Fugacity Coefficients of *n*-Butane

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ALTHOUGH VALUABLE for many purposes, generalized correlations for fugacities frequently do not provide values of sufficient accuracy demanded by many problems. Therefore, recent interest in this area has been directed towards the establishment of precise fugacity coefficients for individual substances. For example, API Project 44 (*6*) has initiated studies which utilize available *P-V-T* data to calculate fugacities and other thermodynamic properties of hydrocarbons. As a result, fugacity coefficients have been obtained for methane, ethane, and propane.

Sage and Lacey (*8*) report fugacities for *n*-butane for temperatures up to 460° F. and high pressures. These values were calculated from *P-V-T* data which compared favorably with experimental *P-V-T* data reported by Olds, Reamer, Sage, and Lacey (*5*). However, fugacities of *n*-butane are often required at temperatures above 460° F, Therefore, in this study, the previous work has been extended to higher temperatures using experimental *P-V-T* data. In addition, fugacities were calculated from these data for temperatures below 460° F. and were compared with the values reported by Sage and Lacey (*8*). The following presents a brief outline describing the approach and data used in this study.

CALCULATION OF *f/p* VALUES

The *P-V-T* data of Beattie, Simard, and Su (*2*), Kay (*3*), Sage, Webster, and Lacey (*7*), and Olds, Reamer, Sage, and Lacey (*5*) were utilized in this study. The critical constants, T_c = 425.2° K. and p_c = 37.47 atm. reported by Beattie, Simard, and Su (*1*) were used to calculate the reduced temperatures and pressures of *n*-butane. From the *P-V-T* data, the quantity $(1 - z)p_R$ was obtained for each temperature and pressure and was plotted against the reduced pressure p_R for constant temperature parameters as shown in Figure 1 for the lower temperature region and in Figure 2 for the higher temperature region. Values of $(1 - z)/p_R$ at $p_R = 0$ were obtained by extending these curves to $p_R = 0$. Graphical integration of each isotherm from $p_R = 0$ produced fugacity coefficients from the following relationship:

$$\ln \frac{f}{p} = \int_0^{p_R} \frac{1 - z}{p_R} dp_R \qquad (1)$$

An examination of Figures 1 and 2 shows that the values of $(1 - z)/p_R$ obtained from the early data of Sage, Webster, and Lacey (*7*) and Kay (*3*) exhibit inconsistent behavior at pressures approaching $p_R = 0$. This behavior is possibly the result of adsorption effects because of the large volumes of equipment used in their direct volumetric measurements.

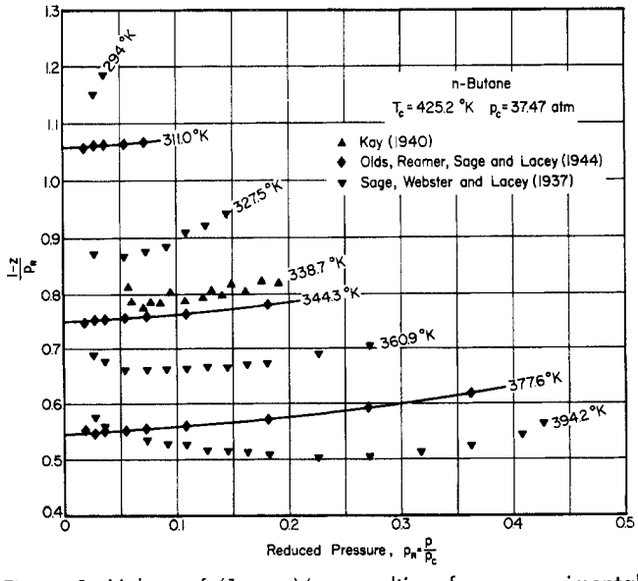

Figure 1. Values of $(1 - z)/p_R$ resulting from experimental *P-V-T* data at temperatures below 200° C.

