virial coefficients conform within about 1% to the theory we are proposing for volumetric and thermodynamic properties generally. In later papers we shall test this scheme against various experimental data and present general tables.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Volumetric and Thermodynamic Properties of Fluids. II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization[1]

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The theoretical considerations of Part I suggested that the compressibility factor of a normal liquid in either gas or liquid state should be expressible as a function of just one parameter in addition to the reduced temperature and reduced pressure. The additional parameter is defined in terms of the vapor pressure at $T_r = 0.7$. This third parameter is required because the intermolecular force in complex molecules is a sum of interactions between various parts of the molecules—not just their centers—hence the name *acentric factor* is suggested. The theory requires that any group of substances with equal values of the acentric factor should conform among themselves to the principle of corresponding states. This result is verified with relatively high accuracy. While a completely analytical expression for the compressibility factor was not obtained, power series expressions in the acentric factor proved satisfactory and the coefficients are tabulated for a wide range of reduced temperature and pressure. The reduced vapor pressure and the entropy of vaporization are also treated similarly. Agreement is obtained to 0.5% over most regions with maximum deviations of about 2%.

A general introduction together with discussion of the theoretical basis for the correlation scheme has been presented in Part I of this series.[3] Although exact theory was available only for the second virial coefficient, those results together with general arguments indicated that a three parameter correlation might well yield at least a factor of ten greater accuracy than is obtained from the simple hypothesis of corresponding states. As was indicated in Part I, we take two critical constants for two of our three independent parameters for each substance. The critical temperature is readily selected as the first parameter which characterizes the intermolecular interaction energy.

While the critical volume would be the simple measure related to intermolecular distance, it is unsatisfactory from the empirical viewpoint. The differential compressibility is infinite at the critical point. Consequently the critical volume is not directly measureable with any accuracy. The values commonly given are extrapolated. The critical pressure is a much more accurately determinable quantity and it suffices just as well for correlation purposes. Hence we choose the critical pressure as our second parameter.

The third parameter is to measure the deviation of the intermolecular potential from that of a simple fluid. An important deviation arises from the fact that the sum of the inverse sixth power terms applying to the various portions of a pair of complex molecules cannot be replaced by a single inverse sixth power term in the distance between molecular centers. Since these forces between noncentral portions of the molecules must be considered, the term *acentric factor* is suggested.

The most convenient empirical quantity is the reduced vapor pressure at a point well removed from the critical point. This in effect gives the slope of the vapor pressure curve, see Fig. 2, Part I. For a *simple fluid*[3] (*e.g.*, A, Kr, Xe, CH_4) the reduced vapor pressure is almost precisely 0.1 at a reduced temperature of 0.7. This point is well removed from the critical yet above the melting point for almost all substances. Consequently it is convenient to take 0.7 as our standard value of reduced temperature for the determination of the *acentric factor* which we define as

$$\omega = -\log P_r - 1.000$$

with P_r the reduced vapor pressure (P/P_c) at $T_r = 0.7$.

The slope of the vapor pressure curve is, of course, closely related to the entropy of vaporization. Thus we may regard our acentric factor as a measure of the increase in the entropy of vaporization over that of a simple fluid. It was also shown in Part I that the acentric factor would depend upon the core radius of a globular molecule, the length of an elongated molecule, or the dipole moment of a slightly polar molecule.

Table I lists the essential parameters for the various substances which were given substantial consideration in our correlations. On the basis of the arguments in Part I it was not expected that the highly polar molecules, ammonia and water, would conform to our scheme. Points for these substances are included on some graphs to illustrate the magnitude of the deviations; however, these points were given no weight in preparing the final tables. The references to Table I include the sources of data for the respective substances for the other tables of this paper.[4]

Compressibility Factor.—The compressibility factor was interpolated graphically to even values

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[1] This research was a part of the program of Research Project 50 of the American Petroleum Institute.

[2] A portion of this paper is abstracted from the Ph.D. Dissertation of David Z. Lippmann, University of California, 1953.

[3] K. S. Pitzer, THIS JOURNAL, **77**, 3427 (1955).

[4] In addition to the substances listed in Table I, supplementary use was made of data for *n*-hexane in certain areas. The sources are S. Young, *Scient. Proc. Roy. Dub. Soc.*, New Series **12**, 374 (1909–1910); E. A. Kelso with W. A. Felsing, *Ind. Eng. Chem.*, **34**, 161 (1942); E. A. Kelso with W. A. Felsing, THIS JOURNAL, **62**, 3132 (1940).

