the liquid base temperature, which is the critical temperature plus half of the 510 degree temperature unit (the same quantity that was utilized in computing the probability unit in paper II), (2) the effective mass is proportional to the fourth power of the base temperature, this relation being analogous to the relation between temperature and radiant energy, and (3) the effectiveness of each mass unit toward increasing the critical temperature varies with the environment and the effective mass added by such a unit is n units, where n may be zero or any small integer. For our purposes it will be convenient to regard the total effective mass as the sum of the actual molecular mass and a positive or negative <u>mass increment</u>, representing the net effect of the environmental factors. Denoting this mass increment by I, we then have the relation

$$T_c + 255.1 = 255.1\ (m + I)^{1/4} \qquad (8)$$

and we may express the critical temperature as

$$Tc = 255.1\ [(m + I)^{1/4} - 1] \tag{9}$$

If the critical temperature thus calculated is below 510.2° K a negative correction amounting to 1/36 of the difference between the calculated value and 510.2° is required.

On this basis evaluation of the critical temperature is reduced to a matter of determining the appropriate mass increment. A purely mathematical method of calculating this increment still remains to be worked out but the general principles, which are involved, are quite well defined. In the smaller atoms the atom as a whole takes part in any modification of the effective mass and the mass increment, if any, is n times the atomic number. We find, for example' that the mass increment of the normal straight chain paraffins is -6, which we may interpret as indicating that in each of these compounds the departure from the normal mass is limited to one carbon atom which has a six-unit negative increment. In Table VI-1 the critical temperatures calculated on this basis are compared with the values obtained experimentally. Following the paraffins in this table are the corresponding olefins which likewise take the -6 mass increment except for ethylene which has -8, the 2-methyl paraffins (-10, except 2-methyl propane) and the 2,2-dimethyl paraffins (-14, except 2~2-dimethyl propane).

These hydrocarbon values bring out two of the general factors, which enter into the determination of the mass increments of all of the organic compounds. First, we note that the increment of the CH2 interior groups is zero and the total increment of the molecule is attributable to the end groups of the chain. Since branched chains have more ends they tend toward larger increments unless the direction of the branch increments is opposite to that of the principal chain. Second, we find that in three of these four hydrocarbon series the first compound has a larger increment than those, which follow. In some of the substituted organic series where the initial increment is considerably greater than 6 this deviation at the lower end of the series extends still farther and the normal series level is not reached before the third or fourth compound. We may conclude from this that the addition of CH2 groups between the end groups of the molecule tends to weaken the influences, which are responsible for the existence of the mass increment. Where the original increment is small this weakening is generally a minor reduction completed with the first CH2 addition as in the hydrocarbon examples; where the original increment is large several CH2 additions may be required in order to attain the maximum effect of separation of the end groups.

As these tabulations indicate, the mass increment of the oxygen atoms is normally positive. The same is true of sulfur and nitrogen. The halogens, on the other hand, normally have negative increments. The increments of carbon and hydrogen can be either positive or negative; positive increments predominating in the acetylenes and the ring compounds and negative in the paraffins and olefins. The factors governing the specific values of the mass increments applicable to particular compounds will be discussed in more detail in subsequent papers dealing with viscosity and surface tension, two liquid properties which are functions of certain controlling temperatures not necessarily identical with the critical temperature but closely related to it.

Unfortunately the amount of experimental data available on critical temperatures is very limited and outside of the aliphatic hydrocarbons there are only a few series, which have been studied extensively, enough to enable any significant comparison between calculated and experimental values. Many of the figures in the table are therefor without direct experimental confirmation but an indirect indication of their validity can be obtained from a consideration of other properties related to the critical temperature and this matter will be covered in subsequent papers in this liquid series, particularly in connection with the discussion of boiling points and other vapor pressure phenomena.

If we compare the divergence between the calculated values and those experimental critical temperatures which are available with the divergence between the results obtained by different observers it is evident that the agreement between theory and observation is about as satisfactory as we can expect. There are a few definite conflicts, one of the most obvious of which is in the results on propane. Here the observed value is consistent with a mass increment of -7 rather than -6. This could well be another instance where a relatively small molecule deviates from the regular pattern of the series to which it belongs but there are also indications to the contrary and it appears that this is a question which will require more detailed study than can be justified in this present work.

Experimental values listed in the table have been taken from many sources, with preference being given to the values selected by Timmermana[36] and those included in the tables of Kobe and Lynn[37]. Beyond the range of the experimental work a few of the values obtained by extrapolation processes have been included but the usefulness of these figures is rather limited since their reliability falls off rapidly as the length of the extrapolation increases.

The critical pressure, the vapor pressure at the critical temperature, can be computed by making use of a relation between two hypothetical quantities: the <u>critical liquid volume,</u> which is the volume that would be occupied by the substance in question if it could exist as a pure liquid at the critical temperature, and the <u>critical gas volume,</u> which is the volume that would be occupied if the substance could exist as a pure or "ideal" gas at that temperature. (The observed critical volume is a composite quantity, which has no particular significance in relation to the subjects being covered in this liquid series.) The critical liquid volume can be calculated from equation 3 (paper II), using the appropriate values of V_0 attained by the methods of Paper III. For use in the pressure computations we next adjust this volume to $V_L + 3V_H$, where V_L is the volume originating below 510° K and V_H is the increment above 510°, if any. The adjusted critical liquid volume, V_{CL}, thus obtained is related to the critical gas volume by a factor K_C and we may express the critical gas volume as $K_C V_{CL}$. Tracing the molar gas volume as 22.4145×10^3 cm³, the value calculated from the natural units developed in the work on which this liquid study is based, we then have the relation

$$T_C = \frac{82.10\ T_C}{K_C\ m\ V_{CL}} \quad \text{atm.} \qquad (10)$$

At the present stage of the development of theory it appears that the factor K_C should be either 5.0 or 5.5 and the value Applicable to each of the series that have been studied thus far does remain constant at one of these two levels, or at the intermediate value 5.25, after the first few members of the series. In some cases these first compounds also take the same factor but more generally there is a positive or negative deviation, which starts at a maximum and decreases toward zero, as the molecule increases in size. Thus we note in Table VI-1 that K_C in the normal paraffin series is methane 5.125, ethane 5.25, propane 5.25, butane and all subsequent compounds 5.50, The acetates have a similar pattern on the positive side of the normal 5.50 value: methyl 5.875, ethyl 5.75, propyl 5.625, butyl et seq., 5.50, and most other organic series approach the normal series value in the same manner. The exact cause of this deviation at the lower ends of the series has not been determined as yet but it is probably another effect of the same influences that modify the mass increment in the smaller molecules.

Preliminary studies of a number of inorganic compounds indicate that the critical constants of these compounds are governed by the same kind of factors that determine the organic constants but for the present we are relying primarily on series relationships for establishing the mass increments and since there are no inorganic series of the necessary length and constancy of structure the present discussion will be confined to the compounds of the organic division.

REFERENCES

36. Timmermans, Jean, Physico-chemical Constants of Pure Organic Compounds, Elsevier Publishing Co., Amsterdam, 1950.

37. Kobe, K. A. and Lynn, R. E. Jr., Chemical Reviews, 52-117.

TABLE VI - 1

CRITICAL CONSTANTS

	I	Critical Temp.		K_C	V_{CL}	Crit. Pressure	
		Calc.	Obs.			Calc.	Obs.
Methane	-6	190.39	191	5.125	4.157	45.73	45.8
Ethane	-6	304.44	305	5.25	3.279	48.29	48.2
Propane	-6	375.04	370	5.25	3.221	41.28	42.0
Butane	-6	428.20	426	5.50	3.051	36.04	35.7
Pentane	-6	471.47	470	5.50	2.958	32.98	33.0

Hexane	-6	508.29	508	5.50	2.890	30.47	30.0
Heptane	-6	539.74	540	5.50	2.951	27.25	27.0
Octane	-6	567.82	569	5.50	3.015	24.61	24.6
Nonane	-6	593.21	595	5.50	3.076	22.45	22.5
Decane	-6	616.58	619	5.50	3.130	20.67	20.8
Undecane	-6	638.23	640	5.50	3.186	19.13	19.2
Doclecane	-6	658.42	659	5.50	3.237	17.83	17.9
Tridecane	-6	677.29	677	5.50	3.289	16.67	17
Tetradecane	-6	695.09	695	5.50	3.337	15.67	16
Pentadecane	-6	711.97	710	5.50	3.383	14.79	15
Hexadecane	-6	724.63	725	5.50	3.412	13.99	14
Ethylene	-8	281.63	282	5.00	3.275	50.34	50.0
Propane	-6	366.29	365	5.125	3.062	45.55	45.6
1-Butene	-6	421.27	420	5.25	3.012	38.99	39.7
1-Pentene	-6	465.69	474	5.50	2.919	33.96	33.0
1-Hexene	-6	503.50	501	5.50	2.804	31.85	29.8
1-Heptene	-6	535.45	535	5.50	2.858	28.49	27.4
1-Octene	-6	563.95	565	5.50	2.931	25.60	25.3
1-Nonene	-6	589.76	594	5.50	2.999	23.26	23.7
1-Decene	-6	613.37	615	5.50	3.059	21.34	21.3
1-Undecene	-6	635.23	637	5.50	3.120	19.70	19.7
1-Dodecene	-6	655.56	657	5.50	3.174	18.32	18.3
1-Tridecene	-6	674.64	674	5.50	3.230	17.10	16.8
1-Tetradecene	-6	692.60	689	5.50	3.281	16.05	15.5
2-Methyl propane	-12	406.98	407	5.125	3.133	35.81	36.0
2-Methyl butane	-10	459.89	461	5.375	2.950	33.01	32.9
2-Methyl pentane	-10	498.31	498	5.50	2.891	29.86	29.9
2-Methyl hexane	-10	531.17	531	5.50	2.923	27.07	27.2
2-Methyl heptane	-10	560.10	561	5.50	2.993	24.45	24.8
2-Methyl octane	-10	586.24	587	5.50	3.058	22.31	21.8

2-Methyl nonane	-10	610.15	609	5.50	3.119	20.52	20.2
2,2-dimethyl propane	-18	434.96	434	5.25	3.020	31.22	31.6
2,2-Dimethyl butane	-14	487.93	489	5.25	2.878	30.77	30.7
2,2Dimethyl pentane	-14	522.30	521	5.25	2.888	28.23	28.4
2,2-Dimethyl hexane	-14	552.17	552	5.25	2.964	25.51	25.6
2,2-Dimethyl heptane	-14	579.03		5.25	3.034	23.27	
2,2-Dimethyl octane	-14	603.53		5.25	3.098	21.41	
Benzene	+28	563.76	562	5.00	2.478	47.83	48.6
Toluene	+30	593.05	593	5.00	2.518	41.97	41.6
Ethylbenzene	+30	616.43	617	5.00	2.610	36.52	38
Propylbenzene	+30	638.16	638	5.00	2.706	32.22	32
Butylbenzene	+30	658.22	661	5.00	2.795	28.81	
Amylbenzene	+30	676.59	679	5.00	2.054	26.26	
Hexylbenzene	+30	697.42	697	5.00	2.924	24.14	
Heptylbenzene	+30	711.83	713	5.00	2.971	22.32	
Octylbenzene	+30	726.85	727	5.00	3.021	20.76	
nonylbenzene	+30	743.14	741	5.00	3.077	19.41	
Decylbenzene	+30	757.76	754	5.00	3.126	18.23	
Miethyl formate	+12	487.61	487	5.75	1.979	58.57	59.2
Ethyl formate	+6	508.06	508	5.75	2.085	46.97	46.75
Propyl formate	+6	539.53	538	5.50	2.293	39.87	40.1
Butyl formate	0	555.97	551	5.50	2.371	34.28	38
Amyl formate	0	582.50		5.50	2.480	30.18	
Hexyl formate	0	606.70		5.50	2.580	26.97	
Heptyl formate	+6	629.04		5.50	2.674	24.35	
Ethyl acetate	-2	522.08	523	5.75	2.235	37.86	38.0
Propyl acetate	-4	547.91	549	5.625	2.344	33.40	33.2
Butyl acetate	-4	575.19	574	5.50	2.491	29.68	
Amyl acetate	-4	600.00		5.50	2.557	26.91	
Hexyl acetate	-4	622.84		5.50	2.650	24.33	

Acetic acid	+64	596.37	595	6.50	2.160	58.06	57.
Propionic acid	+60	613.09	611	5.50	2.306	53.57	53
Butyric acid	+56	628.87	628	5.00	2.416	47.62	52
Valeric acid	+56	649.64	652	5.00	2.531	41.27	
Caproic acid	+56	669.08		5.00	2.623	36.06	
Enanthic acid	+56	687.35		5.00	2.707	32.02	
Caprylic acid	+56	704.62		5.00	2.786	28.80	
Pelargonic acid	+56	721.01		5.00	2.859	26.17	
Capric acid	+56	736.60		5.00	2.928	23.98	
licndecanoic acid	+56	751.51		5.00	2.993	22.13	
Lauriciacid	+56	765.76		5.00	3.055	20.55	
Methyl alcohol	+50	512.75	513	7.00	2.368	79.27	78.5
Ethyl alcohol	+38	517.45	516	6.00	2.466	62.32	63.0
Propyl acohol	+32	535.25	537	5.75	2.480	51.28	50.2
Buty alcohol	+32	563.78	560	5.00	2.553	48.92	49
Amyl alcohol	+32	589.78		5.00	2.658	41.33	
Hexyl alcohol	+32	613.23		5.00	2.745	35.90	
Heptyl alcohol	+32	635.05		5.00	2,829	31.72	
Octyl alcohol	+32	655.45		5.00	2.910	28.40	
Nonyl alcohol	+32	674.52		5.00	2.987	25.70	
Decyl alcohol	+32	692.49		5.00	3.061	23.47	
Methylamine	+22	431.08	430	5.625	2.742	73.88	73.6
Ethylamine	+16	458.95	456	5.625	2.674	55.57	55.5
Propylamine	+16	495.60	497	5.625	2.619	46.73	46.8
Butylamine	+14	524.41		5.50	2.639	40.56	
Anylamine	+14	554.03		5.50	2.731	36.75	
Hexylamine	+14	580.74		5.50	2,820	30.38	
Dimethylamine	+10	438.00	438	5.50	2.805	51.70	52.4
Diethylamine	+2	495.67	496	5.50	2.779	36.40	36.6
Dipropylamine	0	552.10	553	5.50	2.863	28.44	31

Dibutylamine	0	605.14		5.50	2.994	23.35	
Methanethiol	+18	471.39	470	5.25	2.152	71.23	71.4
Ethanethiol	+14	497.18	499	5.375	2.254	54.23	54.2
1-Propancthiol	+14	531.06		5.50	2.422	42.98	
1-Butanethiol	+14	560.01		5.50	2.526	36.70	
1-Pentanethiol	+14	586.17		5.50	2.621	32.04	
1-Hexanethiol	+14	610.07		5.50	2.703	28.49	

VII

Viscosity and Fluidity

One of the most useful findings that has resulted from the development of the general theory of physical state on which this present work is based is the theoretical deduction that there is a linear relation between temperature and each of the temperature-dependent properties of the pure liquid molecule (the molecule which is individually at a temperature somewhere between the melting point and the critical temperature). An approximate linearity has long been recognized in some of these properties, such as surface tension, for example. The present series of papers will not only show that the linearity in these instances is exact rather than approximate but will also demonstrate that a linear relationship exists in the case of those other liquid properties in which such a relation has not hitherto been recognized.

