Enthalpy Data for Polar Compounds

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BECAUSE OF electrical effects, the thermodynamic properties of polar compounds in the gas phase are not well predicted by conventional methods. The correlations of Hougen and Watson (3) and of Lydersen, Greenkorn, and Hougen (8) have no electrical parameter, thus they generally predict values too high for the compressibility factor, Z, and quantities too low for the enthalpy deviation from ideal gas behavior. McCracken and Smith (9) found that correlations (3) and (8) gave average errors of 28 and 18%, respectively, for the enthalpy deviations of methanol as compared with their experimental values. Similar comparisons for ethanol (15) suggested average errors of 32 and 31%, respectively.

In order to develop satisfactory prediction methods for polar substances, enthalpy data are needed for a large number of polar compounds over wide intervals of pressure and temperature. Also, information is desirable for organic compounds in groups other than the alcohols. For this reason, two ethers and two ketones were studied in this work, after first investigating the properties of 1-propanol to be used with the earlier results for methanol and ethanol. The gas-phase data given here have been used to formulate a correlation for polar organic compounds, which is presented elsewhere (2). The objective of this paper is to present enthalpy and entropy data obtained for these five substances.

SCOPE OF EXPERIMENTAL INVESTIGATION

The compounds studied were 1-propanol, ethyl ether, isopropyl ether (IPE), acetone, and methyl ethyl ketone (MEK). The vapor, two-phase, critical, and liquid regions were included. The ranges of conditions covered are as follows: 1-propanol, 50 to 900 p.s.i.a. and 300° to 540° F.; ethyl ether, 50 to 900 p.s.i.a. and 150° to 450° F.; IPE, 50 to 800 p.s.i.a. and 250° to 500° F.; acetone, 50 to 950 p.s.i.a. and 250° to 500° F.; MEK, 50 to 950 p.s.i.a. and 300° to 550° F.

Table I shows the critical constants and the dipole moment for the compounds studied and also for methanol and ethanol.

Purity of Chemicals. All chemicals used were of reagent grade.

BENZENE. Benzene (Merck and Co. Inc.) conformed to ACS reagent grade specifications and was thiophene-free. It had a maximum boiling range of 0.5° C. which included a temperature between 79.5° and 81.0° C.

1-PROPANOL. 1-Propanol (Eastman Kodak) had a boiling range of from 96° to 98° C. and purity of above 99%.

ETHYL ETHER. The ether (Matheson, Coleman, and Bell) had 0.05% of ethyl alcohol as its chief impurity. From the maximum impurities listed, the ether appeared to have a purity over 99.9%.

ISOPROPYL ETHER. Isopropyl ether (Fisher Scientific Co.) had a boiling point range of 67.8° to 69.0° C. and conformed to reagent grade ACS specification. If the impurities listed were the main ones, the purity was well over 99.0%.

ACETONE. Acetone (Baker Chemical Co.) had a boiling point range of 0.2° C. and a purity of 99.5%.

METHYL ETHYL KETONE. MEK or 2-butanone (Eastman Kodak Co.) had a boiling range of 79° to 80° C.

PREVIOUS WORK

The pressure-enthalpy diagrams (Figures 1 to 5) were prepared from measurements taken in this work with the exception of vapor pressure and heat capacity (in the ideal gas state) data taken from the literature. Vapor pressure values, which were available for all the compounds, gave the position of the tie-lines in the two-phase region at the various isotherm temperatures. The ideal gas state heat capacities of 1-propanol and ethyl ether were used to calculate ideal gas state enthalpies. Because the experimental apparatus used for measuring enthalpies could not be operated at pressures below 40 p.s.i.a., ideal gas state enthalpies were useful in extrapolating data down to zero pressure. Figures 1 and 2 show that the ideal gas state enthalpies at zero pressure are in agreement with experimental data.

For 1-propanol, Kobe and his coworkers (6) have published heat capacities in the ideal gas state from 77° to 700° F. Experimental vapor pressures of 1-propanol were taken from the work of Ramsey and Young (12).

The ideal gas state heat capacities (7) and the vapor pressure data (13) for ethyl ether have also been compiled in the Handbook of Chemistry and Physics. Kobe has published vapor pressures for IPE (5), acetone and MEK (4).

