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VOLUMETRIC AND THERMODYNAMIC PROPERTIES OF NORMAL FLUIDS

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Kenneth S. Pitzer

January 1958

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ABSTRACT

A comprehensive system for the prediction of the volumetric and thermodynamic properties of normal fluids has been developed and published in several journal articles. This report draws together the various tables and equations into a convenient unit and provides an introduction to current work on solutions. It is written in the form of an Appendix to a forthcoming revision of the book: Thermodynamics, First Edition, by G. N. Lewis and M. Randall. Occasionally reference is made to equations in the main text by the equation numbers of the revised edition which is not now available. This should not trouble the reader since these are standard equations given in the first edition or in any modern text of chemical thermodynamics.

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Appendix 1*

Properties of Normal Fluids

In Chapters 15 and 16, thermodynamic principles are applied to fluids deviating from ideal gas behavior. Also, the continuity of gas and liquid states is noted. While the properties of many substances have been measured over broad ranges of pressure and temperature, far more substances have not been studied and a system of prediction is to be desired. The very brief discussion of predictive methods in Chapter 16 is extended here. Molecular theory is used to guide forms of equations in some cases, but the final results are based upon the observed properties of numerous substances. It is impractical to repeat here the numerous comparisons with observed data - for that the reader must refer to the original papers cited below.

The prediction of the volumetric and thermodynamic properties of pure fluids has been the subject of many studies over the last hundred years. Although the underlying principles in terms of intermolecular forces are now well understood, the calculation or even the quantitative empirical representation of the resulting macroscopic properties has proven to be unusually difficult. The failure to find a really satisfactory analytical equation of state arises in our opinion, not from any lack of skill in selecting the appropriate combination of common mathematical functions, but rather in the non-existence of any suitable function. Consequently, it is best, in effect, to let nature generate mathematical functions and to develop an equation in which the minimum number of such functions are combined with other precisely defined parameters to yield the desired volumetric and thermodynamic properties for a broad class of pure substances.

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*This material is to constitute Appendix 1 of a forthcoming book on Thermodynamics.

A correlation based on these ideas has been developed and presented in full in two series of papers.[1,2] Statistical theory[3] shows that a group of substances will conform to the principle of corresponding states only if their intermolecular potentials are identical except for distance and energy scale factors characteristic of each substance. Also, their intermolecular motion must be classical, i.e., quantum effects must be negligible. The only group of substances which may be expected to conform to these criteria are the heavier rare gases A, Kr, and Xe which do conform accurately to corresponding states behavior. These are called simple fluids. Various types of molecular shapes and molecular dipole moments might be expected to cause different deviations of macroscopic properties from that of simple fluids. It is found, however, that the reduced theoretical second virial coefficients for a wide variety of these molecular types fall into a single family of curves which may be characterized by a single parameter. The only exception noted is that of molecules with large dipole moments, although there are unusual types of abnormality that have not been tested. The molecules falling into this single family are just those commonly called normal liquids or fluids. Normal fluids are defined more precisely below.

Acentric Factor - The theory thus suggests an extension of the corresponding states correlation involving a third parameter.[4] The slope of the reduced vapor pressure curve is the most sensitive property upon which to base the third parameter and it has the additional advantage that vapor pressures are readily measured with high accuracy. An arbitrary but convenient definition[5] is based upon the reduced vapor pressure at a point well removed from the critical point

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[1] L. Riedel, Chem. Ing. Tech. 26, 83, 259, 679 (1954); 27, 209, 475 (1955); 28, 557 (1956).

[2] K. S. Pitzer, D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, J. Am. Chem. Soc. 77, 3427, 3433 (1955); 79, 2369 (1957); Ind. Eng. Chem.

[3] K. S. Pitzer, J. Chem. Phys. 7, 583 (1939).

[4] A third parameter was first suggested by Nernst in 1907 and by various authors since. See papers[1,2] for references, and for the advantages of the present system over others.

[5] The parameter α_k chosen by Riedel[1] is equivalent but is different in detail of definition. $\alpha_k = 5.808 + 4.93\,\omega$.

and takes the form

$$\omega = -\log (P_s/P_c) - 1.000 \qquad \text{(A1-1)}$$

$$P_s = \text{vapor pressure at } T_r = 0.700.$$

The form is chosen to make $\omega = 0$ for the simple fluids, A, Kr, and Xe, with simple spherical molecules. Other normal fluids have small positive values of ω. The name acentric factor was adopted to indicate that the factor measures the deviation of the intermolecular potential function from that of the simple spherical molecules.

Any property of the fluid, in reduced or dimensionless form, is assumed to be given by a function of the three variables: reduced pressure, reduced temperature, and acentric factor. For example, the compressibility factor, z, may be written

$$z = z(P_r, T_r, \omega). \qquad \text{(A1-2)}$$

It is found that a linear equation in ω is usually adequate.

$$z = z^{(o)}(P_r,T_r) + \omega\, z^{(1)}(P_r,T_r). \qquad \text{(A1-3)}$$

Analytical representation of the functions $z^{(o)}$ and $z^{(1)}$, however, is usually impractical and they are tabulated in most cases.

Vapor Pressure, Heat and Entropy of Vaporization - Where two phases exist in equilibrium the vapor pressure and other properties are given as functions of two variables, T_r and ω.

$$\log P_r = (\log P_r)^{(o)} + \omega(\partial \log P_r/\partial\omega)_T. \qquad \text{(A1-4)}$$

These two functions are tabulated in Table A1-1. From the definition of the acentric factor at $T_r = 0.7$, $(\log P_r)^{(o)} = -1.000$ and $(\partial \log P_r/\partial\omega)_T = -1.000$.

Table A1-1. Data for Coexisting Liquid and Vapor Phases

T_r	$-(\log P_r)^{(o)}$	$-\left(\frac{\partial \log P_r}{\partial \omega}\right)_T$	Vaporization[a] $\Delta S^{(o)}$	$\Delta S^{(1)}$	Vapor $z^{(o)}$	$z^{(1)}$	Liquid $z^{(o)}$	$z^{(o)}$
1.00	0.000	0.000	0.00	0.00	0.291	-0.080	0.291	-0.080
.99	.025	.021	2.57	2.83	.43	- .030	.202	- .090
.98	.050	.042	3.38	3.91	.47	.000	.179	- .093
.97	.076	.064	4.00	4.72	.51	+ .020	.162	- .095
.96	.102	.086	4.52	5.39	.54	.035	.148	- .095
.95	.129	.109	5.00	5.96	.565	.045	.136	- .095
.94	.156	.133	5.44	6.51	.59	.055	.125	- .094
.92	.212	.180	6.23	7.54	.63	.075	.108	- .092
.90	.270	.230	6.95	8.53	.67	.095	.0925	- .087
.88	.330	.285	7.58	9.39	.70	.110	.0790	- .080
.86	.391	.345	8.19	10.3	.73	.125	.0680	- .075
.84	.455	.405	8.79	11.2	.756	.135	.0585	- .068
.82	.522	.475	9.37	12.1	.781	.140	.0498	- .062
.80	.592	.545	9.97	13.0	.804	.144	.0422	- .057
.78	.665	.620	10.57	13.9	.826	.144	.0360	- .053
.76	.742	.705	11.20	14.9	.846	.142	.0300	- .048
.74	.823	.800	11.84	16.0	.864	.137	.0250	- .043
.72	.909	.895	12.49	17.0	.881	.131	.0210	- .037
.70	1.000	1.00	13.19	18.1	.897	.122	.0172	- .032
.68	1.096	1.12	13.89	19.3	.911	.113	.0138	- .027
.66	1.198	1.25	14.62	20.5	.922	.104	.0111	- .022
.64	1.308	1.39	15.36	21.8	.932	.097	.0088	- .018
.62	1.426	1.54	16.12	23.2	.940	.090	.0068	- .015
.60	1.552	1.70	16.92	24.6	.947	.083	.0052	- .012
.58	1.688	1.88	17.74	26.2	.953	.077	.0039	- .009
.56	1.834	2.08	18.64	27.8	.959	.070	.0028	- .007

[a]Strictly there is a small $\Delta S^{(2)}$ which is almost always negligible. See K. S. Pitzer, et al., J. Am. Chem. Soc. 77, 3439 (1955).

Also included in Table A1-1 are values of the compressibility factor functions for the vapor and of the liquid. These are to be used in Eq. (A1-3). The values for z for the liquid are not very accurate at the lower temperatures where they are very small; a better source of volumetric data for liquids is Table A1-16. By combination of the compressibility factor data with the temperature derivative of the vapor pressure, the heat and entropy of vaporization may be calculated. The Claperon

equation rearranges into

$$\Delta S = \frac{R\Delta z}{T_r} \frac{\partial \ln P}{\partial (1/T)_r} \qquad \text{(A1-5)}$$

where Δz is the change in compressibility factor on vaporization. The values of $\Delta S^{(o)}$ and $\Delta S^{(1)}$ in Table A1-1 come from this source. The heat of vaporization is, of course, $T\Delta S$.

The full vapor pressure functions of Table A1-1 make it possible to evaluate the acentric factor from any vapor pressure value at a temperature well below the critical point.

