

Volumetric Properties of Normal Fluids at Low Temperatures: An Extension of Pitzer's Generalized Correlation

The three-parameter tabular correlation of Pitzer et al. for calculating the compressibility factor of pure components has been extended to lower temperatures in the region where T_r is from 0.5 to 0.80 and P_r is from 0 to 9. The compressibility-factor is expressed linearly in the acentric factor $Z = Z^{(0)} + \omega Z^{(1)}$ with values of $Z^{(0)}$ and $Z^{(1)}$ tabulated in terms of T_r and P_r . The generalized correlation has been tested for 21 compounds with a total number of 463 data points. The average deviations in the calculated compressibility factors are 1.63% for the compressed liquids and 0.67% for the gases.

BENJAMIN C.-Y. LU
CHU HSI
SHINN-DER CHANG
and ALBERT TSANG

Department of Chemical Engineering
University of Ottawa
Ottawa, Ontario, Canada

SCOPE

The rapid growth of the petrochemical and natural gas industries has increased the demand for the volumetric properties of normal fluids at the extreme conditions of low temperature and high pressure. These properties, which are necessary for designing equipment, are often unavailable at the desired conditions. Therefore, an ef-

fective correlation was sought for predicting such properties. The well-known three-parameter correlation of Pitzer et al. is commonly employed to serve this purpose over the $0.80 \leq T_r \leq 4.0$ and $0 \leq P_r \leq 9$ region. The purpose of this study is to extend the correlation of Pitzer et al. to lower temperatures.

CONCLUSIONS AND SIGNIFICANCE

The three-parameter tabular correlation of Pitzer et al. for calculating the compressibility factor of pure normal fluid compound has been extended to the low temperature region where $0.5 \leq T_r \leq 0.8$ and $0 \leq P_r \leq 9$. These tables are well subdivided. Thus, linear interpolations

can be easily employed to determine the compressibility factor at a desired condition. Comparison of the results with the existing data indicates that the present correlation is not only reliable and accurate but also simple to use for engineering calculations.

Volumetric properties of gases and compressed liquids are often required for process engineering calculations. Frequently, these properties are required at conditions for which no experimental data exist. The three-parameter correlation of Pitzer et al. (1955) is widely used in such cases for predicting these properties. The correlation of Pitzer et al. is valid over the $0.80 \leq T_r \leq 4.0$ and $0 \leq P_r \leq 9$ region, with the exception of the values for co-existing liquid and vapor phases where the correlation covers the temperature range of T_r from 0.56 to 1.00. The rapid growth of natural gas and petrochemical industries demand volumetric properties of normal fluids at temperatures below $T_r = 0.8$ and at conditions other than saturation. The purpose of this investigation is therefore to extend the correlation of Pitzer et al. to the $0.5 \leq T_r \leq 0.8$ and $0 \leq P_r \leq 9.0$ region.

EVALUATION OF Z , $Z^{(0)}$ and $Z^{(1)}$

The compressibility factor Z is used to represent volumetric properties of fluids. It is expressed as a function

of three variables:

$$\frac{PV}{RT} = Z(T_r, P_r, \omega) \quad (1)$$

Pitzer et al. expanded the compressibility-factor function by means of a power series in the acentric factor.

$$Z = Z^{(0)} + \omega Z^{(1)} + \dots \quad (2)$$

where $Z^{(0)}$ and $Z^{(1)}$ etc. are each functions of T_r and P_r . They reported that the first two terms in the equation are sufficient.

In this investigation it is assumed that in a homogeneous region $Z^{(0)}$ and $Z^{(1)}$ are single-valued and continuous functions of T_r and P_r and that the derivatives with respect to T_r and P_r are also continuous. It is further assumed that the first two terms of Equation (2) are also sufficient in the low temperature region. This simplification may introduce error in the calculation of Z for large molecules.

Gas Phase

The values of Z for the gas phase were obtained from the generalized second virial coefficients reported earlier (Chang and Lu, 1972). In this investigation gas phase

S. Chang is with Canadian General Electric Company, Port Hawkesbury, Nova Scotia, and A. Tsang is with the University of Toronto, Toronto, Ontario, Canada.

exists only in the very low P_r region. It appears that the Z values calculated from the second virial coefficients are adequate for representing the data.