Table I. Fugacity Coefficients, *f/p*, for *n*-Butane

(T_c = 425.2° K. p_c = 37.47 atm.)

p_R	T_R = 1.20	T_R = 1.25	T_R = 1.30	T_R = 1.35	T_R = 1.40
0.00	1.000	1.000	1.000	1.000	1.000
0.05	0.990	0.992	0.993	0.994	0.994
0.10	0.981	0.984	0.985	0.987	0.989
0.15	0.972	0.975	0.978	0.981	0.983
0.20	0.962	0.967	0.971	0.975	0.978
0.25	0.953	0.959	0.964	0.969	0.972
0.30	0.944	0.951	0.957	0.962	0.967
0.35	0.936	0.943	0.950	0.956	0.962
0.40	0.926	0.936	0.943	0.950	0.956
0.45	0.916	0.928	0.936	0.944	0.951
0.50	0.908	0.920	0.930	0.938	0.946
0.60	0.891	0.905	0.916	0.926	0.935
0.70	0.873	0.890	0.903	0.915	0.925
0.80	0.856	0.875	0.890	0.904	0.915
0.90	0.839	0.860	0.878	0.893	0.906
1.00	0.822	0.846	0.866	0.882	0.896
1.20	0.789	0.817	0.840	0.861	0.877
1.40	0.756	0.790	0.816	0.840	0.859
1.60	0.726	0.765	0.793	0.820	0.843
1.80	0.698	0.739	0.772	0.801	0.827
2.00	0.670	0.715	0.750	0.783	0.812
2.20	0.646	0.692	0.730	0.765	0.797
2.40	0.622	0.670	0.711	0.748	0.783
2.60	0.599	0.650	0.692	0.732	0.770
2.80	0.579	0.631	0.675	0.717	0.758
3.00	0.560	0.613	0.660	0.703	0.746
3.20	0.545	0.598	0.646	0.691	0.735
3.40	0.531	0.584	0.634	0.678	0.724
3.60	0.519	0.572	0.622	0.668	0.714
3.80	0.509	0.561	0.612	0.658	0.705
4.00	0.500	0.551	0.602	0.650	0.696
4.20		0.542	0.594	0.642	0.688
4.40		0.534	0.586	0.635	0.681
4.60		0.526	0.579	0.628	0.674
4.80		0.518	0.573	0.623	0.668
5.00		0.511	0.568	0.617	0.663

Therefore only the *P-V-T* data of Beattie, Simard, and Su (*2*) and Olds, Reamer, Sage and Lacey (*5*) were used to calculate the fugacity coefficients for *n*-butane.

RESULTS

In Figure 3, fugacity coefficients calculated from Figures 1 and 2 are plotted *vs.* pressure for isotherms ranging from 160° to 580° F., for 60° F. intervals. The fugacity coefficients reported by Sage and Lacey (*8*) for temperatures of 460° and