Second Virial Coefficient - In Chapter 16 the Berthelot equation for the second virial coefficient was discussed and its limited accuracy was apparent from Fig. 16-1. The acentric factor makes a substantially improved equation possible. A series of inverse powers of T_r is a convenient form. The constants were adjusted[2] to fit both volumetric and thermal data on numerous normal gases.

$$PV = RT + BP + \text{--}$$

$$\frac{BP_c}{RT} = (0.1445 + 0.073\,\omega) - (0.330 - 0.46\,\omega)\,T_r^{-1}$$

$$-(0.1385 + 0.50\,\omega)\,T_r^{-2} - (0.0121 + 0.097\,\omega)\,T_r^{-3}$$

$$-0.0073\,\omega\,T_r^{-8}\,. \qquad \text{(A1-6)}$$

The selection of the term in T_r^{-8} is, of course, somewhat arbitrary, but a very high power is required to fit the low temperature thermal data. Fig. A1-1 compares the curves of Eq. (A1-6) for a few ω values with experimental data for appropriate substances.

Volumetric Data at High Pressure - The volumetric data for a number of substances were interpolated to a series of even reduced pressures and temperatures and plotted against the acentric factor. Fig. A1-2 shows a sample of these plots at $P_r = 3.0$ and a series of reduced temperatures. It is seen that the linear dependence on acentric factor which was assumed in Eq. (A1-3) is a good approximation. The intercepts on the $\omega = 0$ axis constitute the function $z^{(o)}$ and the slopes, the function $z^{(1)}$. The values from the plots were checked for smoothness of variation with P_r

and T_r and adjusted within experimental error if necessary. The resulting functions are given in Tables A1-2 and A1-5. Additional values near the two phase region and the critical point are given in Tables A1-3,4,6,7.

Table A1-2. Values of $z^{(o)}$ for Compressibility Factor Calculation.

(See Tables A1-3 and A1-4 for additional data in the region enclosed by dotted lines)

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0
.80	.851	.066	.100	.133	.164	.192	.225	.258	.287	.318
.85	.882	.067	.101	.134	.165	.194	.226	.258	.287	.316
.90	.904	.778	.102	.135	.167	.198	.229	.258	.288	.316
.95	.920	.819	.697	.145	.176	.205	.235	.262	.292	.321
1.00	.932	.849	.756	.638	.291	.231	.250	.278	.304	.329
1.05	.942	.874	.800	.714	.609	.470	.341	.320	.332	.350
1.10	.950	.893	.833	.767	.691	.607	.512	.442	.408	.402
1.15	.958	.908	.858	.805	.746	.684	.620	.562	.514	.484
1.20	.963	.921	.879	.835	.788	.737	.690	.640	.598	.568
1.25	.968	.930	.896	.858	.820	.778	.740	.702	.664	.636
1.30	.971	.940	.909	.878	.846	.811	.780	.749	.718	.691
1.4	.977	.952	.929	.908	.883	.859	.838	.817	.795	.777
1.5	.982	.963	.945	.927	.909	.892	.875	.859	.844	.831
1.6	.985	.971	.957	.944	.930	.917	.904	.893	.882	.872
1.7	.988	.977	.966	.956	.946	.936	.926	.919	.911	.903
1.8	.991	.982	.974	.966	.958	.950	.944	.937	.931	.926
1.9	.993	.986	.980	.974	.968	.962	.958	.952	.948	.944
2.0	.995	.989	.984	.979	.975	.971	.968	.964	.961	.959
2.5	1.000	.999	.999	.998	.998	.998	.998	.997	.999	1.000
3.0	1.001	1.002	1.003	1.004	1.005	1.007	1.008	1.010	1.012	1.014
3.5	1.002	1.004	1.006	1.008	1.011	1.013	1.015	1.018	1.020	1.022
4.0	1.003	1.005	1.008	1.010	1.013	1.015	1.017	1.020	1.022	1.024

Table A1-2 (Continued)

Values of $z^{(o)}$. Page 2

T_r \ P_r	2.2	2.4	2.6	2.8	3.0	3.2	3.4
.8	.347	.376	.405	.433	.461	.490	.519
.85	.345	.374	.403	.431	.459	.487	.515
.9	.345	.373	.402	.430	.458	.485	.512
.95	.347	.375	.403	.430	.457	.484	.510
1.0	.356	.381	.407	.433	.458	.484	.509
1.05	.372	.393	.417	.441	.466	.489	.512
1.10	.405	.420	.440	.462	.484	.504	.525
1.15	.477	.478	.485	.498	.513	.529	.546
1.2	.553	.545	.544	.548	.554	.563	.574
1.25	.618	.606	.599	.597	.598	.602	.609
1.3	.671	.657	.649	.644	.642	.642	.645
1.4	.759	.745	.734	.725	.720	.718	.718
1.5	.819	.808	.800	.794	.790	.785	.784
1.6	.863	.855	.848	.843	.840	.836	.834
1.7	.896	.889	.883	.879	.875	.873	.872
1.8	.921	.916	.913	.910	.908	.907	.906
1.9	.940	.936	.933	.931	.930	.929	.929
2.0	.956	.954	.953	.953	.952	.952	.953
2.5	1.001	1.001	1.002	1.004	1.006	1.008	1.009
3.0	1.016	1.019	1.022	1.025	1.028	1.030	1.033
3.5	1.024	1.027	1.030	1.033	1.036	1.039	1.042
4.0	1.026	1.029	1.032	1.035	1.038	1.041	1.044

Table A1-2 (Continued)

Values of $z^{(o)}$. Page 3

T_r \ P_r	3.6	3.8	4.0	4.5	5.0	6.0	7.0	8.0	9.0
.8	.547	.576	.605	.675	.746	.883	1.017	1.15	1.28
.85	.542	.569	.597	.663	.730	.861	.990	1.115	1.24
.9	.538	.565	.591	.655	.718	.842	.966	1.089	1.21
.95	.536	.561	.587	.647	.709	.828	.947	1.066	1.185
1.0	.534	.557	.582	.642	.702	.819	.932	1.048	1.166
1.05	.535	.557	.580	.639	.700	.814	.923	1.032	1.147
1.10	.547	.567	.589	.643	.699	.810	.916	1.019	1.129
1.15	.563	.581	.600	.651	.705	.809	.911	1.008	1.113
1.2	.587	.601	.618	.664	.714	.810	.907	1.000	1.100
1.25	.618	.629	.643	.682	.726	.816	.907	.994	1.088
1.3	.651	.659	.668	.701	.740	.824	.910	.992	1.078
1.4	.722	.727	.734	.754	.781	.844	.921	.994	1.071
1.5	.784	.786	.790	.805	.826	.877	.934	1.000	1.070
1.6	.833	.834	.835	.844	.860	.904	.953	1.010	1.075
1.7	.872	.873	.874	.882	.895	.930	.972	1.023	1.082
1.8	.906	.907	.908	.914	.925	.955	.993	1.039	1.091
1.9	.930	.932	.934	.941	.950	.976	1.010	1.051	1.097
2.0	.954	.954	.956	.962	.972	.996	1.027	1.064	1.106
2.5	1.012	1.014	1.018	1.026	1.035	1.055	1.079	1.105	1.136
3.0	1.036	1.038	1.041	1.049	1.058	1.077	1.10	1.124	1.150
3.5	1.045	1.048	1.051	1.058	1.067	1.086	1.105	1.126	1.148
4.0	1.047	1.050	1.053	1.060	1.068	1.086	1.104	1.124	1.143

Table A1-3. Values of $z^{(o)}$ Near the Two Phase Region

T_r	P_r 0.4	0.5	0.6	0.7	0.8	0.9	1.0
.90	.778	.701	.102	.118	.135	.151	.167
.91	.787	.715	.104	.120	.136	.152	.168
.92	.796	.728	.650	.122	.138	.153	.169
.93	.805	.740	.666	.124	.140	.155	.170
.94	.812	.751	.681	.125	.142	.157	.173
.95	.819	.762	.697	.612	.145	.160	.176
.96	.826	.772	.711	.632	.149	.164	.180
.97	.832	.782	.724	.652	.56	.170	.186
.98	.838	.791	.735	.669	.591	.177	.193
.99	.844	.800	.746	.685	.616	.514	.205
1.00	.849	.807	.757	.699	.638	.554	.291
1.01	.854	.813	.767	.713	.654	.583	.476
1.02	.860	.820	.776	.726	.672	.608	.525
1.03	.865	.826	.784	.737	.687	.630	.558
1.04	.870	.833	.793	.748	.701	.648	.586
1.05	.874	.838	.800	.758	.714	.665	.609

Table A1-4. Values of $z^{(o)}$ in the Critical Region

T_r	P_r 1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
.98	.193	.204	.217	.230	.244	.257	.270	.284	.298	.313	.324
.99	.205	.210	.223	.235	.247	.260	.273	.287	.301	.315	.327
1.00	.291	.220	.231	.241	.250	.265	.278	.290	.304	.317	.329
1.01	.476	.283	.243	.248	.259	.271	.283	.294	.307	.319	.332
1.02	.525	.402	.273	.260	.270	.278	.291	.300	.311	.323	.335
1.03	.558	.466	.34	.29	.283	.288	.297	.306	.316	.328	.339
1.04	.586	.509	.41	.33	.307	.302	.307	.314	.324	.334	.343
1.05	.609	.543	.470	.375	.341	.324	.320	.323	.332	.341	.350
1.06	.628	.572	.505	.423	.370	.349	.336	.333	.343	.348	.358
1.07	.645	.597	.534	.468	.408	.379	.358	.349	.356	.358	.367
1.08	.663	.618	.562	.504	.445	.412	.385	.373	.370	.369	.375
1.09	.677	.636	.587	.535	.480	.443	.412	.396	.387	.383	.387
1.10	.691	.652	.607	.561	.512	.473	.442	.422	.408	.400	.402
1.11	.703	.667	.625	.584	.538	.502	.469	.448	.428	.418	.417
1.13	.726	.693	.658	.621	.584	.549	.520	.494	.472	.456	.450
1.15	.746	.715	.684	.652	.620	.589	.562	.536	.514	.495	.484

