# Thermodynamic Properties of Polar-nonpolar Mixtures: Methanol-benzene-hexane System

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Direct enthalpy measurements were carried out for the methanol-benzene system as a function of composition, temperature (250° to 500°F.), and pressure (30 to 1,400 lb./sq. in. abs.). From these data pressure-enthalpy diagrams were prepared to show the enthalpy and entropy above a reference state of saturated liquid at 77°F. Similar results were obtained for a single binary system of methanol and *n*-hexane and a single ternary mixture.

The conventional generalized correlations were not satisfactory for predicting vapor-phase enthalpies for mixtures involving methanol. A new method requiring a knowledge of the heat of dimerization, the equilibrium constant for the reaction, and the interaction constant, is proposed for such polar-nonpolar systems based upon association of the polar component.

The most striking feature of the data for mixtures was the large heat of mixing in the vapor phase for the systems containing methanol. The same type of equation found suitable for the heat of mixing in the vapor phase was applicable to the liquid data.

From the enthalpy data across the two-phase region, it was possible to predict a limited amount of information on the compositions of the liquid and vapor phases in equilibrium. An azeotrope exists in the methanol-benzene system, which at 325°F. contains 75 mole % methanol.

Energy-balance calculations constitute a basic part of process and plant design work. The thermodynamic information necessary for these calculations has been accumulating rapidly during the past two decades, but primarily for hydrocarbon systems. The similarity in structure of the components in such mixtures limits the deviation from ideal solutions in both the gas and liquid phases and probably has hastened the development of correlations and prediction methods for the required thermodynamic properties. In chemically dissimilar mixtures large deviations from ideal-solution behavior may be encountered, and neither adequate data nor satisfactory prediction procedures have appeared. The purpose of this paper is to present enthalpy data for the polar-nonpolar system methanol-benzene and to propose a method of correlating such information.

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## PREVIOUS WORK

While enthalpy data are available for many pure components, experimental information on mixtures over a range of temperatures and pressures is scarce, even for hydrocarbon systems. Nelson and Holcomb (*8*) and Schrader and Gilliland (*13*) report data for ternary and binary hydrocarbon mixtures. Sage, Lacey, and coworkers (*11*) have made several studies for the same type of mixtures. No enthalpy data that covered a range of temperatures and pressures were found for polar-nonpolar systems. Other measurements for the methanol-benzene-*n*-hexane system include the work of Kinoshita and Shimizu (*5*), who determined the *P-V* isotherms at 150°, 200°, 250°, and 300°C. for mixtures of benzene and methanol. Schnaible (*12*) has measured the heats of mixing of the benzene-methanol-*n*-hexane system at 25°C. and atmospheric pressure. Integral isobaric heats of vaporization have been measured (*15*) at atmospheric pressure for benzene-methanol mixtures.

## SCOPE OF THIS INVESTIGATION

Enthalpies were measured for pure methanol, pure benzene, and mixtures of 75, 50, and 25 mole % methanol in benzene. Data were also determined for a binary mixture of 10 mole % methanol and 90 mole % *n*-hexane and for a ternary system of 10 mole % methanol, 30 mole % benzene, and 60 mole % *n*-hexane. The results covered a temperature range of 250° to 500° F. at pressures of 30 to 1,400 lb./sq. in. Data were obtained in the critical region for all but the binary mixture of methanol and *n*-hexane.

The heat of mixing information of Schnaible (*12*) was used to refer all mixture enthalpies to the same basis as for the pure components; that is, the pure liquids at 77°F. and their vapor pressure. Entropies on this basis were computed from the enthalpy data. The results are presented in tabular form and

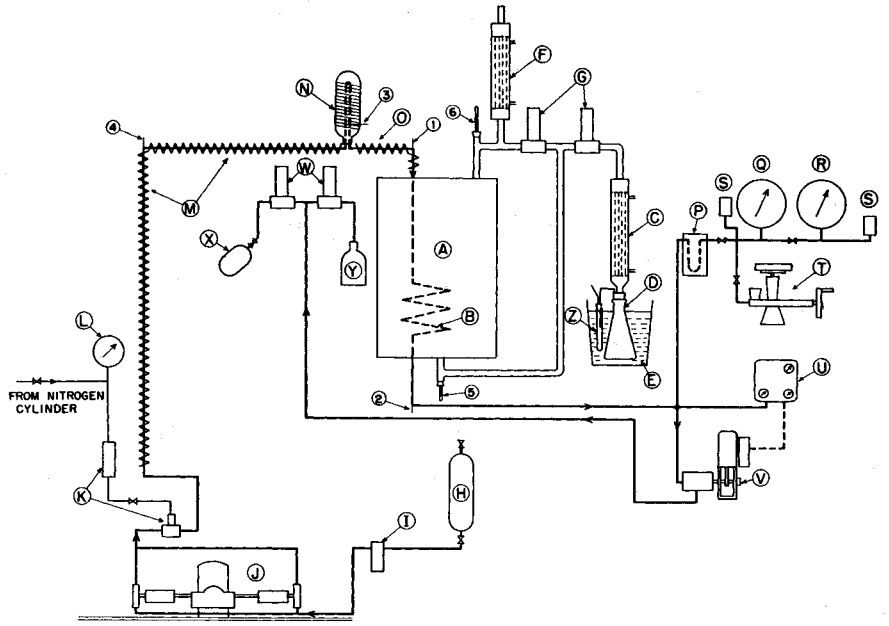


Fig. 1. Schematic equipment diagram.

*A*, calorimeter; *B*, mixture cooling and condensing coil; *C*, Freon sample condenser; *D*, Freon collection bottle; *E*, ice bath; *F*, Freon reflux condenser; *G*, solenoid valves for switching Freon stream; *H*, mixture feed tank; *I*, filter; *J*, mixture pump; *K*, surge tank; *L*, surge-tank pressure gauge; *M*, mixture preheater; *N*, temperature stabilizer; *O*, final temperature control heater; *P*, mercury-filled U tube; *Q*, Heise pressure gauge 3,000 lb.; *R*, Heise pressure gauge 1,000 lb.; *S*, rupture disk; *T*, dead-weight gauge tester; *U*, pressure controller; *V*, pressure control valve; *W*, solenoid valves for switching mixture streams; *X*, mixture sample receiving and weighing bomb; *Y*, mixture receiving bottle; *Z*, ice trap; 1, inlet thermocouple; 2, outlet thermocouple; 3, temperature-stabilizer thermocouple; 4, preheater thermocouple; 5, Freon outlet thermometer; 6, Freon return thermometer.

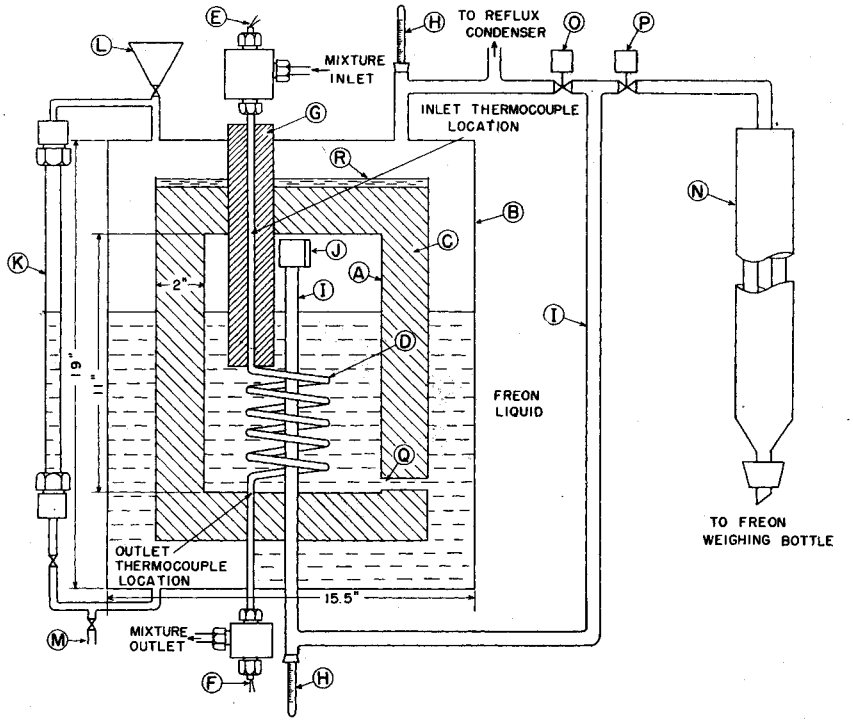


Fig. 2. Calorimeter.