TABLE I

THE ACENTRIC FACTOR AND CRITICAL DATA

(P_r is reduced vapor pressure at $T_r = 0.7$)

Substance	$-\log P_r$	ω	T_c (°K.)	P_c (atm.)
Argon[a]	0.998	−0.002	150.72	48.00
Krypton[b]	0.998	− .002	209.39	54.182
Simple fluid	(1.000)	(.000)		
Xenon[c]	1.002	+ .002	289.75	57.636
Methane[d]	1.013	.013	190.66	45.795
Nitrogen[e]	1.040	.040	126.26	33.540
Hydrogen sulfide[f]	1.100	.100	373.55	88.868
Ethane[g]	1.105	.105	305.75	48.864
Propane[g]	1.152	.152	369.99	42.011
Neopentane[h]	1.195	.195	433.76	31.57
n-Butane[g]	1.201	.201	425.17	37.470
Benzene[i]	1.215	.215	562.66	48.664
Carbon dioxide[j]	1.225	.225	304.16	72.800
n-Pentane[g]	1.252	.252	470.60	33.628
Ammonia[k]	1.250	.250	406.00	112.31
Water[l]	1.348	.348	647.66	219.515
n-Heptane[m]	1.352	.352	539.94	26.882

[a] A. M. Clark, F. Din, J. Robb, A. Michels, T. Wassenaar and Th. Zwietering, *Physica*, **17**, 876 (1951); A. Michels, Hub. Wijker and Hk. Wijker, *ibid.*, **15**, 627 (1949); L. Holborn and J. Otto, *Z. Physik*, **33**, 1 (1925). [b] E. Mathias, C. A. Crommelin and J. J. Meihuizen, *Physica*, **4**, 1200 (1937); J. J. Meihuizen and C. A. Crommelin, *ibid.*, **4**, 1 (1937). [c] A. Michels and T. Wassenaar, *ibid.*, **16**, 253 (1950); J. A. Beattie, R. J. Barriault and J. S. Brierly, *J. Chem. Phys.*, **19**, 1219 (1951); H. W. Habgood and W. G. Schneider, *Can. J. Chem.* **32**, 98 (1954). [d] W. H. Corcoran, R. R. Bowles, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **37**, 825 (1945); A. Stock, F. Henning and E. Kuss, *Ber.*, **54**, 1119 (1921); A. Michels and G. W. Nederbragt, *Physica*, **2**, 1000 (1935); A. Michels and G. W. Nederbragt, *ibid.*, **3**, 569 (1936); R. H. Olds, H. H. Reamer, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **35**, 922 (1943). [e] A. S. Friedman and D. White, THIS JOURNAL, **72**, 3931 (1950); O. T. Bloomer and K. N. Rao, "Thermodynamic Properties of Nitrogen," Institute of Gas Technology, Technology Center, Chicago (1952). [f] H. H. Reamer, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 140 (1950). [g] B. H. Sage and W. N. Lacey, "Thermodynamic Properties of the Higher Paraffin Hydrocarbons and Nitrogen," American Petroleum Institute, New York, N. Y., 1950; B. H. Sage, D. C. Webster and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 658 (1937). [h] J. A. Beattie, D. R. Douslin and S. W. Levine, *J. Chem. Phys.*, **19**, 948 (1951). [i] E. J. Gornowski, E. H. Amick, Jr., and A. N. Nixon, *Ind. Eng. Chem.*, **39**, 1348 (1947). [j] A. Michels, T. Wassenaar, Th. Zweitering and P. Snits, *Physica*, **16**, 501 (1950); A. Michels, B. Blaisse and C. Michels, *Proc. Roy. Soc.* (*London*) **A160**, 358 (1937); A. Michels and C. Michels, *ibid.*, **A153**, 201 (1936); A. Michels, C. Michels and H. Wouters, *ibid.*, **A153**, 214 (1936); B. J. Kendall and B. H. Sage, *Petroleum* (*London*), **14**, 184 (1951). [k] F. G. Keyes and R. B. Brownlee, THIS JOURNAL, **40**, 25 (1918); F. G. Keyes, *ibid.*, **53**, 965 (1931); J. A. Beattie and C. K. Lawrence, *ibid.*, **52**, 6 (1930). [l] J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936. [m] L. B. Smith, J. A. Beattie and W. C. Kay, THIS JOURNAL, **59**, 1587 (1937); S. Young, *Sci. Proc. Roy. Dub. Soc.*, new series **12**, 374 (1909–1910).