Table A1-5. Values of $z^{(1)}$ for Compressibility Factor Calculation
(See Tables A1-6 and A1-7 for additional data in the region enclosed by dotted lines)

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0
.80	-.095	-.028	-.044	-.058	-.07	-.08	-.10	-.11	-.12	-.13
.85	-.067	-.031	-.049	-.064	-.08	-.09	-.11	-.12	-.13	-.14
.90	-.042	-.09	-.053	-.068	-.085	-.10	-.11	-.12	-.13	-.14
.95	-.025	-.050	-.10	-.072	-.091	-.10	-.11	-.12	-.12	-.13
1.00	-.012	-.016	-.020	-.05	-.080	-.090	-.099	-.108	-.115	-.123
1.05	.000	+.001	+.005	+.015	+.02	+.01	-.01	-.04	-.06	-.07
1.10	+.002	.008	.016	.030	.055	.082	+.11	+.082	+.035	.000
1.15	.004	.012	.012	.040	.064	.093	.12	.140	.136	+.100
1.20	.009	.018	.028	.044	.069	.10	.13	.16	.17	.17
1.25	.011	.023	.036	.050	.069	.10	.13	.16	.18	.19
1.30	.013	.027	.041	.055	.072	.10	.13	.16	.18	.20
1.4	.016	.032	.049	.065	.082	.10	.13	.16	.18	.19
1.5	.017	.035	.052	.070	.088	.10	.13	.15	.17	.18
1.6	.018	.036	.054	.07	.08	.10	.12	.14	.16	.17
1.7	.018	.036	.054	.07	.09	.10	.11	.13	.15	.16
1.8	.018	.036	.054	.07	.09	.10	.11	.13	.15	.16
1.9	.018	.035	.05	.07	.09	.10	.11	.13	.15	.16
2.0	.016	.031	.05	.07	.08	.10	.11	.13	.14	.15
2.5	.01	.02	.04	.05	.07	.08	.10	.11	.12	.13
3.0	.01	.02	.03	.05	.06	.07	.08	.09	.10	.11
3.5	.01	.02	.03	.04	.05	.06	.07	.08	.08	.09
4.0	.01	.02	.02	.03	.04	.05	.06	.06	.07	.08

Table A1-5

(Continued - Page 2)

Values of $z^{(1)}$

T_r \ P_r	2.2	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
.80	-.14	-.15	-.16	-.17	-.18	-.23	-.26	-.29	-.32	-.35	-.37
.85	-.15	-.16	-.17	-.18	-.18	-.22	-.25	-.28	-.31	-.34	-.36
.90	-.15	-.16	-.17	-.17	-.18	-.21	-.24	-.27	-.30	-.32	-.35
.95	-.14	-.15	-.15	-.16	-.17	-.20	-.22	-.25	-.28	-.31	-.34
1.00	-.13	-.13	-.14	-.14	-.15	-.17	-.20	-.23	-.26	-.30	-.33
1.05	-.08	-.09	-.10	-.10	-.11	-.14	-.17	-.20	-.24	-.28	-.31
1.10	-.02	-.03	-.05	-.06	-.07	-.10	-.13	-.16	-.21	-.25	-.28
1.15	+.07	+.04	+.02	.00	-.01	-.04	-.08	-.12	-.16	-.20	-.24
1.20	.16	.14	.12	+.09	+.07	.00	-.04	-.08	-.12	-.16	-.19
1.25	.19	.18	.16	.14	+.12	+.05	.00	-.03	-.07	-.11	-.13
1.30	.20	.20	.20	.19	.18	.10	+.04	.00	-.04	-.07	-.09
1.4	.20	.21	.21	.21	.20	.15	.11	+.07	+.04	+.01	-.01
1.5	.20	.20	.21	.21	.21	.20	.17	.14	.11	.09	+.07
1.6	.18	.19	.20	.20	.21	.22	.21	.19	.17	.15	.14
1.7	.17	.18	.19	.20	.21	.24	.25	.26	.25	.24	.22
1.8	.17	.18	.19	.20	.21	.26	.29	.31	.32	.32	.30
1.9	.17	.18	.19	.20	.21	.26	.30	.35	.38	.40	.40
2.0	.16	.17	.19	.20	.21	.26	.30	.35	.40	.43	.45
2.5	.15	.16	.18	.19	.20	.25	.30	.35	.40	.45	.50
3.0	.13	.14	.15	.16	.17	.23	.28	.34	.38	.45	.50
3.5	.10	.11	.12	.13	.14	.19	.24	.28	.33	.38	.42
4.0	.09	.10	.10	.11	.12	.16	.20	.23	.27	.31	.35

Table A1-6. Values of $z^{(1)}$ Near the Two Phase Region

T_r	P_r .4	.6	.8	1.0
.90	-.09	-.053	-.068	-.085
.91	-.08	-.053	-.069	-.087
.92	-.072	-.18	-.070	-.089
.93	-.066	-.15	-.071	-.090
.94	-.058	-.12	-.072	-.091
.95	-.050	-.10	-.072	-.091
.96	-.042	-.08	-.072	-.091
.97	-.035	-.065	-.14	-.091
.98	-.027	-.050	-.11	-.090
.99	-.021	-.033	-.08	-.087
1.00	-.016	-.020	-.05	-.080
1.01	-.012	-.012	-.02	-.02
1.02	-.008	-.006	-.00	-.01
1.03	-.005	-.001	+.005	.00
1.04	-.002	+.002	+.010	+.01
1.05	+.001	+.005	+.015	+.02

Table A1-7. Values of $z^{(1)}$ in the Critical Region

T_r	P_r 1.0	1.2	1.4	1.6	1.8	2.0
.98	-.090	-.099	-.109	-.118	-.125	-.130
.99	-.087	-.095	-.104	-.114	-.121	-.127
1.00	-.080	-.090	-.099	-.108	-.115	-.123
.01	-.02	-.080	-.091	-.102	-.10	-.100
.02	-0.01	-.065	-.082	-.095	-.09	-.09
.03	0.00	-.047	-.068	-.085	-.08	-.09
.04	+.01	-.025	-.050	-.073	-.07	-.08
.05	+.02	+.01	-0.01	-.04	-.06	-.07
.06	+.03	+.06	+.07	-.02	-.05	-.073
.07	+.04	+.08	+.09	.000	-.038	-.059
.08	+.047	+.08	+.10	+.030	-.015	-.041
.09	+.050	+.08	+.11	+.056	+.012	-.022
1.10	+.055	+.082	+.11	+.082	+.035	0.000
.11	+.057	+.085	+.12	+.099	+.062	+.020
.13	+.062	+.089	+.12	+.123	+.105	+.060
.15	+.064	+.093	+.122	+.140	+.136	+.100

Fugacity, Enthalpy, and Entropy - The fugacity and other thermodynamic functions may be calculated from the equation of state. For the low pressure region where the second virial coefficient gives an adequate measure of the deviation from the ideal gas state, Eq. (A1-6) may be substituted into the appropriate thermodynamic equations. In these equations H^*, S^*, C_p^* refer to the properties of the hypothetical ideal gas at the same pressure and temperature as the real gas.

$$\log\left(\frac{f}{P}\right) = \left(\frac{P_r}{2.303}\right)\Big[(.1445 + .073\omega)\,T_r^{-1} - (.330 - .46\omega)\,T_r^{-2} - (.1385 + .50\omega)\,T_r^{-3} - (.0121 + .097\omega)\,T_r^{-4} - .0073\omega\,T_r^{-9}\Big] \qquad \text{(A1-7)}$$

$$\frac{H_p - H^*}{RT_c} = P_r\Big[(.1445 + .073\omega) - (.660 - .92\omega)\,T_r^{-1} - (.4155 + 1.50\omega)\,T_r^{-2} - (.0484 + .388\omega)\,T_r^{-3} - .0657\omega\,T_r^{-8}\Big] \qquad \text{(A1-8)}$$

$$\left(\frac{S_p - S_p^*}{R}\right) = P_r\Big[-(.330 - .46\omega)\,T_r^{-2} - (.2770 + 1.00\omega)\,T_r^{-3} - (.0363 + .29\omega)\,T_r^{-4} - .0584\,T_r^{-9}\Big] \qquad \text{(A1-9)}$$

$$\frac{C_p - C_p^*}{R} = P_r\Big[(.660 - .92\omega)\,T_r^{-2} + (.831 + 3.0\omega)\,T_r^{-3} + (.145 + 1.16\omega)T_r^{-4} + .526\omega T_r^{-9}\Big] \qquad \text{(A1-10)}$$

These equations are valuable in calculating gas imperfection corrections for gases at low pressures. Fig. A1-3 compares a few data for gas heat capacity with the curves of Eq. (A1-10). Since the heat capacity involves the second derivative of the

volume, this is a very sensitive test.