*A*, inner calorimeter can; *B*, outer calorimeter can; *C*, insulation; *D*, fluid cooling and condensing coil; *E*, inlet thermocouple leads; *F*, outlet thermocouple leads; *G*, cork insulation; *H*, thermometers; *I*, Freon-vapor-removal line; *J*, Freon-vapor-entrainment separator; *K*, glass Freon-level indicator; *L*, Freon-liquid-return funnel; *M*, Freon drain; *N*, Freon-sample condenser; *O*, normally open solenoid valve; *P*, normally closed solenoid valve; *Q*, port connecting inner and outer cans; *R*, Freon liquid pool on top of inner can.

on pressure-enthalpy diagrams with lines of constant entropy.

## EXPERIMENTAL

The experimental method was the same as that used by Nelson and Holcomb (*8*) and involved measuring the energy transferred from the mixture as it flowed through a calorimeter containing boiling Freon 11 in the jacket. A knowledge of the latent heat and the weight of Freon evaporated permitted the calculation of the change in enthalpy between the states at the inlet and outlet of the calorimeter. In all cases the fluid leaving the calorimeter had been cooled to within 1°F. of the boiling point of Freon (75°F.). At this temperature the exit stream was liquid, regardless of the pressure. Measurements indicated that the pressure drop through the calorimeter was negligible.

Figure 1 is a schematic diagram of the entire apparatus. The flow through the system was as follows. The mixture left the feed tank *H*, passed through filter *I* and into pump *J*, which operated at elevated pressures, forcing the fluid through surge tank *K* and into preheater *M*. The hot fluid leaving the preheater passed through a temperature stabilizer *N* and a final heater *O* and into the calorimeter inlet. The inlet temperature was measured at thermocouple 1 before the fluid was cooled in coil *B*. Before the fluid left the calorimeter, the outlet temperature was measured with thermocouple 2 and the pressure with gauges *Q* and *R*. The mixture then passed through the control valve *V*, where the pressure was reduced to atmospheric. Finally the fluid passed through the solenoid valves *W* and into either the sample-collecting and -weighing bomb *X* or the receiving bottle *Y*. The Freon which was vaporized by the heat received from the cooling mixture passed out the line at the bottom of the calorimeter and into condenser *F* or *C*.

When a run was in progress, the mixture entered the weighing bomb *X* and the Freon went to condenser *C* and into the collection bottle *D*. When a run was not in progress, the Freon went to condenser *F* and was returned to the calorimeter. The liquid mixture was collected in the receiving bottle and eventually returned to the feed tank.

Figure 2 is a detailed sketch of the calorimeter. It consisted essentially of an outer can *B* and an inner can *A*, separated by a 2-in. thickness of insulation. The cans were interconnected near the bottom through a liquid port *Q*. The inner can contained the cooling and condensing coil, which was constructed of stainless steel tubing of length sufficient to cool the fluid to approximately the temperature of the boiling Freon.

Freon filled both cans and was free to flow from one to another through the bottom port. The spaces above the liquid were sealed from one another so that the vapor evaporated by the mixture in coil *D* had to leave through pipe *I* and hence to the Freon-weighing bottle.

The calorimeter was designed to maintain boiling Freon in both the inner and outer cans in order to approach adiabatic operation. As an insurance against slight tem-

perature differences, a 2-in. thickness of insulation was installed between the two cans. To reduce heat losses from the entering stream, the inlet-mixture tube was insulated with cork to a level below the top of the Freon liquid. A pool of boiling Freon was maintained on top of the inner can to minimize the flow of heat to the calorimeter from the vapor space in the outer can. Tests with no fluid flowing through the calorimeter indicated the absence of measurable amounts of energy entering the inner can. These tests were carried out at room temperatures as high as 95°F., which is 20°F. above the boiling point of Freon.

Temperatures were measured by use of copper-constantan thermocouples installed in thermowells placed coaxially in the flowing mixture at the locations indicated in Figure 2.

The pressure measurements were made with Heise Bourdon pressure gauges, which were calibrated frequently with a deadweight gauge tester. All pressures were reported to the nearest 1 lb./sq. in.

The mixture and Freon samples were weighed on a torsion balance with a precision of 0.1 g.

### PURITY OF CHEMICALS

The methanol used was described by the Commercial Solvents Corporation as follows: purity: 99.85 wt. %, Maximum boiling range: 1.5°C., including 64.5°C. The benzene was stated to be thiophene free and to conform to A.C.S. specifications for reagent grade. The boiling range was 0.5°C. and included 79.5°C. Normal hexane, purchased from Phillips Petroleum Corporation, was guaranteed to contain 99 mole % *n*-hexane. Estimated impurities were six carbon atom hydrocarbons. Matheson Corporation Freon 11 contained not less than 99.99 wt. % trichloro-fluoromethane.

### CALCULATIONS

Neglecting kinetic and potential energy changes, one finds the energy balance over the calorimeter to be

$$\Delta H_c = \frac{-L_f W_f}{W_m} \qquad (1)$$

To convert the values of $\Delta H$ from Equation (1) to enthalpies referred to the chosen standard state, the following corrections must be considered.

#### 1. Entrance and Exit Temperature Deviations

A correction was made to account for the fact that the actual outlet temperature was not exactly at the datum temperature. In all instances this correction, $\Delta h_2$, amounted to about 1 B.t.u./lb. Similarly, small corrections, $\Delta h_1$, were made to account for inlet temperatures different from the desired value.

#### 2. Effect of Pressure upon Enthalpy of Liquid at 77°F.

Hougen and Watson (*3*) present a generalized correlation for determining the change of enthalpy with pressure for a liquid. Calculations for this system indicated the change in enthalpy between an elevated pressure and the vapor pressure at a constant temperature of 77°F. to be negligible, an indication that the enthalpy of the exit stream at the run pressure was equal to that at the vapor pressure at 77°F.

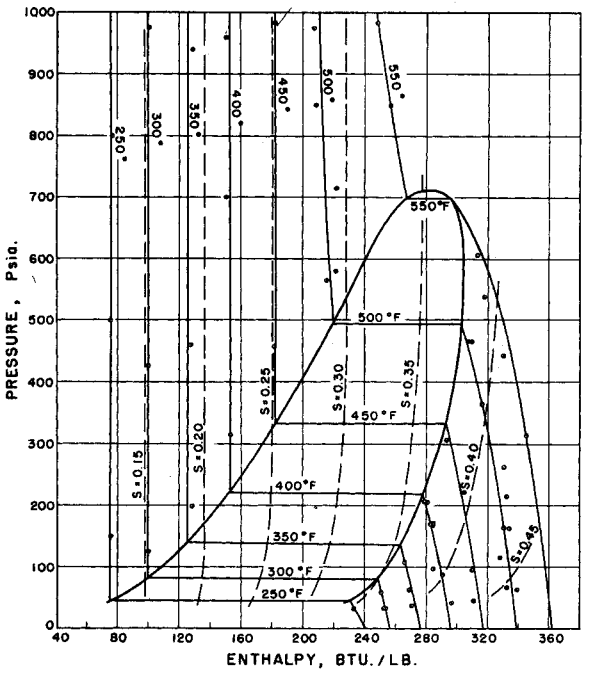


Fig. 3. Pressure-enthalpy diagram, benzene; datum: $H = 0$ and $S = 0$; liquid benzene at 77°F.