of reduced temperature and pressure for the substances listed in Table I. The region T_r from 0.8 to 4.0 and P_r from 0 to 9 was selected for detailed study. This region includes the interesting behavior near the critical point and covers the area of greatest practical interest. Outside of this region the available data become too sparse to give a good test of our theory. Indeed the data are relatively sparse above $P_r = 3$ and $T_r = 2$. For each point in a closely spaced matrix of values of P_r and T_r, the compressibility factor was plotted as a function of the acentric factor. Most of the points fell on smooth curves (and usually on straight lines) within a few tenths of 1%. The largest deviation of experimentally well established points is about 2%. The highly polar H_2O and NH_3 are excepted from this agreement, of course. Two typical sets of these curves are shown in Figs. 1 and 2 which are for $P_r = 1.6$ and 3.0, respectively, and the various values of T_r indicated. Several sets of substances have nearly equal values of the confining factor. In order to avoid undue confusion in Figs. 1 and 2, single points are shown for each set as indicated at the bottom of the figure. The agreement of the individual substances within each set is excellent. For the data in Figs. 1 and 2, the average deviation is between 0.1 and 0.2%.

Figure 1 shows very clearly one advantage of the present system over that of Meissner and Seferian.[5] Any attempt to include such highly polar substances as water and ammonia in a three parameter system will necessarily lead to deviations such as are shown by the open circles in Fig. 1. If such highly polar substances are to be included, a fourth parameter will be necessary for an accurate correlation.

The compressibility factor is expressed generally as a function of three variables.

$$(PV/RT) = z(T_r, P_r, \omega) \qquad (2)$$

The functional dependence on temperature and pressure is very complicated. Indeed this complexity has retarded advances in this field very considerably. No simple analytical equation is adequate. The eight constant Benedict[6] equation is the simplest one which even approaches the desired accuracy. While we expect to examine completely analytical representations further, for the present we will expand the compressibility factor function as a power series in the acentric factor

$$z = z^{(0)} + \omega z^{(1)} + \ldots \qquad (3)$$

where $z^{(0)}$, $z^{(1)}$, etc., are each functions of T_r and P_r.

In almost all regions the first two terms in equation 3 are sufficient. This result corresponds to the straight lines in Figs. 1 and 2. An attempt was made to evaluate the quadratic term $z^{(2)}$ for the small region in which it appeared to be significant. While there was no difficulty at any particular value of T_r and P_r (such as $T_r = 1.10$ in Fig. 1), the resulting values of $z^{(2)}$ showed such irregular behavior as functions of T_r and P_r that there arose considerable doubt as to their validity. Consequently, no values of $z^{(2)}$ are reported at this time, and the data in regions of apparent curvature are fitted with the best straight lines.

The values of $z^{(1)}$ were plotted as functions of T_r and P_r and were adjusted within the limits of experimental error to yield a reasonably smooth function. The values of $z^{(0)}$ were initially much more accurate than those of $z^{(1)}$ and were found to be smooth functions of temperature and pressure without further adjustment. However, large graphs

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(5) H. P. Meissner and R. Seferian, *Chem. Eng. Progress*, **47**, 579 (1951).

(6) M. Benedict, G. B. Webb and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940).

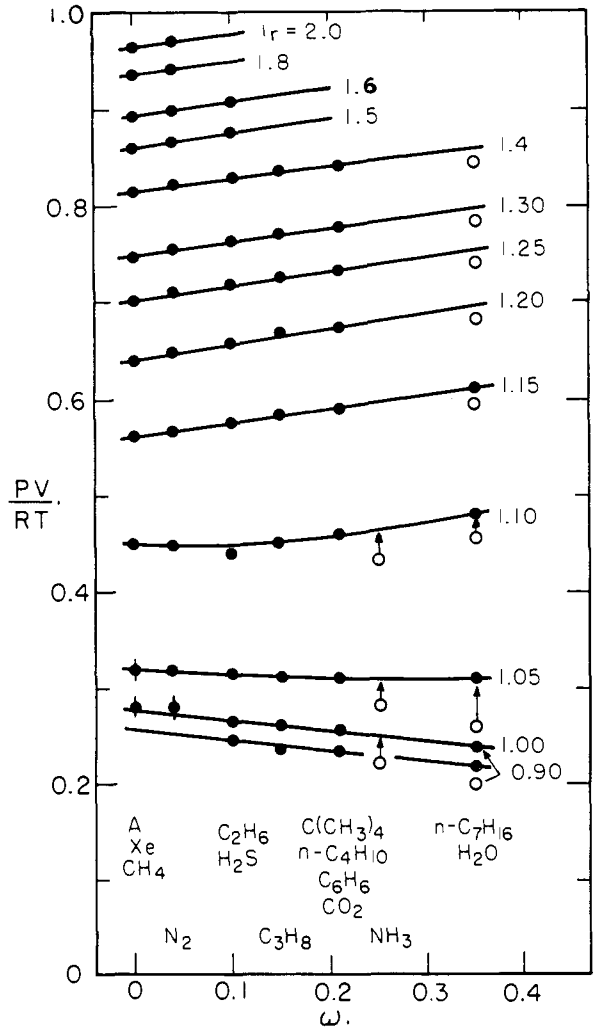

Fig. 1.—The compressibility factor as a function of the acentric factor, ω, at $P_r = 1.6$ and the values of T_r indicated.