Table I. Physical Properties of Polar Compounds

Polar Compound	Critical Pressure, P.S.I.A.	Critical Temperature, ° R.	Dipole Moment, E.S.U.-Cm. $\times 10^{18}$
Methanol	1158	923	1.70
Ethanol	928	930	1.69
1-Propanol	732	967	1.68
Ether	522	841	1.15
IPE	417	900	1.13
Acetone	694	917	2.88
MEK	602	964	2.84

EXPERIMENTAL

The experimental method was the same as that described by McCracken and Smith (9), who presented detailed drawings and a complete description of the apparatus. Energy was transferred from the compound flowing through the center of a double-jacket calorimeter to boiling Freon-11. Measurement of the amount of Freon evaporated, determined the magnitude of the energy transfer. Refluxing Freon-11 was maintained in the annulus between the inner and outer can in order that the Freon in the inner can could be maintained at its atmospheric boiling point. This double jacket arrangement also insulated Freon-11, in the inner can, from the surroundings. The compound entered the calorimeter at some elevated temperature and left as a liquid near 77° F., the reference temperature for all the data. The change in enthalpy of the compound passing from the calorimeter inlet to outlet, ΔH_c, was calculated from a steady state energy balance across the calorimeter, neglecting kinetic and potential energy changes.

$$\Delta H_c = -L_f W_f / W_s \qquad (1)$$

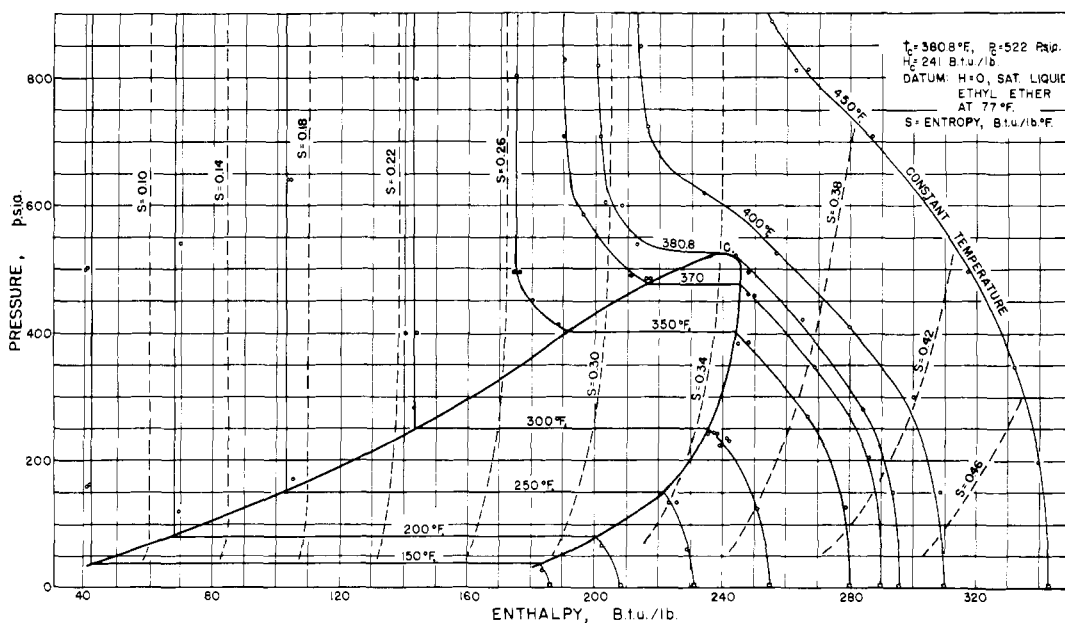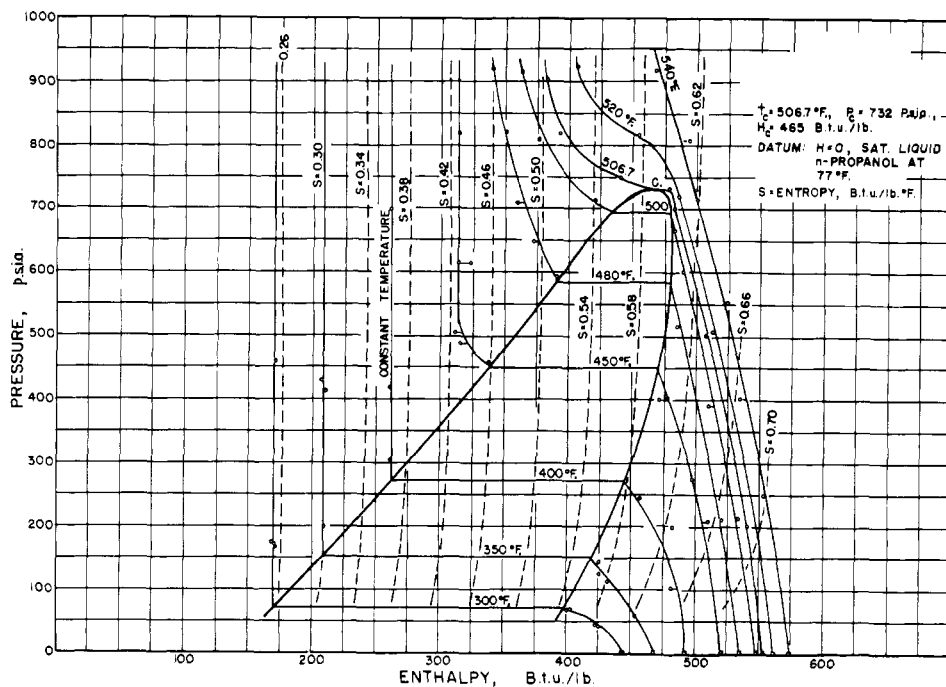Figure 1. Pressure-enthalpy
diagram of 1-propanol

