Thermodynamic Properties of 2-Propanol

M. P. MORELAND,[1] J. J. McKETTA, and I. H. SILBERBERG
Department of Chemical Engineering and Texas Petroleum Research Committee, University of Texas, Austin, Tex.

The compressibility of gaseous 2-propanol was determined by the Burnett method at 25° intervals from 100° to 200° C. From the experimental compressibility data, the deviations of the thermodynamic functions from ideal behavior as well as the fugacity coefficients for 2-propanol were calculated.

THERE has been an increasing need for accurate thermodynamic data because of the rising importance of high pressure and high temperature industrial processes. This type of data for the alcohols has been very sparse and the use of generalized correlations to estimate the properties of these highly polar compounds results in serious error. Data on the volumetric behavior of gaseous 2-propanol have been obtained (*3*) which permit accurate values of the thermodynamic properties to be calculated.

THERMODYNAMIC RELATIONS

The thermodynamic properties calculated from PVT data are obtained in the form of deviations of these properties from ideal behavior. The thermodynamic properties of a substance in the ideal gas state may be calculated from heat capacity data using the methods of statistical mechanics. The deviations from ideal behavior of the thermodynamic properties are determined in dimensionless form as shown in Table I.

The derivation of the expressions relating the functions in Table I to the compressibility factor, pressure, and temperature has been presented in detail by Heichelheim and McKetta (*2*). The resulting relations are as follows:

$$\frac{P}{RT}(V - V^*) = Z - 1 \tag{1}$$

$$\frac{(U - U^*)}{RT} = -T\int_0^P \frac{(\partial Z/\partial T)_p}{P}\,dP - (Z - 1) \tag{2}$$

$$\frac{(H - H^*)}{RT} = -T\int_0^P \frac{(\partial Z/\partial T)_p}{P}\,dP \tag{3}$$

$$\frac{(S - S^*)}{R} = -T\int_0^P \frac{(\partial Z/\partial T)_p}{P}dP - \int_0^P \frac{(Z - 1)}{P}\,dP \tag{4}$$

$$\frac{(G - G^*)}{RT} = \int_0^P \frac{(Z - 1)}{P}\,dP \tag{5}$$

$$\frac{(A - A^*)}{RT} = \int_0^P \frac{(Z - 1)}{P}\,dP - (Z - 1) \tag{6}$$

The fugacity coefficients may also be obtained from the experimental compressibility data by using the relation

$$\nu = \exp\int_0^P \frac{(Z - 1)}{P}\,dP \tag{7}$$

[1] Present address: IBM Corp., Houston, Tex.

CALCULATIONS

Calculation of the values of the thermodynamic functions for 2-propanol was done in several steps. First the measured compressibility factors were plotted *vs.* pressure on a large scale graph. Next a cross plot of the compressibility factors *vs.* temperature for constant values of pressure was made. These compressibility isobars were then fitted as polynomials in T using a least squares procedure, and the resulting expressions were differentiated analytically to give values of $\partial Z/\partial T$ at various pressures. For each isotherm, the values of $(\partial Z/\partial T)_p/P$ were fitted to polynomials in P by a least squares procedure, and the resulting expression was integrated analytically to provide values of

$$\int_0^P \frac{(\partial Z/\partial T)_p}{P}\,dP$$

at various pressures.

To determine the values of the integral used in the free energy calculations, the isothermal values of $(Z - 1)/P$ were first calculated. These values were fitted to a polynomial in P, again using a least squares procedure, and the resulting expression was integrated analytically to provide values of

$$\int_0^P \frac{(Z - 1)}{P}\,dP$$

Table I. Dimensionless Form of Thermodynamic Functions

Function	Dimensionless Form[a]
Volume	$P(V - V^*)/RT$
Internal energy	$(U - U^*)/RT$
Enthalpy	$(H - H^*)/RT$
Entropy	$(S - S^*)/R$
Gibbs free energy	$(G - G^*)/RT$
Helmholtz free energy	$(A - A^*)/RT$

[a] * Indicates property of an ideal gas.

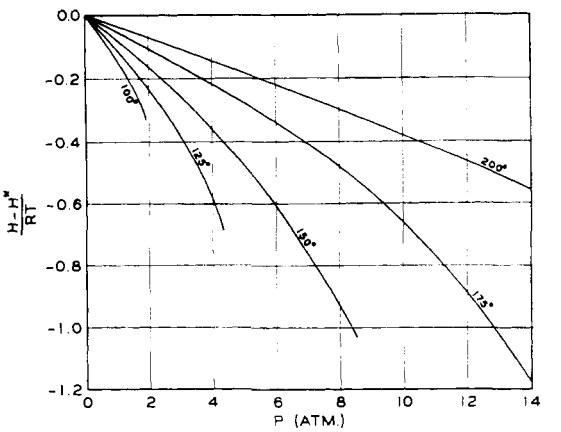

Figure 1. Enthalpy deviation of 2-propanol

at various pressures. In all instances of polynomial fittings, the data were represented within the limits of their precision.