The previous papers in this series have already established the linear nature of the liquid volume-temperature relationship. The liquid aggregate follows a non-linear relation but these papers show that the deviation of the aggregate volume from linearity is not a true liquid characteristic, It is due to the presence of non-liquid molecules in the aggregate: solid molecules at the lower temperatures and critical molecules (see paper II for an explanation of this term) at relatively high temperatures. When the proportion of these foreign molecules is calculated and their volume is subtracted from the volume of the aggregate we find that the remainder, the pure liquid volume, follows the exact linear relation required by theory.

The situation with respect to viscosity is quite similar. Here again we find that the observed values show no indication of a linear relation to temperature but when the effect of the various modifying influences is evaluated and removed the true molecular relationship is seen to be very definitely linear. The underlying theory indicates., however,, that the theoretically significant property is fluidity rather than viscosity and the linear relation is therefore between temperature and fluidity. All of the calculations will be made on the fluidity basis and for convenience in setting up the tabular comparisons of experimental results and calculated values the experimental viscosities will be converted to fluidities.

It is evident that In the tipper part of the liquid temperature range where the number of molecules that have individually reached the critical temperature represents a significant proportion of the total number of molecules the fluidity of the liquid aggregate exceeds the true liquid fluidity because of the greater fluidity of the more mobile critical molecules., just as the liquid aggregate volume in this same region exceeds the volume of the true liquid. In this temperature range,, therefore., the additional fluidity due to the presence of the critical molecules will have to be evaluated and added to the true liquid fluidity in order to arrive at figures comparable with the experimental results. The experimental measurements Of Viscosity have., however., been confined almost entirely to the lower temperature range where this critical component

Is negligible and it seems advisable to limit this present discussion to this range in which the results of the calculations can be verified by comparison with experimental values, leaving the relatively unexplored high temperature range for later treatment.

According to the basic theory a solid molecule has no fluidity under any circumstances. At first glance this may seem to conflict with the observed fact that many solids do have a certain amount of plasticity, which is a low degree of fluidity. It has previously been explained, however, that solids at temperatures in the vicinity of the melting point, the same temperature range in which plasticity is found, contain a significant proportion of liquid molecules. The observed fluidity or plasticity of the solid aggregate is not actually a solid property; it is a property of the liquid molecules existing within the solid aggregate.

The same theoretical considerations, which exclude the possibility of any fluid properties for the solid molecule also, indicate that the liquid molecule has zero fluidity below the liquid temperature, which corresponds to the melting point of the solid. The first requirement in setting up the mathematical relations for calculating fluidity is therefore to establish this liquid equivalent of the melting point: a quantity which we will designate T_0. Preliminary consideration of the theoretical background would seem to indicate that this temperature T_0 should be one-third of the critical temperature. More detailed study discloses that this basic relation is modified in two respects. First, we find that the effective value of the mass increment applicable to fluidity is not necessarily the same as that applicable to the critical temperature and we therefore replace the critical temperature with a temperature T_f computed from equation 9, paper VI, in the same manner as the critical temperature but utilizing the modified mass increment. Second, we find that T_0 is related to the 3/2 power of T_f rather than to T_f. On this basis we may set up the expression

$$T_0 = .015653\ T_f^{\ 3/2}$$

As stated in the introductory paragraph of this paper, the linear relation between temperature and the various liquid properties applies specifically to the liquid molecule. In the case of properties, which are measured in such a way that the number of molecules is variable, it is therefore necessary to introduce a density term into the mathematical expression of the property. Viscosity is measured in terms of force per unit area and to put the corresponding fluidity on a basis proportional to the force per molecule we multiply the experimental value by the 2/3 power of the density. The product $fd^{2/3}$ thus obtained in the quantity, which varies linearly with the temperature. For convenience the fluidity will be expressed in reciprocal centipoises and the symbol f will refer to the fluidity in terms of these units.

From further theoretical considerations we next deduce that in organic compounds and others of similar general characteristics the linear increase in the quantity $fd^{2/3}$ takes place at such a rate that this quantity reaches the equivalent of one natural unit at $2T_0$. The value of the natural units previously developed[3] enables us to compute the unit of $fd^{2/3}$ in terms of reciprocal centipoises times $(g/cm^3)^{3/2}$ as 4.116. The temperature-fluidity equation is then

$$fd^{2/3} = 4.116\ (T-T_0)/T_0 \qquad (12)$$

and we may express the theoretical fluidity of the pure liquid at any temperature T as

$$f = 4.116\ V^{2/3}\ (T-T_0)/T_0 \qquad (13)$$

In comparing the values calculated from equation 13 with experimental results we note that the experimental fluidities diverge from the linear relation in the vicinity of T_0 and approach zero by a gradual curve rather than showing a sharp cut-off at T_0. It is obvious that this is another result of the distribution of molecular velocities due to the operation of the probability principles. When the temperature of the liquid aggregate is T_0 the temperatures of the individual molecules (their thermal energy levels) arc distributed over a range of values above and below T_0, that temperature being merely the average of the individual temperatures. Those molecules with individual temperatures above T_0 have the positive fluidities which correspond to the prevailing temperatures but there is no such thing as negative fluidity hence this fluidity contributed by the molecules above T_0 cannot be offset by the molecules below T_0 and the total of the positive fluidities manifests itself as the fluidity of the liquid aggregate. Below T_0 this aggregate fluidity follows a probability curve as the number of molecules above T_0 gradually decreases.

As explained in paper II, a determination of the exact probability relations governing such phenomena as this is beyond the scope of a broad general study of this kind and wherever probability is involved it has been considered sufficient for present purposes to establish a reasonably close correlation between the experimental values and some form of the so-called "normal" probability function' thus verifying the theoretical conclusion that the relation is one of the probability type without necessarily implying that the normal function is the exact probability expression applicable to the particular case. In the present instance the contribution of each temperature T shove T_0 to the fluidity deviation depends not only on the number of molecules at this temperature but also on the difference x between T and T_0. The probabilities are therefore computed from the integral of $x\ \phi x\ dx$ rather than the integral of $\phi x\ dx$, which was, used in most of the previous probability applications. The probability unit in which x is expressed has been taken as 510n/72 degrees and the numerical coefficient as 6.116n/18. For all of the compounds included in the tables accompanying this paper the value of n is 4.

From the foregoing it will be noted that in the class of compounds covered by the tables the fluidity at temperatures below T_0 is independent of the composition of the liquid and is a function only of the temperatures difference T_0-T. In the range immediately above T_0 the probability increment adds to the normal fluidity corresponding to the temperature T. Aside from the effect of the density, a quantity which can be evaluated by methods independent of the viscosity, the entire fluidity pattern of these normal organic liquids through the full temperature range of the pure liquid is completely defined by a single numerical value: the zero point temperature, T_0. This in turn can be computed from the molecular mass and the appropriate mass increment. As in the case of the critical temperature the whole fluidity question therefore reduces to a matter of determining the mass increment.

Here again we find it necessary, at the present stage of the development, to utilize series relationships as the means of obtaining the increments. The general series pattern is the same as that of the values applicable to the critical temperature, all members of each series beyond the first three or four having the same mess increment, filth slightly higher values for the lower compounds. These series values of the increment are usually close to those previously established for the critical temperature. The paraffin increments, for example, shift about 6 or 8 units in the positive direction, the normal paraffins going from -6 (critical temperature basis) to 0 (fluidity basis), the 2-methyl and 3-methyl paraffins from -10 to -4, and the 2,2-dimenthyl paraffins from -14 to -6.

At this point it may be appropriate to comment briefly on the nature of this quantity which has been called the mass increment. The use of this term is not intended to imply that the actual mass of the molecule is in any way variable. We find that in many physical properties, including fluidity, the relation between mass and the property in question is subject to modification in such a manner that if the normal effect of the mass m of a particular atom is xm the modified value is nxm. The average coefficient applicable to the molecule as a whole is the weighted average of the x and nx values applicable to the individual atoms. It would be entirely possible, and perhaps more logical, to use average numerical coefficients of this nature in conjunction with the actual molecular mass rather than to throw the adjustment into the mass term by treating the difference between nm and m as an increment adding to the effective mass, but the latter has the very great advantage of bringing out clearly and distinctly the regularities and series relationships in the various properties which would be completely obscured by the alternate method of treatment.

Table VII-1 shows the mass increments and the corresponding values of T_0 for a number of common organic series. In Table VII-2 representative values of T_0 from the preceding tabulation together with the appropriate values for some additional compounds are applied to the calculation of fluidities at specific temperatures. Column 2 in this table, headed P, shows the fluidity increment due to the probability distribution, if any significant increment is present. Column 3 is the sum of this increment and the molecular fluidity, $fd^{2/3}$, computed from equation 12. Dividing by the 2/3 power of the density we then obtain the theoretical fluidity (column 4) corresponding to the measured fluidity in column 5.

Most of the calculated fluidities listed in Table VII-2 agree with the experimental values within one or two percent. This degree of correlation is found in at least a substantial part of the experimental temperature range of practically all of the hundreds of liquids that have been studied in the course of this work, but at other temperatures the divergence frequently amounts to five percent or more. The significance of such discrepancies depends, of course, on the degree of accuracy that can be attributed to the experimental results, Timmermans[36] tells us that it is difficult to measure viscosity with an accuracy of better than one percent and he includes among his selections of "precision" data some values from different sources which differ by three to six or eight percent. (See for example the values listed for pentane, ethyl alcohol, ethyl, ether, and methyl butyrate.) A general comparison of the results obtained on identical substances by different observers indicates that the accuracy of the normal run of experimental work is considerably lower than that of Timmermans' selected values, as might be expected. The differences between the experimental fluidities and the values calculated from equation 13 are therefore clearly within the limits of accuracy of the experimental work,

In this connection it should be remembered that agreement with the experimental results is not an and in itself here as it is in the case of those studies which are made specifically for the purpose of devising mathematical expressions that fit the experimental data. An expression, which is provided with a sufficient number of adjustable constants, can be made to fit any set of experimental results, right or wrong, as long as it is not irregular. The aim of this present works on the other hand, is to ascertain the correct values and the calculations produce a rigid pattern with no latitude for adjustment. If this pattern agrees with the general pattern of experimental values and a reasonably large proportion of the figures agree closely (within the one percent deviation suggested by Timmermans, let us say) then individual discrepancies are not significant, even if they are numerous. In a situation where even the "percision" measurements often differ widely it is obvious that the general run of experimental work must have produced many inaccurate values and these will necessarily show up as deviations from the theoretical fluidities.

In addition to the previously mentioned alternate values of the factor n in the expressions from which the probability units are calculated, there are a few other possible variations in the structural factors involved in the fluidity and a number of substances, notably rater and the alcohols, follow a somewhat modified pattern. This initial presentation of the fluidity relations has, however, been confined to those substances, which can be considered regular, and discussion of the liquids with special behavior characteristics will be deferred to a later publication.

REFERENCES

3. Larson, D, B., The Structure of the Physical Universe, published by the author, 755 N. E. Royal Court, Portland 12, Oregon, 1959. Appendix A,

36. Timmermans, Jean, Physico-chemical Constants of Pure Organic Compounds, Elsevier Publishing Co., Amsterdam, 1950.

38. American Petroleum institute Research Project 44, Selected Values, Carnegie Press, Pittsburgh, 1953.

39. Bingham. E, C., and Spooner, L. W., Physics, 4-387.

40. Friend, J. N., and Hargreaves, W. D., Phil. Mag., 35-619.

41. Friend and Hargreaves, ibid., 35-136.

42. Friend and Hargreares, Ibid., 36-731.

43. Lacher, J. R., Walden, C. H., and Park, J. D., J. Am. Chem. Soc., 71-3026.

TABLE VII - 1

Zero Point Temperatures

	I	T_r
Ethane	-2	94.8
Propane	0	126.3
Butane	0	149.1
Pentane	0	169.0
Hexane	0	186.8
Heptane	0	203.1
Octane	0	218.1
Nonane	0	232.1
Docane	0	245.2
Undecane	0	257.6
Dodecane	0	269.4
Tridentine	0	280.5
Tetradecane	0	291.2
Pentadobane	0	301.7
Hexadecane	0	311.7
2-Methyl propane	+2	152.1
2-Methyl butane	-4	163.6
2-Methyl pontane	-4	181.9
2-Methyl hexane	-4	198.6
2-Methyl heptane	-4	213.9
2-Methyl octane	-4	228.2
2-Methyl Mundane	-4	241.5
Benzene	+36	217.9
Toluene	+18	213.8
Ethylenzene	+12	222.1

propylbenzone	+12	235.8
Butylberinene	+12	248.8
Amylbenzene	+12	261.0
Boxylbenzene	+12	272.6
Heptylbenzene	+12	283.7
octylbenzene	+12	294.3
Ethyl bromide	-40	164.7
Propyl bromide	-38	185.4
Butyl bromide	-38	201.8
Arryl bromide	-36	218.9
Heryl bromide	-36	232.9
Heptyl bromide	-36	246.0
Octyl bromide	-36	258.3
Nonyl bromide	-36	270.1
Methyl formate	-16	174.1
Ethyl Chordate	-12	186.6
Propyl formate	-12	202.8
Butyl fornate	-12	218.0
Ethyl Chordate	-12	232.0
Hexyl formate	-12	245.1
Heptyl fornate	-12	257.5
0ctyl formate	-12	269.3
Methyl acetate	-10	184.3
Ethyl acetate	-6	196.2
Propyl acetate	-6	211.7
Butyl acetate	-6	226.1
Amyl acetate	-6	239.6
Hexyl acetate	-6	252.3
Heptyl acetate	-6	264.4
Octyl acetate	-6	275.8

Methyl propionate	-6	196.2
Ethyl propionate	0	205.2
Propyl propionate	0	220.0
Butyl propionate	0	033.9
Amyl propionate	0	247.0
Hexyl propionate	0	259.3
Heptyl propionate	0	211.0
Octyl propionate	0	282.2
Methyl butyrate	-6	211.7
Ethyl butyrate	0	220.0
Propyl butyrate	0	233.9
Butyl butyrate	0	247.0
Amyl butyrate	0	259.3
Hexyl butyrate	0	271.0
Heptyl butyrate	0	282.2
Octyl butyrate	0	292.8
Ethyl valerate	0	233.9
Ethyl casemate	0	247.0
Ethyl heptanoate	0	259.3
Ethyl caprylate	0	271.0
Ethyl pelargonate	0	282.2
Ethyl caprate	0	292.8

<table>
<tr><th colspan="5">TABLE VII - 2</th></tr>
<tr><th colspan="5">FLUIDITY</th></tr>
<tr><th colspan="5">Octane (30)</th></tr>
<tr><th>T</th><th>P</th><th>fd 2/3</th><th>Calc.</th><th>Cbs.</th></tr>
<tr><td>-50</td><td>.36</td><td>.46</td><td>.55</td><td>.54</td></tr>
<tr><td>-40</td><td>.31</td><td>.59</td><td>.71</td><td>.69</td></tr>
<tr><td>-30</td><td>.24</td><td>.71</td><td>.87</td><td>.85</td></tr>
</table>