Liquid Phase

In the development of the generalized correlation, the values of the isothermal coefficient of bulk compressibility, β_T , compiled by Rowlinson (1969) for the following compounds

	ω
Argon	0.00
Methane	0.013
Oxygen	0.021
Nitrogen	0.040
Benzene	0.215
<i>n</i> -Heptane	0.359

were used for evaluating Z values of liquids. The quantity β_T is defined by

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (3)$$

At a given temperature, β_T is a function of pressure and generally decreases with an increase of pressure. However, in the preliminary evaluation, β_T was treated as constant independent of pressure at a given temperature. This approach was necessary due to the lack of experimental data. Therefore,

$$\int_{P_1}^{P_2} \beta_T dP = - \int_{P_1}^{P_2} \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T dP \quad (4)$$

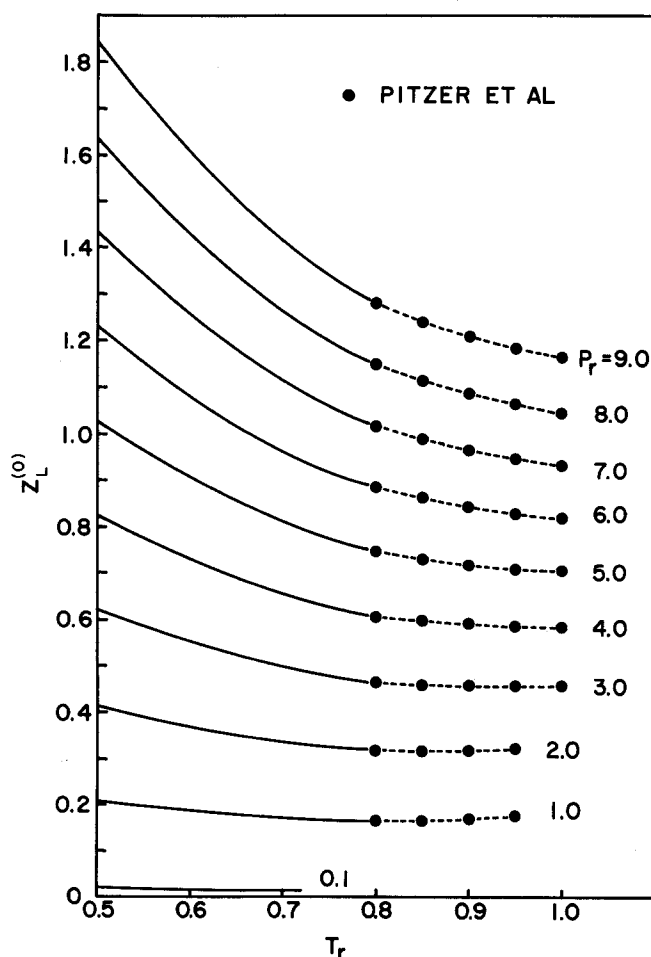


Fig. 1. Generalized plot of $Z^{(0)}$ values for compressed liquids.

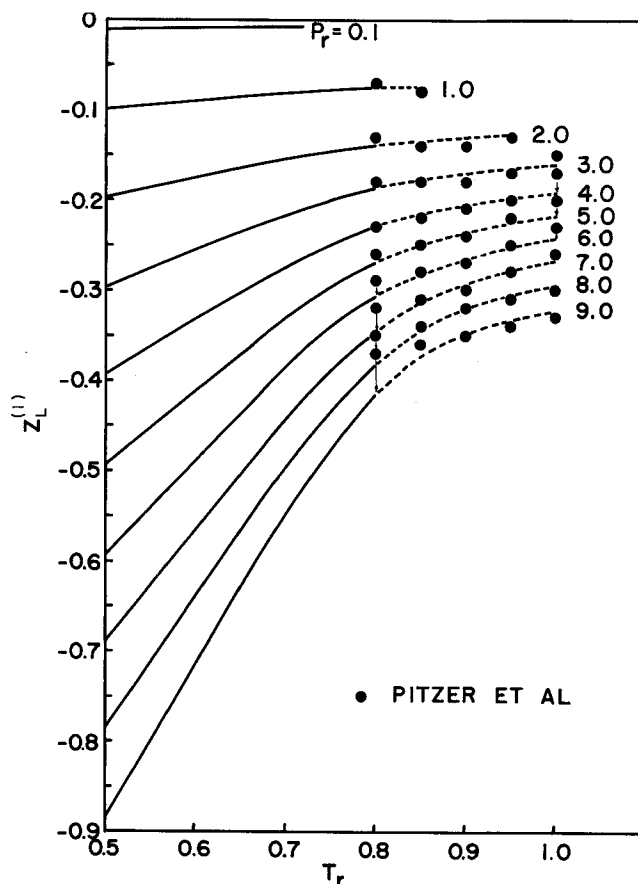


Fig. 2. Generalized plot of $Z^{(1)}$ values for compressed liquids.

and

$$\beta_T(P_2 - P_1) = \ln (V_1/V_2) \quad (5)$$

Vapor pressures and saturated liquid volumes at a given temperature are substituted into Equation (3) as P_1 and V_1 , respectively, for the evaluation of V_2 at any given P_2 . The assumption that β_T is independent of pressure may introduce an error of 3% in the Z values at high pressures where the value of β_T may be reduced by 50%. Without any adjustment, the calculated Z values at high pressures would always be lower than the experimental data. The effect of the assumption at low pressure is, however, not at all significant. Vapor pressures and saturated liquid volumes were taken from the literature (Rowlinson, 1969; Francis, 1957, 1959).

