The Liquid State, Part II Supplement
Volume Relation to Temperature

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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-l 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 $T/510.2n$ 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 n_t and n_v will be used in the following discussion. Most of the common 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 qualify either as organic or inorganic, depending on the definition that is used, and for SO_2 and HC1, 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_o 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_o 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)**	**T**	**V_2**	**V_3**	**V(calc)**	**V(obs)**
-257	.298	3.598	13.21	13.35	-246	.503	7.269	17.09	16.53
-253	.363	4.466	14.15	14.03	-243	.550	8.409	18.28	18.52
-250	.419	5.449	15.19	14.87					
Fluorine V_0 = .5241 - .4939 - .5543 cm^3/g									
-208	.0632	.0233	.611	.610	-193	.0775	.0438	.645	.646
-203	.0677	.0288	.621	.620	-190	.0810	.0510	.656	.657
-198	.0731	.0366	.634	.634	-188	.0825	.0543	.661	.662
Hydrochloric Acid V_0 = .6104 - .6025 - .6498 cm^3/g									
-80	.2283	.0136	.852	.849	-20	.2988	.0884	.998	1.003
-70	.2398	.0195	.870	.869	-10	.3109	.1124	1.034	1.040
-60	.2518	.0273	.890	.891	0	.3229	.1443	1.078	1.082
-50	.2639	.0377	.912	.915	10	.3344	.1891	1.134	1.135
-40	.2753	.0513	.937	.940	20	.3464	.2541	1.211	1.203
-30	.2874	.0676	.965	.970					
Sulfur Dioxide V_0 = .4394 - .4663 - .4932 cm^3/g									

-50	.2042	.0015	.645	.642	50	.2956	.0385	.774	.772
-40	.2131	.0025	.655.	.652	60	.3045	.0483	.792	.792
-30	.2224	.0035	.665	.663	70	.3138	.0617	.815	.814
-20	.2313	.0049	.676	.674	80	.3227	.0764	.839	.838
-10	.2406	.0069	.687	.686	90	.3320	.0942	.866	.866
0	.2499	.0094	.699	.697	100	.3413	.1159	.897	.898
10	.2588	.0128	.711	.710	110	.3502	.1450	.935	.936
20	.2681	.0173	.725	.723	120	.3595	.1850	.984	.982
30	.2770	.0232	.740	.738	130	.3684	.2436	1.051	1.045
40	.2863	.0301	.756	.754	140	.3777	.3191	1.136	1.136
		Carbon Tetrachloride V_0 = .4108 - .3772 - .4108 cm^3/g							
0	.2019	.0004	.613	.612	140	.3054	.0234	.740	.744
10	.2093	.0004	.621	.620	150	.3128	.0292	.753	.757
20	.2167	.0008	.628	.627	160	.3201	.0357	.767	.770
30	.2241	.0012	.636	.635	170	.3275	.0444	.783	.785
40	.2315	.0016	.644	.643	180	.3349	.0534	.799	.802
50	.2388	.0021	.652	.651	190	.3423	.0637	.817	.820
60	.2462	.0029	.660	.660	200	.3497	.0760	.837	.841
70	.2536	.0037	.668	.668	210	.3571	.0904	.858	.864
80	.2610	.0053	.677	.677	220	.3645	.1126	.888	.891
90	.2684	.0070	.686	.687	230	.3719	.1323	.915	.921
100	.2758	.0090	.696	.697	240	.3793	.1651	.955	.958
110	.2832	.0115	.706	.708	250	.3867	.2070	1.005	1.002
120	.2906	.0148	.716	.719	260	.3941	.2604	1.065	1.063
130	.2980	.0189	.728	.731					

Table II-3
Liquid Volume (n_t = 2)