At higher pressures the second virial coefficient does not suffice and we must use the general equation of state defined in Eq. (A1-3) and the Tables. The thermodynamic properties are obtained from the usual equations. In terms of the compressibility factor they are

$$\ln\left(\frac{f}{P}\right) = \int_{o}^{P'_r} \frac{(z-1)}{P_r}\, d\,P_r \quad , \tag{A1-11}$$

$$\left(\frac{H^* - H}{RT_c}\right) = T_r^{\,2} \int_{o}^{P'_r} \left(\frac{1}{P_r}\right)\left(\frac{\partial z}{\partial T_r}\right) d\,P_r \, , \tag{A1-12}$$

$$\left(\frac{S^* - S}{R}\right) = \left(\frac{1}{T_r}\right)\left(\frac{H^* - H}{RT_c}\right) + \ln\left(\frac{f}{P}\right) \quad . \tag{A1-13}$$

In Eq. (A1-11 and 12) the resulting fugacity and enthalpy pertain to the reduced pressure P'_r which is the upper limit of integration. The asterisk, as usual, denotes the ideal gas state. The integration and differentiation must be carried out by graphical and numerical methods, but this causes no fundamental difficulty. A more important feature arises when the path of integration crosses the condensation curve. As ω increases the condensation occurs at a lower pressure for the same temperature. As a result there arises a special contribution to $[\ln(f/P)]^{(1)}$ as follows

$$\Delta\ [\ln(f/P)]^{(1)} = \left[\left(\frac{\partial[\ln(f/P)]^{(o)}}{\partial\, P_r}\right)_{gas} - \left(\frac{\partial\,[\ln(f/P)]^{(o)}}{\partial\, P_r}\right)_{liq.}\right]\left(\frac{\partial P_r}{\partial\omega}\right)_{T,sat} . \tag{A1-14}$$

Corresponding contributions arise for the enthalpy and entropy.

Table A1-8. Values of $[\log (f/P)]^{(o)}$

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4
.80	-.060	-.262	-.425	-.535	-.618	-.683	-.736
.85	-.046	-.120	-.281	-.392	-.474	-.539	-.592
.90	-.042$_5$	-.087$_5$	-.163	-.273	-.356	-.421	-.474
.95	-.033	-.070	-.112	-.173	-.255	-.319	-.372
1.00	-.028	-.059	-.094	-.131	-.175	-.237	-.287
1.05	-.024	-.051	-.079	-.109	-.142	-.178	-.218
1.10	-.021	-.044	-.067	-.093	-.120	-.147	-.177
1.15	-.018	-.037	-.058	-.079	-.101	-.123	-.146
1.20	-.016	-.032	-.050	-.067	-.086	-.104	-.124
1.25	-.014	-.029	-.044	-.059	-.075	-.091	-.107
1.3	-.012	-.025	-.038	-.051	-.065	-.078	-.092
1.4	-.010	-.021	-.031	-.041	-.052	-.062	-.072
1.5	-.008	-.016	-.024	-.032	-.040	-.047	-.055
1.6	-.007	-.013	-.019	-.026	-.032	-.038	-.044
1.7	-.005	-.010	-.015	-.020	-.025	-.030	-.034
1.8	-.004	-.008	-.012	-.015	-.019	-.022	-.026
1.9	-.003	-.006	-.009	-.012	-.015	-.018	-.020
2.0	-.002	-.004	-.007	-.009	-.011	-.013	-.015
2.5	.000	.000	.000	.000	-.001	-.001	-.001
3.0	.000	+.001	+.001	+.002	+.002	+.003	+.003
3.5	+.001	.002	.003	.003	.004	.005	.006
4.0	.001	.002	.003	.005	.006	.007	.008

Table A1-8 (continued)

Values of $[\log (f/P)]^{(o)}$

T_r \ P_r	1.6	1.8	2.0	2.2	2.4	2.6	2.8
.80	-.780	-.817	-.849	-.877	-.901	-.922	-.941
.85	-.636	-.673	-.705	-.733	-.757	-.779	-.797
.90	-.517	-.554	-.587	-.614	-.639	-.680	-.679
.95	-.415	-.452	-.483	-.511	-.535	-.557	-.575
1.00	-.330	-.367	-.398	-.425	-.449	-.470	-.489
1.05	-.257	-.292	-.322	-.349	-.372	-.393	-.411
1.10	-.207	-.237	-.264	-.289	-.311	-.331	-.348
1.15	-.170	-.194	-.217	-.238	-.258	-.276	-.293
1.20	-.143	-.163	-.182	-.200	-.217	-.233	-.247
1.25	-.123	-.139	-.155	-.171	-.186	-.199	-.212
1.3	-.106	-.119	-.133	-.146	-.159	-.171	-.182
1.4	-.082	-.092	-.102	-.111	-.120	-.130	-.138
1.5	-.063	-.070	-.078	-.085	-.092	-.099	-.104
1.6	-.050	-.056	-.062	-.067	-.072	-.077	-.082
1.7	-.039	-.043	-.047	-.051	-.056	-.059	-.063
1.8	-.030	-.033	-.036	-.039	-.042	-.045	-.048
1.9	-.023	-.025	-.028	-.030	-.033	-.035	-.037
2.0	-.017	-.019	-.021	-.023	-.025	-.026	-.028
2.5	-.001	-.001	-.001	-.001	-.001	-.001	-.001
3.0	+.004	+.004	+.005	+.005	+.006	+.007	+.007
3.5	.007	.008	.009	.010	.011	.012	.013
4.0	.009	.010	.011	.012	.013	.014	.015

Table A1-8 (continued)

Values of $[\log (f/P)]^{(o)}$

T_r \ P_r	3.0	3.2	3.4	3.6	3.8	4.0	4.5
.80	-.957	-.972	-.985	-.997	-1.007	-1.016	-1.035
.85	-.814	-.829	-.842	-.854	-.864	-.874	-.893
.90	-.696	-.710	-.724	-.736	-.746	-.756	-.775
.95	-.592	-.607	-.621	-.632	-.643	-.652	-.672
1.00	-.505	-.520	-.534	-.545	-.556	-.566	-.586
1.05	-.428	-.442	-.455	-.467	-.478	-.488	-.508
1.10	-.364	-.378	-.391	-.403	-.413	-.422	-.442
1.15	-.307	-.321	-.333	-.344	-.354	-.363	-.383
1.20	-.261	-.273	-.285	-.295	-.305	-.314	-.332
1.25	-.224	-.236	-.246	-.256	-.264	-.273	-.290
1.3	-.193	-.203	-.212	-.221	-.229	-.237	-.253
1.4	-.146	-.154	-.162	-.169	-.175	-.181	-.194
1.5	-.112	-.117	-.124	-.129	-.134	-.139	-.149
1.6	-.087	-.092	-.096	-.100	-.104	-.108	-.116
1.7	-.067	-.071	-.074	-.077	-.080	-.083	-.089
1.8	-.051	-.053	-.056	-.058	-.060	-.063	-.067
1.9	-.039	-.041	-.043	-.045	-.046	-.048	-.051
2.0	-.029	-.031	-.032	-.033	-.034	-.035	-.037
2.5	-.001	-.001	-.001	.000	.000	.000	+.001
3.0	+.008	+.009	+.010	+.011	+.012	+.012	.015
3.5	.014	.015	.016	.017	.018	.020	.022
4.0	.016	.017	.019	.020	.021	.022	.025

Table A1-8 (continued)

Values of $[\log (f/P)]^{(o)}$

T_r \ P_r	5.0	6.0	7.0	8.0	9.0
.80	-1.048	-1.064	-1.067	-1.063	-1.052
.85	-.907	-.924	-.929	-.926	-.917
.90	-.789	-.807	-.814	-.813	-.805
.95	-.687	-.706	-.713	-.713	-.707
1.00	-.601	-.620	-.629	-.630	-.624
1.05	-.523	-.543	-.552	-.553	-.549
1.10	-.457	-.477	-.487	-.489	-.486
1.15	-.397	-.417	-.427	-.429	-.426
1.20	-.346	-.366	-.375	-.378	-.376
1.25	-.304	-.322	-.331	-.334	-.332
1.3	-.266	-.283	-.292	-.295	-.294
1.4	-.205	-.220	-.228	-.231	-.229
1.5	-.158	-.170	-.176	-.178	-.176
1.6	-.123	-.132	-.137	-.138	-.136
1.7	-.094	-.101	-.105	-.105	-.102
1.8	-.071	-.076	-.078	-.077	-.074
1.9	-.054	-.057	-.057	-.055	-.051
2.0	-.039	-.040	-.039	-.038	-.034
2.5	+.003	+.006	+.011	+.016	+.022
3.0	.017	.023	.028	.035	.042
3.5	.025	.031	.038	.044	.051
4.0	.028	.034	.040	.047	.054

Table A1-9. Values of [log (f/P)][1]

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
.80	-.04	-.47	-.48	-.48	-.48	-.49	-.50	-.50	-.51	-.51	-.52
.85	-.03	-.31	-.31	-.32	-.33	-.33	-.34	-.35	-.35	-.36	-.37
.90	-.02	-.04	-.18	-.20	-.20	-.21	-.21	-.22	-.23	-.23	-.24
.95	-.01	-.02	-.03	-.09	-.10	-.11	-.12	-.12	-.13	-.13	-.14
1.00	-.01	-.01	-.01	-.02	-.03	-.03	-.04	-.05	-.05	-.06	-.06
1.05	.00	.00	.00	.00	+.01	+.01	+.01	+.01	.00	.00	.00
1.10	.00	.00	.00	.01	.01	.02	.02	.03	.03	.03	.03
1.15	.00	.00	.00	.01	.02	.02	.03	.04	.04	.05	.05
1.20	.00	.01	.01	.01	.02	.03	.04	.05	.05	.06	.07
1.25	.00	.01	.01	.02	.03	.03	.04	.05	.06	.07	.07
1.3	.01	.01	.02	.02	.03	.04	.04	.05	.06	.07	.08
1.4	.01	.01	.02	.03	.04	.04	.05	.06	.07	.08	.08
1.5	.01	.02	.02	.03	.04	.05	.05	.06	.06	.07	.08
1.6	.01	.02	.02	.03	.04	.05	.05	.06	.06	.07	.08
1.7	.01	.02	.02	.03	.04	.05	.05	.06	.06	.07	.08
1.8	.01	.02	.02	.03	.04	.05	.05	.06	.06	.07	.08
1.9	.01	.02	.02	.03	.04	.05	.05	.06	.06	.07	.08
2.0	.01	.01	.02	.03	.04	.05	.05	.06	.07	.07	.08
2.5	.01	.01	.02	.02	.03	.04	.04	.05	.06	.06	.07
3.0	.00	.01	.01	.02	.02	.03	.04	.04	.05	.05	.05
3.5	.00	.01	.01	.02	.02	.02	.03	.03	.04	.04	.04
4.0	.00	.01	.01	.02	.02	.02	.02	.03	.03	.03	.04

