The Liquid State, Part 2—Relation to Temperature

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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 far 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 510.2° K. The volume of a liquid *molecule* between absolute zero and the critical temperature can then be expressed as

$$V_L = \left(1 + \frac{T}{510.2}\right) V_0 \tag{1}$$

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

$$V_L = V_1 + \left(\frac{T}{510.2}\right) V_2 \tag{2}$$

The volume of a liquid *aggregate* deviates from the linear relation of Equation (2) in two respects. At

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1   Larson D.B., *The Structure of the Physical Universe*, North Pacific Pub,, Portland, Oregon, U.S.A., 1959.

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 510.2° 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 we designate the larger unit, which we find is $(T_c + 255.1)/9$, as A, the smaller unit as B, and the corresponding probability functions as φ_A and φ_B, we may express the proportion of critical molecules in the saturated or orthobaric liquid aggregate as $\frac{1}{2}(\varphi_A + \varphi_B)$. 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 is $\frac{1}{2}(\varphi_A + \varphi_B)$ the average volume increase for the

liquid aggregate as a whole is ½(φ_A + φ_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

$$V_L = V_1 + \left(\frac{T}{510.2}\right)V_2 + \frac{1}{2}(\phi_A + \phi_B)V_3 \tag{3}$$

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 a 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 of 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 Δ_s in the tabulations included herewith, let us look at the figures for hexane at -50° C. First we divide the melting temperature, 178° K, by 4 to obtain the probability unit 44.5°. Next we divide the 45 degree difference between -50° C and the melting point by the unit value 44.5°, 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 l.41 units. The corresponding value of the integral of the normal probability function, which we will designate φ, 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 -50° 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 +.80. The slightly higher value +.84 will be applied to the paraffins above C_{14}, including hexadecane, one of the compounds covered by the tabulations. The product .079 × .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 84.8°. In the computation for +50° C, for example, we next subtract 50° from the critical temperature, 235° C, obtaining a difference of 185°. Dividing 185 by 84.8, we find that the number of probability units below the critical temperature is 2.18. The corresponding value of $\frac{1}{2}(\varphi_A + \varphi_B)$ 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 +50° C are in the critical condition. We then multiply 0.015 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 the modification of the basic value V_0 by a geometric factor which varies from .8909 to 1.00. In the case of hexane, for example, V_0 is .9778 and the geometric factors for the three dimensions of motion are .9861, .9727, and 1.000 respectively.

Volumetric data for a number of representative liquids are given in Table II-1. In this table the Δ_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.[2] In those cases where the solid-state volume increment, Δ_s, is 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

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2   The experimental values in the Tables have been taken from Timmerman's "Physico-chemical Constants of Pure Organic Compounds" or from the publications of the American Petroleum Institute Research *Project 44*. Most of the other values are either from the *International Critical Tables* or from the extensive work of Vogel and collaborators published in the J. Chemical Soc.

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 $510.2n$ degrees. In such liquids as water, the glycols and many condensed aromatic compounds the value of n is 2.

Table II-1
Hexane

$T_c = 508$ φ unit $= 84.8$ $V_0 = .9645-.9512-.9778$ cm^3/g $V_S-V_L = .080$

T	V_2	V_3	Δ_s	V(calc)	V(obs)	T	V_2	V_3	Δ_s (V calc)	V(obs)
-100	.3229		.031	1.318	1.313	60	.6212	.0196	1.605	1.607
-90	.3415		.024	1.330	1.327	70	.6398	.0254	1.630	1.633
-80	.3601		.018	1.343	1.342	80	.6585	.0332	1.636	1.661
-70	.3788		.014	1.357	1.357	90	.6771	.0430	1.685	1.690
-60	.3974		.010	1.372	1.373	100	.6958	.0548	1.715	1.720
-50	.4161		.006	1.387	1.389	110	.7144	.0694	1.748	1.753
-40	.4347		.004	1.403	1.405	120	.7330	.0851	1.783	1.790
-30	.4534	.0010	.003	1.422	1.422	130	.7517	.1056	1.822	1.829
-20	.4720	.0010	.002	1.440	1.440	140	.7703	.1291	1.864	1.872
-10	.4907	.0020	.001	1.457	1.458	150	.7890	.1564	1.910	1.920
0	.5093	.0029		1.477	1.477	160	.8076	.1877	1.960	1.975
10	.5280	.0039		1.496	1.496	170	.8263	.2278	2.019	2.035
20	.5466	.0059		1.517	1.516	180	.8449	.2767	2.086	2.105
30	.5652	.0078		1.538	1.537	190	.8636	.3461	2.174	2.188
40	.5839	.0108		1.559	1.560	200	.8822	.4351	2.282	2.291
50	.6025	.0147		1.582	1.583	210	.9009	.5593	2.425	2.125

