Refractive Indices of Ethane, Carbon Dioxide, and Isobutane

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Refractive index measurements on ethane, carbon dioxide, and isobutane are reported for temperatures of 100°, 160°, 220°, and 250°F at pressures up to about 1500 psia. Compressibility factors were calculated for ethane and carbon dioxide using densities obtained from the Lorentz-Lorenz relationship. These compared favorably with published values for the same materials.

A number of experimental studies have been made to determine the relationship between density and refractive index. The data have frequently been used to test the validity of the Lorentz-Lorenz theory and to examine by experimental measurement the temperature and density dependence of the Lorentz-Lorenz refractivity. These studies have often involved a lighter gaseous substance which is confined and then compressed so that the refractive index can be obtained over a range of pressures at each of several different temperatures.

Measurements of this kind have been made for carbon dioxide by Michels and Hamers *(3)* at temperatures of 25°, 50°, and 100°C up to pressures of 2400 atm and by Phillips *(4)* at 34°C to pressures of 85 atm. Schmidt and Traube *(7)* and Vukalovich et al. *(9)* have made accurate measurements in the critical region. Measurements of refractive indices and the corresponding densities along the coexisting vapor-liquid curve have been made for ethane and isobutane by Sliwinski *(8)*.

The object of the work reported here was to determine the refractive index of carbon dioxide, ethane, and isobutane along isotherms at 100°, 160°, 220°, and 250°F and at pressures up to about 1500 psia. These data were used with the Lorentz-Lorenz refractivities to calculate compressibility factors for carbon dioxide and ethane which existed in the gaseous region at all conditions.

Experimental

Method. The experimental equipment and method have been described in detail by Besserer and Robinson *(1)*. The sample under investigation was confined in a variable volume temperature-controlled stainless steel cell. The refractive index was measured by a minimum deviation angle method. The measured angles for the refractive index detemination had a repeatability of ±4 sec and a table error of ±2 sec over the measured range giving an overall possible error in the refractive index of $\pm 6 \times 10^{-5}$ in the range 1.0–1.4. The temperature of the cell contents was measured with an iron constantan thermocouple pair with the reference junction placed in an ice bath. The thermocouple pair was calibrated at the triple point and steam point of triple distilled water. The temperatures are believed known to ±0.1°F. The pressure of the system was measured with a strain gage pressure transducer calibrated against the vapor pressure of carbon dioxide at 68°F and the pressure readings are believed known to ±3 psia.

Materials. The isobutane, carbon dioxide, and ethane used in the investigation were obtained from the Matheson Co., Canadian Liquid Air Ltd., and the Phillips Petroleum Co., respectively. In each case the purity was greater than 99.9 mol %.

Results and Calculations

The experimentally determined refractive indices for isobutane, carbon dioxide, and ethane are shown in Figures 1–3, respectively. The curves for isobutane were obtained on the liquid-like region and consequently are terminated along the saturated liquid line. Smoothed values of the refractive indices at uniform increments of pressure up to 1500 psia are given for each material at each of the four temperatures in the range 100–250°F in Tables I–III. All refractive indices are given relative to vacuum using a monochromatic light source from a helium-neon gas laser at a wavelength of 6328Å.

The Lorentz-Lorenz formulation for the relationship between refractive index and density is given by

$$\frac{M}{\rho} \cdot \frac{n^2 - 1}{n^2 + 2} = \text{const} = R_{LL} \tag{1}$$

Experimental data have shown that the refractivity, R_{LL}, is not exactly constant but increases slightly with increasing density, passing through a maximum and declining thereafter. Buckingham and Pople *(2)* have suggested that this effect can be approximated by

$$R_{LL} = R_{LL}^0 + \frac{B}{V} + \frac{C}{V^2} \tag{2}$$

where R_{LL}^0 is the limit of the molar refractivity at zero density, B and C are the second and third virial refractivity coefficients respectively, and V is the molar volume.