Table A1-9 (continued)

Values of [log (f/P)] (1)

T_r \ P_r	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
.80	-.52	-.53	-.53	-.54	-.56	-.59	-.61	-.63	-.65	-.67
.85	-.37	-.38	-.38	-.39	-.41	-.44	-.46	-.48	-.50	-.51
.90	-.24	-.25	-.26	-.26	-.29	-.31	-.33	-.35	-.36	-.38
.95	-.15	-.15	-.16	-.16	-.18	-.20	-.22	-.24	-.26	-.27
1.00	-.07	-.07	-.08	-.08	-.10	-.12	-.13	-.15	-.17	-.18
1.05	.00	-.01	-.01	-.01	-.03	-.05	-.06	-.07	-.09	-.11
1.10	.03	+.03	+.03	+.03	+.02	.00	-.01	-.02	-.03	-.05
1.15	.05	.06	.06	.06	.05	.05	+.04	+.02	+.01	.00
1.20	.07	.08	.08	.08	.09	.09	.08	.07	.07	.06
1.25	.08	.09	.09	.10	.11	.11	.11	.10	.10	.09
1.3	.08	.09	.10	.10	.12	.13	.13	.13	.12	.12
1.4	.09	.10	.11	.11	.13	.15	.15	.16	.16	.16
1.5	.08	.09	.10	.11	.13	.15	.16	.17	.17	.18
1.6	.08	.09	.10	.11	.14	.16	.18	.19	.20	.21
1.7	.08	.09	.10	.11	.14	.16	.18	.20	.21	.23
1.8	.08	.09	.10	.11	.14	.16	.19	.21	.23	.24
1.9	.08	.09	.10	.11	.14	.16	.19	.21	.23	.25
2.0	.08	.09	.09	.10	.13	.16	.19	.21	.23	.26
2.5	.07	.08	.08	.09	.12	.14	.17	.19	.22	.24
3.0	.06	.06	.07	.07	.10	.12	.15	.17	.20	.22
3.5	.05	.05	.06	.06	.08	.10	.13	.15	.17	.19
4.0	.04	.04	.05	.05	.07	.09	.10	.12	.14	.15

Table A1-10. Values of $\left[\frac{H^* - H}{RT_c}\right]^{(o)}$

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8
.80	.37	4.52	4.52	4.52	4.52	4.52	4.52	4.52	4.52
.85	.32	4.35	4.35	4.35	4.34	4.34	4.33	4.32	4.32
.90	.27	.60	4.06	4.10	4.14	4.14	4.15	4.15	4.14
.95	.23	.52	.86	3.69	3.80	3.85	3.87	3.88	3.89
1.00	.21	.45	.76	1.15	2.3_5	3.09	3.32	3.44	3.52
1.05	.19	.40	.64	.95	1.35	1.94	2.54	2.86	3.07
1.10	.17	.36	.57	.82	1.10	1.44	1.83	2.25	2.55
1.15	.14	.30	.49	.70	.93	1.19	1.48	1.78	2.07
1.20	.13	.27	.44	.63	.83	1.03	1.25	1.49	1.73
1.25	.12	.25	.39	.56	.73	.91	1.09	1.29	1.50
1.3	.11	.23	.36	.50	.66	.81	.97	1.14	1.32
1.4	.09	.19	.31	.42	.54	.67	.80	.94	1.08
1.5	.09	.18	.29	.39	.49	.59	.70	.80	.93
1.6	.09	.18	.27	.36	.45	.54	.62	.71	.81
1.7	.08	.16	.25	.33	.41	.48	.56	.64	.71
1.8	.07	.15	.23	.30	.37	.44	.51	.58	.64
1.9	.06	.13	.19	.26	.33	.40	.46	.51	.57
2.0	.06	.12	.18	.24	.30	.36	.42	.46	.51
2.5	.04	.08	.12	.16	.19	.22	.25	.28	.31
3.0	.03	.05	.07	.09	.11	.14	.16	.18	.20
3.5	.02	.04	.05	.06	.07	.09	.10	.11	.12
4.0	.01	.02	.03	.04	.04	.05	.06	.07	.08

Table A1-10 (continued)

Values of $\left[\frac{H^* - H}{RT_c}\right]^{(o)}$

T_r \ P_r	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
.80	4.52	4.52	4.52	4.52	4.52	4.52	4.51	4.51	4.50
.85	4.32	4.32	4.32	4.32	4.32	4.32	4.32	4.31	4.31
.90	4.13	4.13	4.12	4.12	4.12	4.11	4.10	4.10	4.10
.95	3.90	3.90	3.90	3.90	3.90	3.90	3.90	3.90	3.89
1.00	3.57	3.60	3.63	3.65	3.68	3.70	3.71	3.71	3.70
1.05	3.21	3.30	3.36	3.39	3.42	3.44	3.46	3.47	3.49
1.10	2.75	2.89	3.00	3.08	3.15	3.20	3.24	3.27	3.29
1.15	2.33	2.52	2.67	2.78	2.86	2.93	2.98	3.02	3.05
1.20	1.95	2.13	2.30	2.44	2.56	2.66	2.73	2.78	2.82
1.25	1.70	1.87	2.03	2.17	2.29	2.39	2.48	2.55	2.61
1.3	1.49	1.64	1.79	1.93	2.05	2.16	2.24	2.32	2.39
1.4	1.23	1.36	1.47	1.59	1.70	1.79	1.88	1.96	2.04
1.5	1.04	1.15	1.26	1.36	1.45	1.53	1.61	1.68	1.75
1.6	.91	1.00	1.09	1.18	1.26	1.33	1.39	1.44	1.51
1.7	.80	.87	.95	1.02	1.08	1.15	1.21	1.27	1.33
1.8	.71	.78	.84	.90	.95	1.01	1.06	1.12	1.18
1.9	.63	.68	.73	.78	.82	.87	.92	.97	1.02
2.0	.55	.59	.64	.69	.74	.78	.82	.85	.89
2.5	.34	.37	.40	.43	.45	.47	.50	.52	.54
3.0	.22	.24	.26	.28	.30	.31	.33	.34	.36
3.5	.13	.15	.16	.17	.18	.19	.20	.21	.22
4.0	.08	.09	.10	.10	.11	.11	.11	.12	.12

Table A1-10 (continued)

Values of $\left[\frac{H^* - H}{RT_c}\right]^{(o)}$

T_r \ P_r	3.8	4.0	4.5	5.0	6.0	7.0	8.0	9.0
.80	4.50	4.49	4.46	4.43	4.38	4.34	4.29	4.24
.85	4.31	4.30	4.28	4.24	4.20	4.16	4.10	4.04
.90	4.10	4.10	4.09	4.05	4.02	3.99	3.92	3.85
.95	3.89	3.89	3.85	3.85	3.84	3.81	3.76	3.71
1.00	3.70	3.70	3.69	3.68	3.67	3.64	3.60	3.57
1.05	3.50	3.51	3.51	3.50	3.49	3.48	3.46	3.45
1.10	3.30	3.32	3.34	3.34	3.34	3.33	3.32	3.32
1.15	3.09	3.12	3.17	3.18	3.18	3.19	3.19	3.20
1.20	2.87	2.91	2.99	3.02	3.05	3.07	3.07	3.08
1.25	2.67	2.72	2.82	2.87	2.92	2.93	2.95	2.98
1.3	2.45	2.52	2.63	2.72	2.79	2.81	2.84	2.88
1.4	2.11	2.18	2.32	2.43	2.53	2.58	2.62	2.65
1.5	1.82	1.88	2.01	2.12	2.25	2.33	2.39	2.41
1.6	1.57	1.64	1.78	1.87	2.01	2.12	2.19	2.21
1.7	1.39	1.45	1.57	1.66	1.79	1.91	2.00	2.03
1.8	1.24	1.31	1.42	1.50	1.62	1.74	1.83	1.86
1.9	1.08	1.13	1.23	1.32	1.44	1.54	1.63	1.67
2.0	.93	.97	1.07	1.14	1.25	1.33	1.43	1.46
2.5	.56	.58	.63	.67	.75	.81	.87	.91
3.0	.37	.38	.41	.44	.50	.53	.56	.58
3.5	.23	.23	.25	.26	.28	.30	.30	.29
4.0	.12	.13	.13	.14	.14	.14	.13	.12

Table A1-11. Values of $\left[\frac{H^* - H}{RT_c}\right]^{(o)}$ in the Critical Region

T_r \ P_r	.8	.9	1.0	1.1	1.2	1.3	1.4
.98	1.25	3.2	3.3_5	3.43	3.50	3.55	3.59
.99	1.19	1.6	3.1	3.20	3.31	3.39	3.46
1.00	1.15	1.5	2.3_5	2.9	3.09	3.23	3.32
1.01	1.11	1.38	1.8	2.5	2.86	3.05	3.18
1.02	1.07	1.31	1.6	2.1	2.59	2.85	3.02
1.03	1.03	1.24	1.52	1.88	2.33	2.63	2.87
1.04	.99	1.18	1.43	1.74	2.12	2.47	2.71
1.05	.95	1.13	1.35	1.62	1.94	2.27	2.54
1.06	.92	1.08	1.29	1.53	1.80	2.09	2.37
1.07	.89	1.04	1.23	1.45	1.69	1.96	2.22
1.08	.87	1.02	1.18	1.37	1.59	1.83	2.07
1.09	.84	.99	1.14	1.33	1.51	1.72	1.94
1.10	.82	.96	1.10	1.26	1.44	1.64	1.83
1.11	.80	.93	1.06	1.21	1.38	1.55	1.74
1.13	.74	.87	1.00	1.14	1.28	1.44	1.59
1.15	.70	.82	.93	1.06	1.19	1.33	1.48