-20	.16	.82	1.01	1.02
-10	.10	.95	1.17	1.21
0	.05	1.09	1.36	1.40
10	.02	1.25	1.57	1.61
20	.01	1.43	1.81	1.83
30		1.61	2.05	2.06
40		1.79	2.30	2.29
50		1.98	2.57	2.53
60		2.17	2.83	2.79
70		2.36	3.11	3.05
80		2.55	3.39	3.33
90		2.74	3.67	3.61
100		2.93	3.96	3.91
110		3.12	4.26	4.23
120		3.30	4.59	4.56

TABLE VII - 2

FLUIDITY

Nonane (39)

T	P	fd 2/3	Calc.	Cbs.
0	.12	.85	1.04	1.03
10	.07	.98	1.21	1.21
20	.03	1.11	1.38	1.41
30	.01	1.27	1.60	1.61
40	.01	1.45	1.83	1.825
60		1.79	2.30	2.28
80		2.15	2.81	2.78
100		2.50	3.32	3.35

TABLE VII - 2

FLUIDITY				
1-PENTANE (38)				
I = -8		T_0 = 155.0		
T	P	fd 2/3	Calc.	Cbs.
-90	.21	.96	1.16	1.18
-30	.14	1.15	1.40	1.43
-70	.08	1.36	1.67	1.69
-60	.04	1.59	1.97	2.00
-50	.02	1.83	2.30	2.33
-40	.01	2.09	2.65	2.63
-30		2.34	2.99	3.03
-20		2.61	3.37	3.33
-10		2.87	3.74	3.70
0		3.14	4.13	4.17

TABLE VII - 2				
FLUIDITY				
Methyl Cyclallexane (38)				
I = +28		T_0 = 230.1		
T	P	fd 2/3	Calc.	Cbs.
-20	.25	.66	.76	.71
-10	.18	.77	.89	.85
0	.11	.88	1.03	1.01
10	.06	1.01	1.19	1.18
20	.03	1.16	1.38	1.36
30	.01	1.32	1.58	1.56
40		1.49	1.80	1.77
50		1.67	2.04	2.00
60		1.84	2.26	2.24
70		2.02	2.50	2.50

80		2.20	2.75	2.78
90		2.38	3.00	3.03
100		2.56	3.25	3.33

TABLE VII - 2				
FLUIDITY				
Hexyl Cyclopentane (38)				
I = +16		T_0 = 269.4		
T	P	fd 2/3	Calc.	Cbs.
-20	.30	.30	.34	.32
-10	.35	.35	.40	.36
0	.36	.42	.48	.47
10	.32	.53	.61	.56
20	.25	.61	.71	.67
30	.17	.69	.81	.80
40	.10	.77	.91	.93
50	.06	.88	1.05	1.07
60	.03	1.00	1.20	1.22
70	.01	1.14	1.38	1.37
80		1.28	1.56	1.54
90		1.43	1.76	1.69
100		1.59	1.97	1.85

TABLE VII - 2				
FLUIDITY				
Toluene (39)				
T	P	fd 2/3	Calc.	Cbs.
0	.04	1.18	1.28	1.30
10	.02	1.36	1.49	1.49
20	.01	1.54	1.70	1.70

30		1.72	1.91	1.92
40		1.91	2.13	2.14
60		2.30	2.61	2.62
80		2.68	3.08	3.14
100		3.07	3.58	3.70

TABLE VII - 2				
FLUIDITY				
Ethylbenzane (39)				
T	P	fd 2/3	Calc.	Cbs.
0	.08	1.02	1.11	1.14
10	.04	1.17	1.28	1.315
20	.02	1.33	1.47	1.495
30	.01	1.50	1.66	1.68
40		1.68	1.88	1.88
60		2.05	2.32	2.31
80		2.43	2.79	2.77
100		2.80	3.26	3.27

TABLE VII - 2				
FLUIDITY				
Propyl Bromide (39)				
I = -36		T_0 = 185.4		
T	P	fd 2/3	Calc.	Cbs.
0		1.95	1.57	l.545
10		2.17	1.76	1.73
20		2.39	1.95	1.925
30		2.62	2.16	2.13
40		2.84	2.37	2.34
60		3.28	2.79	2.805

TABLE VII - 2

FLUIDITY

Ethyl Iodide (39)

I = -76 T_0 = 179.2

T	P	fd 2/3	Calc.	Cbs.
0		2.16	1.37	1.385
10		2.39	1.53	1.545
20		2.62	1.69	1.71
30		2.85	1.85	1.88
40		3.06	2.02	2.06
60		3.54	2.36	2.435
70		3.77	2.53	2.55

TABLE VII - 2

FLUIDITY

Prionitrile (40)

I = +40 T_0 = 179.3

T	P	fd 2/3	Calc.	Cbs.
20.1		2.00	2.35	2.32
31.2		2.23	2.65	2.61
43.9		2.50	3.00	2.96
57.4		2.78	3.38	3.35
69.5		3.03	3.73	3.71
83.0		3.31	4.12	4.13
93.1		3.53	4.44	4.44

TABLE VII - 2

FLUIDITY

1-Butanethiol (39)

I = +12 T_0 = 205.3

T	P	fd 2/3	Calc.	Cbs.
0	.02	1.39	1.54	1.545
10	.01	1.58	1.76	1.75
20		1.77	1.99	2.00
30		1.97	2.23	2.23
40		2.17	2.47	2.46
60		2.57	2.98	2.95
80		2.97	3.50	3.49

TABLE VII - 2

FLUIDITY

Ethyl Formate (39)

T	P	fd 2/3	Calc.	Cbs.
0		1.91	1.97	1.98
10		2.13	2.22	2.22
20		2.35	2.47	2.48
30		2.57	2.73	2.76
40		2.79	2.99	3.04
50		3.01	3.26	3.25

TABLE VII - 2

FLUIDITY

Ethyl Propionate (39)

T	P	fd 2/3	Calc.	Cbs.
0	.02	1.38	1.47	1.44
10	.01	1.57	1.69	1.55
20		1.77	1.92	1.87
30		1.97	2.15	2.11
40		2.17	2.40	2.36
60		2.57	2.89	2.89

80		2.97	3.40	3.49

TABLE VII - 2

FLUIDITY

Ethyl Butyrate (39)

T	P	fd 2/3	Calc.	Cbs.
20	.01	1.38	1.50	1.50
30		1.56	1.71	1.69
40		1.74	1.92	1.91
60		2.12	2.38	2.38
80		2.49	2.85	2.89

TABLE VII - 2

FLUIDITY

Ethyl Valerate (39)

T	P	fd 2/3	Calc.	Cbs.
0	.13	.82	.88	.87
10	.07	.94	1.02	1.035
20	.04	1.08	1.18	1.20
30	.02	1.24	1.37	1.38
40	.01	1.41	1.57	1.57
60		1.75	1.98	1.985
80		2.10	2.41	2.415
100		2.45	2.87	2.89

TABLE VII - 2

FLUIDITY

Acetone (39) (43)

I = +22 $T_0 = 179.3$

T	P	fd 2/3	Calc.	Cbs.
-80	.32	.64	.68	.65

-40	.06	1.30	1.44	1.40
0		2.16	2.48	2.53
10		2.39	2.77	2.80
20		2.62	3.07	3.09
30		2.84	3.36	3.405
40		3.07	3.67	3.72

TABLE VII - 2				
FLUIDITY				
Acctic Acid (39)				
I = +84		T_0 = 246.8		
T	P	fd 2/3	Calc.	Cbs.
20	.09	.86	.83	.82
30	.04	.98	.95	.96
40	.02	1.13	1.11	1.11
60		1.44	1.44	1.42
80		1.77	1.79	1.78
100		2.11	2.18	2.18

TABLE VII - 2				
FLUIDITY				
Propione Acid (39)				
I = +70		T_0 = 246.8		
T	P	fd 2/3	Calc.	Cbs.
0	.23	.67	,66	.66
10	.15	.76	.76	.78
20	.09	.86	,86	.91
30	.04	.98	.99	1.04
40	.02	1.13	1.15	1.185
60		1.44	1.49	1.59

80		1.77	1.36	1.83
100		2.11	2.26	2.21
120		2.44	2.66	2.63
140		2.78	3.08	3.11

TABLE VII - 2				
FLUIDITY				
Chlorobenzene (39)				
I = +6		T_0 = 222.5		
T	P	fd 2/3	Calc.	Cbs.
0	.07	1.01	.91	.95
10	.03	1.15	1.05	1.095
20	.01	1.32	3.22	1.25
30	.01	1.50	1.39	1.42
40		3.68	1.57	1.58
60		2.05	1.95	1.95
80		2.42	2.34	2.34
100		2.79	2,74	2.79
120		3.16	3.16	3.27

TABLE VII - 2				
FLUIDITY				
Bromobenzcne (39)				
I = -30		T_0 = 230.9		
T	P	fd 2/3	Calc.	Cbs.
0	.31	.86	.63	.625
10	.06	.99	.74	.75
20	.03	1.14	.86	.87
30	.01	1.30	.98	1.00
40		1.47	1.12	1.14

60		1.82	1.41	1.42
80		2.18	1.72	1.72
100		2.54	2.03	2.04
110		2.89	2.35	2.39
140		3.25	2.68	2.78

TABLE VII - 2				
FLUIDITY				
Dibutyl Ether (39)				
I = -6		T_0 = 228.1		
T	P	fd 2/3	Calc.	Cbs.
0	.10	.90	1.06	1.06
10	.05	1.04	1.23	1.245
20	.02	1.19	1.42	1.445
30	.01	1.36	1.64	1.65
40		1.54	1.87	1.86
60		1.90	2.35	2.33
80		2.26	2.84	2.86
100		2.62	3.34	3.41

TABLE VII - 2				
FLUIDITY				
Mitrobenzene (39) (41)				
I = +52		T_0 = 273.3		
T	P	fd 2/3	Calc.	Cbs.
0	.36	.36	.31	.32
10	.34	.49	.43	.40
20	.28	.58	.51	.50
30	.20	.65	.58	.995
40	.13	.73	.66	.695

60	.04	.95	.87	.91
80	.01	1.22	1.13	1.15
100		1.51	1.52	1.42
96.4		1.55	1.34	1.34
139.5		2.10	1.99	1.97
160.9		2.42	2.32	2.30
180.0		2.71	2.64	2.61
199.5		3.01	2.97	2.95

TABLE VII - 2				
FLUIDITY				
p-Nitrotoluene (42)				
I = +46		T_0 = 279.7		
T	P	fd 2/3	Calc.	Cbs.
99.0		1.36	1.29	1.33
124.2		1.73	1.67	1.60
138.6		1.94	1.88	2.39
150.3		2.12	2.07	2.08
162.2		2.29	2.25	2.26
177.5		2.52	2.54	2.505
187.7		2.67	2.67	2.675
200.5		2.06	2.88	2.89
215.5		3.08	3.14	3.14

TABLE VII - 2				
FLUIDITY				
p-Dichlorobenzene (42)				
I = -10		T_0 = 240.4		
T	P	fd 2/3	Calc.	Cbs.
60.7		1.60	1.38	1.385

81.7		1.96	1.72	1.705
101.3		2.30	2.04	2.02
120.0		2.61	2.34	2.33
130.0		2.79	2.92	2.51
139.9		2.96	2.70	2.69
150.2		3.13	2.87	2.87
159.8		3.30	3.05	3.05

VIII

Surface Tension

The study of a phenomenon such as surface tension by the application of a broad general theory encompassing a variety of associated phenomena has a significant advantage over a more restricted approach to the subject because an understanding of the interrelations between these various phenomena usually carries with it a very definite indication of the nature and magnitude of the factors governing the particular physical process under consideration. In this case we find from theory that surface tension and viscosity are very similar properties of matter; in fact it can be said that each is essentially the complement of the other. The findings with respect to viscosity which were described in paper VII can therefore be transferred en bloc to surface tension with appropriate modifications to compensate for the existing differences between the two phenomena.

As pointed out in the first paper of this liquid series, development of the consequences of the fundamental postulates on which this work is based indicates that physical state is a property of the individual molecule determined by its thermal energy level. In the solid state the inward-directed cohesive forces exceed the outward-directed thermal forces in all dimensions and the molecule therefore maintains a constant spatial relationship with its neighbors. In the gaseous state the net force is outward" permitting each molecule to break all ties and pursue its own independent course. The liquid state is the intermediate situation in which the molecule has sufficient thermal energy to escape from the solid state limitations in at least one dimension but not enough to break loose in all dimensions. Fluidity a measure of mobility, is a reflection of the amount of progress toward the gaseous state and it necessarily has zero value at a temperature analogous to the melting point, rising in linear relation to the temperature from there on.

Surface tension, a measure of the inter-molecular attraction, is obviously the in-verse property, a reflection of the degree to which the substance still retains its solid properties. It follows that the surface tension is zero at a temperature analogous to the critical temperature, rising in linear relation to the decrease in temperature below this point.

As in the case of fluidity these relations apply specifically to the surface tension per molecule. Since surface tension is customarily measured in terms of force per unit of length, we multiply the conventional measurement by the cube root of the density, obtaining the quantity $\gamma d^{1/3}$, which is, proportional to the surface tension per molecule and corresponds to the quantity $fd^{2/3}$ used in the fluidity study.

By analogy with the findings concerning fluidity we can deduce that the controlling temperature, at which the surface tension is zero can be evaluated from equation 9, paper VI, in the same manner as T_c and T_f, using an appropriate value of the mass increment. The unit value of the surface tension is reached at the point where the difference T_r - T is equal to the liquid base temperature, which has been defined as the value obtained from equation 9 with the mass increment equal to zero. From the previously developed natural units3 we then compute the numerical coefficient of the surface tension equation as 58.314, which gives us

$$\gamma d^{1/3} = 58.314\ (T_r - T)/T_{base} \qquad (14)$$

and the theoretical equivalent of the surface tension as measured is

$$\gamma = 58.314\ V^{1/3}\ (T_r - T)/T_{base}\ \text{dynes/cm} \qquad (15)$$

The resemblance to equation 13, the fluidity equation, is obvious.

It was brought out in the fluidity discussion that the mass increment effective in the fluidity relations is determined entirely by the end groups of the molecule, the interior groups having no effect except in the smallest molecules, where they may cause a modification of the increments applicable to the end groups by increasing the separation between the ends of the molecules. Surface tension, however, is a property of the solid-state type and in the solid state each structural group acts independently. This means that from a surface tension standpoint each structural group is an end group and is a potential contributor to the mass increment. Instead of settling down to a constant series level after the first few added CH_2 groups in the manner of the mass increments applicable to fluidity, the increments applicable to surface tension continue to increase (or decrease) as the molecule becomes larger.

In the normal paraffins, for example, methane has the same mass increment, for surface tension as for fluidity and for the critical temperature. But whereas the increment for the critical temperature remains constant at -6 for the entire normal paraffin series, and the increment for fluidity remains constant at zero after dropping to this point as a result of the first two CH_2 additions the negative increment for surface tension rises continuously as the chain lengthens, at the rate of two units per added CH_2 group as far as octane and four units per CH_2 group beyond this point. The 1-olefin pattern is almost identical but two units lower.

Table VIII-1 shows the liquid base temperatures, the mass increments, and the corresponding values of T_r for several common organic series. Table VIII-2 compares the experimental surface tensions with the results obtained from equation 15 using selected values from the preceding table and similar data on other representative organic compounds. The densities used are those given in the reports of the surface tension measurements, except where accurate theoretical values are available from the volumetric work described in previous papers of this series. These density values have not been listed in the table, as they are readily available from other sources.