Values of Z were obtained at regular intervals of T_r and P_r and used to obtain $Z^{(0)}$ and $Z^{(1)}$ values by means of Equation (2). A cross-plotting procedure was employed to obtain reasonably smooth curves. These curves were further adjusted using the available volumetric data for 21 compounds as a guide. This step was necessary to overcome the drawbacks of the assumption used above in the evaluation of Z . It should be mentioned that these available data are not sufficient by themselves for extending the correlation of Pitzer et al. to the desired region of this investigation. An attempt was made to draw the curves through the values reported by Pitzer et al. (1955) at $T_r = 0.8$. The final values of $Z^{(0)}$ and $Z^{(1)}$ obtained are expressed in terms of T_r and P_r and are presented in Tables 1 and 2 respectively. In addition, they are also depicted in Figures 1 and 2 with the values of Pitzer et al. (1955) included for the purpose of comparison.

TABLE 1. VALUES OF $Z^{(0)}$ FOR COMPRESSIBILITY FACTOR CALCULATION

$Tr \backslash Pr$	0.001	0.002	0.004	0.006	0.008	0.010	0.012	0.014	0.016	0.018
0.50	0.9975	0.9949	0.0009	0.0013	0.0017	0.0022	0.0026	0.0030	0.0034	0.0038
0.52	0.9978	0.9955	0.0008	0.0012	0.0016	0.0020	0.0024	0.0028	0.0032	0.0036
0.54	0.9980	0.9960	0.9921	0.0011	0.0015	0.0018	0.0023	0.0026	0.0030	0.0034
0.56	0.9982	0.9964	0.9930	0.9893	0.0014	0.0017	0.0021	0.0025	0.0029	0.0033
0.58	0.9984	0.9967	0.9936	0.9904	0.9874	0.0016	0.0020	0.0024	0.0028	0.0032
0.60	0.9985	0.9970	0.9942	0.9914	0.9885	0.9857	0.9828	0.9796	0.0028	0.0032
0.62	0.9987	0.9974	0.9947	0.9921	0.9895	0.9870	0.9843	0.9817	0.9791	0.9764
0.64	0.9988	0.9977	0.9952	0.9928	0.9904	0.9880	0.9856	0.9833	0.9809	0.9785
0.66	0.9989	0.9979	0.9956	0.9935	0.9912	0.9890	0.9869	0.9847	0.9825	0.9802
0.68	0.9990	0.9980	0.9960	0.9940	0.9920	0.9900	0.9880	0.9860	0.9838	0.9819
0.70	0.9991	0.9982	0.9963	0.9945	0.9927	0.9909	0.9890	0.9871	0.9852	0.9833
0.72	0.9992	0.9983	0.9966	0.9949	0.9932	0.9915	0.9898	0.9881	0.9864	0.9846
0.74	0.9992	0.9984	0.9969	0.9953	0.9937	0.9922	0.9905	0.9890	0.9875	0.9857
0.76	0.9993	0.9986	0.9971	0.9956	0.9942	0.9928	0.9913	0.9898	0.9883	0.9867
0.78	0.9994	0.9987	0.9973	0.9960	0.9946	0.9933	0.9919	0.9905	0.9891	0.9877
0.80	0.9994	0.9988	0.9975	0.9963	0.9950	0.9938	0.9925	0.9912	0.9899	0.9887

$Tr \backslash Pr$	0.020	0.040	0.060	0.080	0.10	0.12	0.14	0.16	0.18	0.20
0.50	0.0043	0.0085	0.0127	0.0169	0.0211	0.0253	0.0295	0.0337	0.0380	0.0420
0.52	0.0040	0.0081	0.0122	0.0164	0.0205	0.0247	0.0288	0.0328	0.0370	0.0409
0.54	0.0038	0.0078	0.0119	0.0159	0.0200	0.0240	0.0280	0.0320	0.0361	0.0399
0.56	0.0037	0.0076	0.0116	0.0156	0.0195	0.0235	0.0273	0.0312	0.0352	0.0391
0.58	0.0036	0.0074	0.0114	0.0153	0.0191	0.0230	0.0268	0.0306	0.0344	0.0383
0.60	0.0036	0.0073	0.0112	0.0150	0.0187	0.0225	0.0262	0.0300	0.0338	0.0375
0.62	0.0733	0.0072	0.0110	0.0147	0.0184	0.0221	0.0258	0.0295	0.0331	0.0368
0.64	0.9758	0.0071	0.0108	0.0145	0.0181	0.0217	0.0254	0.0289	0.0326	0.0361
0.66	0.9779	0.9546	0.0107	0.0142	0.0178	0.0215	0.0250	0.0286	0.0321	0.0355
0.68	0.9798	0.9588	0.0106	0.0140	0.0175	0.0211	0.0247	0.0281	0.0317	0.0351
0.70	0.9814	0.9623	0.9426	0.0138	0.0173	0.0209	0.0243	0.0278	0.0312	0.0348
0.72	0.9829	0.9652	0.9474	0.9282	0.0170	0.0207	0.0240	0.0274	0.0309	0.0343
0.74	0.9842	0.9679	0.9512	0.9339	0.9157	0.0205	0.0239	0.0271	0.0305	0.0340
0.76	0.9853	0.9703	0.9548	0.9387	0.9222	0.9053	0.8880	0.0269	0.0302	0.0336
0.78	0.9864	0.9724	0.9581	0.9433	0.9280	0.9122	0.8960	0.8790	0.0300	0.0333
0.80	0.9874	0.9744	0.9611	0.9474	0.9333	0.9187	0.9035	0.8879	0.8716	0.8529