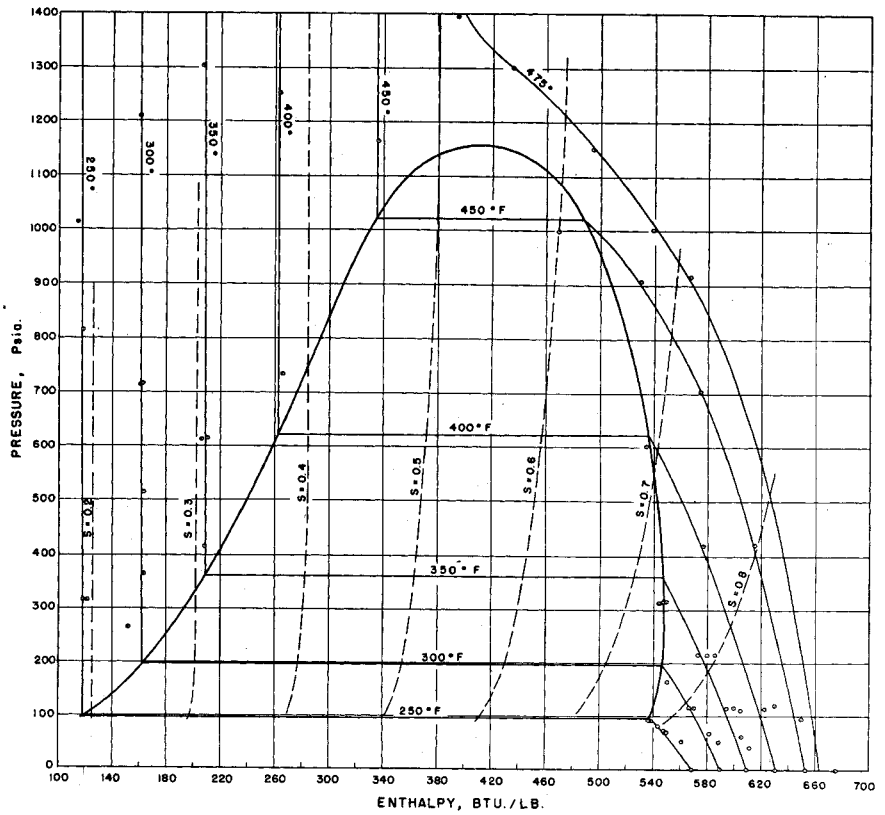


Fig. 4. Pressure-enthalpy diagram, methanol; datum: $H = 0$ and $S = 0$; liquid at 77°F.

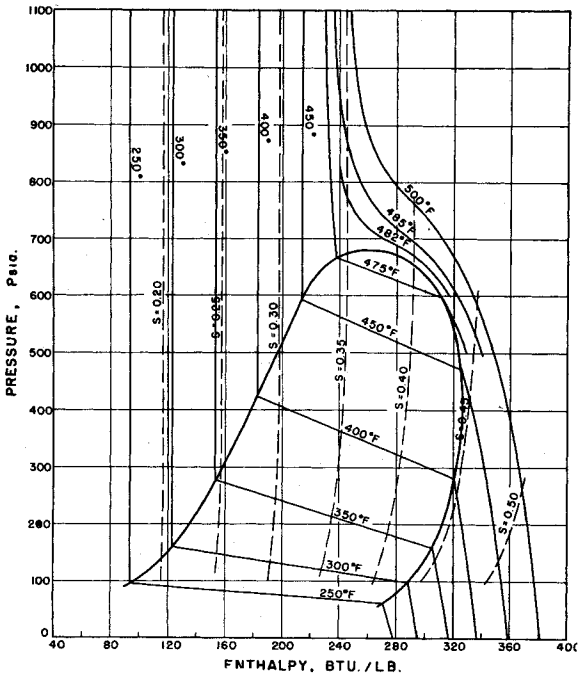


**Fig. 5. Pressure-enthalpy diagram, mixture: 25 mole % methanol; 75 mole % benzene; datum: $H = 0$ and $S = 0$; pure liquid components at 77°F.**

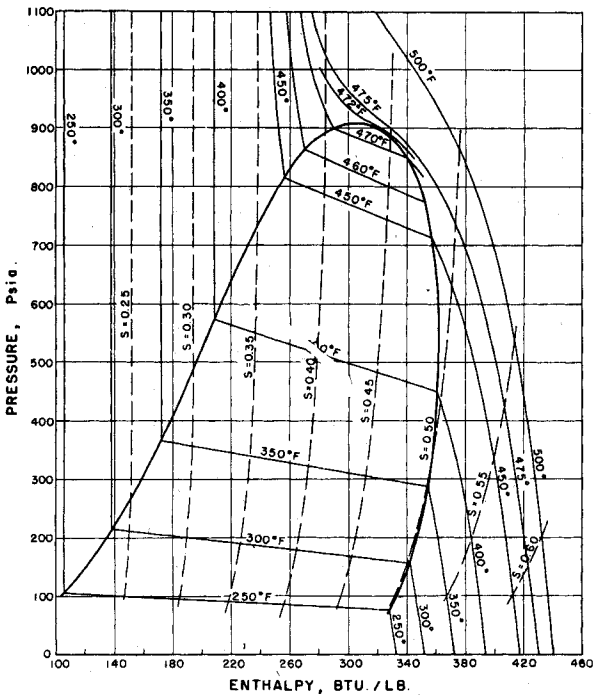


**Fig. 6. Pressure-enthalpy diagram, mixture: 50 mole % methanol; 50 mole % benzene; datum: $H = 0$ and $S = 0$; pure liquid components at 77°F.**

### 3. Heat of Mixing

The enthalpy of the exit stream corrected to 77°F. and the vapor pressure according to 1 and 2 is related to the pure component enthalpies by the heat of mixing at 77°F., $\Delta H_m{}^0$.

$$H^0 - \sum X_i H_i{}^0 = \Delta H_m{}^0 \quad (2)$$

The superscript zero identifies the datum state and the subscript refers to pure component $i$. The enthalpy of the mixture at the datum state is $H^0$. The summation of $X_i H_i{}^0$ is zero.

When the corrections described in 1 and 3 are combined, the enthalpy $H_1$ of the mixture at any state, referred to the pure liquids at 77°F., is

$$H_1 = \frac{L_f W_f}{W_m} + \Delta h_1 + \Delta h_2 + \Delta H_m{}^0 \quad (3)$$

The most convenient way to operate the equipment was to run at a constant inlet temperature and to vary the pressure for each run. A series of runs at constant temperature but at many different pressures would then represent an isotherm on a pressure-enthalpy diagram. If the isotherm were below the critical temperature, three distinct curves would be obtained—one in each of the liquid, two-phase, and vapor regions. The intersections of the curves represented points on the phase envelope. Thus a series of isotherms determined the phase envelope. Figures 3 to 8 show the results on pressure-enthalpy diagrams, and Tables 1 through 6 present the smoothed enthalpies in tabular form.*

## PRECISION OF RESULTS

No direct measurements of enthalpy were available for comparison with the data on mixtures. However, the results for pure benzene were compared with enthalpies calculated by Organick and Studhalter (*9*) from *P-V-T* data fitted to an equation of state. The standard deviation of the experimental data with respect to the computed values (*9*) was 3.9 B.t.u./lb. The comparison of the experimental enthalpies for methanol with those computed by Smith (*14*) from *P-V-T* data was good for the lower isotherms but poor for the higher isotherms. For the 250° and 300°F. isotherms only, the standard deviation was 3.0 B.t.u./lb. In view of the inaccuracies introduced in computing enthalpies from volumetric data, these deviations are not excessive.