Hexadecane

$T_c = 728$ φ unit $= 109.2$ $V_0 = .8195-.7764-.8373$ cm^3/g $V_S-V_L = .084$

T	V_2	V_3	Δ_s	V(calc)	V(obs)	T	V_2	V_3	Δ_s	V(calc)	V(obs)
20	.4461		.028	1.294	1.293	160	.6592	.0033	.001	1.483	1.483
30	.4613		.024	1.305	1.305	170	.6744	.0042		1.498	1.499
40	.4766		.020	1.316	1.316	180	.6896	.0050		1.514	1.516
50	.4918		.017	1.328	1.328	190	.7048	.0067		1.531	1.533
60	.5070		.014	1.341	1.341	200	.7201	.0084		1.548	1.551
70	.5222		.011	1.353	1.353	210	.7353	.0109		1.566	1.570
80	.5374		.009	1.366	1.366	220	.7505	.0134		1.583	1.590
90	.5527		.007	1.379	1.379	230	.7657	.0167		1.602	1.611
100	.5679		.005	1.392	1.392	240	.7809	.0201		1.621	1.633
110	.5831	.0008	.004	1.407	1.407	250	.7961	.0251		1.641	1.655
120	.5983	.0008	.003	1.422	1.421	260	.8114	.0310		1.662	1.679
130	.6135	.0008	.002	1.436	1.436	270	.8266	.0385		1.685	1.704
140	.6287	.0017	.002	1.452	1.451	280	.8418	.0461		1.707	1.730
150	.6440	.0025	.001	1.467	1.466	290	.8570	.0553		1.732	1.759

Benzene

$T_c = 564$ φ unit $= 91.0$ $V_0 = .7208\text{-}.7208\text{-}.8091$ cm³/g $V_S\text{-}V_L = 0$

T	V₂	V₃	Δₛ V(calc)	V(obs)	T	V₂	V₃	Δₛ V(calc)	V(obs)
0	.3859	.0000	1.107	1.111	140	.5837	.0388	1.343	1.344
10	.4000	.0008	1.121	1.124	150	.5978	.0494	1.368	1.368
20	.1042	.0008	1.136	1.138	160	.6120	.0607	1.394	1.392
30	.4283	.0016	1.151	1.151	170	.6261	.0744	1.421	1.420
40	.1424	.0024	1.166	1.166	180	.6402	.0898	1.451	1.448
50	.4566	.0032	1.181	1.181	190	.6544	.1084	1.484	1.480
60	.4707	.0049	1.196	1.197	200	.6685	.1295	1.519	1.514
70	.4848	.0065	1.212	1.212	210	.6826	.1545	1.558	1.555
80	.4989	.0081	1.228	1.228	220	.6967	.1837	1.601	1.599
90	.5131	.0113	1.245	1.244	230	.7109	.2217	1.653	1.649
100	.5272	.0146	1.263	1.262	240	.7250	.2702	1.716	1.709
110	.5413	.0186	1.281	1.281	250	.7391	.3358	1.796	1.783
120	.5555	.0243	1.301	1.300	260	.7532	.4215	1.896	1.877
130	.5696	.0307	1.321	1.321	270	.7674	.5292	2.017	2.006

Acetic Acid

$T_c = 596$ φ unit $= 94.55$ $V_0 = .6346\text{-}.5496\text{-}.7016$ cm³/g $V_S\text{-}V_L = 0$

T	V₂	V₃	Δₛ V(calc)	V(obs)	T	V₂	V₃	Δₛ V(calc)	V(obs)
20	.3143	.0000	.949	.953	170	.4751	.0372	1.147	1.150
30	.3250	.0007	.960	.962	180	.4858	.0463	1.167	1.169
40	.3357	.0007	.971	.972	190	.4965	.0554	1.187	1.189
50	.3464	.0014	.982	.983	200	.5072	.0681	1.210	1.210
60	.3571	.0021	.994	.994	210	.5179	.0807	1.233	1.233
70	.3679	.0028	1.005	1.005	220	.5287	.0968	1.260	1.259
80	.3786	.0035	1.017	1.017	230	.5394	.1151	1.289	1.288
90	.3893	.0049	1.029	1.029	240	.5501	.1361	1.321	1.321
100	.4000	.0063	1.041	1.042	250	.5608	.1621	1.358	1.358
110	.4107	.0084	1.054	1.055	260	.5715	.1936	1.400	1.401
120	.4215	.0112	1.067	1.068	270	.5823	.2343	1.451	1.449
130	.4322	.0147	1.082	1.083	280	.5930	.2884	1.516	1.509
140	.4429	.0182	1.096	1.100	290	.6037	.3578	1.596	1.579
150	.4536	.0239	1.112	1.116	300	.6314	.4448	1.694	1.681
160	.4643	.0302	1.129	1.133					