$Tr \backslash Pr$	0.40	0.60	0.80	1.0	1.2	1.4	1.6	1.8	2.0	2.2
0.50	0.0841	0.126	0.168	0.210	0.250	0.293	0.333	0.375	0.415	0.455
0.52	0.0817	0.123	0.164	0.205	0.245	0.285	0.325	0.365	0.405	0.443
0.54	0.0796	0.120	0.160	0.199	0.238	0.278	0.318	0.356	0.395	0.433
0.56	0.0777	0.117	0.156	0.195	0.233	0.271	0.310	0.347	0.386	0.422
0.58	0.0761	0.115	0.152	0.190	0.227	0.265	0.303	0.340	0.377	0.412
0.60	0.0747	0.113	0.149	0.186	0.223	0.260	0.297	0.332	0.369	0.403
0.62	0.0732	0.111	0.146	0.183	0.218	0.254	0.290	0.325	0.360	0.395
0.64	0.0721	0.110	0.144	0.180	0.214	0.249	0.284	0.320	0.353	0.387
0.66	0.0710	0.108	0.141	0.176	0.211	0.245	0.279	0.315	0.347	0.380
0.68	0.0707	0.106	0.139	0.174	0.208	0.242	0.274	0.309	0.341	0.375
0.70	0.0694	0.105	0.138	0.171	0.205	0.238	0.271	0.305	0.336	0.369
0.72	0.0686	0.104	0.137	0.170	0.202	0.235	0.267	0.300	0.332	0.365
0.74	0.0680	0.103	0.136	0.169	0.199	0.233	0.265	0.297	0.329	0.360
0.76	0.0673	0.102	0.135	0.167	0.196	0.230	0.262	0.294	0.325	0.355
0.78	0.0667	0.101	0.134	0.165	0.194	0.228	0.260	0.290	0.321	0.351
0.80	0.0660	0.100	0.133	0.164	0.192	0.225	0.258	0.287	0.318	0.347

$Tr \backslash Pr$	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	0.497	0.538	0.579	0.619	0.822	1.025	1.230	1.432	1.636	1.840
0.52	0.484	0.525	0.565	0.604	0.802	1.000	1.199	1.392	1.592	1.791
0.54	0.471	0.511	0.550	0.591	0.784	0.975	1.168	1.357	1.549	1.743
0.56	0.460	0.498	0.536	0.578	0.765	0.950	1.138	1.320	1.507	1.696
0.58	0.450	0.486	0.523	0.564	0.747	0.927	1.108	1.286	1.467	1.649
0.60	0.440	0.476	0.510	0.552	0.730	0.904	1.080	1.253	1.428	1.602
0.62	0.430	0.465	0.500	0.540	0.713	0.882	1.053	1.221	1.388	1.559
0.64	0.421	0.456	0.490	0.528	0.698	0.862	1.028	1.191	1.353	1.519
0.66	0.414	0.447	0.481	0.517	0.680	0.844	1.003	1.163	1.320	1.480
0.68	0.406	0.440	0.473	0.506	0.668	0.826	0.980	1.136	1.288	1.443
0.70	0.400	0.434	0.465	0.497	0.653	0.808	0.959	1.111	1.260	1.410
0.72	0.395	0.427	0.458	0.489	0.642	0.794	0.940	1.092	1.234	1.379
0.74	0.390	0.422	0.451	0.481	0.631	0.781	0.924	1.072	1.210	1.350
0.76	0.385	0.416	0.445	0.475	0.620	0.769	0.910	1.054	1.189	1.325
0.78	0.381	0.411	0.439	0.469	0.613	0.758	0.898	1.038	1.168	1.301
0.80	0.376	0.405	0.433	0.461	0.605	0.746	0.883	1.017	1.150	1.280