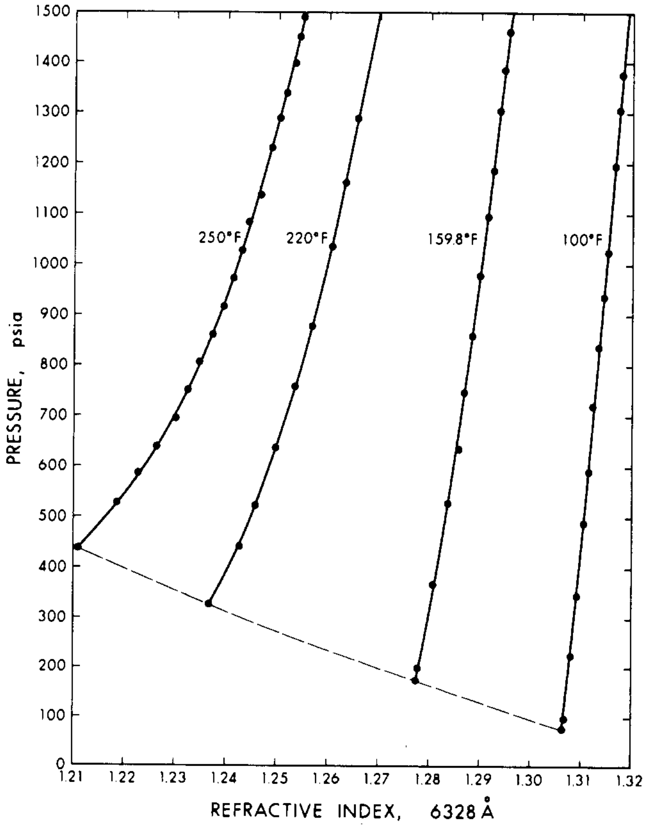

Figure 1. Effect of temperature and pressure on the refractive index of liquid isobutane

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Table I. Effect of Temperature and Pressure on the Refractive Index of Liquid Isobutane

Pressure, psia	Refractive index[a]			
	100.0°F	159.8°F	220.0°F	250.0°F
100	1.3068	. . .	. . .	. . .
200	1.3078	1.2779	. . .	. . .
300	1.3088	1.2800	. . .	. . .
400	1.3097	1.2820	1.2406	. . .
500	1.3107	1.2838	1.2449	1.2166
600	1.3117	1.2852	1.2486	1.2239
700	1.3125	1.2866	1.2519	1.2300
800	1.3132	1.2878	1.2548	1.2349
900	1.3141	1.2889	1.2576	1.2389
1000	1.3149	1.2901	1.2599	1.2422
1100	1.3158	1.2913	1.2620	1.2452
1200	1.3165	1.2925	1.2641	1.2480
1300	1.3173	1.2937	1.2661	1.2506
1400	1.3181	1.2948	1.2680	1.2530
1500	1.3190	1.2960	1.2700	1.2553

[a] Relative to vacuum at 6328Å.