The maximum sources of error in the experimental work, assignable to various causes, are as follows:

| Source | Maximum error, B.t.u./lb. |
|---|---|
| Temperature measurement | 1.0 |
| Pressure measurement | 0.5 |
| Freon collection and weighing | 0.2–1.0 |
| Sample collection and weighing | 1.0–6.0 |
| | 2.7–8.5 |

The high value in the range of maximum error due to sample collection corresponds to runs with pure methanol for which the enthalpy of the vapor is relatively high. For the mixture data and for pure benzene, the maximum total error should approach the lower figure of 2.7 B.t.u./lb.

*Tabular material (Tables 1 to 6) has been deposited as document 5051 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

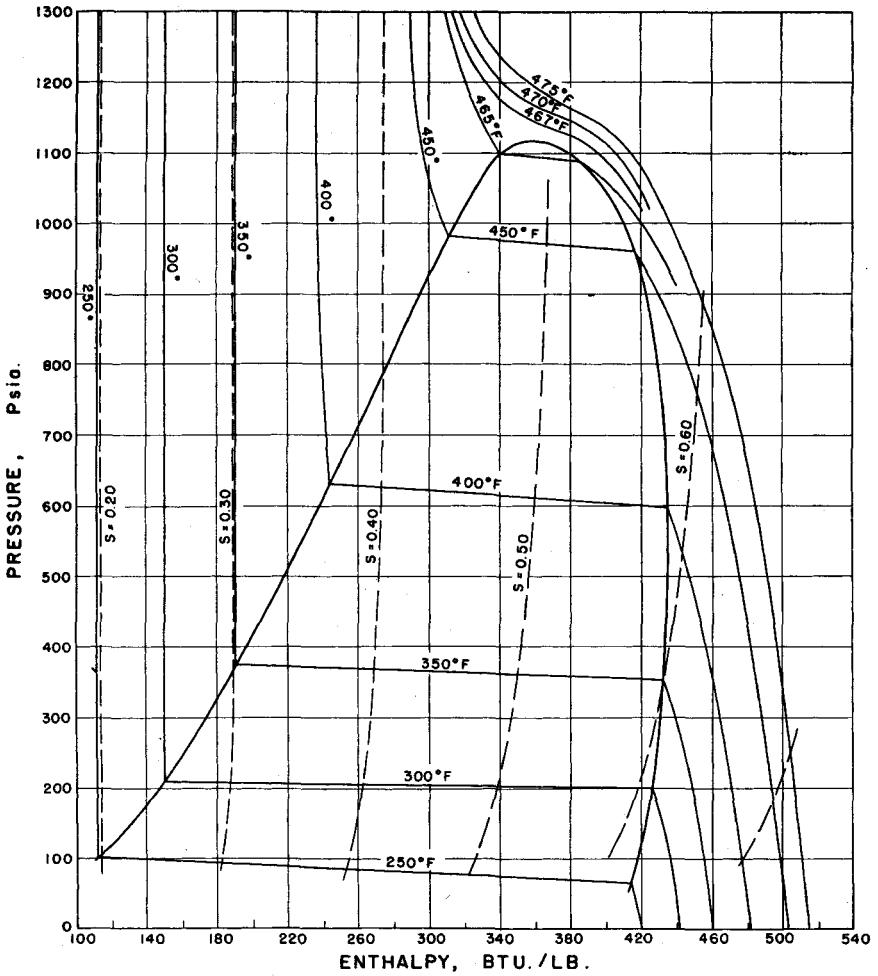


Fig. 7. Pressure-enthalpy diagram, mixture: 75 mole % methanol, 25 mole % benzene; datum: $H = 0$ and $S = 0$; pure liquid components at 77°F.

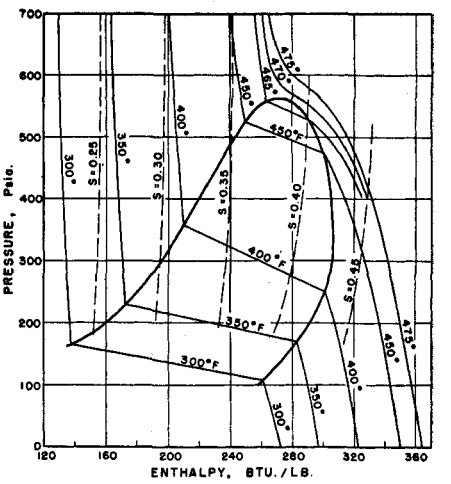


Fig. 8. Pressure-enthalpy diagram, mixture: 10 mole % methanol, 30 mole % benzene, 60 mole % *n*-hexane; datum: $H = 0$ and $S = 0$; pure liquid components at 77°F.

#### ENTROPY CALCULATIONS

Entropies were calculated from the experimental enthalpies according to the following equation, applied at constant pressure,

$$dS = \frac{dH}{T} \qquad (4)$$

The correlations of Hougen and Watson (*3*) permitted an estimation of the effect of pressure on the entropy of the liquid at 77°F. This was found to be within the experimental error and was neglected.

The entropies obtained from Equation (4) will not include the effect of mixing. The true entropy of the mixture is related to the entropy of mixing of the liquid at 77°F., $\Delta S^0$, and Equation (4) by the expression

$$S - \sum_i X_i S_i^{\,0} = \Delta S^0 + \int_{537^\circ\text{R.}}^{T} \frac{dH}{T} \qquad (5)$$

where $S$ represents the entropy of the mixture and $i$ designates a pure component.

The entropy of mixing is defined, as

$$\Delta S^0 = S_m^{\,0} - \sum X_i S_i^{\,0} \qquad (6)$$

This same type of equation may be written for a state in the gaseous region, where the deviations from ideality are small.

$$\Delta S^+ = S_m^{\,+} - \sum X_i S_i^{\,+} \qquad (7)$$

This gaseous state, designated by the cross, should be taken at the lowest pressure and highest temperature for which enthalpy data were available in order to minimize the value of $\Delta S^+$. Subtracting Equation (7) from Equation (6) gives

$$\Delta S^0 = \Delta S^+ - (S_m^{\,+} - S_m^{\,0}) + \sum X_i (S_i - S_i^{\,0}) \qquad (8)$$

The terms $(S_m^{\,+} - S_m^{\,0})$ and $(S_i - S_i^{\,0})$ can be obtained by integration of Equation (4) by use of the mixture and pure-component enthalpy data.

The value of $\Delta S^+$ may be estimated by an equation of state valid at low pressures:

$$PV = RT - \frac{AP}{RT} \qquad (9)$$

in which the constant $A$ is independent of pressure and determined for each temperature. Combining Equation (9) with the conventional thermodynamic equations for the effect of pressure on enthalpy and entropy leads to the following expression for the entropy of mixing in the near-ideal gaseous state:

$$\Delta S^+ = -R \sum_i X_i \ln X_i + \frac{P^+}{2T^+}\left[\left(\frac{\partial H}{\partial P}\right)_{T^+} - \sum_i X_i \left(\frac{\partial H_i}{\partial P}\right)\right]_{T^+} \qquad (10)$$

Thus, from the slope of the isotherm, $(\partial H/\partial P)_T$, on the pressure-enthalpy diagram, it is possible to calculate the entropy of mixing at 77°F. in the liquid state by use of Equations (10) and (8). This value of $\Delta S^0$ was then used in Equation (5) to determine entropies of the mixtures relative to the pure-liquid components. The gaseous mixing state was chosen as $P^+ = 100$ lb./sq. in. abs. and $t^+ = 450$°F. for the binary mixtures and 200 lb./sq. in abs. and 475°F. for the ternary mixture.

The final results are listed in Tables 1 to 6.* Lines of constant entropy are given on Figures 3 to 8.

#### PHASE EQUILIBRIA

The discontinuities in the isotherms on the pressure-enthalpy diagrams (Figures 3 to 8) represent points of equilibrium between liquid and vapor. Plotted on a *P-T* diagram, these points determine the phase envelope shown in Figure 9.