Table A1-11. (continued)

Values of $\left[\frac{H^* - H}{RT_c}\right]^{(o)}$

T_r \ P_r	1.5	1.6	1.7	1.8	1.9	2.0
.98	3.63	3.65	3.67	3.68	3.70	3.71
.99	3.51	3.55	3.58	3.61	3.63	3.64
1.00	3.39	3.44	3.48	3.52	3.54	3.57
1.01	3.27	3.34	3.39	3.44	3.47	3.50
1.02	3.14	3.23	3.30	3.36	3.40	3.44
1.03	3.02	3.12	3.21	3.27	3.32	3.36
1.04	2.87	2.99	3.09	3.17	3.23	3.28
1.05	2.73	2.86	2.98	3.07	3.14	3.21
1.06	2.58	2.74	2.88	2.98	3.06	3.13
1.07	2.43	2.61	2.76	2.88	2.97	3.04
1.08	2.29	2.49	2.64	2.77	2.86	2.95
1.09	2.16	2.37	2.54	2.66	2.77	2.86
1.10	2.05	2.25	2.42	2.55	2.66	2.75
1.11	1.94	2.15	2.31	2.45	2.57	2.66
1.13	1.77	1.95	2.11	2.25	2.38	2.50
1.15	1.62	1.78	1.92	2.07	2.20	2.33

Table A1-12. Values of $\left[\frac{H^* - H}{RT_c}\right]^{(1)}$

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
.80	.44	5.05	5.04	5.02	4.98	4.97	4.94	4.93	4.90	4.88	4.87
.85	.37	4.74	4.71	4.70	4.67	4.65	4.63	4.63	4.63	4.60	4.57
.90	.31	.71	4.33	4.32	4.31	4.31	4.30	4.30	4.30	4.30	4.29
.95	.25	.55	1.01	3.83	3.80	3.81	3.84	3.84	3.87	3.87	3.88
1.00	.20	.41	.68	.95	2.66	3.17	3.27	3.33	3.38	3.41	3.45
1.05	.14	.27	.40	.54	.68	1.22	1.77	2.19	2.45	2.59	2.71
1.10	.12	.22	.29	.36	.42	.52	.69	.92	1.32	1.71	1.97
1.15	.09	.17	.23	.28	.32	.36	.39	.45	.58	.81	1.08
1.20	.08	.14	.20	.24	.28	.29	.29	.32	.37	.47	.59
1.25	.06	.13	.18	.21	.25	.25	.26	.28	.28	.30	.36
1.3	.03	.06	.10	.13	.17	.19	.24	.23	.24	.25	.27
1.4	.02	.04	.06	.08	.10	.11	.11	.12	.12	.12	.14
1.5	.01	.01	.02	.03	.04	.04	.04	.04	.04	.04	.05
1.6	0	0	0	0	0	0	0	0	-.01	-.01	-.01
1.7	-.01	-.01	-.02	-.03	-.04	-.04	-.05	-.05	-.06	-.06	-.07
1.8	-.01	-.02	-.03	-.04	-.06	-.07	-.08	-.09	-.10	-.10	-.11
1.9	-.02	-.03	-.05	-.07	-.09	-.11	-.13	-.15	-.17	-.19	-.20
2.0	-.02	-.04	-.06	-.08	-.10	-.13	-.16	-.19	-.22	-.25	-.25
2.5	-.03	-.06	-.10	-.13	-.17	-.20	-.23	-.26	-.29	-.32	-.35
3.0	-.04	-.08	-.13	-.17	-.21	-.25	-.29	-.33	-.37	-.41	-.45
3.5	-.04	-.08	-.13	-.17	-.21	-.25	-.29	-.34	-.37	-.42	-.47
4.0	-.04	-.08	-.13	-.17	-.21	-.25	-.29	-.34	-.37	-.42	-.46

Table A1-12 (continued)

Values of $\left[\frac{H^* - H}{RT_c}\right]^{(1)}$

T_r \ P_r	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
.80	4.86	4.84	4.83	4.82	4.83	4.85	4.86	4.88	4.90	4.91
.85	4.57	4.56	4.56	4.56	4.57	4.61	4.63	4.65	4.68	4.71
.90	4.28	4.29	4.30	4.30	4.36	4.39	4.43	4.43	4.50	4.53
.95	3.90	3.90	3.93	3.93	4.04	4.12	4.19	4.23	4.28	4.32
1.00	3.49	3.53	3.58	3.61	3.76	3.88	3.97	4.02	4.07	4.10
1.05	2.79	2.88	2.94	2.99	3.26	3.48	3.57	3.66	3.75	3.81
1.10	2.11	2.24	2.30	2.39	2.74	3.01	3.17	3.30	3.42	3.53
1.15	1.32	1.52	1.67	1.78	2.24	2.52	2.73	2.93	3.09	3.23
1.20	.74	.91	1.08	1.21	1.70	1.98	2.21	2.41	2.59	2.79
1.25	.43	.51	.63	.76	1.26	1.56	1.79	1.98	2.15	2.41
1.3	.32	.39	.46	.53	.85	1.11	1.43	1.60	1.83	2.10
1.4	.16	.19	.22	.25	.45	.73	.98	1.15	1.40	1.66
1.5	.06	.07	.08	.09	.20	.47	.68	.86	1.10	1.36
1.6	-.01	-.02	-.02	-.02	.05	.28	.45	.64	.88	1.10
1.7	-.08	-.09	-.10	-.10	-.07	.11	.25	.43	.63	.85
1.8	-.12	-.13	-.14	-.16	-.16	-.03	.08	.23	.42	.61
1.9	-.20	-.21	-.21	-.21	-.21	-.15	-.07	.06	.22	.39
2.0	-.25	-.26	-.26	-.26	-.28	-.26	-.19	-.10	.03	.18
2.5	-.39	-.43	-.45	-.48	-.53	-.55	-.57	-.59	-.63	-.61
3.0	-.49	-.53	-.57	-.60	-.74	-.85	-.95	-1.05	-1.14	-1.21
3.5	-.51	-.55	-.59	-.63	-.83	-1.02	-1.19	-1.37	-1.50	-1.67
4.0	-.50	-.54	-.58	-.62	-.84	-1.03	-1.25	-1.47	-1.66	-1.86

Table A1-13. Values of $\left[\frac{H^* - H}{RT_c} \right]^{(1)}$ in the Critical Region

T_r \ P_r	.8	1.0	1.2	1.4	1.6	1.8	2.0
.98	1.15	3.28	3.39	3.48	3.55	3.57	3.59
.99	1.0	3.05	3.28	3.39	3.44	3.47	3.51
1.00	.95	2.66	3.17	3.27	3.33	3.38	3.41
1.01	.84	1.47	2.97	3.11	3.18	3.24	3.29
1.02	.75	1.19	2.61	2.92	3.00	3.08	3.14
1.03	.68	.99	2.10	2.67	2.82	2.91	3.00
1.04	.60	.82	1.60	2.30	2.55	2.66	2.80
1.05	.54	.68	1.22	1.77	2.19	2.45	2.59
1.06	.49	.61	.96	1.40	1.89	2.18	2.42
1.07	.44	.57	.80	1.12	1.58	1.95	2.25
1.08	.42	.51	.69	.95	1.35	1.71	2.07
1.09	.38	.46	.59	.83	1.10	1.52	1.91
1.10	.36	.42	.52	.69	.92	1.32	1.71
1.11	.33	.40	.47	.61	.80	1.08	1.47
1.13	.29	.34	.40	.47	.59	.78	1.04
1.15	.28	.32	.36	.39	.45	.58	.81

Table A1-14. Values of $\left[\frac{S^* - S}{R}\right]^{(o)}$

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8
.80	.33	5.04	4.66	4.41	4.23	4.08	3.94	3.85	3.76
.85	.27	4.85	4.47	4.21	4.01	3.86	3.73	3.62	3.53
.90	.20	.47	4.13	3.92	3.78	3.63	3.52	3.42	3.32
.95	.17	.39	.64	3.48	3.41	3.32	3.22	3.13	3.05
1.00	.14	.31	.54	.85	1.95	2.55	2.66	2.68	2.68
1.05	.12	.27	.43	.66	.96	1.44	1.91	2.13	2.25
1.10	.11	.23	.36	.53	.73	.97	1.25	1.57	1.77
1.15	.08	.17	.30	.43	.57	.75	.95	1.16	1.36
1.20	.07	.15	.25	.37	.49	.62	.76	.91	1.07
1.25	.07	.14	.21	.31	.41	.52	.62	.75	.88
1.30	.06	.12	.19	.27	.36	.44	.53	.63	.74
1.4	.04	.09	.15	.21	.26	.34	.41	.49	.56
1.5	.04	.09	.14	.19	.23	.28	.34	.39	.45
1.6	.04	.08	.12	.17	.21	.25	.29	.33	.38
1.7	.03	.07	.11	.15	.18	.21	.25	.29	.32
1.8	.03	.06	.09	.13	.16	.19	.22	.26	.28
1.9	.03	.05	.08	.11	.14	.17	.19	.22	.24
2.0	.03	.05	.08	.10	.13	.15	.18	.19	.21
2.5	.02	.03	.05	.06	.07	.09	.10	.12	.13
3.0	.01	.02	.03	.04	.04	.05	.06	.07	.08
3.5	.01	.02	.02	.03	.03	.04	.04	.05	.05
4.0	.005	.01	.01	.02	.02	.03	.03	.04	.04