The great majority of organic liquids and many of the common inorganic liquids follow this pattern without deviation and to simplify this initial presentation the discussion has been confined to these "regular" liquids. The compounds with special behavior characteristics including those chronic dissenters water and the alcohols, will be covered in a later publication.

Since the accuracy of the surface tension measurements is considerably greater than that of the measurements of viscosity we can draw some more definite conclusions from the comparisons of calculated and experimental values than were possible in the preceding paper on viscosity. To those who are interested in this situation primarily from the standpoint of liquid theory these questions as to the exact degree of correlation have little meaning. It is obvious that we cannot prove the validity of the theory by such a comparison; all that we can do is to show that the differences between the calculated and experimental values are within the uncertainty limits of the latter, which indicates that the theory could be correct. Actual evidence of its validity will have to be derived from other sources, the nature and significance of which will be discussed in the next paper in this series. In addition to its theoretical aspects however, the development of an accurate method of calculating the magnitudes of the various physical properties of liquids has a considerable practical value and those who are interested principally in the practical utilization of the figures are likely to give considerable weight to the actual degree of correlation between theory and experiment. Some discussion of this matter is therefore in order.

The important point that should be recognized in this connection is that a closer agreement is not necessarily a better agreement. Everyone realizes that if the differences between the calculated and experimental values are greater than the experimental uncertainty the theoretical results cannot be correct " but it is not always appreciated that too close an agreement has exactly the same meaning. The results obtained from a theoretically correct method of calculation will, of course, show very close agreement with the experimental values in many, cases but if the agreement is consistently much closer than the margin of experimental uncertainty it is clear that method of calculation gives us nothing more than a restatement of the experimental results.

This emphasizes the importance of a realistic evaluation of the magnitude of the experimental uncertainty. For this purpose the most reliable guide is the extent of agreement between competent observers. The investigators' own estimates of uncertainty usually have to be taken with a grain of salt. As B. N. da C. Andrade puts it, the last significant figure reported is often nothing more than an "expression of a genial optimism". Timmermans[36] has made a close study of this subject and states that it is difficult to measure surface tension with an accuracy greater than about 0.2 percent. If the surface tension is in the neighborhood of 25 dynes/cm this amounts to approximately .05 dynes/cm. Examination of his selections of "precision" data discloses that in a very large percentage of those cases where two or more values are given for the same temperature the difference between the minimum and maximum is .10 dynes/cm or more. In the normal paraffin hydrocarbons, which are as Timmermans says "a first rate physico-chemical material" and have been extensively studied, the average difference between his 20º values is .033 dynes/cm where only two values are given, but when we look at heptane and octane, which are represented by 4 and 5 values respectively, we find that the difference between the high and low values in both cases is .09 dynes/cm. Since there is no reason to believe that the measurements are any more difficult on these two compounds than on others in the series it is evident that the law figure of .033 dynes/cm is merely a result of selection and that the true uncertainty in the most accurate measurements of surface tension is at least .09 dynes/cm.

This conclusion is corroborated by the fact that the differences between the "best" experimental values for other organic compounds are much higher. The average difference between the 20º values selected by Timmermans for the branched paraffins is .122 dynes/cm, and in other organic families we find deviations up to .45 dynes/am. Since these are "precision" measurements in the most favorable temperature range and have undergone a selection process which has eliminated the most discordant values, it is obvious that the uncertainty in the general run of experimental work is substantially higher.

Let us now see whether the differences between the experimental results and the calculated values (which are the correct values if the theory is valid) are consistent with these experimental uncertainties. Again we will look first at the experimental results which are presumably the most accurate. A recent study by Jasper, Kerr and Gregorich[44] covered the normal paraffins from pentane to octadecane and from 0º to 80º C. If ire average the differences between the results of this investigation and the calculated values for each compound and then give these averages equal weight in computing an overall average difference we arrive at a figure of .074 dynes/cm. A similar calculation for the 1-olefins using data of the same investigators gives us an average deviation of .110 dynes/cm. The API values for the normal paraffins (propane and beyond) which cover a larger number of compounds and extend to higher and lower temperatures where measurement is more difficult show an average deviation of .149 dynes/cm. The monumental work of Vogel and collaborators produces results such as the following: normal paraffins .118, acetylenes .128, alkyl benzenes .097, propyl esters .134, ethyl diesters .128.

Although uncertainty is a very difficult thing to measure, the foregoing figures leave little doubt but that the average differences between the experimental results and the values calculated by the methods of this paper are consistent with realistic estimates of the uncertainties. The calculated values are therefore within the area in which they should fall if they are correct. The next paper in this series will utilize other methods to show that these values probably are correct.

The particular merit of the new development from the standpoint of practical utilization rests upon this point since it means that the new methods are able to distinguish correct from incorrect values. This is not true of any of the mathematical expressions previously developed for the representation of liquid properties. Such expressions smooth out the experimental values and eliminate minor irregularities but the general degree of accuracy of the results obtained from them is completely determined by the accuracy of the experimental data from which their constants were derived. The equations developed in this work, on the contrary, are primarily theoretical. They are not entirely independent of the experimental results but they utilize these data only for the purpose of finding the general area within which the correct values are located and the specific magnitudes of these correct values are then precisely determined by the equations. The accuracy or lack of accuracy of the experimental work has no bearing on this latter operation.

To illustrate this point let us look at some very interesting and significant data on the normal paraffins from C_{11} to C_{16} inclusive. When equation 15 was first formulated several years ago the results obtained from calculations on this group of compounds were checked against the API values, which are a composite of experimental data selected from the literature. At 20º C, which is probably the temperature most favorable for accurate observation, the differences between the calculated and experimental values ranged from .02 to .04 dynes/cm, with an average of .027, If we accept Timmemans' estimate of the maximum accuracy normally obtainable at the present time arid take .05 dynes/cm as the dividing line between correct and incorrect values, the calculations indicate that all of the API values at 20º are correct. When we examine the results at other temperatures, however, we find that only 7 out of a total of 44 measurements in the range from 0º to 80º f all within the limits which we have taken as defining the correct values .9 and the average deviation is .088 dynes/cm. This comparison therefore leads to the conclusion that most of the API values for these compounds at temperatures other than 20º C are incorrect.

Ordinarily the only support which is available for such conclusions as the foregoing comes from the general considerations -which indicate that the results produced by the new system are correct and if these conclusions had been announced at the time they were originally reached they undoubtedly would have been challenged, but the subsequent work of Jasper. et al, fully substantiates the accuracy of the calculations and the validity of the conclusions reached therefrom, Almost 80 percent of the individual, measurements on these six compounds reported by the Jasper group are within .05 dynes/cm, of the calculated values and the average deviation is only .35 dynes/cm. On the other hand the differences between the Jasper and API values average .10 dynes/cm with individual discrepancies as high as .30 dynes/cm. This recent work thus provides a very striking confirmation of the points which ' have been brought out in the foregoing discussion and, together with the theoretical evidence of the validity of the calculated results which will be discussed in paper number nine, justifies the assertion that wherever a homologous series of compounds is long enough or closely enough related to another series to enable establishing the values of the mass increments on a firm basis the calculations from equation 15 produce the correct values of the surface tension and if there is any lack of agreement with the experimental results the error is in the experimental work.

Although the true situation with respect to viscosity is obscured to some extent because of the greater experimental uncertainties in the measurement of that property, it is quite apparent that the theoretical development in this work unites the surface tension and viscosity phenomena and the conclusions with respect to surface tension are therefore valid for viscosity as well.

This ability of the new equations to discriminate between correct and incorrect values has some important implications with respect to their applicability. Obviously such expressions have a potential field of usefulness considerably broader than that of any expressions which merely enable interpolation and a limited amount of extrapolation of the experimental data.

TABLE VIII - 1

Zero Point Temperatures

	T_{base}	I	T_r
Methane	255.48	-6	199.03
Ethane	342.33	-8	297.87
Propane	402.34	-10	361.38
Butane	449.34	-12	409.77
Pentane	488.47	-14	449.43
Hexane	522.24	-16	483.32
Heptane	552.10	-18	513.12
Octane	578.98	-22	535.56
Nonane	603.49	-24	560.14
pecane	626.06	-28	579.09
Undecane	647.02	-32	596.80
Dodecane	666.61	-36	613.49
Tridecane	685.03	-40	629.27
Tetradecane	702.42	-44	644.23
Pentadecane	718.91	-48	658.50
Hexadecane	734.61	-52	672.13
Heptadecane	749.59	-56	685.16
Octadecane	763.94	-60	697.69
Nonadecane	777.70	-64	709.73
Eicosane	790.93	-68	721.35
Ethylene	332.05	-8	284.76
Propane	394.69	-9	356.76
1-Butene	443.15	-10	409.69
1-Pentene	483.22	-12	449.37
1-Hexene	517.65	-14	483.30

1-Heptene	548.01	-16	513.07
1-0ctene	575.28	-20	535.51
Argonne	600.10	-22	560.12
1-Decene	622.92	-26	579.05
1-Undecene	644.10	-30	596.78
1-Dodecene	663.87	-34	613.46
1-Tetradecone	699.97	-42	644.20
1-Hexadecene	732.39	-50	672.08
Acetylene	321.23	-2	309.82
Propyne	386.76	0	386.76
1-Butyne	436.80	-2	430.31
1-Pentyne	477.84	-4	466.84
Teledyne	512.98	-6	498.55
1-Heptyne	543.86	-8	526.70
1-Octyne	571.52	-10	552.09
1-Nonyne	596.66	-12	575.30
1-Decyne	619.74	-16	593.24
1-Undecyne	641.14	-20	610.14
l-Dodecyne	661.11	-24	626.10
Methyl acetate	493.40	+6	508.12
Ethyl	526.55	-6	512.89
Proyl	555.97	-10	535.34
Butyl	582.49	-14	556.03
Amy1	606.70	-18	575.23
Hexyl	629.04	-22	593.19
Propyl formate	526.55	-2	522.08
Prowl acetate	555.97	-10	535.34
Propyl propionate	582.49	-16	552.03
Prowl butyrate	606.70	-22	567.72
Proper valerate	629.04	-28	582.58

Me Me ketone	449.22	+14	488.30
Me Et	488.35	+10	512.89
He Pr	522.15	+6	535.34
Me Bu	552.03	+2	556.03
He Am	578.90	-2	575.23
He Hexyl	603.42	-8	589.70
Me Heptyl	625.98	-12	606.78
Et Et	522.15	+6	535.34
Et Pr	552.03	0	552.03
Et Bu	578.90	-4	571.50
Et Am	603.42	-8	589.70
Et Hexyl	625.98	-12	606.78
Et Heptyl	646.96	-16	622.92
Ethyl chloride	467.98	-5	453.55
Propyl	504.42	-6	489.48
Butyl	536.28	-8	518.60
Amyl	564.70	-10	544.76
Hexyl	590.42	-12	568.56
Heptyl	614.01	-14	590.47
Octyl	635.80	-18	607.51
Nonyl	656.11	-20	626.72
Decyl	675.15	-24	641.82
Undecyl	693.08	-28	656.18
Dodecyl	710.05	-32	669.91
Hexadecyl	770.28	-48	719.16
Dimethyl ether	409.59	-4	394.66
Diethyl	493.50	-14	455.25
Dipropyl	556.05	-22	508.33
Dibutyl	606.77	-30	552.15
Diamyl	649.86	-38	589.83

Dihexyl	687.53	-46	623.03
Diheptyl	721.17	-54	652.85
Dioctyl	751.65	-62	679.98

TABLE VIII - 2		
Surface Tension		
Butane (38)		
T	Calc.	Obs.
-100	27.25	27.2
-90	25.98	25.9
-80	24.72	24.6
-70	23.46	23.4
-60	22.20	22.1
-50	20.99	20.88
-40	19.76	19.65
-30	18.56	18.43
-20	17.35	17.22
-10	16.15	16.02
0	14.97	14.84

TABLE VIII - 2		
Surface Tension		
Hexane (44)		
T	Calc.	Obs.
0	20.56	20.50
10	19.51	19.46
20	18.44	18.41
30	17.40	17.37
40	16.36	16.32
50	15.32	15.28

60	14.29	14.24

TABLE VIII - 2

Surface Tension

Octane (36)

T	Calc.	Obs.
10	22.70	22.73
20	21.70	21977
30	20.74	20.76
40	19.75	19.84
50	18.78	18.82

TABLE VIII - 2

Surface Tension

Decane (44) (38)

T	Calc.	Obs.
0	25.88	25.73
10	24.94	24.81
20	23.99	23.89
30	23.07	22.98
40	22.34	22.06
50	21.21	21.14
60	20.31	20.22
70	19.39	19.29
80	18.50	18.43
90	17.61	17.6

TABLE VIII - 2

Surface Tension

Dodecane (44)

T	Calc.	Obs.

0	27.29	27.24
10	26.36	26.36
20	25.47	25.48
30	24.57	24.60
40	23.69	23.73
50	22.80	22.85
60	21.93	2.97
70	21.06	21.09
80	20.20	20.21

<table>
<tr><td colspan="3">TABLE VIII - 2</td></tr>
<tr><td colspan="3">Surface Tension</td></tr>
<tr><td colspan="3">1-Octene (45)</td></tr>
<tr><td>T</td><td>Calc.</td><td>Obs.</td></tr>
<tr><td>0</td><td>24.00</td><td>23.83</td></tr>
<tr><td>10</td><td>22.98</td><td>22.87</td></tr>
<tr><td>20</td><td>21.97</td><td>21.91</td></tr>
<tr><td>30</td><td>20.99</td><td>20095</td></tr>
<tr><td>40</td><td>19.99</td><td>19.99</td></tr>
<tr><td>50</td><td>19.01</td><td>19.03</td></tr>
<tr><td>60</td><td>18.04</td><td>18.08</td></tr>
<tr><td>70</td><td>17.07</td><td>17.12</td></tr>
<tr><td>80</td><td>16.13</td><td>16.16</td></tr>
<tr><td>90</td><td>15.16</td><td>15.20</td></tr>
<tr><td>100</td><td>14.22</td><td>14.24</td></tr>
</table>

<table>
<tr><td colspan="3">TABLE VIII - 2</td></tr>
<tr><td colspan="3">Surface Tension</td></tr>
<tr><td colspan="3">1-Heptyne (46)</td></tr>
<tr><td>T</td><td>Calc.</td><td>Obs.</td></tr>
</table>

20	22.58	22.67
40	20.47	20.61
60	18.50	18.50

TABLE VIII - 2		
Surface Tension		
1-0ctyne (46)		
T	Calc.	Obs.
20	23.95	23.86
40	21.93	21.78
60	19.94	19.70

TABLE VIII - 2		
Surface Tension		
Anodyne (46)		
T	Calc.	Obs.
20	25.13	25.00
40	23.21	23.02
60	21.26	21.05
85	18.88	18.60

TABLE VIII - 2		
Surface Tension		
1-Decene (45)		
T	Calc.	Obs.
0	26.13	25.97
10	25.18	25.05
20	24.23	24.14
30	23.29	23.22
40	22.34	22.30
50	21.41	21.39

60	20.50	20.47
70	19.58	19.55
80	18.68	18.64
90	17.77	17.72
100	16.88	16.81

TABLE VIII - 2		
Surface Tension		
1-Dodecene (45)		
T	Calc.	Obs.
0	27.47	27.48
10	26.57	26.59
20	25.65	25.71
30	24.76	24.82
40	23.85	23.94
50	22.93	23.05
60	22.08	22.17
70	21.22	21.28
80	20.34	20.40
90	19.49	19.51
100	18.63	18.63