RESULTS

The calculations were carried out with the aid of a CDC 1604 digital computer. The thermodynamic deviation functions and fugacity coefficients were calculated from the values of the integrals and are listed in Table II along with the values obtained for the integrals. The enthalpy, Gibbs free energy, and entropy functions are shown in Figures 1, 2, and 3, and the fugacity coefficients in Figure 4.

Because of the method of computation, the thermodynamic deviation functions in Table II are internally consistent to 0.0001; however, they should be considered accurate to no more than 0.001. The compressibility factor data from which the properties were calculated were estimated to be in error by less than 0.2% (*3*). Good accuracy in evaluating the integral

Table II. Thermodynamic Properties of 2-Propanol

Temp., °C.	Press., Atm.	$Z-1$	$\int_0^P \frac{(Z-1)}{P}dP$	$\int_0^P \frac{(\partial Z/\partial T)_P}{P}dP$	$\frac{U-U^*}{RT}$	$\frac{H-H^*}{RT}$	$\frac{A-A^*}{RT}$	$\frac{G-G^*}{RT}$	$\frac{S-S^*}{R}$	Fugacity Coeff.
100	0	0	0	0	0	0	0	0	0	1.0000
100	0.2	−0.0057	−0.0059	0.0000735	−0.0217	−0.0274	−0.0002	−0.0059	−0.0215	0.9941
100	0.4	−0.0113	−0.0119	0.0001484	−0.0441	−0.0554	−0.0006	−0.0119	−0.0434	0.9881
100	0.6	−0.0173	−0.0180	0.0002248	−0.0666	−0.0839	−0.0007	−0.0180	−0.0659	0.9821
100	0.8	−0.0237	−0.0241	0.0003032	−0.0895	−0.1132	−0.0004	−0.0241	−0.0891	0.9762
100	1.0	−0.0304	−0.0302	0.0003848	−0.1132	−0.1436	0.0002	−0.0302	−0.1134	0.9703
100	1.2	−0.0377	−0.0365	0.0004705	−0.1379	−0.1756	0.0012	−0.0365	−0.1391	0.9642
100	1.4	−0.0454	−0.0429	0.0005622	−0.1644	−0.2098	0.0025	−0.0429	−0.1668	0.9580
100	1.6	−0.0550	−0.0495	0.0006641	−0.1928	−0.2478	0.0055	−0.0495	−0.1983	0.9517
100	1.7	−0.0618	−0.0530	0.0007222	−0.2077	−0.2695	0.0088	−0.0530	−0.2165	0.9484
100	1.8	−0.0714	−0.0568	0.0007886	−0.2229	−0.2943	0.0146	−0.0568	−0.2375	0.9448
125	0	0	0	0	0	0	0	0	0	1.0000
125	0.5	−0.0111	−0.0118	0.0001342	−0.0423	−0.0534	−0.0007	−0.0118	−0.0417	0.9883
125	1.0	−0.0228	−0.0232	0.0002752	−0.0868	−0.1096	−0.0004	−0.0232	−0.0864	0.9771
125	1.5	−0.0349	−0.0348	0.0004253	−0.1344	−0.1693	0.0001	−0.0348	−0.1345	0.9658
125	2.0	−0.0478	−0.0466	0.0005872	−0.1860	−0.2338	0.0012	−0.0466	−0.1872	0.9545
125	2.5	−0.0618	−0.0586	0.0007651	−0.2428	−0.3046	0.0032	−0.0586	−0.2460	0.9430
125	3.0	−0.0765	−0.0712	0.0009655	−0.3079	−0.3844	0.0053	−0.0712	−0.3132	0.9313
125	3.5	−0.0932	−0.0842	0.0012000	−0.3846	−0.4778	0.0090	−0.0842	−0.3935	0.9192
125	3.8	−0.1047	−0.0923	0.0013644	−0.4385	−0.5432	0.0124	−0.0923	−0.4509	0.9118
125	4.0	−0.1140	−0.0979	0.0014873	−0.4782	−0.5922	0.0161	−0.0979	−0.4943	0.9068
125	4.1	−0.1202	−0.1008	0.0015535	−0.4983	−0.6185	0.00194	−0.1008	−0.5177	0.9041
125	4.2	−0.1294	−0.1038	0.0016232	−0.5169	−0.6463	0.0256	−0.1038	−0.5425	0.9014
125	4.3	−0.1510	−0.1070	0.0016969	−0.5385	−0.6756	0.0440	−0.1070	−0.5686	0.8985