were used to interpolate values of $z^{(0)}$ at intermediate points. The final values of the functions in equation 3 are given in Tables II–V. In view of the omission of the quadratic term one must regard the results in the region $T_r = 1.05$–1.10; $P_r = 1.4$–2.0 as less precise.

Outside of the critical region the spacing of points in Tables II and IV are close enough to allow linear interpolation without significant error. Tables III and V provide more closely spaced values in regions of large curvature. Even this close spacing is not sufficient to allow linear interpolation at all points, but simple graphs should suffice.

In certain regions either the data are poor or more commonly the data deviate from the linear correlation in ω. In such regions values are given to only the second decimal place and correspondingly lower accuracy must be expected in the calculated results.

Coexisting Phases.—Separate studies were made of the vapor pressure and of the compressibility factor for both liquid and gas along the saturation curve. The vapor pressure data are generally quite accurate and log P_r *vs.* ω plots give good straight lines even at temperatures well removed from 0.7 where ω is defined. The values are summarized in Table VI where log P_r for $\omega = 0$ and $(\partial \log P_r/\partial\omega)_T$ are tabulated. Second-order terms are not needed for the vapor pressure. The volumetric data are less accurate and the correlation plots show random deviations as high as 3% but averaging less than 1%. The greatest deviations occur in the range where the values are rounded to the hundredths place.

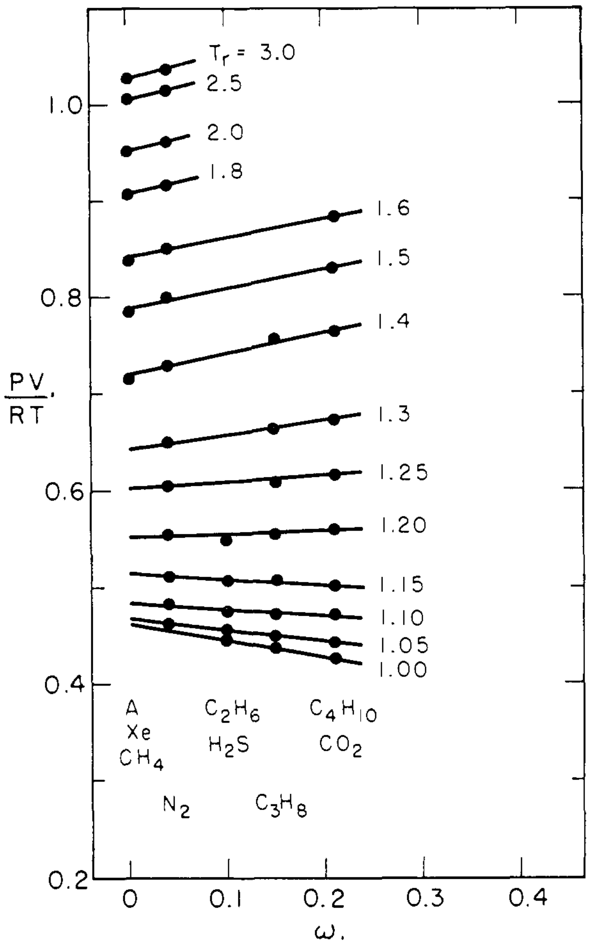

Fig. 2.—The compressibility factor as a function of the acentric factor at $P_r = 3.0$ and the indicated values of T_r.

The volumetric data for the two-phase region are repeated for convenience in Table VII as a function of reduced pressure. It should be noted that the functions $z_T^{(1)}$ and $z_P^{(1)}$ are partial derivatives where the subscript indicates the variable held constant, thus

$$
\begin{aligned}
z_T^{(1)} &= (\partial z/\partial\omega)_T \\
z_P^{(1)} &= (\partial z/\partial\omega)_P \\
&= z_T^{(1)} + (\partial z/\partial T)_\omega(\partial T/\partial\omega)_P
\end{aligned}
\qquad (4)
$$

The last equation gives a relationship between $z_P^{(1)}$ and $z_T^{(1)}$; however, we found it more convenient to evaluate each of the z functions directly from volumetric data.

We expect to treat the volumetric data for liquids at low temperatures in greater detail later. The present approximate values in this region suffice, however, for calculations of Δz of vaporization.