TABLE VIII - 2		
Surface Tension		
1-Tetradecene (45)		
T	Calc.	Obs.
0	28.62	28.64
10	27.74	27.77
20	26.85	26.90
30	25.99	26.03

40	25.12	25.16
50	24.26	24.29
60	23.41	23.43
70	22.57	22.56
80	21.74	21.69
90	20.90	20.82
100	20.09	19.95

TABLE VIII - 2		
Surface Tension		
1-Decyne (46)		
T	Calc.	Obs.
20	25.83	25.95
40	23.95	24.00
60	22.08	22.07
85	19.95	19.67

TABLE VIII - 2		
Surface Tension		
Ethyl Chloride (36)		
T	Calc.	Obs.
5	21.20	21.20
10	20.51	20.64

TABLE VIII - 2		
Surface Tension		
Propyl Chloride (36)		
T	Calc.	Obs.
15	22.46	22.45
20	21.84	21.78
30	20.63	20.48

TABLE VIII - 2		
Surface Tension		
Butyl Chloride (47)		
T	Calc.	Obs.
23.3	23.15	23.29
42	21.05	20.88
61	18.92	18.75

TABLE VIII - 2		
Surface Tension		
Amyl Chloride (47)		
T	Calc.	Obs.
12.9	25.69	25.81
23	24.59	24.57
41.9	22.55	22.44

TABLE VIII - 2		
Surface Tension		
Hexyl Chloride (47)		
T	Calc.	Obs.
20.4	26.02	26.14
42.6	23.74	24.02
62.7	21.68	21.77
87.3	19.21	19.25

TABLE VIII - 2		
Surface Tension		
Heptyl Chloride (47)		
T	Calc.	Obs.
12.3	27.80	27.73

21.5	26.88	26.95
41.6	24.86	24.89
62.3	22.85	22.92
87.2	20.42	20.60

TABLE VIII - 2		
Surface Tension		
Pr Formate (48)		
T	Calc.	Obs.
26.1	23.80	23.83
33.2	22.99	23.13
41.5	22.02	22.04
61.2	19.76	19.94

TABLE VIII - 2		
Surface Tension		
Pr Acetate (48)		
T	Calc.	Obs.
22.1	24.17	24.13
41.1	22.11	22.03
62.0	19.83	19.57
87.3	17.13	16.87

TABLE VIII - 2		
Surface Tension		
Pr Propionate (48)		
T	Calc.	Obs.
25.8	24.24	24.15
40.7	22.68	22.52
61.0	20.57	20.40
86.5	17.99	17.70

TABLE VIII - 2		
Surface Tension		
Pr Butyrate (48)		
T	Calc.	Obs.
15.9	25.63	25.49
24.0	24.81	24.70
40.8	23.12	22.91
61.2	21.09	20.94
86.9	18.58	18.38

TABLE VIII - 2		
Surface Tension		
Pr Valerate (48)		
T	Calc.	Obs.
18.3	25.77	25.95
29.1	24.72	24.95
40.9	23.59	23.64
61.3	21.64	21.67
86.7	19.24	19.23

TABLE VIII - 2		
Surface Tension		
Pr Castrate (48)		
T	Calc.	Obs.
16.5	28.40	28.69
20.1	28.10	28.28
40.7	26.36	26.41
61.4	24.61	24.49
88.8	22.34	22.38

TABLE VIII - 2

Surface Tension

Acetone (36)

T	Calc.	Obs.
15	24.09	23.92
20	23.43	23.32
30	22.13	22.01

TABLE VIII - 2

Surface Tension

Me Ketone (49)

T	Calc.	Obs.
24.80	23.83	23.97
34.85	22.61	22.88
50.15	20.78	21.13

TABLE VIII - 2

Surface Tension

MP Ketone (49)

T	Calc.	Obs.
24.80	24.61	24.21
34.85	23.46	23.38
50.15	21.74	21.68

TABLE VIII - 2

Surface Tension

MB Ketone (49)

T	Calc.	Obs.
24.80	25.41	25.50
34.85	24.32	24.32
50.15	22.69	22.72

TABLE VIII - 2

Surface Tension

MA Ketone (49)

T	Calc.	Obs.
24.80	26.04	26.17
34.85	25.00	25.02
50.15	23.44	23.48

TABLE VIII - 2

Surface Tension

ES Ketone (36)

T	Calc.	Obs.
15	25.83	25.87
20	25.26	25.26
30	24.12	24.37

TABLE VIII - 2

Surface Tension

EP Ketone (49)

T	Calc.	Obs.
24.80	25.03	25.03
34.85	23.95	24.01
50.15	22.30	22.32

TABLE VIII - 2

Surface Tension

EB Ketone (49)

T	Calc.	Obs.
24.80	25.75	25.72
34.85	24.70	24.69

50.15	23.05	23.17

REFERENCES

3. Larson, D. B., The Structure of the Physical Universes, published by the author. 755 N. E. Royal Court, Portland 12, Oregon. 1959, Appendix A.

36. Historians, Jeans Physico-chemical Constants of Pure Organic Compounds, Elsevier Publishing Co, Amsterdam, 1950.

38. American Petroleum Institute Research Project 44, Selected Values, Carnegie Press, Pittsburgh 1953,

44. Jasper, J. J., Kerr, E. R., and Gregorian, F. J., Am. Chem. Soc., 75-5252.

45. Jasper, J. J., and Kerr, E. R., Ibid., 76-2659.

46. Grzeskowiak, R., Jeffery, G. H., and Vogel, A. I., J. Chem. Soc., 1960-4719.

47. Vogel, A. I., Ibid., 1948-644.

48. Vogel, A. I., Ibid., 1948-624.

49. Owen, K., Quayle, O. R., and Clegg, W. J., J. Am. Chem. Soc., 64-1294.

IX

Review and Appraisal

The previous eight papers in this series may be regarded as constituting the basic framework of the liquid theory developed from the fundamental postulates of the work. Once such a general framework of theory has been erected, practically every new development, no matter how minor it may be in itself, serves to corroborate or clarify some part of what has gone before, and in order to facilitate recognition of the manner in which the new information to be presented in the subsequent papers fits in with the previous findings it has seemed advisable to undertake a general review and appraisal of the results described in the preceding papers.

0rdinarily the investigator himself is not the beat person to appraise the results of an investigation, but the purpose of this particular appraisal is primarily explanatory rather than argumentative. The exposition of a new system of thought on any subject is usually difficult to follow, since it requires a certain amount of mental reorientation which is not easily accomplished, and it should therefore be helpful to have the author's own analysis of the work. On this basis the following are the salient features of the findings reported in this series of papers:

1. (a) The entire development is carried out on a theoretical basis and all mathematical expressions are derived from theory, consequently

(b) There are no unexplained terms and no arbitrary or adjustable constants in any of these expressions.

Every term and every constant has a definite physical meaning. Aside from the conversion constants which are required for the purpose of expressing the results in terms of whatever conventional system of units is being used, the only constants that enter into the equations relating the various properties are what we may call structural constants: relatively small integral or half-integral values which represent the actual numbers of the different kinds of physical units entering into the particular phenomena under consideration.

(c) These expressions contain no exponential functions other than simple 2nd, 3rd, and 4th power values, which are readily explained theoretically.

All properties which vary with distance, for example, follow the inverse square relation; the system contains no such things as inverse sixth or eighth power functions or terms with decimal exponents,

2. (a) All phases of the development are based on the <u>same</u> general liquid theory, consequently

(b) The same general principles apply to all liquid properties.

Example: Paper I stated that the relation between temperature and any temperature-dependent property of a liquid molecule (a molecule which is individually at a temperature somewhere between the melting point and the critical temperature) is linear, Subsequent papers showed that this principle applies to volume, to viscosity, and to surface tension. The papers to follow will still further enlarge this list of properties for which the relation has been verified.

(c) The basic numerical values entering into the mathematical equations are identical.

Example: Wherever the liquid unit of temperature enters into the calculations, as it does frequently, this unit always has the same value, 510.20º C, irrespective of the nature of the other property involved in the relation under consideration.

(d) The equations representing different properties are closely related.

Example: Viscosity and surface tension are calculated by means of expressions which are essentially nothing more than modified forms of the same equation.

(e) Because of this close relation between the equations, the results obtained in each area serve as confirmation and support for the results obtained in related areas.

The close correlation between the calculated and experimental surface tension values, for instance, not only establishes the validity of the surface tension calculations but also supports the results obtained from the saw basic sources in the viscosity field, where direct experimental verification is more difficult because of the larger experimental uncertainties.

3. (a) The latitude for variability in the equations expressing the various relationships is very small, yet they produce results which agree with the experimental findings within the margin of uncertainty of the latter, consequently.

(b) There is a high degree of probability that these results are correct or nearly correct.

Since current scientific thinking runs along somewhat different lines, this point probably needs some elaboration. Present-day practice in developing mathematical expressions to represent physical properties is to start with some basic relation of a theoretical or semi-theoretical nature and then to modify this relation by additional terms and "adjustable constants" to secure better agreement with the experimental data. For instance the "equations of state" for gasses which have gone farther in this direction than any other physical expressions have as their foundation the general gas law $PV = RT$. To this base an increasing number and variety of additional terms and the constructors of the equations have added constants. The Beattie-Bridgeman equation has four adjustable constants the Benedict-Webb-Rubin equation has eight. The development of expressions to represent other physical properties is in general proceeding along similar lines.

If we regard the objective of this activity as the attainment of close agreement with the experimental values for the purpose of facilitating interpolation and extrapolation of the experimental results, the prevailing policy has been successful, since the correlation is usually increasingly better as the number of constants is increased. The fact that seems to be generally overlooked is that if the objective is to ascertain the correct relationships and numerical values, this program of adding more and more constants is definitely proceeding in the wrong direction. Every constant makes it easier for the equation to fit the experimental data, but in so doing it correspondingly decreases the probability that the products-the equation and the results it produces-are correct. This is an inescapable mathematical result of the increase in the number of possible variations of the experimental data, which will agree with the equation.

In order to make progress toward the correct answers it is essential to reduce rather than increase the adjustability of the equation, and the ultimate goal of a completely defined system cannot be reached until all terms and all constants that enter into the mathematical expression of the property in question are specifically determined by the basic structural constants of the molecules, and all latitude for adjustment is eliminated. As we move in this direction we must obviously keep the results of the calculations within the limits of experimental uncertainty, but so long as this requirement is met every additional restriction that can be placed on the quantities entering into the calculations increases the probability that the values obtained from these calculations are correct.

This is, of course, the hard road to follow. Unlike the conventional "more and better constants" approach, which follows a well-defined pattern and is practically certain to produce results of some kind most attempts to make progress toward the difficult goal of a more restrictive equation will inevitably end in nothing but frustration and disappointment. The preference for the currently popular easy route is therefore quite understandable) but here, as in so marry other lines of human endeavor, true forward progress can only be made in the hard way.

Let us then consider what has been accomplished in this liquid study in the way of progress toward the goal of a more completely defined set of equations; that is, equations in which the latitude for "adjustment" is minimized. The first and undoubtedly the most important of the steps that have been taken toward this goal was made possible by the previously mentioned theoretical deduction as to the linear relation between temperature and the temperature-dependent properties of the true liquid molecule. But the equations presented in these papers are not only limited by the requirement of linearity; each is still further restricted to a specific kind of a linear relation. Such linear expressions are defined by two values: the slope of the line and the temperature at which it intersects the zero axes. If either of these defining values can be related to some specific quantity or if the two can be related to each other, the range of variability is very greatly reduced and as long as the values calculated from these expressions still fall within the limits of the experimental uncertainty so that they <u>can</u> be correct, the probability that they are correct is greatly increased. Limitations of this kind have been established in the preceding papers for each of the properties covered. The slope of the temperature volume relation is fixed by the unit temperature value, 510.20, the slope of the surface tension curve is a specific function of the molecular mass, while the slope of the fluidity curve is reciprocally related to the zero point temperature.

Although the general nature of the curves which express the relations between temperature and the liquid properties is thus established, a complete definition of each curve requires one more item of information: the coordinates of some point on the curve. When these can be unequivocally evaluated from some basic molecular constants such as the mass or the number of constituent atoms the ultimate objective will have been reached. In the meantime each additional restriction that can be placed on the values for the individual liquids is a step toward that objective.

The first move in this direction carried out during the present project was to develop a means of expressing the variable factor in each equation in a manner that would bring out the underlying cause of the variations between individual substances. In the case of viscosity, for example, it was found in the initial phase of the study that the slope of the fluidity-temperature curve is inversely proportional to the zero point temperature, To. This one value therefore defines the entire curve, but an intensive study of the To values applicable to different liquids failed to disclose any direct connection between the individual values and the basic constants of the molecular composition and structure. The scope of the investigation was therefore broadened and with the help of some deductions from the basic theory it was ultimately determined that the To values could be expressed in of the molecular mass plus a mass increment I. a quantity which did have characteristics that could be related to the molecular composition and structure.

Development of methods which would enable a direct determination of the values of I and similar quantities appearing in other equations has been found to be a difficult problem and considerable additional work will be necessary in this area. In the meantime, however, it has been possible to establish certain general characteristics of these values. and in this way the range of variability has been reduced to the point where evaluation by indirect means is feasible. The increment I applicable to fluidity has been found to be (1) an integer or zero, (2) a property of the individual atom, (3) related to and limited by the atomic weight, and (4) subject to modification in a systematic and regular way by the molecular structure, These items of information, each of which restricts the range of variability of the values produced by the viscosity equation and therefore represents some advance toward the objective of the work, have then been applied to a study of homologous series of compounds and some further restrictions of major importance have been derived from this study. In total these various items of information are sufficient to establish unique values for most liquids.

Every step in this long process of development which has been described is a move in the direction of restricting the amount of variability or possibility of "adjustment" and each step has therefore increased the probability that the mathematical expressions which have been developed are correct representations of the physical properties to which they correspond, and that the values obtained from the calculations based on these expressions are, within the degree of accuracy of the mathematical processes employed, the correct magnitudes of these properties.

4. (a) The liquid theory is merely one aspect of a broad general theory of the

structure-of the universe, consequently

(b) The liquid equations are not only closely inter-related among themselves, as indicated in item 2. but are also closely related to similar expressions in non-liquid areas.

A striking example will be provided by the next paper in this series, which will present the results of a study of the effect of pressure on the melting point. Here it will be shown that the equation, which represents the pressure-melting point relation, is not merely similar to, but is identical with the equation previously developed for solid compressibility, which was described in a privately circulated paper that preceded this liquid series. We simply substitute T_m for the term V where it appears in the compressibility equation and change the numerical coefficient to conform to temperature units rather than volume units, and we then have the complete melting point equation. The values of the initial pressure applicable to the solid-liquid transition are somewhat different from those applicable to either the solid or the liquid, as might be expected, but they can be derived in a similar manner.

5. (a) Although the achievements of the new liquid theory, even in the incomplete form in which they are presented in the eight previous papers and summarized in the numbered statements preceding, add up to a very impressive total, they are actually the results of only a relatively small amount of development work applied to the basic assumptions: a single-handed effort almost infinitesimal in comparison with the collective amounts of time and energy that have been applied to the development of previous theories.

(b) It is therefore evident that the potentialities of the new theory are a long way from being fully exploited, and that further work toward development of the details of the theoretical structure can be expected to be very fruitful.