The intersection of the bubble-point portion of one envelope with the dew-point section of another represents a point of equilibrium between the vapor

*See footnote on page 501.

and liquid compositions corresponding to the two envelopes. For example, Point A on Figure 9 gives the temperature and pressure at which a liquid of 25 mole % methanol and a vapor of 50 mole % methanol are in equilibrium. Table 7 lists the phase equilibria obtained in this manner.

TABLE 7. VAPOR-LIQUID EQUILIBRIUM COMPOSITION

| Temperature, °F. | Pressure, lb./sq. in. abs. | % Methanol in benzene | |
|---|---|---|---|
| | | Liquid | Vapor |
| 319 | 205 | 25 | 50 |
| 325 | 270 | 75 | 75 |
| 375 | 477 | 50 | 75 |

The phase envelope for a mixture of 75 mole % methanol is of special interest. The bubble- and dew-point curves converge to a point and then diverge, indicating an azeotrope of this composition at 325°F.

#### ENTHALPY OF PURE COMPONENTS (VAPOR PHASE)

Several generalized correlations have been developed for predicting the effect of pressure on the enthalpy of pure substances. The experimental data were compared with three of these: Hougen and Watson (*3*), Edmister (*1, 2*), and Lydersen, Greenkorn, and Hougen (*7*). These correlations all present the difference between the actual enthalpy and that of an ideal gas at the same temperature divided by the critical temperature as a function of the reduced temperature and pressure. The first two methods give this information on charts; Lydersen et al. (*7*) list values in tabular form. In addition to the reduced temperature and pressure, the latter tables include a third parameter, $Z_c$, the compressibility factor at the critical point.

Table 8 shows the percentage errors for benzene with the various methods. Table 9 gives the same information for methanol.

The comparison for benzene is as good as can be expected for correlations of this type, except in the third case. The best agreement is obtained with Edmister's method, which is based on a residual volume correlation of $P$-$V$-$T$ data. The results for methanol are poor for all methods, although the Lydersen, Greenkorn, and Hougen tables gave the best results. The generalized correlations are prepared from calculations involving a generalized equation of state. These calculations require differentiation of the equation of state and hence magnify the error introduced by fitting the $P$-$V$-$T$ data to a generalized equation.

The poor comparison for methanol is not unexpested, as it is a polar molecule. For such cases association has been frequently used to explain the abnormal behavior. This concept is applied here to account for the enthalpy results for methanol.

Lambert and co-workers (*6*) experimentally determined second virial coefficients for a large number of polar and nonpolar gases. They were able to predict the virial coefficient of the nonpolar compounds, but large discrepancies were noted between the predicted and experimental values for polar substances. The predicted coefficients were calculated from the Berthelot equation and the critical temperature and pressure of the fluid. The poor agreement for polar compounds was satisfactorily explained by assuming that dimerization occurred to

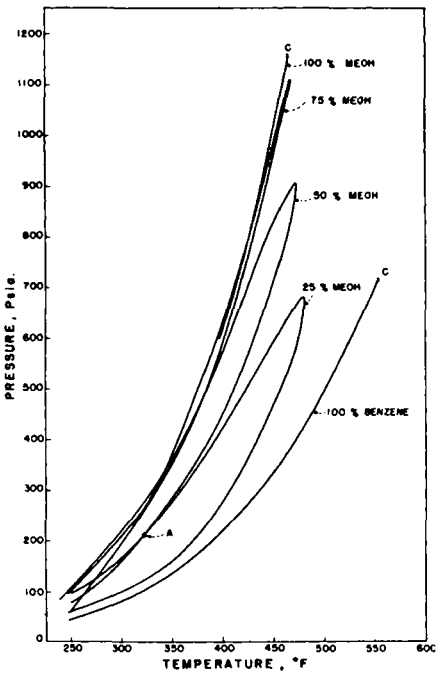


**Fig. 9. Pressure-temperature diagram, methanol-benzene system.**

an appreciable extent, according to the reaction:

$$2A = A_2$$

The same authors derived an equation similar to

$$B_e = B - KRT \qquad (11)$$

where $K$ = equilibrium constant for the dimerization in terms of partial pressures

$$K = \frac{P_{A_2}}{P_A^2}$$

The essential assumption involved was that the degree of dimerization was small. Equation (11) suggests that the effect of dimerization can be superimposed on the effect normally expected for forces between molecules. If the same reasoning is applied to the enthalpy of a polar molecule, the following expression can be developed:

$$\Delta H_T = \Delta H_s + \Delta H' \qquad (12)$$

If $\Delta H_0$ is the heat of dimerization for 1 mole of dimer, and $\alpha$ the number of moles of dimer per mole of mixture, considered as monomer, then

$$\Delta H' = \alpha \Delta H_0 \qquad (13)$$

If, for the purpose of evaluating $\alpha$, it is assumed that $\alpha$ is small and that the gas mixture is ideal, the equilibrium constant is

$$K = \frac{\alpha}{P} \qquad (14)$$

Substituting this result into Equation (13) gives

$$\Delta H' = KP\Delta H_0 \qquad (15)$$

The relation between the heat of dimerization and the equilibrium constant is

$$\frac{d \ln K}{dT} = \frac{\Delta H_0}{RT^2} \qquad (16)$$

If $\Delta H_0$ is assumed to be independent of temperature, this may be integrated to give

$$\log_{10} K = -\frac{\Delta H_0}{2.3RT} + C \qquad (17)$$

Thus if $\Delta H_0$ and $C$ are known, Equations (17), (15), and (12) may be used to calculate the actual enthalpy of the polar gas.

Values of $\Delta H'$ were calculated from Equation (12) by use of the experimental data to determine $\Delta H_T$. The term $\Delta H_s$ was established from the generalized correlations of Lydersen et al. (*7*) by using $Z_c = 0.222$ and the critical point of methanol. These results for $\Delta H'$ were then used to calculate the following values for the constants in Equation (17):

$$\Delta H_0 = -17{,}000 \text{ B.t.u./lb.-mole}$$

$$C = -8.79$$

Figure 10 compares the observed values of $\Delta H'$ with those obtained using the preceding numbers for $\Delta H_0$ and $C_1$. The last column of Table 9 shows that the average error was reduced from 18 to 6.6% by taking association into account by this method. The 6.6% error is approximately that predicted for nonpolar gases by the generalized correlations (benzene results, Table 8).

Lambert et al. (*6*) found the heat of dimerization to vary from −5,800 to −13,000 B.t.u./lb.-mole between 40° and 140°C. Pauling (*10*) gave the bond energies of the O—H . . . O bond in the association of methanol as 11,000 B.t.u./lb.-mole. These values compare with −17,000 B.t.u./lb.-mole obtained in this investigation.

#### ENTHALPY OF GASEOUS MIXTURES

The most striking feature of the mixture data is the large heat of mixing

Table 8. Differences Between Predicted and Experimental Enthalpy Deviations from the Ideal-gas Values

Benzene

| Temperature, °F. | Pressure, lb./sq. in. abs. | % Error (3) | (2) | (7) $Z_c = 0.27$ |
|---|---|---|---|---|
| 300 | 50 | +10 | −16 | −31 |
| 350 | 50 | +20 | 0 | −13 |
| | 100 | +12 | − 7 | −20 |
| 400 | 100 | + 7 | − 5 | −14 |
| | 200 | + 7 | −10 | −18 |
| 450 | 100 | + 9 | 0 | − 6 |
| | 200 | + 9 | 0 | − 5 |
| | 300 | + 6 | − 6 | −14 |
| 500 | 100 | + 2 | − 2 | − 7 |
| | 200 | − 1 | − 9 | −10 |
| | 300 | + 3 | −11 | −14 |
| | 400 | + 5 | − 9 | −17 |
| 550 | 100 | − 3 | − 6 | − 6 |
| | 200 | − 4 | − 9 | − 9 |
| | 300 | − 8 | − 4 | −12 |
| | 400 | −11 | −17 | −14 |
| | 500 | −10 | −10 | −14 |
| | 600 | − 9 | − 6 | −12 |
| | 700 | −14 | − 4 | − 4 |
| Average error* | | 7.9% | 6.9% | 12.6% |

*Average error disregarding sign.