150	0	0	0	0	0	0	0	0	0	1.0000
150	1.0	−0.0164	−0.0167	0.0001818	−0.0605	−0.0769	−0.0003	−0.0167	−0.0602	0.9834
150	2.0	−0.0337	−0.0334	0.0003815	−0.1277	−0.1614	0.0003	−0.0334	−0.1280	0.9671
150	3.0	−0.0519	−0.0505	0.0006033	−0.2034	−0.2553	0.0014	−0.0505	−0.2048	0.9507
150	4.0	−0.0708	−0.0681	0.0008519	−0.2897	−0.3605	0.0027	−0.0681	−0.2924	0.9342
150	5.0	−0.0910	−0.0861	0.0011319	−0.3879	−0.4789	0.0049	−0.0861	−0.3929	0.9175
150	6.0	−0.1130	−0.1047	0.0014474	−0.4994	−0.6124	0.0083	−0.1047	−0.5078	0.9006
150	7.0	−0.1374	−0.1240	0.0018029	−0.6255	−0.7629	0.0134	−0.1240	−0.6389	0.8834
150	7.5	−0.1509	−0.1339	0.0019974	−0.6943	−0.8452	0.0170	−0.1339	−0.7113	0.8747
150	8.0	−0.1661	−0.1441	0.0022042	−0.7666	−0.9327	0.0220	−0.1441	−0.7886	0.8658
150	8.5	−0.1850	−0.1546	0.0024245	−0.8409	−1.0259	0.0304	−0.1546	−0.8713	0.8567
175	0	0	0	0	0	0	0	0	0	1.0000
175	1.0	−0.0127	−0.0129	0.0001165	−0.0395	−0.0522	−0.0002	−0.0129	−0.0393	0.9871
175	2.0	−0.0258	−0.0256	0.0002349	−0.0795	−0.1053	0.0002	−0.0256	−0.0797	0.9747
175	3.0	−0.0391	−0.0384	0.0003562	−0.1205	−0.1596	0.0007	−0.0384	−0.1213	0.9623
175	4.0	−0.0527	−0.0514	0.0004821	−0.1633	−0.2160	0.0013	−0.0514	−0.1646	0.9499
175	5.0	−0.0669	−0.0647	0.0006144	−0.2084	−0.2753	0.0022	−0.0647	−0.2106	0.9373
175	6.0	−0.0816	−0.0782	0.0007559	−0.2571	−0.3387	0.0034	−0.0782	−0.2606	0.9248
175	7.0	−0.0969	−0.0919	0.0009094	−0.3107	−0.4076	0.0050	−0.0919	−0.3157	0.9122
175	8.0	−0.1130	−0.1058	0.0010785	−0.3703	−0.4833	0.0072	−0.1058	−0.3776	0.8996
175	9.0	−0.1297	−0.1199	0.0012668	−0.4380	−0.5677	0.0098	−0.1199	−0.4478	0.8870
175	10.0	−0.1472	−0.1344	0.0014781	−0.5152	−0.6624	0.0128	−0.1344	−0.5280	0.8742
175	11.0	−0.1656	−0.1493	0.0017162	−0.6035	−0.7691	0.0163	−0.1493	−0.6198	0.8613
175	12.0	−0.1851	−0.1645	0.0019847	−0.7043	−0.8894	0.0206	−0.1645	−0.7249	0.8483
175	13.0	−0.2062	−0.1801	0.0022868	−0.8186	−1.0248	0.0261	−0.1801	−0.8447	0.8352
175	14.0	−0.2296	−0.1961	0.0026250	−0.9468	−1.1764	0.0335	−0.1961	−0.9802	0.8219
175	15.0	−0.2587	−0.2129				0.0458	−0.2129		0.8082
200	0	0	0	0	0	0	0	0	0	1.0000
200	2.0	−0.0206	−0.0205	0.0001533	−0.0520	−0.0726	0.0001	−0.0205	−0.0502	0.9797
200	4.0	−0.0416	−0.0411	0.0003085	−0.1044	−0.1460	0.0005	−0.0411	−0.1049	0.9597
200	6.0	−0.0632	−0.0621	0.0004671	−0.1578	−0.2210	0.0011	−0.0621	−0.1589	0.9398
200	8.0	−0.0860	−0.0836	0.0006308	−0.2125	−0.2985	0.0024	−0.0836	−0.2148	0.8997
200	10.0	−0.1103	−0.1057	0.0008021	−0.2692	−0.3795	0.0046	−0.1057	−0.2739	0.8997
200	12.0	−0.1356	−0.1282	0.0009839	−0.3299	−0.0074	0.0074	−0.1282	−0.3373	0.8796
200	14.0	−0.1627	−0.1514	0.0011795	−0.3954	−0.5581	0.0113	−0.1514	−0.4067	0.8595
200	16.0	−0.1818	−0.1752				0.0166	−0.1752		0.8393
200	18.0	−0.2232	−0.1997				0.0235	−0.1997		0.8190
200	20.0	−0.2571	−0.2250				0.0321	−0.2250		0.7985
200	22.0	−0.2949	−0.2513				0.0436	−0.2513		0.7778
200	24.0	−0.3383	−0.2787				0.0596	−0.2787		0.7567