TABLE 2. VALUES OF $Z^{(1)}$ FOR COMPRESSIBILITY FACTOR CALCULATION

$Tr \backslash Pr$	0.001	0.002	0.004	0.006	0.008	0.010	0.012	0.014	0.016	0.018
0.50	-0.0067	-0.0127	-0.0004	-0.0007	-0.0009	-0.0012	-0.0014	-0.0017	-0.0019	-0.0021
0.52	-0.0052	-0.0103	-0.0003	-0.0006	-0.0008	-0.0011	-0.0013	-0.0016	-0.0018	-0.0020
0.54	-0.0040	-0.0082	-0.0172	-0.0005	-0.0007	-0.0011	-0.0013	-0.0015	-0.0017	-0.0019
0.56	-0.0030	-0.0065	-0.0141	-0.0216	-0.0007	-0.0010	-0.0012	-0.0014	-0.0016	-0.0018
0.58	-0.0024	-0.0053	-0.0114	-0.0176	-0.0240	-0.0010	-0.0012	-0.0013	-0.0015	-0.0017
0.60	-0.0019	-0.0042	-0.0091	-0.0141	-0.0190	-0.0244	-0.0295	-0.0347	-0.0014	-0.0016
0.62	-0.0016	-0.0034	-0.0072	-0.0111	-0.0148	-0.0191	-0.0234	-0.0277	-0.0324	-0.0370
0.64	-0.0014	-0.0029	-0.0059	-0.0090	-0.0121	-0.0153	-0.0185	-0.0219	-0.0254	-0.0288
0.66	-0.0012	-0.0025	-0.0049	-0.0074	-0.0100	-0.0126	-0.0151	-0.0178	-0.0205	-0.0231
0.68	-0.0010	-0.0022	-0.0041	-0.0062	-0.0085	-0.0106	-0.0127	-0.0149	-0.0170	-0.0193
0.70	-0.0009	-0.0019	-0.0034	-0.0051	-0.0071	-0.0089	-0.0107	-0.0124	-0.0143	-0.0161
0.72	-0.0008	-0.0016	-0.0029	-0.0043	-0.0059	-0.0075	-0.0089	-0.0105	-0.0121	-0.0135
0.74	-0.0006	-0.0014	-0.0025	-0.0036	-0.0049	-0.0062	-0.0074	-0.0086	-0.0100	-0.0113
0.76	-0.0005	-0.0012	-0.0021	-0.0030	-0.0041	-0.0052	-0.0062	-0.0072	-0.0083	-0.0094
0.78	-0.0005	-0.0010	-0.0017	-0.0026	-0.0034	-0.0044	-0.0052	-0.0060	-0.0069	-0.0077
0.80	-0.0004	-0.0008	-0.0014	-0.0022	-0.0028	-0.0036	-0.0043	-0.0050	-0.0058	-0.0065

$Tr \backslash Pr$	0.020	0.040	0.060	0.080	0.10	0.12	0.14	0.16	0.18	0.20
0.50	-0.0024	-0.0048	-0.0071	-0.0094	-0.0118	-0.0138	-0.0159	-0.0180	-0.0200	-0.0220
0.52	-0.0023	-0.0046	-0.0069	-0.0092	-0.0114	-0.0134	-0.0155	-0.0175	-0.0194	-0.0214
0.54	-0.0022	-0.0045	-0.0067	-0.0089	-0.0110	-0.0130	-0.0151	-0.0171	-0.0190	-0.0209
0.56	-0.0020	-0.0043	-0.0065	-0.0086	-0.0107	-0.0127	-0.0148	-0.0166	-0.0185	-0.0204
0.58	-0.0019	-0.0042	-0.0062	-0.0084	-0.0104	-0.0124	-0.0144	-0.0162	-0.0180	-0.0199
0.60	-0.0018	-0.0040	-0.0061	-0.0082	-0.0101	-0.0120	-0.0140	-0.0157	-0.0175	-0.0194
0.62	-0.0416	-0.0038	-0.0059	-0.0079	-0.0098	-0.0116	-0.0135	-0.0153	-0.0171	-0.0189
0.64	-0.0323	-0.0037	-0.0057	-0.0077	-0.0095	-0.0113	-0.0132	-0.0149	-0.0167	-0.0185
0.66	-0.0259	-0.0550	-0.0055	-0.0074	-0.0093	-0.0110	-0.0128	-0.0145	-0.0164	-0.0181
0.68	-0.0216	-0.0463	-0.0053	-0.0072	-0.0090	-0.0108	-0.0125	-0.0142	-0.0160	-0.0177
0.70	-0.0180	-0.0385	-0.0620	-0.0070	-0.0088	-0.0105	-0.0123	-0.0139	-0.0157	-0.0174
0.72	-0.0150	-0.0316	-0.0509	-0.0714	-0.0085	-0.0103	-0.0120	-0.0136	-0.0154	-0.0170
0.74	-0.0126	-0.0261	-0.0415	-0.0580	-0.0758	-0.0100	-0.0116	-0.0134	-0.0151	-0.0167
0.76	-0.0105	-0.0217	-0.0339	-0.0471	-0.0616	-0.0770	-0.0930	-0.0131	-0.0148	-0.0164
0.78	-0.0088	-0.0180	-0.0279	-0.0386	-0.0500	-0.0628	-0.0760	-0.0900	-0.0145	-0.0161
0.80	-0.0072	-0.0148	-0.0227	-0.0313	-0.0407	-0.0509	-0.0615	-0.0720	-0.0836	-0.0952