Table 9. Differences Between Predicted and Experimental Enthalpy Deviations from the Ideal-gas Values

Methanol

| Temperature, | Pressure, | % Error (3) | (2) | (7) $Z_c = 0.222$ | Assoc.* |
|---|---|---|---|---|---|
| 250 | 50 | −49 | −59 | −41 | + 8 |
| | 80 | −53 | −54 | −43 | + 2 |
| 300 | 50 | −33 | −40 | −23 | +11 |
| | 100 | −38 | −24 | −30 | + 2 |
| | 150 | −52 | −23 | −32 | − 3 |
| 350 | 100 | −23 | −33 | −21 | 0 |
| | 200 | −36 | −39 | −22 | − 5 |
| | 300 | −44 | −39 | −20 | − 4 |
| 400 | 100 | −28 | −27 | −24 | − 7 |
| | 200 | −31 | −30 | −23 | − 7 |
| | 300 | −34 | −34 | −23 | −10 |
| | 400 | −24 | −37 | −24 | −11 |
| | 500 | −29 | −35 | −24 | −14 |
| | 600 | −29 | −34 | −22 | −11 |
| 450 | 100 | −21 | −18 | −18 | − 8 |
| | 300 | −24 | −23 | −12 | 0 |
| | 500 | −18 | −21 | − 6 | + 5 |
| | 700 | −15 | −23 | − 8 | + 1 |
| | 900 | −26 | −31 | −10 | − 3 |
| | 1000 | −25 | −25 | − 2 | + 4 |
| 475 | 100 | −13 | −13 | −17 | − 5 |
| | 300 | −10 | − 7 | − 6 | + 6 |
| | 500 | −14 | − 6 | + 2 | +10 |
| | 700 | −17 | −17 | − 2 | +11 |
| | 900 | −25 | −22 | − 6 | + 4 |
| | 1100 | −32 | −28 | −17 | −11 |
| | 1300 | −11 | − 8 | + 9 | +14 |
| Average error† | | 28% | 28% | 18% | 6.6% |

*Calculated, considering association in conjunction with method of Lydersen, Greenkorn, and Hougen (7).
†Average error disregarding sign.

observed in the vapor phase. The enthalpy deviation vs. composition data shown in Figures 13, 14, and 15 illustrate the extent of deviation from ideal-solution behavior. These results suggest that the conventional correlations developed for hydrocarbons are not suitable for mixtures containing polar components such as methanol, a conclusion borne out by the data of Table 10, in which the expermental data are compared with the correlations of Edmister and Hougen and Watson, by means of both the true critical point and the pseudocritical concept introduced by Kay (4). From its definition, the pseudocritical point will always be proportionally located between the critical points of the components of the mixture. Reference to Figure 9 shows that for the methanol-benzene system, such pseudocritical points will always be at a higher temperature and pressure than the true critical point. Therefore, the use of a pseudocritical concept leads to a large error for systems of this type. A more plausible correlation method is one which would take into account the significant heats of mixing.

The heat of mixing $\Delta H_m$ is related to the enthalpy $H$ of the mixture and the pure components $H_i$ by the equation

$$H = \Delta H_m + \sum_i X_i H_i \quad (18)$$

Subtracting the ideal-gas enthalpy from each side of Equation (18) results in

$$\Delta H = \Delta H_m + \sum_i X_i \Delta H_i \quad (19)$$

where $\Delta H$ and $\Delta H_i$ are the enthalpy differences between the actual and ideal-gas state for the mixture and pure components, respectively. The determination of the enthalpy of a mixture is, thus, reduced to determining the heat of mixing, provided the enthalpy of the pure components can be estimated.

Preliminary calculations indicated that a one-constant equation could adequately represent the heat of mixing in the vapor region. Such an equation for a binary system is

$$\frac{\Delta H_m}{X_1 X_2} = W_0 \quad (20)$$

This equation has been derived from statistical mechanics where $W_0$ was called the exchange energy.

Letting

$$W_0 = 2\Delta H_{12} - \Delta H_1 - \Delta H_2 \quad (21)$$

and applying Equation (19) to a binary system leads to the form

$$\Delta H = X_1^2 \Delta H_1 + 2X_1 X_2 \Delta H_{12} + X_2^2 \Delta H_2 \quad (22)$$

The quantity $\Delta H_{12}$ may be considered the energy of interaction between molecule 1 and molecule 2. It is independent of

composition, but a function of the temperature and pressure.

Equation (22) may be applied in a binary mixture where one component associates. $\Delta H_1$ and $\Delta H_2$ are the values of the actual enthalpy deviations from the ideal gas state for the pure components. For an associating component $\Delta H_2$, for example, would be given by Equations (12) and (15), which may be combined into the form

$$\Delta H_{T_2} = \Delta H_{g_2} + K_2 P \Delta H_{0_2} \quad (23)$$

Introducing this expression into Equation (22) for component 2 gives

$$\Delta H = X_1^2 \Delta H_1 + 2X_1X_2\Delta H_{12} + X_2^2 \Delta H_{g_2} + X_2^2 KP\Delta H_{0_2} \quad (24)$$

Since the amount of dimer is presumed to be small, the interaction term is not affected by the association of component 2.

Comparing Equations (22) and (24) one finds that the effect of association on the enthalpy of the mixture is

$$\Delta H' = X_2^2 KP\Delta H_0 \quad (25)$$

This result may also be derived from equilibrium considerations if the second component in the mixture is considered to act as a diluent.

Various methods may be proposed for determining the interaction term from the pure-component values. The simplest form is

$$\Delta H_{12} = \tfrac{1}{2}(\Delta H_1 + \Delta H_2) \quad (26)$$

When this is introduced into Equation (22), the result is

$$\Delta H = X_1\Delta H_1 + X_2\Delta H_2 \quad (27)$$

which represents the case of ideal mixing.

Other common combining laws are

$$\Delta H_{12} = \sqrt{\Delta H_1 \Delta H_2} \quad (28)$$

and

$$\Delta H_{12} = \tfrac{1}{8}[\Delta H_1^{1/3} + \Delta H_2^{1/3}]^3 \quad (29)$$

Figure 11 shows the shape of the curves obtained for Equations (27), (28), and (29) for hypothetical values of $\Delta H_1$ and $\Delta H_2$ and indicates that only slight differences result for the three combining laws. However, curve IV suggests that if $\Delta H_{12}$ is treated as an empirical constant, substantially different values may be obtained for the enthalpy deviation of the mixture. The particular curve shown in the figure is one for which $\Delta H_{12}$ has been taken equal to zero.

In view of the foregoing considerations, Equation (24) was used to correlate the binary mixture data in the vapor region up to pressures of about 600 lb./sq. in. abs. at 450°F. Values of $\Delta H_{12}$ were determined from the experimental data by averaging the results for different compositions of the methanol-benzene system. Figure 12 shows the interaction term so obtained as a function of temperature and pressure.

Values of this interaction term can then be used in Equation (24) to calculate the enthalpy deviation from the ideal-gas law for any mixture of methanol and benzene. This has been done for a number of points, and the differences between the computed and experimental values of $\Delta H$ are summarized in Table 11. The values of $\Delta H_1$ and $\Delta H_{2_g}$ for the unassociated pure components were determined from the Lydersen correlation (7). No comparisons were made for the ternary mixture since the interaction constants were not known for all the constituent binaries. The agreement is very good for mixtures of 25 and 75% methanol, but larger deviations occur for the 50% mixture. Better agreement could be obtained by utilizing a two-constant equation for the heat-of-mixing expression rather than the simple one-constant expression, Equation (20).