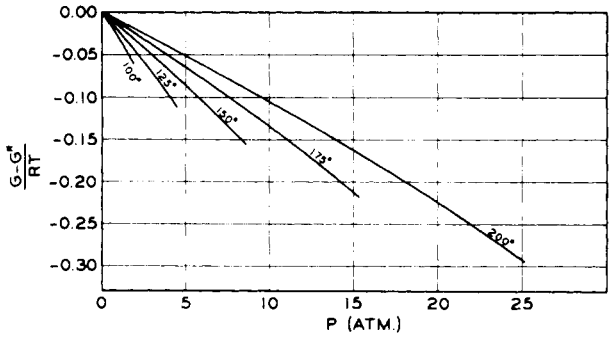

Figure 2. Gibbs free energy deviation of 2-propanol

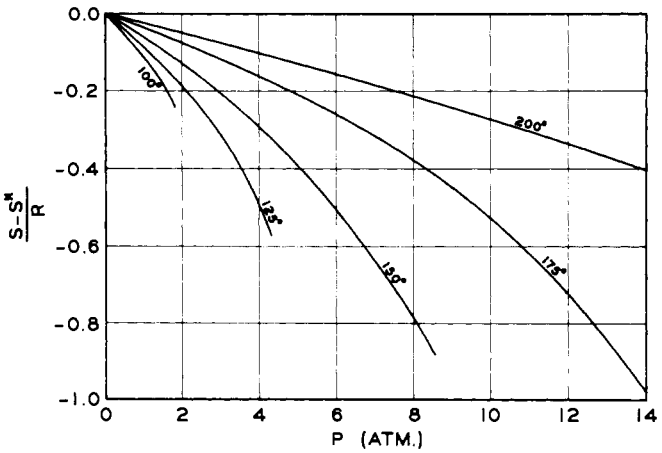

Figure 3. Entropy deviation of 2-propanol

$$\int_0^P \frac{Z-1}{P}\,dP$$

should have allowed no more than 1% error in the Gibbs free energy function. The Helmholtz free energy function should be somewhat more accurate because of the cancellation effect of errors in $Z - 1$. As a result of the differentiation, evaluation of the integral

$$\int_0^P \frac{(\partial Z/\partial T)_P}{P}\,dP$$

was subject to greater uncertainties. The error in the internal energy and enthalpy functions is therefore estimated not to exceed 2%. The entropy function consequently may be in error by as much as 3%. The minimum accuracy of the fugacity coefficient f/P should be 0.3%.

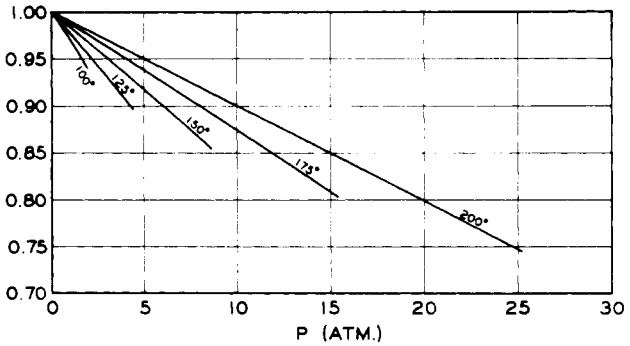

Figure 4. Fugacity coefficients of 2-propanol

Calculation of the thermodynamic properties of 2-propanol vapor from the data of Table II requires only the corresponding properties of the ideal gas state. Green has computed the ideal gas constant pressure heat capacity, enthalpy, Gibbs free energy, and entropy from 0° to 1000° K.(*1*).

NOMENCLATURE

- A = Helmholtz free energy
- f = fugacity
- G = Gibbs free energy
- H = enthalpy
- P = pressure
- R = gas constant
- S = entropy
- T = absolute temperature
- U = internal energy
- V = molal volume
- Z = compressibility factor, PV/RT
- ν = fugacity coefficient, f/P

Superscripts

- * = property of ideal gas state

LITERATURE CITED

(1) Green, J.H.S., *Trans. Faraday Soc.* **59**, 1559 (1963).
(2) Heichelheim, H.R., McKetta, J.J., *Chem. Eng. Progr. Symp. Ser.* **59**, No. 44, 23 (1963).
(3) Moreland, M.P., McKetta, J.J., Silberberg, I.H., J. CHEM. ENG. DATA **12**, 329 (1967).

RECEIVED for review December 12, 1966. Accepted March 28, 1967. Research supported in part by the National Science Foundation.