The values in Table VI can be compared with the tabulations of Riedel.[7] His parameter α_k is related to our ω since both measure the slope of the vapor pressure curve. Application of our equation 1 to his formula yields

$$\alpha_k = 5.808 + 4.93\omega \qquad (5)$$

Riedel's tables yield values of log P_r agreeing with our results within 0.001 except at the lowest temperatures where the difference still remains within 0.1%. While the precision of agreement in the derivative (∂ log $P_r/\partial\omega$) is not quite as high, it yields agreement in log P_r within the above limits over the entire range of ω of practical interest. Thus, so far as vapor pressures are concerned, our treatment is essentially equivalent to Riedel's.

Entropy of Vaporization.—Given the vapor pressure function and the volumetric data for both gas and liquid, one may calculate the entropy of vaporization from the thermodynamic equation

$$\begin{aligned}\Delta S &= \Delta V(\partial P/\partial T) \\ &= \frac{R\Delta z}{T_r}\,\frac{\partial \ln P}{\partial (1/T_r)} \qquad (6)\end{aligned}$$

where ΔV and Δz are the change in volume and compressibility factor on vaporization, respectively.

TABLE II

VALUES OF $z^{(0)}$ FOR COMPRESSIBILITY FACTOR CALCULATION

(See Tables III-A and III-B for additional data in the region enclosed by dotted lines.)

T_r	P_r 0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.80	0.851	0.066	0.100	0.133	0.164	0.192	0.225	0.258	0.287	0.318
.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	.331
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

T_r	P_r 2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4
0.8	0.318	0.347	0.376	0.405	0.433	0.461	0.490	0.519
.85	.316	.345	.374	.403	.431	.459	.487	.515
.9	.316	.345	.373	.402	.430	.458	.485	.512
.95	.320	.347	.375	.403	.430	.457	.484	.510
1.0	.331	.356	.381	.407	.433	.458	.484	.509
1.05	.351	.372	.393	.417	.441	.466	.489	.512
1.10	.408	.410	.421	.440	.462	.484	.504	.525
1.15	.486	.477	.478	.485	.498	.513	.529	.546
1.2	.569	.553	.545	.544	.548	.554	.563	.574
1.25	.636	.618	.606	.599	.597	.598	.602	.609
1.3	.691	.671	.657	.649	.644	.642	.642	.645
1.4	.777	.759	.745	.734	.725	.720	.718	.718
1.5	.831	.819	.808	.800	.794	.790	.785	.784
1.6	.872	.863	.855	.848	.843	.840	.836	.834
1.7	.903	.896	.889	.883	.879	.875	.873	.872
1.8	.926	.921	.916	.913	.910	.908	.907	.906
1.9	.944	.940	.936	.933	.931	.930	.929	.929
2.0	.959	.956	.954	.953	.953	.952	.952	.953
2.5	1.000	1.001	1.001	1.002	1.004	1.006	1.008	1.009
3.0	1.014	1.016	1.019	1.022	1.025	1.028	1.030	1.033
3.5	1.022	1.024	1.027	1.030	1.033	1.036	1.039	1.042
4.0	1.024	1.026	1.029	1.032	1.035	1.038	1.041	1.044

It is well known that the logarithm of the vapor

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(7) L. Riedel, *Chem. Ing. Tech.*, **26**, 83 (1954).

TABLE II (*Continued*)

T_r	P_r								
	3.6	3.8	4.0	4.5	5.0	6.0	7.0	8.0	9.0
0.8	0.547	0.576	0.605	0.675	0.746	0.883	1.017	1.15	
.85	.542	.569	.597	.663	.730	.861	0.990	1.115	
.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	0.994	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 IIIA

VALUES OF $z^{(0)}$ NEAR THE TWO-PHASE REGION

T_r	P_r						
	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.90	0.778	0.701	0.102	0.118	0.135	0.151	0.167
.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 IIIB

VALUES OF $z^{(0)}$ 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
0.98	0.193	0.204	0.217	0.230	0.244	0.257	0.270	0.284	0.299	0.313	0.326
0.99	.205	.210	.223	.235	.247	.260	.273	.287	.301	.315	.328
1.00	.291	.220	.231	.241	.250	.265	.278	.290	.304	.317	.331
1.01	.476	.283	.243	.248	.259	.271	.283	.294	.307	.319	.331
1.02	.525	.402	.273	.260	.270	.278	.291	.300	.311	.323	.334
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

pressure is very nearly a linear function of the reciprocal of the temperature, hence the second form of the equation is most convenient.

