The Liquid State, Part III
Volume – Relation to Composition

Dewey B. Larson

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.[1] 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 volume, V_0, as

$$V_0 = V_s + \Delta \tag{1}$$

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 will 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 distances range from ½ unit to 2½ units. The great majority of the structural 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 groups 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. Same very striking illustrations of this fact can be produced by replacing the heavy atoms in metal-organic compounds by

light organic groups. Far 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 0.707, 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 0.707, or 0.891, 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 k_s and the number of liquid groups by n, we have the relation

$$V_0 = 0.707\, n\, k_s \quad \textit{natural units of volume} \tag{2}$$

In order to convert Equation (2) to conventional units so that comparisons can be made between theoretical and observed volumes, it is necessary to multiply the expression $0.707\ n k_s$ 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,[2] Equation (2) becomes

$$V_0 = 10.5326 \frac{n\, k_s}{m} \quad \frac{cm^3}{g} \tag{3}$$

Where the inter-atomic bonds are all alike, the value of n can be calculated from the solid-state inter-atomic 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 $C(CH_3)_2$, 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 dose relationship to the solid state. Each volumetric group must conform to one of the two possible k_s values, 0.891 or 1.00, but in a multi-group molecule, the number of groups taking each value may vary all the way from 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 k_s is generally lower than in the initial dimension. The minimum value 0.891 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 k_s 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. Methyl chloride thus occupies 3½ volumetric units and each added CH_2 group increases the volume by one unit. Applying these values of *n* to Equation (3) 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 separately in the tabulations. As indicated in the column headed n_s, 2½ of the 3½ volumetric units in methyl chloride have the 0.891 factor in the first dimension, but in the higher compounds of the series all groups take the full 1.00 factor. The second dimension factor is 0.891 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 0.891. By applying these k_s 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 paper.

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 become 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.

Table III-1
Initial Volumes – Alkyl Chlorides

	n	V_0 (and V_3)	Dimension 1 n_s	Dimension 1 Av. k_s	V_1	Dimension 2 n_s	Dimension 2 Av. k_s	V_2
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
Heptyi	9½	.7431	0	1.000	.7431	7½	.914	.6791
Octyl	10½	.7439	0	1.000	.7439	8½	.912	.6782
Nonyl .	11½	.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

	n	n_s	T	V(calc)	V(obs.)
		Paraffins			
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
Hexane	8	1-2	0	1.477	1.477
Heptane	9	1-3	50	1.519	1.5L9
Octane	10	1-4	50	1.474	1.474
Nonane	11	1-5	100	1.531	1.530
Decane	12	l½-6	100	1.496	1.497
Undecane	13	l½-7	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

	n	n_s	T	V(calc)	V(obs.)
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-l4	200	1.521	1.523
Nonadecane	21	5-15	200	1.510	1.511
Eicosane	22	5½-16	200	1.501	1.501
		Olefins			
Ethylene	3½	0-3½	-100	1.756	1.774
Propene	4½	0-0	0	1.830	1.834
1-Butene	5½	0-0	0	1.611	1.616
1-Pentene	6½	0-0	0	1.507	1.512
1-Hexene	7½	0-0	50	1.545	1.551
1-Heptene	8½	0-1	50	1.490	1.491
1-Octene	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	1.434
1-Tetradecene	15½	l½-8	120	1.429	1.429
1-Pentadecene	16½	2-9	120	1.416	1.416
		Ketones			
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			
Methyl	3	2-2½	20	1.511	1.511
Ethyl	4	½-1	20	1.461	1.464

	n	n_s	T	V(calc)	V(obs.)
Propyl	5	0-1½	20	1.394	1.390
Butyl	6	0-l½	20	1.351	1.351
Amyl	7	0-1½	20	1.323	1.322
Hexyl	8	0-1½	40.5	1.336	1.335
		Thiols			
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			
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
Butyl	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			
Ethyl	5	5-5	30	.690	.694
Propyl	6	5-5	62	.779	.781
Butyl	7	5-5	89	.855	.853
Amyl	8	4-8	87	.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			
Methyl	4½	0-2½	90	1.310	1.309
Ethyl	7	3½-7	90	1.305	1.307
Propyl	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			
Hexyl formate	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 valerate	9½	2½-9½	64	1.201	1.200
Methyl caproate	9½	4½-9½	61	1.180	1.182