The three most serious obstacles that have hitherto stood in the way of a complete understanding of the physical and mathematical relationships between the various liquid properties are first, the large degree of uncertainty in many of the experimental values, second, the great variety of behavior exhibited by different liquids, and third, the existence of transitions, some evident, some not evident, in which the factors controlling the behavior of individual liquids are modified and the trend of the observed values is altered accordingly. Heretofore the only significant tests that could be applied to the experimental values were those of reproducibility and regularity. The currently accepted physical values listed in the handbooks and other reference volumes are generally considered to be reproducible but, as pointed out in previous papers, the variations between the results of competent investigators are normally much larger than each investigator's own estimates of uncertainty, and the possible margin of error is therefore considerably greater than is generally admitted. Furthermore, many measurements, particularly under extreme conditions where the theoretical significance is the greatest, have been made by only one method, which leaves us with an added degree of uncertainty as to the accuracy of the method itself. The criterion of regularity is based on the assumption that the values of the liquid properties change continuously and can therefore be represented by a-smooth curve (aside from definite transitions). This test enables its to eliminate minor irregularities in the measured values, but neither of the available criteria gives us any protection against systematic errors where only one method has been used or where results are available from only one investigator (as in much of Bridgman's work, for example), nor do they necessarily distinguish simple curves from compound curves containing one or more transitions.

As a result of the absence of any positive method of checking the accuracy of the experimental results the theorist has been practically at the mercy of the experimenter. In general it has been necessary for purposes of theory to assume the validity of the experimental work since the degree of correlation with the experimental values has been the only test which could be applied to theory. Furthermore, it has been necessary to assume, or at least it has in practice been assumed, that unless there is a discontinuity in some physical property or other definite evidence of a transition, the shape of the experimental curve indicates the true pattern of behavior of the liquid property under consideration: a very misleading assumption.

The findings of this work have in essence liberated the theorist from this complete dependence on the experimental values and, aside from their value as a forward base from which to make further advances in theory, their principal claim to merit rests upon this fact, which opens up a wide field of potential usefulness. It is still necessary, at least for the present, to utilize the experimental results as the raw material to which the theoretical processes are applied, but it is no longer necessary to accept all experimental values as authentic or as accurate; we now have theoretical criteria which are capable of separating authentic and applicable values from erroneous and inapplicable results, and we have processes which are able to convert approximate and uncertain values into correct and accurate values.

In undertaking to apply the general liquid theories to a study of any specific property we must first identify the quantity to which the linear relation characteristic of the liquid applies. It is essential, for instance, to establish the fact that it is the fluidity rather than the viscosity which varies linearly with the temperature. We then compare the experimental data with this theoretical linear relation and invariably we find that a large proportion of the curves representing the values for different liquids are definitely linear or, if they approach the zero axis as in the case of fluidity, have a linear upper section and make the transition to zero at the lower end by way of a probability curve, as the fluidity or any other property of the liquid aggregate must do if the curve for each individual molecule, is linear. This experimentally verified linearity of a substantial proportion, usually the great majority, of the curves confirms the validity of the theoretical linear relation, since the probability that this could be a chance result is essentially zero.

Having established the linear relation as correct, we now go back to the nonconforming experimental results and examine the deviations from the theoretical linear curves. Aside from the minor deviations due to experimental errors, the most common situation that we find is that the experimental curve consists of two linear sections connected by a transition curve. Such second order transitions without discontinuities are often recognized in solids by collateral evidence of one kind or another, but rarely in liquids, and where they do exist in liquids without being recognized their effects are automatically absorbed into the adjustable constants of conventional equations, giving the behavior of the liquid properties involved an appearance of complexity which is not at all justified by the facts.

The foregoing procedure enables us to identify the basic elements of the curves, the linear sections, and to select the most accurate values of the points on these linear sections from the experimental data. All of this information is then studied to determine the nature and magnitude of the controlling factors, which define the exact position of each curve. In principle it should be possible to deduce the values of these factors directly from the fundamental theory, but at the present incomplete stage of the theoretical development this is not feasible. The theory does, however. give some definite clues to the correct answers and in the studies that have been made thus far it has always been possible to establish the factors for at least the majority of the organic liquids. The application of this procedure to the property of fluidity has already been described in a previous paragraph. Here we find that each curve is completely defined by the molecular mass plus an increment I, originating from increased effectiveness of some of the individual mass units under certain conditions. We further find that the value of this increment is constant for all of the members of each organic series beyond the first two or three. All that we need to know, therefore to calculate the viscosity of any normal paraffin (propane or beyond) at any temperature is that the value of I for the normal paraffin series is 6.

Again the probability principles confirm the validity of the conclusions which have been reached. The probability that mere chance would enable us to reproduce the experimental values of the viscosity of all of these normal paraffins by the use of a single integer in conjunction with the molecular mass, with close agreement in many cases and approximate agreement in practically all cases, is infinitesimal. We are therefore justified in concluding that the calculated values are essentially correct and that whatever divergence may exist between these and the experimental values is a measure of the experimental error.

When this procedure is repeated for several organic series and in each case the series value of the increment I is found to be integral, the same kind of reasoning justifies accepting this fact as a confirmation of the theoretical deduction that <u>all</u> such values are integral. This finding, together with the previously established linearity of the curves, then eliminates the necessity of relying entirely on uncertain experimental values. As long as these experimental results are anywhere near the correct values, so that the controlling integral factors can be identified, the exact values can be computed.

It should be noted that the foregoing is possible only because all latitude for adjustment is eliminated. We cannot prove the validity of the conventional type of equation containing, one or more adjustable constants by probability mathematics, as an adjustable equation can be <u>made</u> to fit any set of values, right or wrong, which conforms to the general pattern for which the equation was constructed. An equation, which is not adjustable, cannot be forced into a fit; it can agree with the experimental values within the margin of experimental uncertainty, only (1) by chance, or (2) because it correctly represents the physical facts. Under the circumstances which have been discussed it is possible to demonstrate that chance cannot be responsible.

Of course, a great many liquids are not members of any large and thoroughly studied homologous series comparable to the normal paraffins, and identification of the controlling factors for the various physical properties of these less gregarious liquids is a more difficult matter. There are, however, other useful relations similar to those within series, and there are also inter-relations between the factors applicable to different properties of the same liquid, from which considerable information can be extracted. Extension of the work to the additional liquids that can be reached by such means is going ahead as rapidly as the tine that can be allocated to this particular phase of the total project will permit, and steady forward progress is being made, not only in the organic division but also among the more complex liquid structures of the elements and inorganic compounds.

This rate of progress will no doubt be greatly accelerated as soon as the results of the original work are sufficiently well known to encourage other investigators to explore additional consequences of the new liquid theories. Some very broad fields, which have had to be excluded from this initial project in order to keep the work within reasonable limits, are wide open for attack by anyone who wishes to undertake the task. It should be relatively simple, for instance. to extend the relations developed for pure liquids to liquid mixtures. Solutions will present some more complicated problems, but the general principles involved are already fairly well defined-the concept of physical state as a property of the individual molecule is obviously the key to an understanding of the nature of solid-liquid solutions-and some very interesting and significant results can undoubtedly be attained in this field with a minimum of effort.

It should be understood, however, that the data, which it has been possible to include in the tabulations accompanying the text of the previous papers, does not by any means reflect the full amount of information already available. The surface tension values given in paper VIII, for example, are representative of the results obtained in detailed studies made on over 500 liquids. Similarly, the presentation of the mathematical relations developed for the various liquid properties has in most cases been confined to the "regular" liquids because of the necessity for economy of space, but the relations applicable to many of the compounds with special behavior characteristics, such as water and the alcohols, have been determined with the same accuracy as those of the regular liquids and are also available far publication. The case for the new theories will, of course, be strengthened considerably when it becomes possible to release this material in one way or another. It will be necessary, however, to limit the forthcoming papers in this present series to new subjects. leaving the more extended treatment of the previous subjects for future publication.

X

The Melting Point - Relation to Pressure

Attached herewith is paper number ten in my liquid series which shows that the melting points under pressure can be accurately computed by means of a very simple equation. This paper makes a highly significant contribution to the work as a whole, as the melting point equation is not only a purely theoretical expression derived directly from the basic postulates of the work, but it is also the same equation that was used to calculate solid compressibilities in previous papers. It is difficult to visualize the possibility that such an equation could successfully reproduce the full range of experimental values in either field unless it were an essentially correct representation of the physical facts; the possibility that an incorrect expression could accomplish these results in both fields is wholly inconceivable.

It appears to me that this occasion, on which I am submitting some striking new evidence of the validity of the fundamental postulates on which my work is based, is an appropriate time to make some comments regarding those aspects of currently accepted physical theory with which my findings are in conflict. It is true; of course, that these conflicts are quite numerous, and there is a very understandable reluctance to believe that accepted theory can be wrong in so many important respects. But it is not difficult to prove this point. It is quite a task to prove that any of the current theories are wrong, because long years of effort on the part of the theorists have enabled them to adjust their theories to fit the facts in most cases and to devise means of evading most of the many contradictions that still remain, but it is quite simple to show that the particular theories in question are lacking in factual support and therefore can be wrong. As long as this is true, it is clearly in order to consider conflicting theories.

The case in favor of my new theoretical structure rests primarily on the contention that not a single one of the thousands of necessary and unavoidable consequences of my fundamental postulates is inconsistent with any positively established fact. It becomes very important, therefore, to distinguish clearly between items that are definitely known to be factual and those, which do not qualify. The enclosed memorandum is a discussion of this situation as it applies to the points of conflict. The memorandum does not attempt to discuss all of the points at issue, nor to make an exhaustive analysis of any case; nothing short of a book-length presentation could cover that much ground. However, the various categories of pseudo-facts commonly encountered are described and illustrated by examples, and it should not be difficult to see that every one of the accepted ideas with which my findings are in conflict is one of these pseudo facts: a hypothesis, assumption, or extrapolation masquerading in the guise of an established fact.

Perhaps it will be regarded as presumptuous for me to suggest that the strict and critical tests which will be applied to my new theory be applied to the conflicting parts of currently accepted theory as well, but I believe that by this time the new developments which I have covered in the liquid papers add up to an impressive enough total to justify a full and comprehensive examination of the underlying theories, including a careful consideration of this question as to the true status of conflicting ideas.

D. B. Larson

Strictly speaking, the melting point is a phenomenon of the solid state rather than of the liquid state and in general its behavior follows the solid state pattern, but since this temperature constitutes the point of transition between the two physical states it has some close relations with various liquid properties which justify giving it some consideration in this survey of the liquid state,

If the melting point were actually a property of the liquid, we could expect that it would be linearly related to the pressure, just as the true liquid component of the volume and other liquid properties are so related. Solid state properties, however, are directly or inversely related to the square root of the pressure, rather than to the first power, for reasons that are explained in the author's book "The Structure of the Physical Universe", which develops the general physical theories underlying the liquid principles that form the basis for this series of papers. It has already been brought out in a paper which preceded this liquid series[5] that the solid state equivalent of Bole's Law, $PV = k$, is $PV^2 = k$, from which we obtain the relation $V/V_0 = P_0^{1/2}(P + P_0)^{1/2}$. In terms of density this becomes

$$d = \frac{(P + P_0)^{1/2}}{P_0^{1/2}} d_0$$

The previous solid compressibility paper showed that this equation is able to reproduce the experimental values of the compression, within the existing margin of uncertainty, over the entire range of temperatures, pressures and substances for which data are available.

According to the basic theory, this is a characteristic relationship applying to solid state properties in general, rather than merely a volume relation, and we may therefore rewrite the equation, substituting T_m, the normal melting point, for d_0, and T_p, the melting point under an externally applied pressure P, for d. We then have

$$T_p = \frac{(P + P_0)^{1/2}}{P_0^{1/2}} T_m \qquad (16)$$

It will be noted that this expression is identical with the well-known Simon melting point equation, except for the substitution of a constant for one of the two variables of the Simon equation, which the originator expresses as

$$\frac{P}{a} = \left(\frac{T}{T_0}\right)^C - 1$$

Simon's factor a corresponds to the initial pressure, as is generally recognized, His factor c (unexplained theoretically) has usually been assigned a value somewhere between 1.5 and 2 in application to organic compounds and other low melting point substances, and replacing this variable factor by the constant value 2 is not a major modification of the equation, so far as the effect on the calculated values is concerned, as these values are not very sensitive to changes in c if accompanied by corresponding changes in a. The situation with respect to the high melting point elements, which are often assigned considerably higher values of the factor c. will be discussed later.

No satisfactory theoretical explanation has thus far been discovered for the Simon equation, but this expression agrees with the experimental results over a wide range of pressures and substances, and it is generally conceded that such a theoretical explanation must exist. Strong and Bundy state the case in these words, "Simon's fusion equation has now endured a considerable amount of experimental and theoretical examination. Because it applies in so many cases... it must contain fundamentally correct concepts concerning some of the properties of matter".[50]

In the areas previously covered by this series of papers, the new equations, which have been developed, are to a large degree filling a vacuum, as no generally applicable mathematical representations of these properties have hitherto been available. It is therefore quite significant that when we reach an area where an equation of recognized standing does already exist, the new development does not produce something totally new; the general liquid principles on which the work is based lead to a melting point expression which is essentially a modified form of the previously existing equation. Here, as in so many places outside the liquid field, genuine knowledge already in existence coincides with the products of the development of the postulates of this work, and can simply be incorporated into the new theoretical structure with nothing more than minor modifications. What the new development actually does, in essence, is to establish the exact nature of those "fundamentally correct concepts" to which Strong and Bundy refer.

But even though the required modification of the Simon equation is minor, it does not necessarily follow that it is unimportant. As brought out in paper IX of this series, the more restrictive the mathematical expression of a physical property can be made, the more likely it is to be a correct representation of the true physical facts, providing, of course, that it produces results which agree with the experimental values within the margin of uncertainty of the latter. Replacement of one of the two adjustable factors in the Simon equation by the constant value 2 as required by the new theory is an important move in this direction.

Now that this value has been fixed, the only additional requirement for a complete and unequivocal definition of the pressure-melting point relation for each substance is a means of calculating the initial pressure applicable in each case. In the solid compressibility paper previously mentioned, the following equation for the initial pressure applicable to compression of solids was developed:

$$P_0 = \frac{16649\ abc}{s_0^3}\ \text{atm.}$$

The initial pressure applicable to liquid compressibility is considerably lower and paper IV in this series expressed this relation as

$$P_0 = 415.84\ n/V_0\ \text{atm.}$$

Since the melting point is at the boundary between the liquid and solid states, it is to be expected that the initial pressure applicable to this property will lie somewhere between the true liquid and true solid values, and a study of this situation leads to an equation of an intermediate type:

$$P_0 = 664.28\ \frac{abc}{nV_0^{2/3}}\ \text{atm.}$$

The symbols in this equation have the same significance as in the expressions for the true liquid and true solid initial pressures. The factors a, b, and c are the effective displacements in the three dimensions of space, a concept that is explained in the author's book previously mentioned. V_0 is the initial specific volume of the liquid as defined in paper II of this series, and n is the number of independent units in the molecule at the melting temperature.