Figure 13 shows the experimental and calculated curves at a fixed pressure for varying temperatures. The curve at 250°F. indicates again that the errors are largest for the 50% mixture. Figure 14 illustrates experimental and calculated curves at a fixed temperature for different pressures. Comparison of the two figures shows that a high temperature as well as a low pressure are criteria for "regularity"

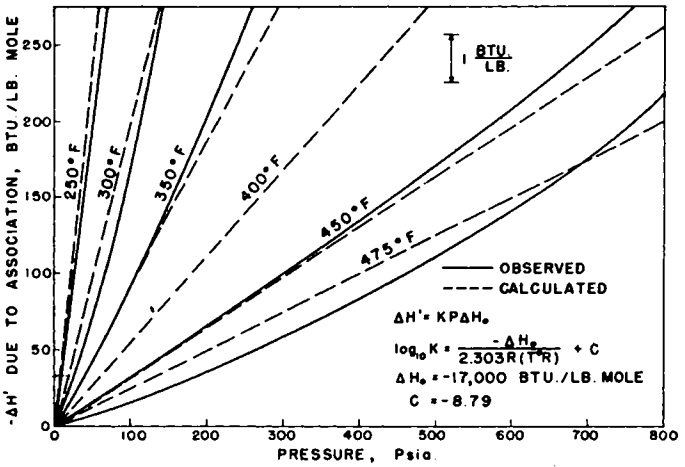


Fig. 10. Heat effect due to association of methanol.

TABLE 10. ENTHALPY DEVIATIONS FROM IDEAL-GAS VALUES

Average Percentage of Errors for Methanol-benzene System

| Composition | True critical method (3) | (1, 2) | Pseudocritical method (3) |
|---|---|---|---|
| 25 Mole % methanol | 38 | 28 | 42 |
| 50 Mole % methanol | 21 | 17 | 32 |
| 75 Mole % methanol | 17 | 13 | 45 |
| 10 Mole % methanol, 30 mole % benzene, 60 mole % *n*-hexane | 13 | 15 | 15 |

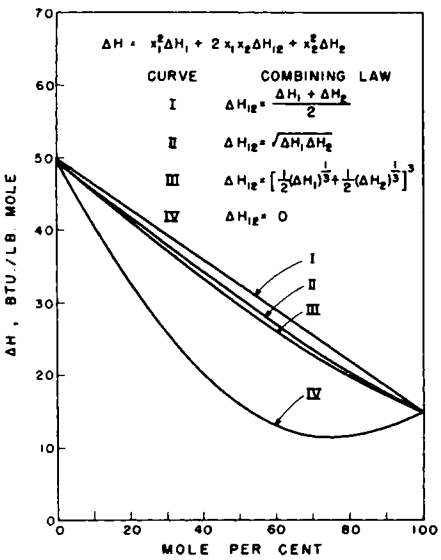


Fig. 11. Combining laws for interaction constant.

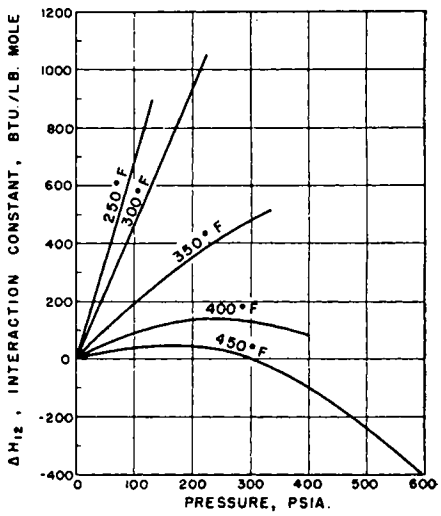


Fig. 12. Interaction constant, $\Delta H_{12}$; methanol-benzene.

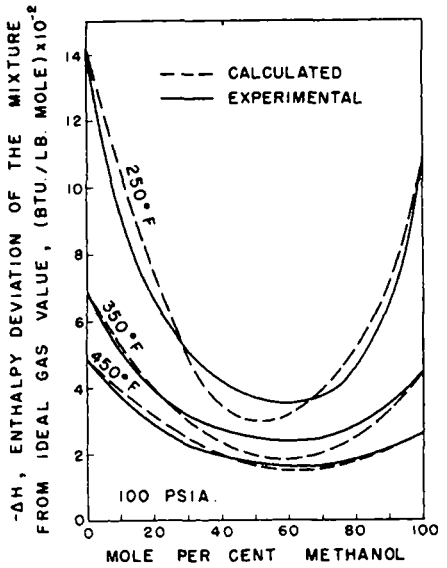


Fig. 13. Effect of temperature on enthalpy deviations of the mixture from the ideal-gas values, methanol-benzene.

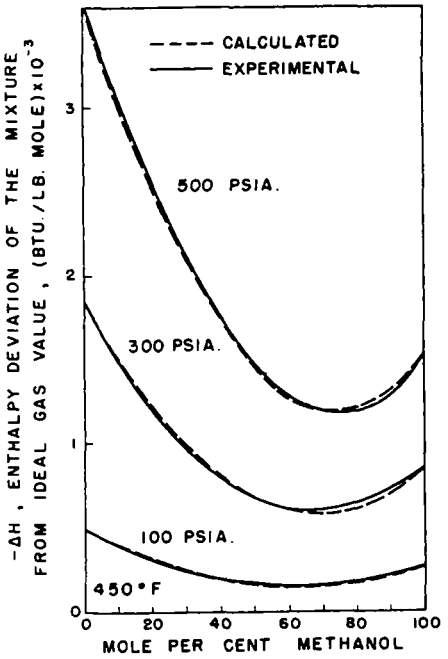


Fig. 14. Effect of pressure on enthalpy deviations of the mixture from the ideal-gas values, methanol-benzene.

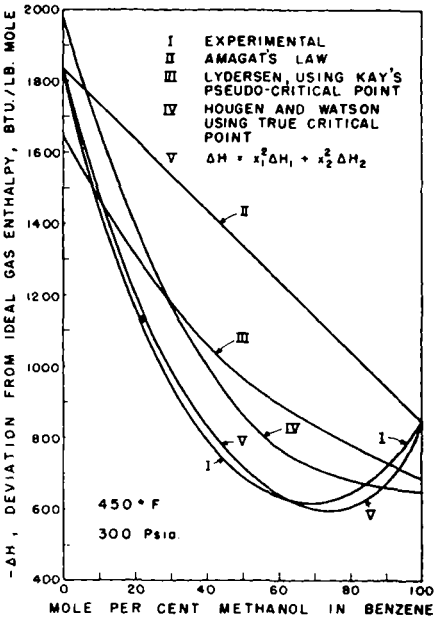


Fig. 15. Comparison of methods for estimating enthalpies of a gaseous mixture.

of this system. It should be stated that in several instances the experimental enthalpies were obtained by extrapolating into the two-phase region. For instance, at 450°F. and 500 lb./sq. in. abs. benzene exists as a liquid. The experimental value was obtained by extrapolating the vapor curve to the given conditions.

Figure 15 compares several methods of predicting the enthalpy of a gas mixture, including the proposal developed in this paper (curve V). The experimental curve for methanol-benzene at 450°F. and 300 lb./sq. in. abs. is also shown for comparison purposes.

## PREDICTION OF ENTHALPY OF NONIDEAL VAPOR MIXTURES

The results of this investigation have suggested a method for estimating the enthalpy of mixtures, as follows.

1. Estimate enthalpy deviations from the ideal-gas state, for nonpolar compounds, directly from a generalized correlation such as that of Edmister (*1, 2*) or Lydersen, Greenkorn, and Hougen (*7*).