The substitution of our functional relationships for z and P yields a quadratic formula for the entropy.

$$\Delta S = \Delta S^{(0)} + \omega \Delta S^{(1)} + \omega^2 \Delta S^{(2)} \qquad (7)$$

Each of the coefficients is readily derived and, upon appropriate numerical calculations, yields the values given in the last three columns of Table VI. The unit is cal./degree mole.

Since the available data for the volume of the saturated vapor at very low reduced temperatures are scanty, use was made of calorimetric values of the entropy of vaporization in this region. However, once $z^{(0)}$ and $z^{(1)}$ are fixed at the lowest temperature to agree with entropy data, the remainder of their values follow from volumetric data and a requirement of reasonable smoothness.

Discussion.—The advantage of this scheme over simple corresponding states correlations is readily seen from Figs. 1 and 2. On the simpler basis

TABLE IV

VALUES OF $z^{(1)}$ FOR COMPRESSIBILITY FACTOR CALCULATION

(See Tables VA and VB for additional data in the region enclosed by dotted lines.)

T_r	P_r									
	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
0.80	−0.095	−0.028	−0.044	−0.058	−0.07	−0.08	−0.10	−0.11	−0.12	−0.13
.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	.021	.040	.064	.093	.12	.140	.136	+ .100
1.20	.006	.014	.025	.043	.07	.10	.13	.16	.17	.17
1.25	.007	.016	.028	.046	.07	.10	.13	.16	.18	.19
1.30	.008	.018	.031	.05	.07	.10	.13	.16	.18	.20
1.4	.012	.025	.039	.05	.07	.10	.13	.16	.18	.19
1.5	.016	.032	.051	.06	.08	.10	.13	.15	.17	.18
1.6	.018	.035	.051	.07	.08	.10	.12	.14	.16	.17
1.7	.018	.035	.051	.07	.08	.10	.11	.13	.15	.16
1.8	.018	.035	.051	.07	.08	.10	.11	.13	.14	.15
1.9	.018	.035	.051	.07	.08	.10	.11	.13	.14	.15
2.0	.018	.035	.051	.07	.08	.10	.11	.13	.14	.15
2.5	.018	.035	.051	.07	.08	.10	.11	.13	.14	.15
3.0	.018	.035	.051	.07	.08	.10	.11	.13	.14	.15
3.5	.018	.035	.051	.07	.08	.10	.11	.13	.14	.15
4.0	.018	.035	.051	.07	.08	.10	.11	.13	.14	.15

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
0.80	−0.14	−0.15	−0.16	−0.17	−0.18	−0.23	−0.26	−0.29	−0.32	−0.35	−0.37
.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	.17	.18	.19	.20	.21	.26	.30	.35	.40	.43	.45
2.5	.17	.18	.19	.20	.21	.26	.30	.35	.40	.45	.50
3.0	.17	.18	.19	.20	.21	.26	.30	.35	.40	.45	.50
3.5	.17	.18	.19	.20	.21	.26	.30	.35	.40	.45	.50
4.0	.17	.18	.19	.20	.21	.26	.30	.35	.40	.45	.50

horizontal lines would have to be drawn through each set of points at a given reduced temperature, since the acentric factor is not considered. At the lowest temperatures, the range of values of the compressibility factor from methane to heptane is about 15% even when water and ammonia are excluded. Thus a corresponding states correlation could not possibly yield a maximum error less than 7% at this point. We see that our formulation in terms of the acentric factor, which is determined independently from the vapor pressure data, yields agreement in this region within about 1%. At higher temperatures the agreement on both bases is better, but we have still reduced the error by about a factor of ten.

It should be emphasized that this improvement is attained at very little expense in terms of complexity. Vapor pressure data near the normal boiling point are even more generally available than are reliable critical data. Thus there is no difficulty in obtaining the acentric factor. As is illustrated later, the vapor pressure datum need not be at the point of definition, $T_r = 0.7$. Two coefficients must be interpolated instead of a single quantity, but this is a simple procedure. The principal increase in effort required by the present system

TABLE VA

VALUES OF $z^{(1)}$ NEAR THE TWO PHASE REGION

T_r	P_r 0.4	0.6	0.8	1.0
0.90	−0.09	−0.053	−0.068	−0.085
.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 VB