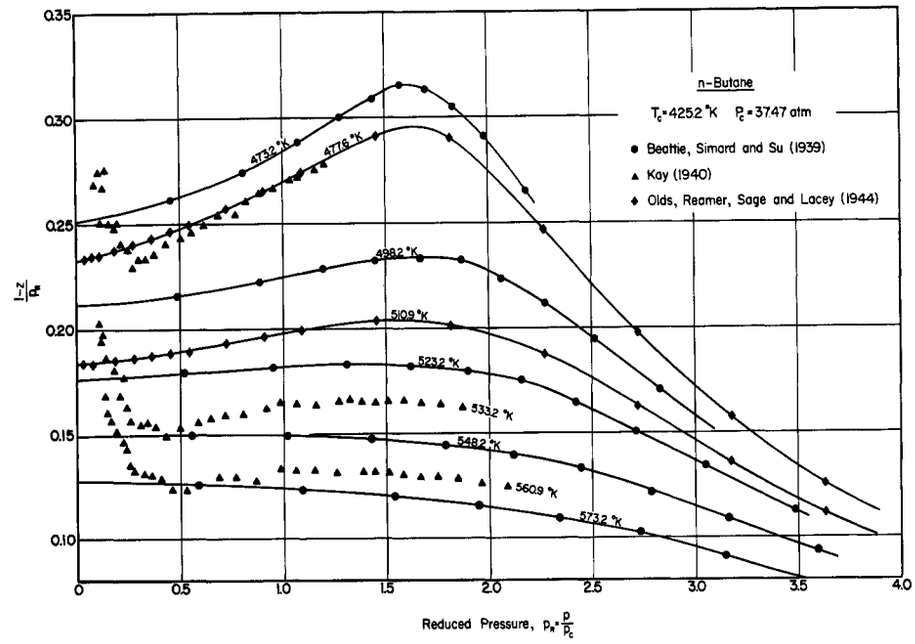

Figure 2. Values of $(1 - z)/p_R$ resulting from experimental *P-V-T* data at temperatures above 200° C.

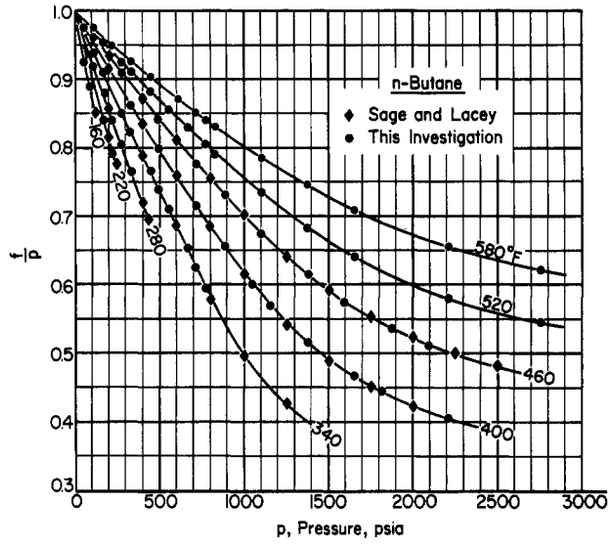

Figure 3. Fugacity coefficients from this work and that of Sage and Lacey

Table II. Comparison of Fugacity Coefficients

		f/p		
T_R	P_R	Lydersen, others (4)	This work	% Dev.
1.20	0.30	0.958	0.944	1.48
1.20	1.00	0.838	0.822	1.95
1.20	2.40	0.629	0.622	1.12
1.25	1.40	0.794	0.790	0.51
1.25	3.50	0.581	0.578	0.52
1.25	5.00	0.518	0.511	1.37
1.30	1.60	0.801	0.793	1.00
1.30	3.00	0.669	0.660	1.36
1.30	4.00	0.609	0.602	1.16
1.35	1.80	0.811	0.801	1.25
1.35	3.00	0.710	0.703	1.00
1.35	5.00	0.618	0.617	0.16
1.40	0.80	0.928	0.915	1.42
1.40	3.00	0.752	0.746	0.80
1.40	5.00	0.667	0.663	0.60

below are also plotted on these isotherms from 160° to 460° F. and indicate that the calculated values obtained in this study for this region are consistent with the results of their investigation.

The fugacity coefficients of *n*-butane from 460° to 612° F. which extend the work of Sage and Lacey (*8*) are presented in Table I for reduced temperatures, T_R = 1.20, 1.25, 1.30, 1.35, and 1.40 and for reduced pressures up to p_R = 5.0 (2754 p.s.i.a.). Fifteen representative fugacity coefficients obtained from Table I were compared with values available from the generalized reduced state correlations presented by Lydersen, Greenkorn, and Hougen (*4*) and produced the positive deviations presented in Table II, ranging from 0.16 to 1.95%.

NOMENCLATURE

- f = fugacity
- p = pressure
- p_c = critical pressure
- p_R = reduced pressure, p/p_c
- T = absolute temperature
- T_c = critical temperature
- T_R = reduced temperature, T/T_c
- z = compressibility factor

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RECEIVED for review July 22, 1960. Accepted March 6, 1961.