Figure 2. Pressure-enthalpy
diagram of ethyl ether

Three corrections were made to values of ΔH_c in order to refer the enthalpies to the standard state of saturated liquid at 77° F. A small correction, Δh_1, was made for deviations of the actual inlet temperature from the desired isotherm temperatures. A similar correction, Δh_2, was necessary for deviations of the outlet temperature from the 77° F. reference temperature. Finally, the correlation of Watson (16) for the isothermal effect of pressure on liquid enthalpies, was employed to correct the enthalpy to the reference pressure. This correlation is based upon the law of corresponding states. Although this correction, Δh_3 never exceeded 2 B.t.u. per pound, it was necessary, since the actual outlet pressure at the calorimeter was only slightly below the inlet pressure and, therefore, usually considerably above the vapor pressure chosen for the reference state.

The corrected enthalpy at any state, H_1, based on the desired reference state is thus given as:

$$H_1 = L_f W_f / W_s + \Delta h_1 + \Delta h_2 + \Delta h_3 \qquad (2)$$

The data so obtained were immediately plotted on a large pressure-enthalpy diagram to insure against insufficient and faulty data. The curves were cross-plotted on temperature-entropy diagrams. Then, the chosen enthalpy values were obtained from the final, consistent P-H and T-S diagrams. The average deviation of experimental points from the final curves was 0.8%.

Entropy values were calculated, as a function of pressure and temperature, from experimental enthalpy data using the equation,