The values of n applicable to the solid-liquid transition are usually less than those applicable to liquid compressibility, as would be expected since the number of effective units per molecule is normally less in the solid, particularly at low temperatures, than it is in the liquid, and an intermediate value is appropriate for the boundary state. There is also a marked tendency toward a constant value in each of the various homologous series of compounds, at least in those portions of these series for which experimental data are available. Thus the value for most of the aliphatic acids is 4, and for the normal alcohols it is 3. Most elements have n = 1, the principal exceptions being such elements as sulfur and phosphorus which have quite complex liquid structures.

In the majority of substances on which experimental results are available for comparison including most of the common organic compounds, the a and c factors take the theoretical maximum values 4 and 8 respectively. The factor b is usually 1 at low pressures, except for the elements in the middle of each periodic group, which have the same tendency toward higher values that was noted in the case of solid compressibility.

Some of the low melting point elements have a-c-b values at or near the theoretical minimum, a point which is of particular interest; first, because it provides a definite reference point for these factors which helps to demonstrate that they have a real physical significance, and second, because the wide spread between the possible values of the factors at the lower end of the scale makes identification of the applicable factors a very simple matter. Helium, for example, takes the minimum values, 1-1-1. The next higher combination that is theoretically possible 1½-1-1 would result in a reduction of more than 20 percent in the melting temperature at the upper end of the experimental temperature range. This is, of course, far outside the margin of experimental uncertainty, which is normally in the neighborhood of one or two percent and the 1-1-1 factors are therefore definitely the ones that are applicable.

The situation with respect to the other elements of very low melting point is similar, and the theoretical melting point pattern for these substances is therefore positively established. It does not necessarily follow, however, that the divergence between the experimental melting points and the values thus calculated is always chargeable to experimental error. The theoretical values are those which would result from the application of pressure only, without any "second order" effects such as those due to the presence of impurities, to consolidation of molecules under pressure, to polymorphic transitions, etc, and they will not necessarily coincide exactly with the results of accurate measurements made on a substance which is subject to extraneous influences of this kind.

It should also be recognized that correlation of the theoretical and experimental values is not as simple a matter in the melting point field as it is for a property such as surface tension, on which we have a large volume of reasonably accurate experimental data. Only a comparatively small amount of work has been done on the melting curves, and most of that has been confined to the range below 1000 atm. Outside of the recent work with the metallic elements and the elements of very low melting point, Bridgman's investigations are practically the only source of information at the higher pressures. This, of course, introduces some serious uncertainties into any correlations that we may attempt. If the calculated and experimental values agree, each serves to some extent as a corroboration for the other, but where there is a divergence it is not immediately apparent which of the two is in error.

The correlations of theory against experiment in the areas covered by previous papers in this series have been of the, massive type, Calculations have been carried out for hundreds of substances of many different classes and, although it has not been possible to show all of these data in the tabulations accompanying the papers, a reasonably good sample has been included in each case. Where the experimental data are scarce and to a large degree unconfirmed 2 as in the present instance) it will be necessary to use a more selective technique, and to examine the evidence of the validity of each phase of the theoretical relationship separately, rather than verifying the entire development in one operation by a massive demonstration of agreement with the results of observation.

The first point, which we will want to consider, is the validity of the square root relationship. For this purpose the most significant experimental results are those in which the percentage increase in the melting point is the greatest. Where the ratio of the melting point at the upper end of the experimental pressure range to the normal melting point is less than 2, the difference between a square root curve and some other possible exponential curve, or a linear curve, is small, and unless the experimental values are extremely accurate it is difficult to determine which relation these values actually follow. The divergence of the curves increases rapidly, however, as the ratio rises, and if this ratio is 4 or more the nature of the curve is readily ascertained.

For this particular purpose, therefore, the work at the highest pressures is of no particular value. Even where pressures in the neighborhood of 150,000 atm. have been reached in the study of the metallic elements, the corresponding melting point ratio is only about 1.2. In the range from 1.0 to 1.2 the difference due to even a fairly large change in the exponent of the melting point expression is negligible. It is not surprising, therefore, that there is much difference of opinion as to just what this exponent should be. In the case of iron, for example, Gilvarry arrives at an exponent of 1.9 for the Simon formula, Simon himself selects 4, and Strong gives us the value 8 (which corresponds to 1/8 on the basis of equation 16).[51] On first consideration this seems to be an extreme case of disagreement, but if the value of Simon's constant a is adjusted empirically (as is always done, of course), the differences between these various exponential curves in this range are so much less than the experimental uncertainty that the curves are for all practical purposes coincident. For example, the square root of 1.1 is 1.0488 and the square root of 1.2 is 1.0954. If the curve from 1.0 to 1.2 were linear, the value at 1.1 would be 1.0477, which differs from 1.0448, the value on the square root basis, by only one-tenth of one percent. A similar calculation using an exponent of 1/8 (equivalent to Strong's value 8) shows that the deviation from the linear curve is still less, only about ½0 of one percent. Where the normal melting point is in the vicinity of 20000, a change from Gilvarry's exponent 1.9 to Strong's exponent 8 changes the position of the midpoint of the curve only about one degree if the value of a is fitted to the maximum experimental value of the melting temperature. It is therefore clear that within the experimental pressure range all of the exponents selected by previous investigators are in agreement with each other and with the exponent of equation 16, But where the experimental data fit everything they prove nothing.

The definite verification of the square root relationship is furnished by the elements of very law melting point, the most conclusive demonstration coming from helium and hydrogen. Helium does not melt at all except under pressure, and its melting curve cannot be referred to the normal melting point in the usual manner, but a study of the situation indicates that the melting point of this element can be calculated from equation 16 by the use of a pseudo-melting point which has been evaluated empirically as 11.1° K. We first calculate the melting point under pressure just as if 11.1° were the normal melting point, and then we subtract 11.1° from the result. At 5000 atm. for example, we find that the quantity $(P + P_0)^{1/2}/P_0^{1/2}$ amounts to 4.516. Multiplying by 11.1° we obtain 50.13°, and subtracting 11.1° we arrive at a theoretical melting point of 39.03° K. A measurement at this pressure is reported as 39° K. If the value of the expression

$$\frac{(P + P_0)^{1/2}}{P_0^{1/2}} - 1$$

is less than 1.0 (that is, if the true melting point is below the pseudo-melting point), the true melting point is proportional to the 2/3 power of the foregoing expression instead of the first power. The reasons for this behavior are not clear, although it is not surprising to find that the values below the reference temperature, which correspond in some degree to negative temperatures, are abnormal, Table X-1 compares the calculated and experimental melting points of helium. Here we see that although the maximum pressure of observation is only 7270 atm, the melting point ratio (designated as R in this and the following tables) at this pressure is 4.4, which is well above the minimum requirement for positive identification of the nature of the melting curve.

Also included in this table are the values for He^3 which are computed in the same manner, except that the pseudo-melting point is slightly higher, 11.5° K, and the 5/6 power is substituted for the 2/3 power below the pseudo-melting point. It will be noted that for both isotopes the differences between the theoretical and experimental values are abnormally high in the vicinity of the pseudo-melting point. This is a mathematical effect of the distribution of molecular velocities in the neighborhood of a transition point, similar to the effect on the fluidity values discussed in paper VIII, page 3, and rough calculations indicate that when the transition is studied in detail so that the proper corrections for this effect can be determined, the agreement at these temperatures will be found just as close in this range as it is where the transition effect is absent.

Aside from hydrogen, which will be discussed later, there is no other substance on which the melting curve has been followed farther than a ratio of about 2.5. In the range from around 2.0 to 2.5 we find such substances as nitrogen, which shows an agreement within 1° over the full experimental pressure range (if we use Bridgman's values up to his pressure limit); carbon tetrachloride, which agrees within 1° to 6000 kg/cm², with somewhat larger deviations above this pressure ethyl bromide, which agrees within 2° to 25,000 kg/cm² and shows a deviation of 5° at 30,000 kg/cm², beyond what appears to be a transition of some kind; chloroform, which agrees with the results of one set of measurements by Bridgman to within 2° but differs substantially from another set of results; and two of the normal alcohols, ethyl and butyl, for which the agreement is within 4° and 3° respectively up to 25,000 kg/cm², beyond which the values diverge. It is not clear whether this divergence is due to experimental error or to a transition to a new value of P_0 similar to the transitions, which were found in the study of compressibility.

The calculated and experimental melting points for these substances are listed in Table X-2,. Also included in this table are values for a few other substances which have been observed up to 11,000 kg/cm² or higher) but only to melting point ratios between 1.25 and 2.0, Even though the information available within the range of significant melting point ratios is quite limited, the comparisons in this table should be sufficient to add considerable weight to the conclusions reached on the basis of the helium values

The melting curves of a large number of substances have been determined with precision to pressures in the neighborhood of 1000 atm. For reasons previously discussed, these determinations are of no value from the standpoint of verifying the square root relation, but now that the validity of this relation has been confirmed by other means, the values in the lower pressure range can be utilized as a test of equation 17, and a number of comparisons of melting points in this range are given in Table X - 3. Since all other factors that enter into the determination of the melting points of the common organic compounds are definitely fixed, identity of the values of n applicable to related compounds) or obvious regularities in the values for such compounds, are strong evidence of the validity of equations 16 and 17 and of the theoretical principles from which these equations were derived. For example, melting points for the first seven of the aliphatic acids computed on the basis of n = 4 agree with the experimental results within 1° in four cases, and in only one of these compounds (propionic acid) is there any deviation as large as 3°

Benzene and some of its simple derivatives contribute additional evidence of the same kind. Benzene itself has n = 5, and a large percentage of the closely related compounds for which melting curves are available take the same values of this factor. Among these are toluene, two of the xylenes, naphthalene, benzophenone, nitrobenzene, and two of the nitrobenzene. Representative examples of both the benzenes and the aliphatic acids are included in Table X-3.

The data for water, Table X - 4, are particularly interesting. The a-c-b values are 4-8-1 as usual, except that there is a transition to 4-8-2 between 8000 and 9000 kg/cm² affecting ice VI only. Disregarding the abnormal forms of ice that exist below 2000 kg/cm², we find that the entire melting point pattern of water, complex as it is, can be reproduced simply on the assumption that the factor n, the number of effective units in the molecule, increases step by step as we pass from one form of ice to the next: ice III - 1, ice V - 2. ice VI - 3, ice VII - 4. (The status of ice IV is questionable; it may not even exist). Except in the range from 20,000 to 28,000 kg/cm², where the effects of a polymorphic transition that takes place at 22,400 kg/cm² are in evidence, the agreement between the calculated and experimental values is within 2º in all cases.

The increase in the factor b from 1 to 2 which was found at a pressure of approximately 9000 kg/cm² in ice VI is one of the very few instances where the existence of a transition of this kind, involving an increase in the initial pressure, appears to be definitely confirmed. The pattern of increase in this factor found in the study of solid compressibility suggests, however, that such transitions may be normal, and that their infrequent appearance in melting phenomena is merely due to the relatively narrow pressure range that has thus far been covered experimentally.

A similar transition in the opposite direction occurs in hydrogen and the inert gases above helium. Here we find that the initial a-c-b values are 1½-1-1, but subsequently these factors drop to the minimum level 1-1-1, What we may regard as the normal pattern for this transition is illustrated by krypton and xenon, Table X-5. In these elements the 1½-1-1 factors prevail up to 170º K (one-third of the liquid temperature unit, 510º). From 170º to 340º (two-thirds of the temperature unit) there is a linear transition to 1-1-1, and above 340º the effective factors remain at this minimum level. The experimental results on argon are erratic and inconclusive, but not inconsistent with values calculated on the same basis. Neon and hydrogen follow the same general pattern, but the transition temperatures are fractional values of those normally applicable. In the case of hydrogen, the transition begins at 28.3º K, one-sixth of the normal 170º, and is completed in 113.3º, two-thirds of the normal interval. Table X-6 compares the hydrogen melting points calculated on this basis with a set of values compiled from experimental data. As the table shows, the two sets of values agree within 1/4 degree up to the two highest pressures of observation, and even in these cases the difference is less than ½ degree.

Table X-7 lists the values of the various factors entering into the calculation of initial pressures and melting points for all of the substances included in the preceding tabulations.

TABLE X - 1			
Melting Points - Helium			
He^4		P_0 = 266.4 kg/cm^2 (52)	
P	R	T_m	Obs.
37.3	.068	1.85	1.91
238.7	.377	5.79	5.70
482.2	.676	8.55	8.75
750.8	.954	10.76	12.54
1018.9	1.197	13.29	13.88
1280.3	1.409	15.64	16.01
1539.2	1.603	17.79	18.01
1746.8	1.749	19.41	19.52
2032.8	1.938	21.51	21.52
2251.5	2.074	23.02	23.01
2480.1	2.211	24.54	24.46
2813.3	2.400	26.64	26.48
2986.4	2.494	27.68	27.50
3323.9	2.671	29.65	29.47
3496.0	2.758	30.61	30.47

TABLE X - 1			
Melting Points - Helium			
He^4		atm. (53)	
P	R	T_m	Obs.
3280	2.704	30.01	30
4170	3.144	34.90	35
5140	3.576	39.69	40
6170	3.993	44.32	45

TABLE X - 1			
Melting Points - Helium			
He^3		P_0 = 294.1 kg/cm^2 (52)	
P	R	T_m	Obs.
75.9	.173	1.99	1.94
232.0	.405	4.66	4.68
322.3	.512	5.89	5.86
535.3	.724	8.33	8.42
729.9	.887	10.20	10.45
1010.9	1.106	12.72	13.00
1251.2	1.292	14.86	15.03
1505.1	1.473	16.94	17.00
1776.0	1.653	19.01	19.00
2054.9	1.826	21.00	21.00
2281.2	1.959	22.53	22.51
2518.3	2.092	24.66	24.02
2759.6	2.222	25.55	25.51
3008.3	2.351	27.04	27.01
3262.3	2.478	28.50	28.50
3253.7	2.603	29.93	30.01

TABLE X - 2

Melting Points

Nitrogen (54)

P M kg/cm^2	R	T_m	Obs.
0	1.000	63	63
1	1.324	83	82
2	1.582	100	99
3	1.806	114	113
4	2.003	126	126
5	2.183	138	138
6	2.350	148	149
M atm.		(55)	
7	2.540	160	157.5
8	2.689	169	169
9	2.830	178	178.5

TABLE X - 2

Melting Points

Carbon Dioxide

P M kg/cm^2	R	T_m	Obs. (54)
0	1.000	217	217
1	1.078	234	236
2	1.151	250	253
3	1.219	265	268
4	1.283	278	282
5	1.345	292	295
6	1.404	205	306
7	1.461	317	317
8	1.514	329	328

9	1.567	340	339
10	1.618	351	349
12	1.715	372	367

TABLE X - 2

Melting Points

Lead

P M kg/cm^2	R	T_m	Obs. (56)
0	1.000	600	600
3	1.036	622	622
6	1.071	643	643
9	1.105	663	663
12	1.138	683	682
15	1.171	703	701
18	1.202	721	719
21	1.232	739	737
24	1.262	757	754
27	1.291	775	770
30	1.320	792	785
33	1.347	808	800

TABLE X - 2

Melting Points

Mercury

P M kg/cm^2	R	T_m	Obs.
0	1.000	234	234
2	1.047	245	245
4	1.092	256	255
6	1.135	266	265

8	1.176	275	275
10	1.216	285	285
12	1.255	294	295

TABLE X - 2

Melting Points

Chloroform

P M kg/cm²	R	T_m	Obs.
0	1.000	210	212
1	1.090	229	228
2	1.173	246	245
3	1.250	263	261
4	1.323	278	277
5	1.392	292	291
6	1.458	306	306
7	1.521	319	319
8	1.581	332	332
9	1.640	344	345
10	1.696	356	357
11	1.750	368	369
12	1.803	379	381