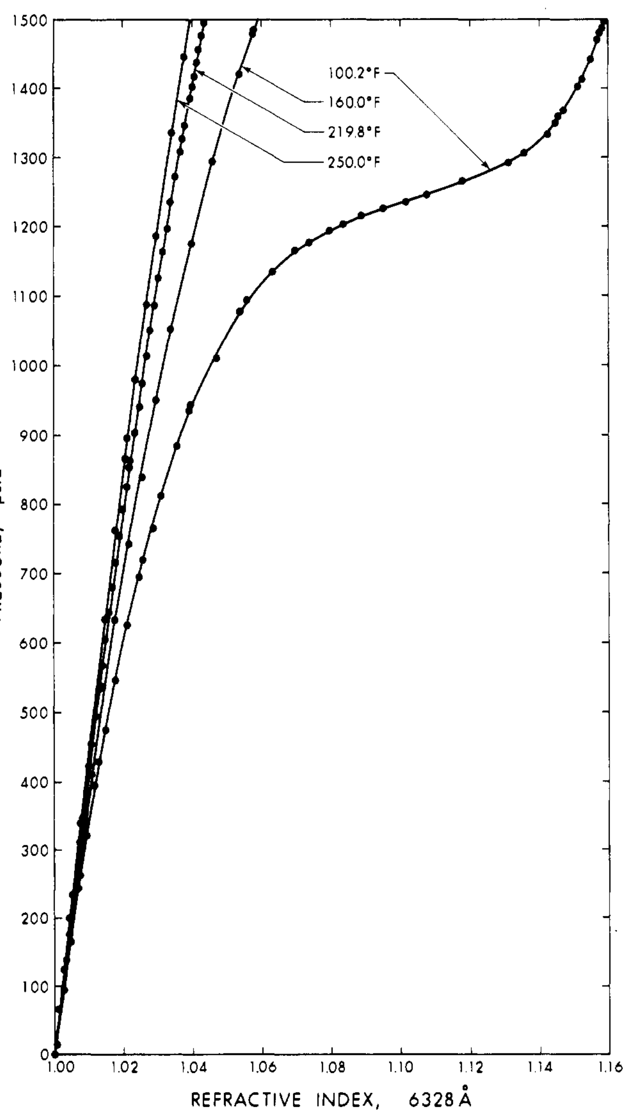

Figure 2. Effect of temperature and pressure on the refractive index of carbon dioxide

Plots of $(R_{LL} = R_{LL}^0)V$ vs. $1/V$ were made for Michels and Hamers' *(3)* high-density data for carbon dioxide and from this the following equation was derived:

$$R_{\rm LL} = \frac{n^2 - 1}{n^2 + 2} \cdot V = 6.600 + \frac{1.25}{V} - \frac{264}{V^2} \quad (3)$$

where V is in cc/g-mol.

A similar expression was used by Sliwinski *(8)* for ethane:

$$R_{LL} = 11.26 + \frac{23.2}{V} - \frac{1670}{V^2} \quad (4)$$

The smoothed experimental values of the refractive indices were used in these expressions to find the molar

Table II. Effect of Temperature and Pressure on Refractive Index of Carbon Dioxide

Pressure, psia	Refractive index[a]			
	100.2°F	160.0°F	219.8°F	250.0°F
100	1.0027	1.0025	1.0023	1.0021
200	1.0055	1.0050	1.0046	1.0042
300	1.0086	1.0077	1.0069	1.0064
400	1.0120	1.0104	1.0093	1.0087
500	1.0158	1.0134	1.0118	1.0110
600	1.0199	1.0165	1.0144	1.0135
700	1.0246	1.0199	1.0172	1.0161
800	1.0299	1.0235	1.0201	1.0187
900	1.0364	1.0274	1.0231	1.0214
1000	1.0454	1.0314	1.0261	1.0241
1050	1.0508	1.0336	1.0276	1.0255
1100	1.0570	1.0358	1.0292	1.0269
1150	1.0657	1.0382	1.0308	1.0283
1200	1.0805	1.0408	1.0324	1.0298
1250	1.1105	1.0434	1.0341	1.0312
1300	1.1333	1.0462	1.0358	1.0327
1350	1.1438	1.0492	1.0376	1.0342
1400	1.1499	1.0520	1.0395	1.0358
1500	1.1580	1.0587	1.0432	1.0390

[a] Relative to vacuum at 6328Å.

Table III. Effect of Temperature and Pressure on the Refractive Index of Ethane

Pressure, psia	Refractive index[a]			
	100.3°F	160.4°F	219.6°F	249.6°F
100	1.0047	1.0043	1.0039	1.0037
200	1.0100	1.0089	1.0080	1.0075
300	1.0159	1.0138	1.0122	1.0115
400	1.0230	1.0191	1.0166	1.0157
500	1.0315	1.0251	1.0212	1.0199
600	1.0438	1.0318	1.0264	1.0245
700	1.0611	1.0395	1.0319	1.0295
750	1.0788	1.0440	1.0348	1.0321
800	1.1365	1.0490	1.0378	1.0348
850	1.1620	1.0540	1.0410	1.0375
900	1.1712	1.0591	1.0443	1.0402
1000	1.1835	1.0716	1.0514	1.0461
1100	1.1916	1.0865	1.0587	1.0521
1200	1.1979	1.1023	1.0665	1.0585
1300	1.2025	1.1180	1.0747	1.0652
1400	1.2063	1.1321	1.0831	1.0723
1500	1.2100	1.1440	1.0919	1.0795

[a] Relative to vacuum at 6328Å.