Table A1-14 (continued)

Values of $\left[\frac{S^* - S}{R}\right]^{(o)}$

P_r / T_r	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6
.80	3.69	3.63	3.56	3.53	3.48	3.44	3.39	3.36	3.33
.85	3.46	3.39	3.34	3.29	3.25	3.21	3.18	3.13	3.11
.90	3.23	3.18	3.11	3.06	3.01	2.97	2.92	2.89	2.86
.95	2.99	2.93	2.87	2.82	2.78	2.74	2.70	2.67	2.64
1.00	2.65	2.62	2.60	2.57	2.55	2.54	2.51	2.48	2.44
1.05	2.31	2.34	2.34	2.32	2.31	2.30	2.28	2.26	2.25
1.10	1.89	1.96	2.01	2.04	2.06	2.07	2.07	2.07	2.06
1.15	1.53	1.64	1.73	1.18	1.82	1.84	1.85	1.86	1.86
1.20	1.21	1.32	1.42	1.50	1.57	1.62	1.64	1.66	1.67
1.25	1.00	1.10	1.20	1.28	1.34	1.39	1.44	1.47	1.50
1.30	.84	.92	1.01	1.09	1.15	1.22	1.25	1.29	1.33
1.4	.64	.71	.77	.84	.89	.94	.99	1.03	1.07
1.5	.51	.57	.63	.68	.72	.76	.81	.83	.87
1.6	.43	.47	.51	.56	.60	.63	.66	.68	.71
1.7	.36	.39	.43	.46	.49	.52	.55	.58	.61
1.8	.31	.34	.37	.39	.42	.44	.47	.49	.52
1.9	.27	.28	.31	.33	.35	.37	.39	.41	.43
2.0	.23	.24	.27	.29	.31	.33	.34	.35	.37
2.5	.14	.15	.16	.17	.18	.19	.20	.21	.22
3.0	.08	.09	.10	.11	.12	.12	.13	.14	.15
3.5	.06	.07	.08	.08	.09	.09	.10	.10	.11
4.0	.05	.05	.05	.06	.06	.06	.07	.07	.07

Table A1-14 (continued)

Values of $\left[\frac{S^* - S}{R}\right]^{(o)}$

T_r \ P_r	3.8	4.0	4.5	5.0	6.0	7.0	8.0	9.0
.80	3.30	3.26	3.19	3.12	3.01	2.96	2.91	—
.85	3.08	3.05	2.98	2.90	2.82	2.76	2.70	
.90	2.83	2.81	2.76	2.68	2.61	2.56	2.48	2.42
.95	2.61	2.58	2.57	2.48	2.43	2.37	2.31	2.29
1.00	2.42	2.40	2.34	2.30	2.24	2.19	2.14	2.13
1.05	2.23	2.22	2.17	2.13	2.08	2.05	2.02	2.02
1.10	2.05	2.05	2.02	1.98	1.94	1.91	1.89	1.90
1.15	1.87	1.88	1.88	1.85	1.81	1.79	1.78	1.80
1.20	1.69	1.70	1.72	1.72	1.70	1.69	1.68	1.70
1.25	1.53	1.55	1.59	1.60	1.59	1.58	1.59	1.62
1.30	1.35	1.39	1.44	1.48	1.49	1.48	1.51	1.54
1.4	1.11	1.14	1.21	1.26	1.30	1.32	1.34	1.37
1.5	.91	.93	.99	1.05	1.11	1.15	1.18	1.20
1.6	.74	.78	.84	.89	.95	1.01	1.05	1.07
1.7	.64	.66	.72	.76	.82	.88	.94	.96
1.8	.55	.58	.63	.67	.73	.79	.84	.86
1.9	.46	.48	.53	.57	.63	.68	.73	.76
2.0	.39	.41	.45	.48	.54	.58	.63	.65
2.5	.23	.23	.25	.27	.31	.35	.37	.41
3.0	.16	.16	.18	.19	.22	.24	.27	.29
3.5	.11	.11	.12	.13	.15	.17	.19	.20
4.0	.08	.08	.09	.10	.11	.13	.14	.15

Table A1-15. Values of $\left[\frac{S^* - S}{R}\right]^{(1)}$

T_r \ P_r	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
.80	.46	5.23	5.20	5.16	5.12	5.08	5.03	5.00	4.96	4.92	4.89
.85	.37	4.86	4.82	4.79	4.74	4.70	4.66	4.63	4.61	4.58	4.54
.90	.30	.70	4.38	4.36	4.33	4.31	4.29	4.27	4.26	4.24	4.22
.95	.24	.53	.98	3.81	3.77	3.76	3.76	3.76	3.76	3.76	3.76
1.00	.19	.39	.65	.90	2.60	3.09	3.18	3.23	3.26	3.28	3.31
1.05	.13	.26	.38	.51	.67	1.18	1.71	2.11	2.34	2.47	2.58
1.10	.11	.20	.27	.35	.41	.51	.68	.91	1.27	1.63	1.86
1.15	.09	.16	.22	.28	.32	.36	.41	.48	.60	.81	1.06
1.20	.08	.14	.20	.24	.28	.31	.33	.38	.44	.53	.65
1.25	.06	.12	.17	.22	.26	.28	.30	.33	.35	.39	.46
1.3	.04	.07	.10	.13	.16	.18	.20	.22	.24	.26	.31
1.4	.03	.05	.07	.09	.11	.13	.14	.15	.16	.17	.20
1.5	.02	.03	.05	.06	.07	.07	.08	.09	.09	.10	.11
1.6	.01	.0	.03	.04	.04	.04	.05	.05	.06	.06	.07
1.7	.00	.01	.01	.02	.02	.02	.02	.03	.03	.03	.04
1.8	0.0	0.0	.01	.01	.01	.01	.01	.01	.01	.01	.01
1.9	0.0	0.0	-.01	-.01	-.01	-.01	-.02	-.02	-.03	-.03	-.02
2.0	0.0	0.0	-.01	-.01	-.01	-.02	-.03	-.04	-.05	-.06	-.05
2.5	-.01	-.02	-.02	-.03	-.04	-.04	-.05	-.06	-.06	-.07	-.08
3.0	-.01	-.02	-.03	-.04	-.05	-.06	-.07	-.08	-.09	-.09	-.10
3.5	-.01	-.02	-.02	-.03	-.04	-.05	-.06	-.07	-.08	-.08	-.09
4.0	-.01	-.01	-.02	-.02	-.03	-.04	-.05	-.06	-.07	-.08	-.08

Table A1-15 (continued)

Values of $\left[\frac{S^* - S}{R}\right]^{(1)}$

T_r \ P_r	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
.80	4.86	4.83	4.81	4.79	4.74	4.71	4.68	4.65	4.62	4.60
.85	4.52	4.50	4.48	4.46	4.43	4.41	4.39	4.37	4.36	4.35
.90	4.20	4.19	4.19	4.18	4.18	4.17	4.17	4.16	4.16	4.15
.95	3.76	3.76	3.77	3.77	3.83	3.87	3.90	3.90	3.91	3.92
1.00	3.34	3.37	3.41	3.42	3.53	3.61	3.66	3.67	3.68	3.68
1.05	2.65	2.72	2.77	2.82	3.03	3.20	3.26	3.32	3.36	3.39
1.10	1.99	2.11	2.16	2.23	2.53	2.75	2.86	2.96	3.04	3.10
1.15	1.28	1.45	1.58	1.68	2.07	2.30	2.46	2.60	2.71	2.81
1.20	.79	.94	1.09	1.21	1.62	1.85	2.03	2.18	2.31	2.38
1.25	.53	.61	.71	.83	1.25	1.50	1.68	1.82	1.95	2.02
1.3	.36	.41	.46	.51	.77	.98	1.23	1.36	1.53	1.74
1.4	.22	.24	.26	.29	.45	.67	.85	.98	1.16	1.34
1.5	.12	.13	.15	.17	.26	.46	.61	.74	.90	1.09
1.6	.08	.08	.09	.10	.17	.33	.46	.59	.74	.90
1.7	.04	.04	.05	.05	.10	.22	.33	.45	.59	.73
1.8	.01	.01	.02	.02	.05	.14	.23	.34	.46	.58
1.9	-.02	-.01	-.01	0	.03	.08	.15	.24	.35	.46
2.0	-.05	-.04	-.04	-.03	-.01	.03	.09	.16	.25	.35
2.5	-.09	-.09	-.10	-.10	-.09	-.08	-.06	-.05	-.03	0
3.0	-.11	-.11	-.12	-.13	-.15	-.16	-.17	-.18	-.18	-.18
3.5	-.09	-.10	-.11	-.12	-.16	-.19	-.21	-.24	-.26	-.29
4.0	-.09	-.10	-.10	-.11	-.14	-.17	-.21	-.25	-.28	-.32

The resulting functions are given in Tables A1-8 to 15. Because of the lower vapor pressure for liquids of high acentric factor at a given temperature, it is sometimes necessary to extrapolate the functions on the liquid side. This extrapolation should be taken with respect to pressure at constant temperature. The complete equations have the form of Eq. (A1-3).

$$\log (f/P) = [\log (f/P)]^{(o)} + \omega [\log (f/P)]^{(1)} \qquad \text{(A1-15)}$$

$$\left[\frac{H^* - H}{RT_c} \right] = \left[\frac{H^* - H}{RT_c} \right]^{(o)} + \omega \left[\frac{H^* - H}{RT_c} \right]^{(1)} \qquad \text{(A1-16)}$$

$$\left[\frac{S^* - S}{R} \right] = \left[\frac{S^* - S}{R} \right] + \omega \left[\frac{S^* - S}{R} \right]^{(1)} \qquad \text{(A1-17)}$$

Fig. A1-4 shows a comparison of the calculated enthalpy difference from the ideal gas with experimental values from Joule-Thomson expansion and other methods.