TABLE X - 2

Melting Points

Ethyl Bromide

P M kg/cm²	R	T_m	Obs.
0	1.000	154	154
5	1.318	203	203
10	1.572	242	244

15	1.791	276	278
20	1.986	306	307
25	2.164	333	331
30	2.327	358	353

TABLE X - 2

Melting Points

Aniline

P M kg/cm^2	R	T_m	Obs.
0	1.000	267	267
1	1.070	286	286
2	1.136	303	305
3	1.198	320	322
4	1.257	336	338
5	1.313	351	352
6	1.368	365	366
7	1.420	379	380
8	1.470	392	392
9	1.518	405	405
12	1.655	442	439

TABLE X - 2

Melting Points

Chlorobenzene

P M kg/cm^2	R	T_m	Obs.
0	1.000	228	228
1	1.071	244	245
2	1.138	259	261
3	1.201	274	276

4	1.261	288	290
5	1.318	301	303
6	1.373	313	315
7	1.426	325	327
8	1.476	337	337
9	1.525	348	348
10	1.573	359	358
11	1.619	369	367
12	1.664	379	377

TABLE X - 2			
Melting Points			
Nitrobenzene			
P M kg/cm²	R	T_m	Obs.
0	1.000	279	279
1	1.080	301	300
2	1.155	322	321
3	1.225	342	342
4	1.291	360	361
5	1.354	378	379
6	1.414	395	396
7	1.472	411	411
8	1.528	426	427
9	1.581	441	443
10	1.633	456	458
11	1.683	470	472

TABLE X - 2
Melting Points
Bromobenzene

P M kg/cm²	R	T_m	Obs.
0	1.000	242	242
1	1.071	259	261
2	1.139	276	279
3	1.202	291	295
4	1.262	305	309
5	1.320	319	323
6	1.375	333	335
7	1.428	346	347
8	1.479	358	359
9	1.528	370	370
10	1.576	381	381
11	1.623	393	391
12	1.668	404	401

TABLE X - 2

Melting Points

Carbon Tetrachloride

P M kg/cm²	R	T_m	Obs.
0	1.000	250	251
1	1.145	286	287
2	1.274	319	319
3	1.391	348	349
4	1.498	375	376
5	1.599	400	400
6	1.694	424	423
7	1.783	446	444
8	1.868	467	465
9	1.950	488	485

TABLE X - 2

Melting Points

Bromoform

P M kg/cm^2	R	T_m	Obs.
0	1.000	281	281
1	1.086	305	305
2	1.166	328	327
3	1.241	349	348
4	1.311	368	368
5	1.378	387	387
6	1.442	405	404
7	1.502	422	421
8	1.561	439	436
9	1.618	455	452
10	1.672	470	467
11	1.725	485	482

TABLE X - 2

Melting Points

Ethyl Alcohol

P M kg/cm^2	R	T_m	Obs.
0	1.000	156	156
5	1.290	201	197
10	1.525	236	234
15	1.729	270	268
20	1.911	298	298
25	2.078	324	327
30	2.232	348	355

35	2.375	371	382

TABLE X - 2

Melting Points

Butyl Alcohol

P M kg/cm^2	R	T_m	Obs.
0	1.000	188	183
5	1.278	240	240
10	1.505	283	285
15	1.703	320	322
20	1.880	353	353
25	2.041	384	381
30	2.191	412	405
35	2.331	438	428

TABLE X - 3

Melting Points

Benzene

P M kg/cm^2	R	T_m	Obs. (57)
0	1.000	279	279
166	1.015	283	283
349	1.033	288	288
538	1.050	293	293
728	1.066	297	298
993	1.090	304	305

TABLE X - 3

Melting Points

p-Nitrotoluene

P M kg/cm²	R	T_m	Obs. (57)
0	1.000	325	325
112	1.009	328	328
297	1.024	333	333
483	1.039	338	338
671	1.054	343	343
857	1.068	347	348
972	1.077	350	351

TABLE X - 3			
Melting Points			
Rutures Acid			
P M kg/cm²	R	T_m	Obs. (57)
0	1.000	268	268
290	1.021	274	213
567	1.041	279	278
837	1.060	284	283
986	1.071	287	286

TABLE X - 3			
Melting Points			
o-Xylene			
P M kg/cm²	R	T_m	Obs. (57)
0	1.000	248	248
220	1.021	253	253
437	1.042	258	258
654	1.063	264	263
865	1.082	268	268

1080	1.101	273	273

TABLE X - 3

Melting Points

m-Nitrotoluene

P M kg/cm²	R	T_m	Obs. (57)
0	1.000	289	289
164	1.013	293	293
372	1.031	298	298
578	1.047	303	303
781	1.063	307	308
982	1.079	312	313

TABLE X - 3

Melting Points

Caproic Acid

P M kg/cm²	R	T_m	Obs. (57)
0	1.000	269	269
218	1.016	273	273
487	1.036	279	278
760	1.056	284	283
890	1.065	286	286
996	1.073	289	288

TABLE X - 3

Melting Points

p-Xylene

P M kg/cm²	R	T_m	Obs. (57)
0	1.000	286	286

49	1.006	288	288
197	1.024	293	293
343	1.041	298	298
495	1.058	303	303
647	1.075	307	308
803	1.093	313	313
957	1.110	317	318

TABLE X - 3

Melting Points

Acetic Acid

P M kg/cm^2	R	T_m	Obs. (57)
0	1.000	290	290
168	1.011	293	293
415	1.029	298	298
663	1.045	303	303
957	1.064	309	309

TABLE X - 3

Melting Points

Caprylic Acid

P M kg/cm^2	R	T_m	Obs. (57)
0	1.000	289	289
190	1.014	293	293
434	1.033	299	298
669	1.050	303	303
922	1.068	309	308

TABLE X - 5

Melting Points

Krypton

P M kg/cm^2	R_1	R_2	2%	T_m	Obs. (58)
0	1.000	1.000	0.0	116	116
2	1.414	1.581	2.4	164	165
4	1.732	2.000	27.1	209	209
6	2.000	2.345	48.2	251	252
8	2.236	2.646	66.5	291	293
10	2.449	2.915	82.9	329	332
12	2.646	3.162	100.0	367	370

TABLE X - 5

Melting Points

Xenon

P M kg/cm^2	R_1	R_2	2%	T_m	Obs. (58)
0	1.000	1.000	0.0	166	161
1	1.183	1.265	19.4	199	198
2	1.342	1.484	37.6	232	231
3	1.483	1.674	54.1	263	262
4	1.612	1.844	68.8	294	292
5	1.732	2.000	82.3	324	322
6	1.844	2.146	94.7	353	351
7	1.949	2.281	100.0	379	379
8	2.049	2.409	100.0	400	406

TABLE X - 4

Melting Points

Water (54) Ice III

P M kg/cm^2	R	T_m	Obs. (57)

0	1.000	241	
2	1.038	250	251
2.5	1.048	253	253
3	1.057	255	255
3.5	1.066	257	256

TABLE X - 4			
Melting Points			
Water (54) Ice VI (4-8-1)			
P M kg/cm²	R	T_m	Obs. (57)
0	1.000	206	
4.5	1.237	255	255
5	1.261	260	260
5.5	1.283	264	266
6	1.306	269	270
6.5	1.329	274	274
7	1.351	278	278
8	1.394	287	286

TABLE X - 4			
Melting Points			
Water (54) Ice V			
P M kg/cm²	R	T_m	Obs. (57)
0	1.000	226	
3.5	1.129	255	256
4	1.146	259	260
4.5	1.163	263	263
5	1.180	267	266
5.5	1.197	271	269

6	1.213	274	272

TABLE X - 4

Melting Points

Water (54) Ice VI (4-8-2)

P M kg/cm²	R	T_m	Obs. (57)
0	1.000	237	
9	l.237	293	293
10	1.261	299	299
15	1.372	325	326
16	1.394	330	330
18	1.435	340	339
20	1.476	350	347
22	1.515	359	354

TABLE X - 4

Melting Points

Water (54) Ice VII

P M kg/cm²	R	T_m	Obs. (57)
0	1.000	172.5	
22.4	2.125	367	355
24	2.183	377	369
26	2.254	389	384
28	2.323	401	397
30	2.389	412	410
32	2.454	423	423
34	2.517	434	434
36	2.579	445	445
38	2.639	455	456

40	2.690	465	466

TABLE X - 6

Melting Points

Hdrogen (59)

P M kg/cm^2	R	T_m	Obs. (57)
0	l.000	14.00	14
33.2	1.077	15.08	15
67.3	1 150	16.10	16
103.5	1:223	17.12	17
142.3	1.297	18.16	18
183.6	1.371	19.19	19
227.1	1.445	20.23	20
272.3	1.518	21.25	21
318.6	1.589	22.25	22
366.0	1.659	23.23	23
415.0	1.729	24.20	24
465.6	1.797	25.16	25
518	1.866	26.12	26

TABLE X - 6

Melting Points

Xenon

P M kg/cm^2	R_1	R_2	2%	T_m	Obs. (58)
572	1.934	2.261	0.7	27.11	27
628	2.002	2.348	1.5	28.10	28
685	2.069	2.434	2.2	29.08	29
744	2.136	2.519	3.0	30.06	30
867	2.270	2.689	4.5	32.04	32

996	2.402	2.856	6.0	34.01	34
1131	2.534	3.021	7.4	35.97	36
1274	2.605	3.186	8.9	37.96	38
1422	2.795	3.350	10.4	39.94	40
1821	3.118	3.753	14.0	44.89	45
2258	3.438	4.150	17.5	49.87	50
2735	3.755	4.544	21.0	54.89	55
3249	4.070	4.935	24.5	59.95	60
3801	4.382	5.321	27.9	65.02	65
4389	4.693	5.704	31.4	70.14	70
5014	5.002	6.085	34.8	75.30	75
5674	5.308	6.463	38.2	80.48	s0

TABLE X - 7

Initial Pressures

	a-c-b	n	V_0	P_0
Hydrogen	1½-1-1	1	9.318	208.8
	1-1-1	1	9.318	139.2
Helium (He4)	1-1-1	1	3.519	266.4
(He3)	1½-1-1	1	6.256	294.1
Nitrogen	2-1-1	1	1.0048	1327
Krypton	1½-1-1	1	.3359	2066
	1-1-1	1	.3359	1378
Xenon	1½-1-1	1	.2407	2581
	1-1-1	1	.2407	1720
Mercury	2-4-1	1½	.0702	20859
Lead	4-6-1	2	.0876	40510
C02	4-8-1	5	.5722	6180
C014	4-4-1	6	.4108	3212
Ice III	4-8-1	1	.7640	25486

Ice V	4-8-1	2	.7640	12743
Ice VI	4-8-1	3	.7640	8495
	4-8-2	3	.7640	16990
Ice III	4-8-1	4	.7640	6371
Ethyl alcohol	4-8-1	3	.9145	7537
Butyl alcohol	4-8-1	3	.8526	7897
Acetic acid	4-8-1	4	.6346	7211
Butyric acid	4-8-1	4	.7043	6727
Caproic acid	4-8-1	4	.7254	6596
Caprylic acid	4-8-1	4	.7304	6566
Benzene	4-8-1	5	.7208	5299
o-Xylene	4-8-1	5	.7721	5061
p-Xylene	4-8-1	6	.7937	4141
Nitrobenzene	4-8-1	5	.5989	5996
m-Nitrotoluene	4-8-1	5	.5977	6004
p-Nitrotoluerie	4-8-1	5	.5893	6061
Aniline	4-8-1	4	.6786	6895
Chlorobenzene	4-8-1	4½	.5827	6784
Bromobenzene	4-8-1	5½	.4360	6735
Chloroform	4-8-1	7	.4315	5328
Bromoform	4-8-1	10	.2364	5567
Ethyl bromide	4-8-1	5½	.4305	6792

REFERENCES

5. Larson, D. B., Compressibility of Solids, privately circulated paper available from the author on request.

50. Strong, H. M., and Bundy, F. P., Phys. Rev., 115-278.

51. See discussion by Strong in Nature, 183-1381.

52. MiIls, R. L., and Frilly, E. R., Phys. Rev., 99-480. Numerical values supplied by Dr, Mills in private communication.

53. Holland, Huggill and Jones, Proc. Roy, Soc. (London), A 207-268.

54. Bridgman, P. W., various, For a bibliography of Bridgman's reports see his book "The Physics of High Pressure". 0. Bell & Sons., London, 1958. All values in Table X-2 are from Bridgman unless otherwise specified.

55. Robinson., D. W., Proc. Roy. Soc. (London), A 225-393. Butuzov, V. P., Doklady Akad. Nauk, S.S.S.R., 91-1083

57. Deffet, Ll, Bull, Soc. Chim. Belg., 44-41.

58. Lahr, P. H. and Eversolet W. 0., J. Chem. Engr. Data, 7-42.

59. Compiled from original sources by Wooley, Scott and Brickwedde, J. Res. N.B.S., 41-3790

DEWEY B. LARSON: THE COLLECTED WORKS

Dewey B. Larson (1898-1990) was an American engineer and the originator of the Reciprocal System of Theory, a comprehensive theoretical framework capable of explaining all physical phenomena from subatomic particles to galactic clusters. In this general physical theory space and time are simply the two reciprocal aspects of the sole constituent of the universe–motion. For more background information on the origin of Larson’s discoveries, see Interview with D. B. Larson taped at Salt Lake City in 1984. This site covers the entire scope of Larson’s scientific writings, including his exploration of economics and metaphysics.

D.B. Larson

Physical Science

The Structure of the Physical Universe
The original groundbreaking publication wherein the Reciprocal System of Physical Theory was presented for the first time.

The Case Against the Nuclear Atom
“A rude and outspoken book.”

Beyond Newton
“...Recommended to anyone who thinks the subject of gravitation and general relativity was opened and closed by Einstein.”

New Light on Space and Time
A bird’s eye view of the theory and its ramifications.

The Neglected Facts of Science
Explores the implications for physical science of the observed existence of scalar motion.

Quasars and Pulsars
Explains the most violent phenomena in the universe.

Nothing but Motion
The first volume of the revised edition of
The Structure of the Physical Universe, developing the basic principles and relations.

Basic Properties of Matter
The second volume of the revised edition of
The Structure of the Physical Universe, applying the theory to the structure and behavior of matter, electricity and magnetism.

The Universe of Motion
The third volume of the revised edition of
The Structure of the Physical Universe, applying the theory to astronomy.

The Liquid State Papers
A series of privately circulated papers on the liquid state of matter.

The Dewey B. Larson Correspondence
Larson's scientific correspondence, providing many informative sidelights on the development of the theory and the personality of its author.

The Dewey B. Larson Lectures
Transcripts and digitized recordings of Larson's lectures.

The Collected Essays of Dewey B. Larson
Larson's articles in *Reciprocity* and other publications, as well as unpublished essays.

Metaphysics

Beyond Space and Time
A scientific excursion into the largely unexplored territory of metaphysics.

Economic Science

The Road to Full Employment
The scientific answer to the number one economic problem.

The Road to Permanent Prosperity
A theoretical explanation of the business cycle and the means to overcome it.

These works are free at; http://www.reciprocalsystem.com/dbl/index.htm

Special Thanks to the folks who set up the Dewey B Larson website!