VALUES OF $z^{(1)}$ IN THE CRITICAL REGION

T_r	P_r 1.0	1.2	1.4	1.6	1.8	2.0
0.98	−0.090	−0.099	−0.109	−0.118	−0.125	−0.130
0.99	− .087	− .095	− .104	− .114	− .121	− .127
1.00	− .080	− .090	− .099	− .108	− .115	− .123
1.01	− .02	− .080	− .091	− .102	− .10	− .100
1.02	− .01	− .065	− .082	− .095	− .09	− .09
1.03	.00	− .047	− .068	− .085	− .08	− .09
1.04	+ .01	− .025	− .050	− .073	− .07	− .08
1.05	+ .02	+ .01	− .01	− .04	− .06	− .07
1.06	+ .03	+ .06	+ .07	− .02	− .05	− .073
1.07	+ .04	+ .08	+ .09	.000	− .038	− .059
1.08	+ .047	+ .08	+ .10	+ .030	− .015	− .041
1.09	+ .050	+ .08	+ .11	+ .056	+ .012	− .022
1.10	+ .055	+ .082	+ .11	+ .082	+ .035	.000
1.11	+ .057	+ .085	+ .12	+ .099	+ .062	+ .020
1.13	+ .062	+ .089	+ .12	+ .123	+ .105	+ .060
1.15	+ .064	+ .093	+ .122	+ .140	+ .136	+ .100

TABLE VI

DATA FOR COEXISTING PHASES

$(PV/RT)_T = z^{(0)} + \omega z_T^{(1)}$ $\log P_r = (\log P_r)^{(0)} + \omega(\partial \log P_r/\partial\omega)_T$ $\Delta S = \Delta S^{(0)} + \omega\Delta S^{(1)} + \omega^2\Delta S^{(2)}$

			Liquid		Gas				
T_r	$-(\log P_r)^{(0)}$	$-\left(\frac{\partial \log P_r}{\partial\omega}\right)_T$	$z^{(0)}$	$z_T^{(1)}$	$z^{(0)}$	$z_T^{(1)}$	$\Delta S^{(0)}$	$\Delta S^{(1)}$	$\Delta S^{(2)}$
1.00	0.000	0.000	0.291	−0.080	0.291	−0.080	0.00	0.00	0.0
0.99	.025	.021	.202	− .090	.43	− .030	2.57	2.83	.6
.98	.050	.042	.179	− .093	.47	.000	3.38	3.91	.9
.97	.076	.064	.162	− .095	.51	+ .020	4.00	4.72	1.1
.96	.102	.086	.148	− .095	.54	.035	4.52	5.39	1.3
.95	.129	.109	.136	− .095	.565	.045	5.00	5.96	1.4
.94	.156	.133	.125	− .094	.59	.055	5.44	6.51	1.5
.92	.212	.180	.108	− .092	.63	.075	6.23	7.54	1.8
.90	.270	.230	.0925	− .087	.67	.095	6.95	8.53	2.0
.88	.330	.285	.0790	− .080	.70	.110	7.58	9.39	2.2
.86	.391	.345	.0680	− .075	.73	.125	8.19	10.3	2.4
.84	.455	.405	.0585	− .068	.756	.135	8.79	11.2	2.5
.82	.522	.475	.0498	− .062	.781	.140	9.37	12.1	2.6
.80	.592	.545	.0422	− .057	.804	.144	9.97	13.0	2.7
.78	.665	.620	.0360	− .053	.826	.144	10.57	13.9	2.8
.76	.742	.705	.0300	− .048	.846	.142	11.20	14.9	2.9
.74	.823	.800	.0250	− .043	.864	.137	11.84	16.0	2.9
.72	.909	.895	.0210	− .037	.881	.131	12.49	17.0	2.8
.70	1.000	1.00	.0172	− .032	.897	.122	13.19	18.1	2.8
.68	1.096	1.12	.0138	− .027	.911	.113	13.89	19.3	2.7
.66	1.198	1.25	.0111	− .022	.922	.104	14.62	20.5	2.6
.64	1.308	1.39	.0088	− .018	.932	.097	15.36	21.8	2.5
.62	1.426	1.54	.0068	− .015	.940	.090	16.12	23.2	2.4
.60	1.552	1.70	.0052	− .012	.947	.083	16.92	24.6	2.3
.58	1.688	1.88	.0039	− .009	.953	.077	17.74	26.2	2.2
.56	1.834	2.08	.0028	− .007	.959	.070	18.64	27.8	2.1

arises directly from the greater accuracy expected. Modest sized graphs no longer suffice. Also the interpolations must be made with greater care to avoid loss in accuracy.

The principles of thermodynamics allow the calculation of a number of functions from the compressibility factor and its derivatives. It is this point which emphasizes the desirability of analytical representation. A program is currently under way in coöperation with Professor B. H. Sage of the California Institute of Technology which involves the application of the Benedict equation. Expressions will be obtained for each of the eight coefficients of that equation in terms of our three fundamental variables, the critical temperature, the critical pressure and the acentric factor. Attention will be given to such derived functions as the fugacity, entropy, and heat content as soon as this analytical function has been obtained.