$Tr \backslash Pr$	0.40	0.60	0.80	1.0	1.2	1.4	1.6	1.8	2.0	2.2
0.50	-0.0420	-0.0620	-0.0810	-0.100	-0.120	-0.140	-0.160	-0.179	-0.199	-0.219
0.52	-0.0410	-0.0607	-0.0792	-0.0978	-0.117	-0.136	-0.156	-0.175	-0.194	-0.213
0.54	-0.0403	-0.0594	-0.0773	-0.0956	-0.114	-0.133	-0.152	-0.171	-0.189	-0.207
0.56	-0.0395	-0.0580	-0.0756	-0.0937	-0.112	-0.130	-0.148	-0.166	-0.184	-0.202
0.58	-0.0387	-0.0568	-0.0740	-0.0918	-0.109	-0.127	-0.145	-0.162	-0.179	-0.196
0.60	-0.0379	-0.0556	-0.0722	-0.0900	-0.107	-0.124	-0.142	-0.158	-0.175	-0.191
0.62	-0.0370	-0.0544	-0.0710	-0.0881	-0.105	-0.122	-0.139	-0.154	-0.171	-0.186
0.64	-0.0363	-0.0533	-0.0699	-0.0864	-0.103	-0.119	-0.136	-0.151	-0.166	-0.181
0.66	-0.0355	-0.0522	-0.0684	-0.0849	-0.101	-0.117	-0.133	-0.147	-0.162	-0.176
0.68	-0.0347	-0.0511	-0.0670	-0.0834	-0.0991	-0.115	-0.130	-0.144	-0.158	-0.172
0.70	-0.0339	-0.0501	-0.0660	-0.0820	-0.0972	-0.112	-0.127	-0.142	-0.155	-0.167
0.72	-0.0331	-0.0492	-0.0648	-0.0810	-0.0958	-0.110	-0.125	-0.139	-0.151	-0.163
0.74	-0.0324	-0.0481	-0.0639	-0.0799	-0.0941	-0.109	-0.122	-0.136	-0.148	-0.159
0.76	-0.0315	-0.0476	-0.0627	-0.0789	-0.0928	-0.107	-0.120	-0.133	-0.145	-0.157
0.78	-0.0308	-0.0468	-0.0619	-0.0779	-0.0915	-0.105	-0.118	-0.130	-0.142	-0.152
0.80	-0.0300	-0.0460	-0.0611	-0.0769	-0.0900	-0.104	-0.116	-0.127	-0.139	-0.149

$Tr \backslash Pr$	2.4	2.6	2.8	3.0	4.0	5.0	6.0	7.0	8.0	9.0
0.50	-0.238	-0.258	-0.278	-0.297	-0.394	-0.495	-0.595	-0.690	-0.788	-0.887
0.52	-0.232	-0.251	-0.271	-0.288	-0.382	-0.478	-0.574	-0.665	-0.758	-0.853
0.54	-0.226	-0.244	-0.263	-0.280	-0.368	-0.462	-0.552	-0.640	-0.728	-0.819
0.56	-0.220	-0.237	-0.255	-0.271	-0.357	-0.446	-0.531	-0.614	-0.699	-0.784
0.58	-0.213	-0.230	-0.247	-0.262	-0.344	-0.430	-0.510	-0.589	-0.669	-0.750
0.60	-0.207	-0.223	-0.239	-0.254	-0.333	-0.413	-0.488	-0.565	-0.640	-0.715
0.62	-0.201	-0.216	-0.232	-0.246	-0.320	-0.397	-0.468	-0.540	-0.611	-0.681
0.64	-0.196	-0.210	-0.224	-0.238	-0.308	-0.380	-0.447	-0.515	-0.581	-0.647
0.66	-0.190	-0.203	-0.217	-0.230	-0.297	-0.364	-0.426	-0.490	-0.553	-0.612
0.68	-0.185	-0.197	-0.210	-0.223	-0.285	-0.348	-0.406	-0.466	-0.525	-0.580
0.70	-0.179	-0.191	-0.203	-0.216	-0.274	-0.331	-0.386	-0.443	-0.498	-0.548
0.72	-0.174	-0.186	-0.197	-0.209	-0.263	-0.316	-0.367	-0.421	-0.472	-0.518
0.74	-0.170	-0.181	-0.192	-0.203	-0.252	-0.302	-0.349	-0.399	-0.448	-0.490
0.76	-0.166	-0.176	-0.186	-0.197	-0.244	-0.290	-0.333	-0.380	-0.425	-0.465
0.78	-0.162	-0.172	-0.181	-0.192	-0.236	-0.279	-0.319	-0.362	-0.404	-0.441
0.80	-0.158	-0.168	-0.177	-0.187	-0.229	-0.268	-0.307	-0.346	-0.385	-0.418

