Table VII. Activity Coefficients for Carbon Dioxide in Alcohols at 25° C.

Solvent	α	X_2, Mole Fraction $\times 10^3$	$f_2^L X_2$	γ_2
Methanol	3837	6.36	0.311	3.22
Ethanol	2706	6.52	0.319	3.14
Propanol	2498	7.66	0.375	2.67
Isobutanol	1849	7.01	0.343	2.92
Pentanol	1831	8.10	0.396	2.52
Cyclohexanol	1017	4.42	0.216	4.62

the data. If either of these physical properties correctly represents the behavior of the solvent, it is possible to predict the solubility for an organic solvent, provided the solubilities in other homologs of similar chemical structure are known. In fact, the solubility of carbon dioxide in cyclohexanol corresponds to its extrapolated value in Figure 4. The solubility in ethanol is lower than expected and is attributed to the fact that the purity of this alcohol was only 97%. The solubility of carbon dioxide in water is much lower ($\alpha = 826$) than in alcohol, and it is very probable that the solubility in the pure alcohol would be greater than 2706 cc./liter.

The activity coefficient is the fundamental quantity of interest in studies of behavior of liquid mixtures. In Table VII, the activity coefficients are listed for carbon dioxide in the various alcohols. The activity coefficients at 25° C. were calculated by use of the following equation from Prausnitz and Shair.

$$\frac{1}{X_2} = \frac{f_2^L}{f_2^o}\gamma_2 \qquad (8)$$

Where

X_2 = mole fraction of solute
f_2^L = fugacity of the hypothetical liquid carbon dioxide at 1 atm. = 48.9 atm. at 25° C.
f_2^o = fugacity of the pure gas at 1 atm.
γ_2 = activity coefficient for the gas in solution

Although the activity coefficients for carbon dioxide in the straight chain alcohols appear to be a smooth function of molar volume, the values for isobutanol and cyclohexanol fall above the curve for the linear molecules. Therefore, it appears that the correlation of the solubility coefficient in this case would be preferred in an attempt to predict values for other solvents in a series of alcohols of straight chain, branched, or cylic structure.

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Physical Properties of Saturated Solutions of Magnesium Chloride in *n*-Propanol–Water

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DETERMINATIONS reported in this communication were conducted as part of a program of investigation of the effect of salt addition on vapor-liquid equilibrium data of binary systems.

Binary solutions of *n*-propanol–water of known concentrations were prepared. These solutions were introduced into flasks (capacity of about 17 ml.) containing sufficient weights of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) to assure saturation. All reagents used in this investigation were analytical grade ones. The *n*-propanol was the analytical grade manufactured by J.T. Baker Chemical Co. (boiling point: 97.2° C., boiling range: 0.8° C.). It was further purified by fractionation in a multiple plate still, the first 10% distilled and a 10% residue being discarded. The physical constants (density, refractive index, and boiling point) of the purified *n*-propanol agreed with data in the literature. The distilled water was obtained from a Barnstead laboratory distillation apparatus, and its specific conductivity was between 200,000 and 600,000 ohm-cm. The magnesium chloride was Fisher Chemical Co., Certified A.C.S. F.W. 203, actual lot analysis reported on label.

Table I. Properties of Saturated Solutions of Magnesium Chloride in *n*-Propanol–Water

Mole Fraction of *n*-Propanol (Salt-Free Basis)	Solubility, Grams of $MgCl_2 \cdot 6H_2O$ 100 Ml. Salt-Free Solvent (25° C.)	Density, Grams/Cm.^{3} (25° C.)	Refractive Index, $n_{\mathrm{D}}^{25^\circ}$
0.000	329.1	1.3343	1.4318[a]
0.074	263.9	1.2987	1.4318
0.138	211.3	1.2649	1.4302
0.265	150.6	1.1998	1.4266
0.360	120.7	1.1586	1.4243
0.491	90.46	1.1046	1.4210
0.577	73.02	1.0692	1.4187
0.685	58.13	1.0339	1.4162
0.762	53.17	1.0144	1.4151
0.821	46.98	0.9967	1.4135
0.922	42.08	0.9779	1.4130
1.000	39.79	0.9692	1.4129

[a] This figure is the refractive index of water (no salt). Because there is no salt in this case, this point does not plot on the same smooth curve as the rest of the data.

The flasks were sealed and thermostated for at least 24 hours and, in some cases, 2 to 3 days in a constant temperature bath (Sargent S-84805) which was maintained at 25 ± 0.01° C. The samples were frequently stirred. Samples of the saturated solutions were carefully withdrawn so as not to remove any of the precipitated salt. Two determinations were made at each concentration, the results being averaged.

Densities were determined by means of Weld-type pycnometer bottles. Refractive indices ($n_{\mathrm{D}}^{25^\circ}$) were determined by a Bausch and Lomb refractometer (BL 7762). All these determinations were conducted isothermally at 25 ± 0.01° C.

The salt solubilities were determined by titrating for the chloride according to Mohr's procedure. The salt is reported as $MgCl_2 \cdot 6H_2O$, since this is the stable form at 25° C. The data obtained are presented in Table I and plotted as smooth curves.

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Thermodynamic Properties of the Helium-Nitrogen System

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Thermodynamic properties of helium-nitrogen mixtures were calculated for eight compositions at 10° increments from 240° through 560° R. and over the pressure range from 14.7 through 7500 p.s.i.a. These properties included specific volume, enthalpy, entropy, internal energy, fugacity coefficient, Joule-Thomson coefficient, enthalpy of mixing, excess entropy of mixing, and isobaric specific heat. Sets of coefficients of an equation of state are presented for eight compositions.

THERMODYNAMIC properties of gases, as a function of temperature and pressure, can be determined from direct calorimetric measurements, from compressibility data plus ideal-gas specific heat data, or from Joule-Thomson coefficient data plus ideal-gas specific heat data. Joule-Thomson coefficients have been reported for helium-nitrogen mixtures by Roebuck (*18*) from −125° to 250° C. up to 200 atm., and work is in progress at the University of Michigan (*10*) on direct calorimetric measurements. The present paper reports the thermodynamic properties of helium-nitrogen mixtures from 240° to 560° R. at 14.7 to 7500 p.s.i.a. as calculated from compressibility data and ideal-gas specific heat data.

The results presented in this paper will be useful in future attempts to predict the thermodynamic properties of mixtures by the theory of corresponding states. A more immediate and practical application of the results will be in the design of efficient equipment for purifying crude helium.

The thermodynamic properties reported here were calculated by fitting experimental compressibility data to an especially developed equation of state. The least squares fit was performed using an orthogonalization scheme. Compressibility data for the helium-nitrogen system have been reported by many investigators (*3, 8, 9, 13, 14, 16, 20*); however, to restrict the upper temperature to 100° F. and because high pressure data were not available above 100° F., the data from three sources (*3, 8, 13*) were used in evaluating the coefficients of the equation of state.

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