$$\Delta S = \int_{T_0}^{T_1} dH/T \qquad (3)$$

at constant pressure. In order to integrate Equation 3 graphically, plots of $1/T$ vs. H were prepared for different pressures. The entropy values obtained in this manner were also based on a reference state of saturated liquid at 77° F.
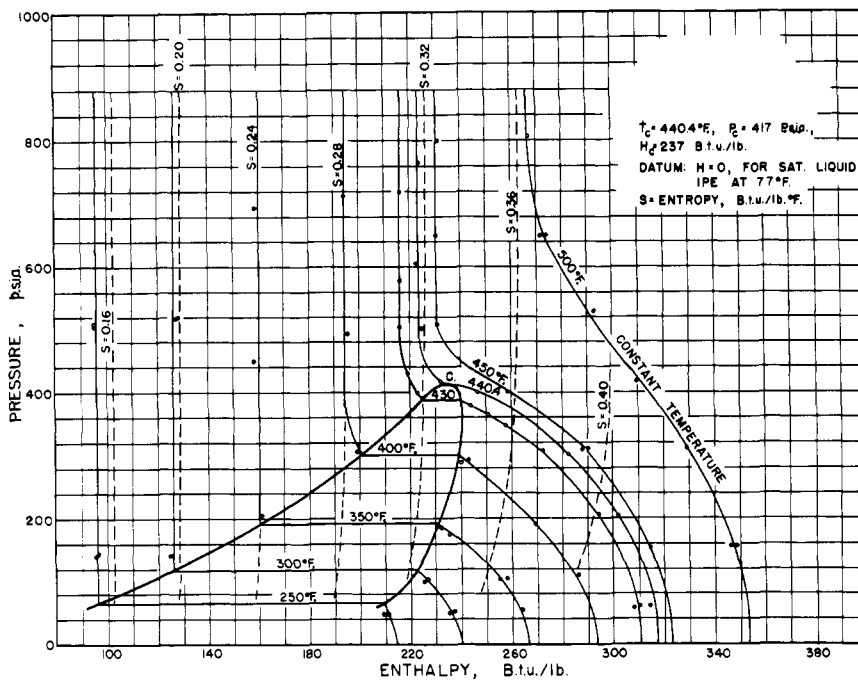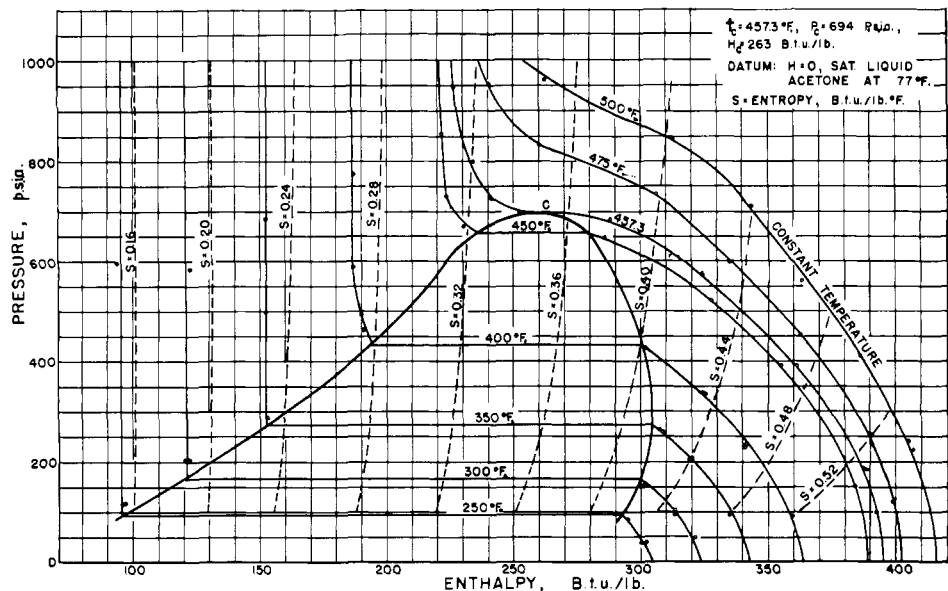
Figure 3. Pressure-enthalpy diagram of isopropyl ether

Figure 4. Pressure-enthalpy diagram of acetone

ACCURACY AND PRECISION

The accuracy of the apparatus was checked by measuring enthalpy values of benzene at two points, one in the liquid phase and the other in the gas phase. The first point was at 250° F. and about 160 p.s.i.a. The gas point was at 350° F. and 95.0 p.s.i.a. The available benzene data have been reviewed by Organick and Studhalter (*10*). Based on the reference state used here, values of 77.8 and 266.1 B.t.u. per pound were obtained for the two chosen, check points. The average of numerous experimental values at these two conditions was 77.7 and 269.7 B.t.u. per pound. On this basis it was possible to obtain an average accuracy of about 0.7% with the apparatus.

Multiple runs at the same conditions indicated an experimental precision of about 0.7%. These values for accuracy and precision are somewhat dependent on pressure and temperature. The latter were measured within 1 p.s.i.a. and 0.3° F.

Most of the experimental error was due to the sampling and weighing of the Freon-11 and the compound. Some heat from the surroundings, no doubt, leaked into the inner can of the calorimeter causing high readings. These errors, however, were not thought to be significant as compared to those due to sampling and weighing.

DIAGRAMS AND TABLES

Figures 1 to 5 show the smoothed *P-H* diagrams obtained for 1-propanol, ethyl ether, IPE, acetone, and MEK. The smoothed *T-S* diagrams have been presented elsewhere (*1*).