T	V_2	V_3	Δ_s	V(calc)	V(obs)	T	V_2	V_3	V(calc)	V(obs)
0	.2048		.0312	1.0000	1.0002	160	.3239	.0140	1.1019	1.1021
10	.2124		.0242	1.0006	1.0004	170	.3316	.0184	1.1140	1.1144
20	.2193		.0185	1.0018	1.0018	180	.3392	.0228	1.1260	1.1275
30	.2269		.0137	1.0046	1.0044	190	.3469	.0289	1.1398	1.1415
40	.2345		.0099	1.0084	1.0079	200	.3545	.0360	1.1545	1.1565
50	.2422	.0009	.0068	1.0139	1.0121	210	.3614	.0447	1.1701	1.1726
60	.2491	.0009	.0048	1.0188	1.0171	220	.3690	.0544	1.1874	1.1900
70	.2567	.0009	.0032	1.0248	1.0228	230	.3767	.0658	1.2065	1.2087
80	.2643	.0018	.0020	1.0321	1.0290	240	.3842	.0789	1.2272	1.2291
90	.2720	.0018	.0012	1.0390	1.0359	250	.3919	.0947	1.2506	1.2512
100	.2796	.0026	.0007	1.0469	1.0435	260	.3988	.3114	1.2742	1.2755
110	.2865	.0035	.0004	1.0544	1.0515	270	.4064	.1315	1.3019	1.3023
120	.2941	.0053	.0002	1.0636	1.0603	280	.4141	.1543	1.3324	1.3321
130	.3018	.0061		1.0719	1.0697	290	.4217	.1806	1.3663	1.3655
140	.3094	.0079		1.0813	1.0798	300	.4294	.2131	1.4065	1.4036
150	.3171	.0114		1.0925	1.0906					

Table II-4

LIQUID VOLUME (n_t = 4 to 16)

T	**V2**	**V(calc)**	**V(obs)**
Sulfur $n_t = 4$ $V_0 = .4578$			
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
Lithium $n_t = 9$ $V_0 = 1.7729$			
200	.1826	1.96	1.97
400	.2606	2.03	2.04
600	.3369	2.11	2.11
800	.4149	2.19	2.19
1000	.4911	2.26	2.27

T	**V_2**	**V(calc)**	**V(obs)**
Silver $n_t = 16$ $V_0 = .0923$			
960	.0139	.106	.105
1092	.0154	.108	.109
1195	.0166	.109	.110
1300	.0178	.110	.111
Tin $n_t = 16$ $V_0 = .1331$			
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
Temperature 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)		T	V_0	V_2	V(calc)	V(obs)
LiF	887	.3617	.2058	.568	.558	KI	700	.2538	.1614	.415	.411
	1058		.2358	.598	.587		751		.1698	.424	.420
LiCl	626	.4697	.2071	.677	.668	RbF	820	.2245	.1374	.362	.347
	900		.2701	.740	.727		1006		.1610	.386	.372
LiBr	547	.2701	.1240	.394	.392	RbCl	734	.2858	.1881	.474	.476
	700		.1472	.417	.410		822		.2046	.490	.493
NaF	1017	.3351	.2118	.547	.517	RbBr	697	.2269	.1439	.371	.372
	1214		.2443	.579	.549		780		.1561	.383	.384
NaCl	809	.4013	.2432	.645	.650	RbI	700	.2177	.1385	.356	.357
	1010		.2885	.690	.697		800		.1526	.370	.372
NaBr	785	.2735	.1625	.436	.433	CsF	720	.2238	.1452	.369	.368
	954		.1882	.462	•46o		824		.1605	.384	.386
NaI	675	.2267	.l406	.367	.367	CsCl	66l	.2229	.1360	.359	.360
	724		.1478	.375	.374		741		.1478	.371	.372
KF	913	.3230	.2145	.538	.534	CsBr	662	.1984	.1212	.320	.321
	1054		.2400	.563	.563		743		.1317	.330	.333
KC1	785	.4161	.2467	.663	.658	CsI	639	.1806	.1291	.310	.315
	958		.2871	.703	.706		701		.1380	.319	.323
KBr	751	.2856	.1911	.477	.473						
	945		.2273	.513	.512						