Tables A1-11 and 13 give more closely spaced values for the enthalpy functions in the critical region. Simple graphs are still desirable for accurate interpolation here. The fugacity functions are interpolated easily in the critical region. The entropy is, of course, related to the fugacity and enthalpy. General entropy tables are given for convenience, but in the critical region the entropy should be calculated from the detailed enthalpy tables and the fugacity.

Internal energy and work content values can be obtained by appropriate combination of the functions tabulated. Also temperature derivatives of the enthalpy will yield rough heat capacity values.

Liquid Density- This completes the results for the gas phase and the compressed liquid. The properties of the liquid at low pressure are especially accessible to measurement and have particular interest. Strictly, we consider the liquid under its own vapor pressure, but usually the properties under atmospheric pressure are not significantly different. These results are based upon the correlations of Riedel.[1] For the ratio of the density of the liquid to that of the critical point, the equation is

$$\frac{d}{d_c} = 1 + 0.85 (1 - T_r) + (1 - T_r)^{1/3} (1.89 + .91\omega) . \qquad \text{(A1-18)}$$

If we substitute $T_r = 0$ we find a hypothetical density d_o for the liquid at 0^oK. It turns out that the ratio of the actual density to d_o is effectively independent of the acentric factor at temperatures lower than $T_r = 0.8$. The resulting values are listed in Table A1-16. This table together with Eq. (A1-18) summarizes the correlation of liquid density. They allow prediction of the density variation over the full range of temperature from a single measured value. Thus the coefficient of expansion is determined and may be obtained by differentiating Eq. (A1-18).

Table A1-16. Values of (d/d_o)

T_r	0	.01	.02	.03	.04	.05	.06	.07	.08	.09	.10
.3	.875	.870	.866	.862	.858	.853	.849	.844	.840	.835	.830
.4	.830	.826	.821	.816	.812	.807	.802	.797	.792	.787	.782
.5	.782	.777	.772	.767	.762	.757	.752	.747	.742	.737	.731
.6	.731	.726	.720	.715	.709	.703	.698	.692	.686	.680	.674
.7	.674	.668	.662	.656	.649	.642	.636	.629	.622	.613	.608

Surface Tension, A Criterion of a Normal Fluid - Another important property of the liquid is the surface tension. It is well represented by the equation

$$\sigma/\sigma_o = (1 - T_r)^{11/9} \qquad \text{(A1-19)}$$

where σ_o is a hypothetical surface tension at 0^oK. The constant σ_o may be predicted from the equation

$$\sigma_o V_\sigma^{2/3}/T_c = 1.86 + 1.18\omega, \ (\text{dynes/cm})(\text{cc/mole})^{2/3}(^oK)^{-1} \ . \qquad \text{(A1-20)}$$

The quantity V_o is the hypothetical molal volume at 0^oK as calculated from d_o. Given a density at a known reduced temperature one may obtained (d/d_o) from Table A1-16; then from the definitions one has

$$V_o = (M/d)(d/d_o) \ . \qquad \text{(A1-21)}$$

A test of Eq. (A1-20) is shown in Fig. A1-5. We note that typical normal liquids agree with the predicted line quite well whereas the values of

$(\sigma_o V_o^{2/3}/T_c)$ for hydrogen bonding liquids are as low as 50% of that predicted. Thus the surface tension represents a sensitive test for a normal liquid. A deviation of over 5% from Eq. (A1-20) appears to indicate significant abnormality. This relationship for σ_o is recommended as the operational test of a normal liquid.

Estimating Critical Constants - We have already noted that the vapor pressure need not be known at exactly the temperature of definition in order to obtain the acentric factor since the entire vapor pressure function is given in Table A1-1. Similarly, other observations may be substituted for the critical temperature and pressure which we have assumed to be known. Riedel[1] has proposed several systems for predicting T_c and P_c of which the following seems most useful. The underlying equations are just those presented above; they are now recast for convenience in another form.

To estimate T_c, P_c, and ω for a fluid three pieces of information are required. These are its liquid density at some temperature near or below the boiling point, the normal boiling point, T_{760} and the temperature, T_{100} at which the vapor pressure is 100 mm. T_{100} may be calculated from a vapor pressure equation for the substance.

The density is used to calculate a characteristic molal volume for the substance. We use the V_o defined in Eq. (A1-21).

The calculation of a set of critical constants is a rapidly converging sequence of approximations. One starts with the assumption that $T_c = T_{760}/.65$, and calculates an approximate value of T_r at which the liquid density is known. One then obtains from Table A1-16 the values of (d/d_o) at this reduced temperature and the volume $V_o = M(d/d_o)/d$ where M is the molecular weight. Next the values of $\log(T_{760}/V_o)$ and (T_{100}/T_{760}) are calculated and their intersection found on Fig. A1-6. In the first expression T_{760} is in ^oK and V_o in cc/mole. This gives a new estimate of (T_{760}/T_c) and a value of ω.

This estimate of (T_{760}/T_c) is used to calculate a new value of T_r for the temperature at which the density is measured. This T_r is used to look up d/d_o. $\text{Log}(T_{760}/V_o)$ is then recalculated and a new estimate of (T_{760}/T_c) and ω is found. This process is continued until no further change is found.

T_c is given by $T_c = \left(\frac{T_{760}}{T_c}\right)^{-1} T_{760}$. P_c is then found by using the calculated values of T_c and ω, and the equation $\log P_c = (\log P_c)^{(o)} + \omega(\log P_c)^{(1)}$,

together with Table A1-17 which is merely a convenient rearrangement of the vapor pressure equation of Table A1-1. Riedel[1] calculated the critical parameters of twenty-six substances. The root-mean-square percentage error for these substances for T_c = .8%, for P_c = 3.3%.

Table A1-17. Dependence of P_c(atm) on T_{760}/T_c and ω

$$\log P_c = (\log P_c)^{(o)} + \omega(\log P_c)^{(1)}$$

T_{760}/T_c	$(\log P_c)^{(o)}$	$(\log P_c)^{(1)}$
.76	.742	.705
.74	.823	.800
.72	.909	.895
.70	1.000	1.00
.68	1.096	1.12
.66	1.198	1.25
.64	1.308	1.39
.62	1.426	1.54
.60	1.552	1.70
.58	1.688	1.88
.56	1.834	2.08

<u>Examples</u> - The calculation of the critical constant of toluene is given as an example of this procedure.

$T_{760} = 383.8^{o}K$ $\qquad$ $T_{100} = 325.1^{o}K$

$d = .866$ g/cc at $293.2^{o}K$

$$\frac{T_{100}}{T_{760}} = .847$$

Assume $\quad T_{760} = .65\ T_c$

$$T_r = .65\frac{293.2}{383.8} = .496 \text{ for the density value.}$$

From Table A1-16,

$$\log\left(\frac{T_{760}}{V_o}\right) = \log\left(\frac{383.8 \times .866}{.784 \times 93}\right) = .659.$$

From Fig. A1-6,

$$\frac{T_{760}}{T_c} = .643 \qquad \omega = .233$$

$$T_r = .643 \; \frac{293.2}{383.8} = .491 \text{ for the density value.}$$

From Table A-16,

$$\log\left(\frac{T_{760}}{V_o}\right) = \log\left(\frac{383.8 \times .866}{93 \times .786}\right) = .658 \; .$$

There is no change in this approximation, therefore

$$\omega = .233$$

$$T_c = \frac{383.8}{.643} = 597^{o}K \; .$$

From Table A1-17,

$$\text{at } T_r = .643$$

$$\log P_c = 1.291 + \omega\,(1.37)$$

$$= 1.610$$

$$P_c = 40.8 \text{ atm.}$$

In addition let us calculate V_c.

$$z_c = z_c^{(o)} + \omega z_c^{(1)}$$

$$= .291 + \omega\,(-.080)$$

$$= .272$$

$$V_c = \frac{z_c R T_c}{P_c} = \frac{(.272)(.082)(597)}{(40.8)}$$

$$= .326 \text{ liter/mole.}$$

	T_c	P_c	V_c
Estimate	597°K	40.8 atm	.326 liter/mole
Experimental	594.0	40.	.32

We may continue the example by predicting the properties of toluene at 600°K and 80 atm. We take $\omega = .233$ and the experimental critical properties.

$$T_r = \frac{600}{594} = 1.01$$

$$P_r = \frac{80}{40} = 2.00$$

$$z = .332 + .233\ (-.100) = .309$$

$$V = RT/P = 82.0\ (600)/80(.309) = 1990 \text{ cc/mole}$$

$$\log\ (f/P) = -.382 - .233\ (-.05) = -.370$$

$$f = 80(.427) = 34.1 \text{ atm}$$

$$\left(\frac{H^* - H}{RT_c}\right) = 3.50 + .233\ (3.29) = 4.27$$

$$H^* - H = 1.987\ (594)(4.27) = 5040 \text{ cal/mole}$$

$$S^* - S = 1.987\ \left[\left(\frac{4.27}{1.01}\right) + 2.303\ (-.370)\right]$$

$$= 6.7 \text{ cal/deg mole}$$