Table IV. Effect of Temperature and Pressure on the Compressibility Factor of Carbon Dioxide

Pressure, psia	Compressibility factor[a] z 100.2°F	160.0°F	219.8°F	250.0°F
100	0.971	0.980	0.984	0.987
200	0.940	0.959	0.969	0.974
300	0.908	0.937	0.953	0.961
400	0.874	0.913	0.938	0.949
500	0.839	0.890	0.922	0.936
600	0.799	0.865	0.906	0.923
700	0.755	0.840	0.890	0.910
800	0.708	0.814	0.874	0.896
900	0.657	0.788	0.857	0.884
1000	0.597	0.762	0.841	0.871
1050	0.560	0.748	0.834	0.864
1100	0.516	0.734	0.826	0.857
1150	0.465	0.720	0.818	0.850
1200	0.390	0.706	0.810	0.843
1250	0.305	0.691	0.801	0.837
1300	0.264	0.671	0.793	0.830
1350	0.254	0.662	0.785	0.823
1400	0.252	0.646	0.777	0.816
1500	0.256	0.616	0.764	0.803

[a] Calcd using V obtained from refractive index data where $\frac{n^2-1}{n^2+2}V = 6.600 + 1.25/V - 264/V^2$.

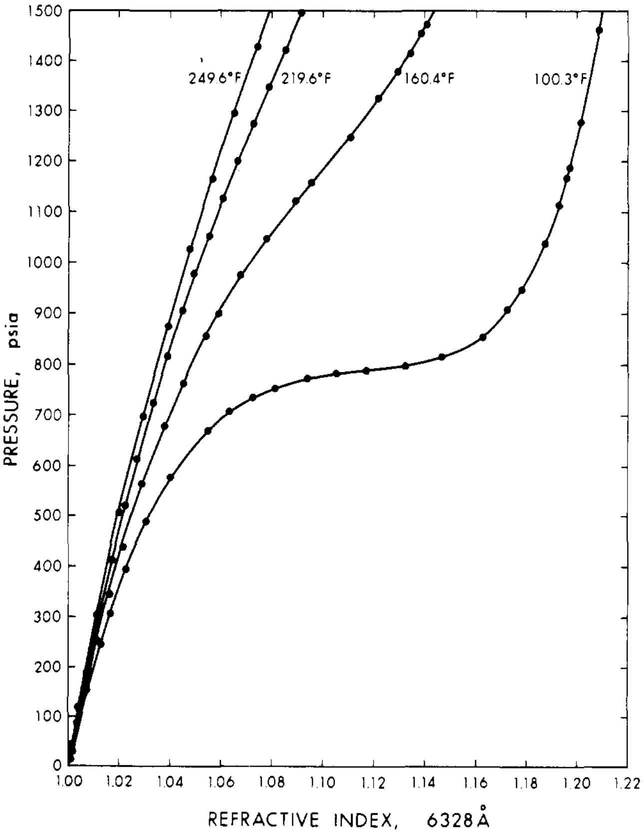

Figure 3. Effect of temperature and pressure on the refractive index of ethane

volumes at each pressure and temperature, and from this the compressibility factors were calculated. Values are tabulated in Table IV for carbon dioxide and Table V for ethane. Figures 4 and 5 show a comparison between the compressibility factors calculated from the refractive indices and those obtained by the direct volumetric measure-