The class of substances for which this correlation succeeds is just that which has been designated *normal liquids*[8] and it would seem desirable to use that term in the present connection. We know that highly polar or hydrogen bonding molecules such as H_2O and NH_3 do not form normal

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(8) See J. H. Hildebrand, "Solubility," First edition, The Chemical Catalog Co., New York, 1924, pp. 90–95, or F. Daniels, "Outlines of Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 182–186.

TABLE VII

DATA FOR COEXISTING PHASES

$(PV/RT)_P = z^{(0)} + \omega z_P^{(1)}$

P_r	Liquid $z^{(0)}$	Liquid $z_P^{(1)}$	Gas $z^{(0)}$	Gas $z_P^{(1)}$
1.00	0.291	−0.080	0.291	−0.080
0.99	.244	− .074	.35	− .083
.98	.228	− .071	.38	− .085
.97	.218	− .069	.40	− .087
.96	.210	− .067	.41	− .088
.95	.203	− .065	.42	− .089
.94	.197	− .063	.43	− .089
.92	.188	− .060	.45	− .090
.90	.180	− .058	.47	− .091
.85	.164	− .055	.50	− .090
.80	.150	− .053	.53	− .087
.75	.137	− .050	.56	− .081
.70	.125	− .047	.59	− .075
.65	.114	− .044	.615	− .069
.60	.104	− .041	.64	− .063
.55	.0945	− .038	.665	− .056
.50	.0850	− .036	.688	− .049
.45	.0758	− .033	.711	− .041
.40	.0670	− .030	.734	− .033
.35	.0584	− .027	.758	− .025
.30	.0500	− .023	.783	− .018
.25	.0416	− .020	.809	− .012
.20	.0334	− .017	.835	− .008
.15	.0253	− .013	.864	− .005
.10	.0175	− .010	.896	− .002
.05	.0093	− .006	.935	.000
.00	.0000	.000	1.000	.000

liquids. In Part I theoretical methods were applied to the questions of the maximum polarity allowable for conformity to our system. The resulting criterion involved molecular parameters not generally available. If we substitute appropriate powers of the critical temperature and pressure for these molecular quantities, we obtain the expression $\mu^4 P_c^2/T_c^4$ as a measure of the ratio of polar to non-polar intermolecular forces. Here μ is the dipole moment. Also, if we take our units as 10^{-18} e.s.u., atm., and degrees K., respectively, we obtain for this ratio the values 0.3, 2.3 and 3.2, all $\times 10^{-6}$ for H_2S, NH_3, and H_2O in that order. We know that H_2S conforms well with our correlation whereas NH_3 and H_2O do not. Hence the maximum value of $\mu^4 P_c^2/T_c^4$ for a normal liquid will be in the vicinity of 0.5×10^{-6}.

Example.—Finally, it seems desirable to present an example both to illustrate the method of use of these tables and to illustrate the accuracy obtained. We consider isobutane[9] which was not used in the construction of the tables. To determine ω we select a single vapor pressure value well removed from the critical point: for example the datum at 0°F. or 459.7°R. Since T_c is 734.65°R, we find $T_r = 0.6257$; and similarly $P_c = 529.1$, $P = 11.53$ lb./sq. in. and $-\log P_r = 1.6617$. Then interpolating to this T_r in Table VI we find values for the equation

$$-\log P_r = -\log P_r^{(0)} + \omega \left(\frac{-\partial \log P_r}{\partial \omega}\right)_T$$

$$1.6617 = 1.392 + 1.50\omega$$
$$\omega = 0.180$$

A similar calculation with the vapor pressure datum[9b] at 100°F. yields $\omega = 0.184$, which is reasonable agreement.

For the calculation of the compressibility factor of isobutane we take an example at 340°F. and 800 lb./sq. in. since this is in the sensitive region a little above critical temperature and pressure. The reduced variables are $P_r = 1.5533$, $T_r = 1.0919$. Interpolation in Tables IIB and VB yields $z^{(0)} = 0.433$ and $z^{(1)} = 0.074$, and substitution into equation 3 yields a calculated value $z = 0.447$ which may be compared with an experimental value[9b] of 0.4517.

NOTE ADDED IN PROOF:—In additional papers Riedel (*Chem. Ing. Tech.*, **26**, 259, 679 (1954)) has treated the volumetric behavior of liquid and vapor along the saturation curve and the entropy of vaporization. While the agreement with our results in these cases is not as precise as for vapor pressures,[7] it is satisfactory.

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[9] (a) F. D. Rossini, *et al.*, "Selected Values of the Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953; (b) Ref. g to Table I.