TABLE 3. DEVIATIONS OF CALCULATED COMPRESSIBILITY FACTORS FROM LITERATURE VALUES

Compound	ω	T_r range	P_r range	No. of pts.	Gas phase			No. of pts.	Liquid phase			Ref.
					Avg. deviation %	Bias	Max. dev. %		Avg deviation %	bias	Max. dev. %	
Methane	0.013	0.788-0.796	0.319-0.599	—	—	—	—	2	0.97	+0.71	+1.68	Vennix et al. (1970)
n-butane	0.201	0.731-0.771	0.018-8.167	6	0.35	+0.35	+0.49	23	0.68	+0.42	+2.35	Olds et al. (1944)
i-butane	0.192	0.762	0.028-8.507	1	1.39	-1.39	-1.39	17	0.78	-0.07	+1.97	Gonzalez and Lee (1966)
i-pentane	0.206	0.701-0.755	0.030-0.121	7	0.35	+0.35	+0.70	—	—	—	—	Silberberg et al. (1959)
Neopentane	0.195	0.717	0.216-8.621	—	—	—	—	16	1.47	-1.02	-5.94	Gonzalez and Lee (1968)
n-hexane	0.290	0.735-0.784	0.187-8.674	—	—	—	—	14	1.01	+0.95	+6.10	Kelso and Felsing (1940)
2-methylpentane	0.295	0.750-0.800	0.187-8.674	—	—	—	—	14	1.75	-1.75	-4.31	Kelso and Felsing (1940)
3-methylpentane	0.277	0.739	0.182-8.420	—	—	—	—	9	1.02	-0.69	-1.94	Day and Felsing (1951)
2,2-dimethylbutane	0.266	0.763	0.326-8.143	—	—	—	—	14	3.74	-3.74	-4.60	Felsing and Watson (1943b)
n-heptane	0.359	0.506-0.783	1.828-7.311	—	—	—	—	15	0.35	-0.23	-0.88	Dolittle (1963)
n-octane	0.395	0.524-0.787	0.041-8.614	—	—	—	—	107	0.66	-0.04	-6.12	Benson and Winnick (1971)
2,2,4-trimethylpentane	0.310	0.686-0.778	0.197-7.874	—	—	—	—	28	2.30	-2.30	-3.44	Felsing and Watson (1942)
2,2,3,3-tetramethylbutane	0.377	0.704-0.723	0.408-6.290	—	—	—	—	13	2.10	+2.10	+3.44	Felsing et al. (1947)
Cyclohexane	0.186	0.562	0.340-8.503	—	—	—	—	17	2.22	+2.21	+2.87	Reamer and Sage (1957)
Propene	0.143	0.761	0.144-8.955	1	1.32	+1.32	+1.32	19	0.63	+0.20	+2.64	Sage and Lacey (1959)
1-butene	0.203	0.741	0.107-8.576	1	0.43	+0.43	+0.43	18	0.93	-0.70	-4.29	Sage and Lacey (1959)
1-pentene	0.238	0.745-0.787	0.140-7.795	—	—	—	—	20	11.29	-11.29	-14.93	Day and Felsing (1951)
Argon	0.0	0.596-0.795	0.021-6.250	10	0.39	-0.39	-0.99	13	0.94	-0.83	-2.18	Michels et al. (1958)
Nitrogen	0.04	0.634-0.792	0.030-8.955	8	1.09	-1.09	-3.47	15	1.33	-1.28	-2.52	Din (1955a)
Hydrogen sulfide	0.100	0.743	0.011-7.657	11	0.9	+0.90	+2.24	25	0.77	+0.77	+2.48	Din (1955b)
Carbon dioxide	0.225	0.776-0.799	0.280-1.120	—	—	—	—	19	0.73	+0.10	-1.86	Sage and Lacey (1959)
			Overall	45	0.67	+0.05	-3.47	418	1.63	-0.78	-14.93	Jenkin (1920)

COMPARISON OF CALCULATED RESULTS

The Z values of 21 compounds were evaluated using the $Z^{(0)}$ and $Z^{(1)}$ values presented in Tables 1 and 2 and compared with the literature values. A summary of the comparison is presented in Table 3. The percentage deviation is defined by $100 [Z_{\text{calc}} - Z_{\text{expt}}]/Z_{\text{expt}}$. The total number of experimental points included in the comparison is 463. The average absolute deviations of the calculated Z values of the vapor and liquid phases are 0.67% and 1.63% respectively. The overall average absolute deviation obtained is 1.53%. If one excludes 1-pentene from the comparison, the average absolute deviation of the Z values of the liquid phase reduces from 1.63% to 1.14% and the overall average absolute deviation reduces from 1.53% to 1.09%. In Table 3 maximum deviations are also included. The average bias deviation indicated is the mean of the deviations taken with their signs.