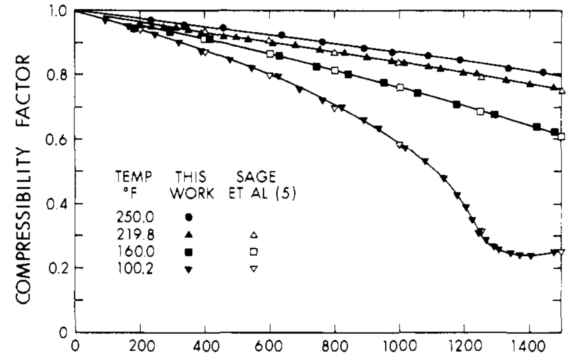

Figure 4. Compressibility factors for carbon dioxide

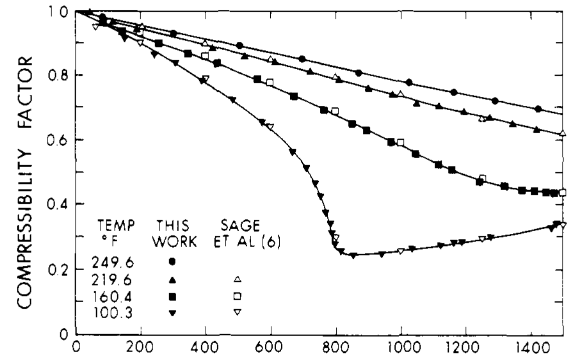

Figure 5. Compressibility factors for ethane

Table V. Effect of Temperature and Pressure on the Compressibility Factor of Ethane

Pressure, psia	Compressibility factor[a] z 100.3°F	160.4°F	210.6°F	249.6°F
100	0.953	0.966	0.976	0.979
200	0.902	0.932	0.951	0.957
300	0.846	0.896	0.926	0.936
400	0.788	0.859	0.901	0.914
500	0.721	0.819	0.874	0.892
600	0.639	0.776	0.848	0.871
700	0.521	0.729	0.820	0.849
750	0.433	0.705	0.807	0.838
800	0.277	0.682	0.793	0.827
850	0.246	0.958	0.778	0.816
900	0.245	0.633	0.765	0.805
1000	0.256	0.584	0.737	0.783
1100	0.272	0.534	0.711	0.762
1200	0.288	0.491	0.685	0.741
1300	0.305	0.462	0.666	0.722
1400	0.322	0.446	0.639	0.704
1500	0.339	0.441	0.621	0.689

[a] Calcd using V obtained from refractive index data where $\frac{n^2-1}{n^2+2}V = 11.26 + 23.2/V - 1670/V^2$.

ments on carbon dioxide and ethane by Reamer et al. *(5, 6)*. Over most of the region, agreement between the two sets of data is very close.

Nomenclature

B, C = second and third virial refractivity coefficients, respectively
ρ = density, g/cc
M = molecular weight
n = refractive index at 6328Å relative to vacuum
R_{LL} = Lorentz-Lorenz molar refractivity, cc/g-mol
R_{LL}^0 = zero density limit of the molar refractivity at 6328Å
V = molar volume, cc/g-mol

Literature Cited

(1) Besserer, G. J., Robinson, D. B., *Can. J. Chem. Eng.*, **49,** 651 (1971).
(2) Buckingham, A. D., Pople, J. A., *Discuss. Faraday Soc.*, **22,** 17 (1956).
(3) Michels, A., Hamers, J., *Physica*, **4,** 995 (1947).
(4) Phillips, P., *Proc. Roy. Soc. (London)*, **97A,** 225 (1920).
(5) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **36** (1), 88 (1944).
(6) Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, p 956.
(7) Schmidt, E., Traube, K., Proc. Intern. Res. Thermodyn. Transp. Prop., 2nd, Princeton, N.J., 1962, p 193.
(8) Sliwinski, P., *Z. Phys. Chem., Neue Folge*, **63,** 263 (1969).
(9) Vukalovich, M. P., Kobelev, V. P., Timoshenko, N. I., *Teploenergetika*, **15** (6), 80 (1968).

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Vapor Pressure of α-Samarium and α-Ytterbium

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The torsion-effusion method was used to determine the vapor pressure of α-samarium and α-ytterbium in the temperature range 1043–1179K and 775–907K, respectively. The proposed heat of sublimation at 298K, obtained as an estimated average between our second- and third-law values, was 49.56 ± 0.50 and 37.20 ± 0.40 kcal/mol for α-samarium and α-ytterbium, respectively.