Tables II to X were prepared for the saturated and superheated properties of the compounds as read from the smoothed *P-H* and *T-S* diagrams, and are available from the American Documentation Institute.

In the liquid phase, there was little variation of enthalpy with pressure at isotherms well below the critical temperature as shown by Figures 1 to 5. At about 50 F. below the critical temperature, the isotherms start to bend towards the bubble point curve as they near it. This continues until the slope is zero for the critical isotherm at the critical point.

In the gas phase, electrical effects, such as dipole-dipole interaction, tend to pull the molecules together. This causes greater decreases in enthalpy as the pressure increases along a given isotherm than would be experienced by hydrocarbons of similar structure. The effect was not as pronounced at higher temperatures where molecules are not close enough together to be greatly influenced by electrical interactions.

Although no direct enthalpy measurements were found in the literature for the compounds investigated, P-V-T data for 1-propanol and ethyl ether exist. Using the relationship,

$$(\partial H/\partial P)_T = V - T(\partial V/T)_p \qquad (4)$$

the change of enthalpy with pressure at constant temperature can be computed. These values are added to the ideal gas state enthalpies calculated from heat capacity measurements. This gives the enthalpies in the vapor phase; liquid phase enthalpies are obtained by subtracting experimental heats of vaporization from dew points enthalpies to obtain the bubble point enthalpies.

The authors have calculated enthalpy values in this manner for 1-propanol from the P-V-T data of Ramsay and Young (11). Comparing 14 values of enthalpy at random in the gas phase, the calculated values were found to be an average of 4.3% greater than the experimental values; all calculated values were at least as great as the corresponding experimental values. Since these calculated values were outside the experimental error, it was assumed that the P-V-T data was not of an accuracy that would withstand differentiation and still maintain high accuracy.

Schnaible and Smith (14) have calculated enthalpy values from P-V-T data for ethyl ether. These values were compared with 26 experimental enthalpy values taken at random; an average absolute error of 2.1% was found.
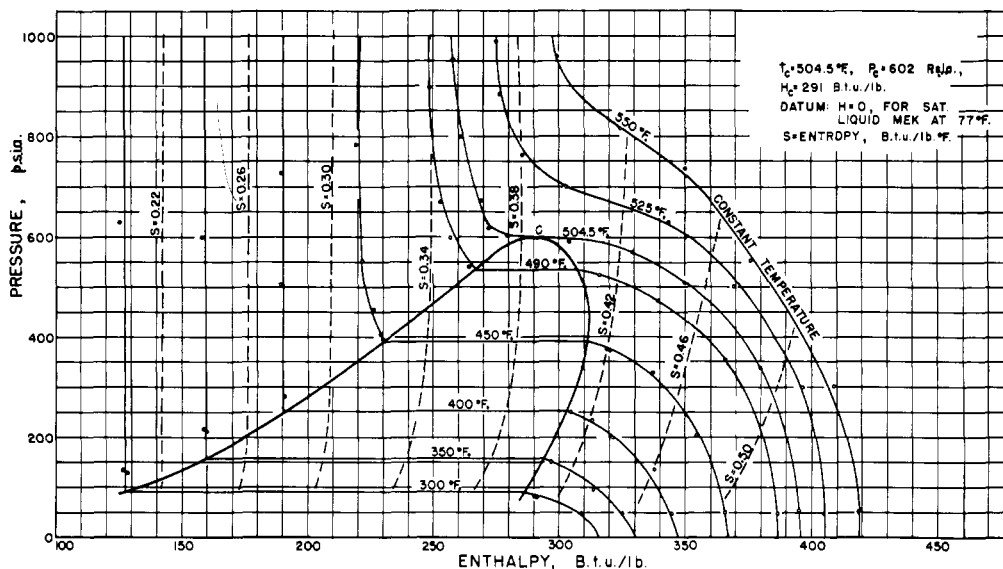

Figure 5. Pressure-enthalpy diagram of methyl ethyl ketone

Subscript

c = critical property; calorimeter in Equation 1
f = Freon-11
s = sample of compound
l = inlet to calorimeter

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NOMENCLATURE

Δh = enthalpy correction applied to data points
H = enthalpy at any pressure, smoothed enthalpy data
L = latent heat of vaporization
P = pressure
S = entropy at any pressure, smoothed entropy data
T = absolute temperature
V = specific volume
W = weight
Z = compressibility factor