ACKNOWLEDGMENT

The authors are indebted to the National Research Council of Canada for financial support.

LITERATURE CITED

- Benson, M. S., and J. Winnick, "PVT Properties of Liquid n-Octane," *J. Chem. Eng. Data*, **16**, 154 (1971).
 Chang, S.-D., and B. C.-Y. Lu, "A Generalized Virial Equation of State and its Application to Vapor-Liquid Equilibria at Low Temperatures," *Adv. Cryogenic Eng.*, **17**, 255 (1972).
 Day, H. O., and W. A. Felsing, "The Compressibility of Pentene-1," *J. Am. Chem. Soc.*, **73**, 4839 (1951).
 ———, "The Pressure-Volume-Temperature Relations of 3-Methylpentane," *ibid.*, **74**, 1951 (1952).
 Din, F., "Thermodynamic Functions of Gases," Vol. 2, pp. 190, Butterworth, London (1955a).
 ———, *ibid.*, Vol. 3, p. 146 (1955b).
 Dolittle, A. K., "Some Thermodynamic Properties of n-Heptane," *Chem. Eng. Progr. Symp. Ser. No. 44*, **59**, 1 (1963).
 Felsing, W. A., and G. M. Watson, "The Compressibility of

- Liquid n-Octane," *J. Am. Chem. Soc.*, **64**, 1822 (1942).
 ———, "The Pressure-Volume-Temperature Relations of 2,2,4-Trimethylpentane," *ibid.*, **65**, 780 (1943a).
 ———, "The Pressure-Volume-Temperature Relations of 2,2-Dimethylbutane," *ibid.*, 1889 (1943b).
 ———, A. M. Cuellar, and W. N. Newton, "The Pressure-Volume-Temperature Relations of 2,2,3,3-Tetramethylbutane," *ibid.*, **69**, 1972 (1947).
 Francis, A. W., "Pressure-Temperature-Liquid Density Relations of Pure Hydrocarbons," *Ind. Eng. Chem.*, **49**, 1779 (1957).
 ———, "Pressure-Temperature-Density Relations of Pure Liquids," *Chem. Eng. Sci.*, **10**, 37 (1959).
 Gonzalez, M. H., and A. L. Lee, "Viscosity of Isobutane," *J. Chem. Eng. Data*, **11**, 357 (1966).
 ———, "Viscosity of 2,2-Dimethylpropane," *ibid.*, **13**, 66 (1968).
 Jenkin, C. F., "Dilatation and Compressibility of Liquid Carbonic Acid," *Proc. Roy. Soc., London*, **98**, 170 (1920).
 Kelso, E. A., and W. A. Felsing, "The Pressure-Volume-Temperature Relations of n-Hexane and 2-Methylpentane," *J. Am. Chem. Soc.*, **62**, 3132 (1940).
 Michels, A., J. M. Levelt, and W. DeGraaff, "Compressibility Isotherms of Argon at Temperatures between -25°C and -155°C, and at Densities up to 640 Amagat," *Physica*, **24**, 659 (1958).
 Olds, R. H., H. H. Reamer, B. H. Sage and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems—Volumetric Behavior of n-Butane," *Ind. Eng. Chem.*, **36**, 282 (1944).
 Pitzer, K. S., D. Z. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Peterson, "The Volumetric and Thermodynamic Properties of Fluids II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization," *J. Am. Chem. Soc.*, **77**, 3433 (1955).
 Reamer, H. H., and B. H. Sage, "Phase Equilibria in Hydrocarbon Systems—Volumetric Behavior of Cyclohexane," *Chem. Eng. Data Ser.*, **1**, 9 (1957).
 Rowlinson, J. S., *Liquids and Liquid Mixtures*, 2nd ed., Chapt. 2, pp. 34-51, Butterworth, London (1969).
 Sage, B. H., and W. N. Lacey, "Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide," pp. 17, 25, 36, A.P.I., Washington, D. C. (1959).
 Silberberg, H., J. J. McKetta, and K. A. Kobe, "Compressibility of Isopentane with the Burnett Apparatus," *J. Chem. Eng. Data*, **4**, 323 (1959).
 Vennix, A. J., T. W. Leland, and R. Kobayashi, Low-Temperature Volumetric Properties of Methane," *ibid.*, **15**, 238 (1970).

Manuscript received February 14, 1973, revision received March 1 and accepted March 5, 1973.