Few data on the vapor pressure of α-samarium and α-ytterbium are reported in the literature *(3, 4, 6, 9, 10)*. A new series of tensimetric data, obtained by the Knudsen torsion-effusion method, is given in this paper. The basis of the method and the experimental apparatus have been described elsewhere *(7, 8)*. Vapor pressures were calculated from the torsion-effusion data by means of the equation

$$P = 2\,K\beta/(a_1d_1f_1 + a_2d_2f_2) \tag{1}$$

where P is the pressure; β the deflection; K the torsion constant of the suspension; a_1, a_2, d_1, and d_2 the orifice area and distances from the axis of rotation; and f_1 and f_2 the Freeman and Searcy *(1)* correction factor for orifice geometry.

The metals were vaporized from tantalum cells placed in the constant-temperature zone of the furnace. The samarium and ytterbium samples were from Koch-Light Lab certified to be at least 99% pure with respect to total impurities. The loading of the cell was carried out with samples (~1 gram) mechanically cleaned and reduced to small pieces (~2 mm) to increase the evaporating surface. Loading in inert atmosphere was not necessary *(4)*. An ambient vacuum less than 10^{-5} mm Hg was maintained during the runs. The temperature of the operating cell was taken to be the temperature determined by a calibrated iron-constantan thermocouple placed inside an identical but empty cell located directly beneath the operating cell. This procedure was tested putting a second thermocouple in the operating cell and measuring the differences in emf values. All the temperature uncertainties were estimated to be ±2°C at about 1200K. The effusion cell was suspended on a 30-μ diam tungsten wire, 33.0 cm long, with a torsion constant of 0.358 ± 0.004 dyn cm/rad. The details of the effusion cells are given as a footnote in Table I.

The vapor pressures of α-samarium and α-ytterbium, determined in the temperature range 1043–1179K and 775–907K, respectively, are reported in Table I, considering the vapor constituted by a monoatomic species only *(10)*. The corresponding values of $\Delta H_{298}°$ (subl) of both elements, calculated using the free energy function, $(G_T° - H_{298}°)/T$, (fef), selected by Hultgren et al. *(5)*, are reported in the same table. The average third-law $\Delta H_{298}°$ (subl) values for Sm and Yb are 49.60 ± 0.20 and 37.01 + 0.11 kcal/mol, respectively, where the associated errors are standard deviations. The least-squares lines through the pressure data over the experimental temperature range are given by the equations:

$$\log P\ (\text{atm}) = 5.33 \pm 0.19 - \frac{(10.39 \mp 0.21) \times 10^3}{T}, \text{ samarium} \tag{2}$$

$$\log P\ (\text{atm}) = 5.61 \pm 0.17 - \frac{(7.97 \mp 0.14) \times 10^3}{T}, \text{ ytterbium} \tag{3}$$

The lines are drawn in Figure 1 and the relative slopes give the sublimation enthalpy values, $\Delta H_{298}°$ (Sm) =

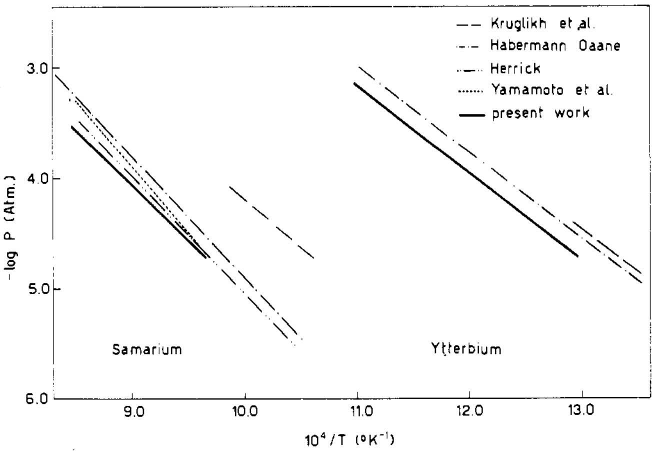

Figure 1. Vapor pressure of solid samarium and ytterbium

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