2. For polar compounds, the effect of pressure on enthalpy for the unassociated gas may be determined from the generalized correlation. The effect of association is predicted by use of

$$\Delta H' = KP\Delta H_0 \qquad (15)$$

and

$$\log_{10} K = -\frac{\Delta H_0}{2.3RT} + C \qquad (17)$$

The value of $\Delta H_0$ is preferably determined from experimental data for the heat of dimerization. If this is not feasible, it may be estimated from the bond energies of Pauling (*10*). An experimental value of $K$ is required to determine the constant in Equation (17), which may be obtained by direct enthalpy measurement or from $P$-$V$-$T$ data at low pressures.

The effect of association, $\Delta H'$, evaluated in this way, may then be added to the result for the unassociated gas according to Equation (23) to give the total enthalpy deviation from the ideal-gas state for the particular component.

3. The enthalpy of the mixture then is estimated from Equation (22) by means of the pure-component values of $\Delta H$, as previously determined. Enthalpy measurements on one mixture are required to estimate the interaction term, $\Delta H_{12}$.

The following example illustrates the method of calculation.

### Sample Calculation

The enthalpy of a mixture of 25 mole % methanol and 75 mole % benzene as a vapor at 450°F. and 400 lb./sq. in. abs. is to be estimated.

*Data*

| | |
|---|---|
| Critical temperature, benzene | 553°F. |
| Critical pressure, benzene | 715 lb./sq. in. abs. |
| Critical temperature, methanol | 464°F. |
| Critical pressure, methanol | 1,155 lb./sq. in. abs. |

Table 11. Differences Between Calculated and Experimental Enthalpy Deviations from the Ideal-Gas Values

Methanol-benzene System

| Temperature, °F. | Pressure, lb./sq. in. abs. | Mole % methanol 25% | 50% | 75% |
|---|---|---|---|---|
| | | % Error | | |
| 250 | 50 | + 4 | −33 | +17 |
| 250 | 50 | − 2 | −59 | −24 |
| | 100 | + 6 | −49 | −10 |
| 300 | 50 | + 8 | −32 | 0 |
| | 100 | + 6 | −29 | +21 |
| | 150 | + 4 | −26 | 0 |
| 400 | 100 | +10 | −17 | − 3 |
| | 200 | +12 | −10 | 0 |
| | 300 | 0 | −15 | 0 |
| 450 | 100 | +10 | − 8 | − 5 |
| | 200 | + 2 | − 5 | − 3 |
| | 300 | + 2 | − 3 | − 2 |
| | 400 | + 1 | − 3 | − 2 |
| | 500 | − 3 | − 2 | + 1 |
| | 600 | −13 | + 4 | + 8 |
| Average error* | | 5.6% | 19% | 6.4% |

*The average was calculated disregarding the sign.

| | | |
|---|---|---|
| Heat of dimerization | −17,000 B.t.u./lb. mole | |
| Constant in Equation (17) | −8.79 | |
| Interaction constant $\Delta H_{12}$ (Figure 12) | −100 B.t.u./lb. mole | |
| Compressibility factor at critical points ($Z_c$) | | |
| Benzene | 0.274 | (7) |
| Methanol | 0.222 | (7) |

*Pure-component Calculations*

The enthalpy deviations from the ideal gas may be estimated from the tables of Lydersen, Greenkorn, and Hougen (7)

BENZENE

$$Pr = \frac{400 \text{ lb./sq. in. abs.}}{715} = 0.56$$

$$Tr = \frac{910°\text{R.}}{1{,}013°\text{R.}} = 0.896$$

From the tables, with $Z_c = 0.27$

$$-\frac{\Delta H_1}{T_c} = 2.6 \frac{\text{B.t.u.}}{(\text{lb. mole})(°\text{R.})}$$

$$\Delta H_1 = -2{,}640 \text{ B.t.u./lb. mole}$$

METHANOL

$$Pr = \frac{400}{1{,}155} = 0.346$$

$$Tr = \frac{910}{929} = 0.986$$

From the tables, with extrapolation to $Z_c = 0.222$

$$-\frac{\Delta H_2}{T_c} = 1.1$$

$$\Delta H_2 = -1{,}020 \text{ B.t.u./lb. mole}$$

*Correction for Association*

The value for methanol may be corrected for association according to the equations

$$\Delta H' = KP\Delta H_0 \qquad (15)$$

where

$$\log_{10} K = -\frac{\Delta H_0}{(2.3)(R)T} - 8.79 \qquad (17)$$

and

$$\Delta H_0 = -17{,}000 \text{ B.t.u./lb. mole}$$

Solving for $K$ at 450°R. gives

$$\log_{10} K = +\frac{17{,}000}{(2.3)(1.987)(910)} - 4.70$$

$$K = 1.99 \times 10^{-5} \text{ (lb./sq. in. abs.)}^{-1}$$

$$\Delta H' = (1.99 \times 10^{-5})(400)(-17{,}000)$$

$$= -135 \text{ B.t.u./lb. mole}$$

The total-enthalpy deviation of methanol vapor from the ideal-gas value, according to Equation (23), is

$$\Delta H_2 = -1{,}020 - 135$$

$$= -1{,}155 \text{ B.t.u./lb. mole}$$

*Mixture Calculations*

$$\Delta H = X_1^2 \Delta H_1 + 2X_1X_2\Delta H_{12} + X_2^2 \Delta H_2$$

$$= (0.75)^2(-2{,}640) + (2)(0.75)(0.25)(-100) + (0.25)^2(-1{,}155)$$

$$= -1{,}480 - 38 - 72$$

$$= -1{,}590 \text{ B.t.u./lb. mole}$$

*Comparison of Computed and Experimental Values*

| | Calc. B.t.u./lb. mole | Exp. B.t.u./lb. mole |
|---|---|---|
| Benzene | −2,640 | (liquid at this condition) |
| Methane | −1,155 | −1180 |
| Mixture (25% methanol, 75% benzene) | −1,590 | −1530 |

## CORRELATION OF LIQUID-PHASE ENTHALPY

The data in Tables 1 to 6 include information for the effect of composition on the enthalpy of liquid mixtures. The deviation from ideal-solution behavior in this case is positive in contrast to the negative vapor-phase deviations. The data may be correlated by use of a one-constant heat-of-mixing equation similar to Equation (20).


## ACKNOWLEDGMENT

This work was carried out with the aid of a Shell Fellowship Committee Award in Chemical Engineering at Purdue University. The Engineering Experiment Station also provided financial support. The advice and counsel of Professor H. C. Van Ness are also asknowledged.


## NOTATION

$\alpha$ = mole fraction dimer in associating gas
$A$ = constant, independent of pressure, in Equation (9)
$B$ = second-virial coefficient for a nonassociating gas
$B_e$ = effective second-virial coefficient for an associating gas
$C$ = constant of integration in equilibrium constant equation, Equation (17)
$\Delta h_1$ = enthalpy correction for deviation from selected inlet temperature
$\Delta h_2$ = enthalpy correction for deviation of exit temperature from datum value of 77°F.
$H$ = enthalpy of mixture referred to reference state of pure components
$\Delta H_0$ = heat of dimerization per mole of dimer
$\Delta H'$ = heat effect due to association as defined by Equation (15)
$\Delta H_e$ = change in enthalpy of fluid passing through the calorimeter
$\Delta H_g$ = difference between enthalpy in the unassociated state at pressure $P$ and in the ideal-gas state
$\Delta H_m$ = heat of mixing
$\Delta H_T$ = difference between enthalpy of the actual gas at pressure $P$ and the enthalpy in the ideal-gas state
$K$ = equilibrium constant for dimerization
$L_f$ = latent heat of Freon 11 at 75°F.
$P$ = absolute pressure
$R$ = gas constant per mole
$S$ = entropy of mixture referred to reference state of pure components
$\Delta S$ = heat of mixing
$T$ = absolute temperature, °R.
$V$ = volume per mole
$W_f$ = mass of Freon evaporated during a run
$W_m$ = mass of sample collected a run
$X$ = mole fraction
$Z_c$ = compressibility factor at the critical point

**Subscripts and Superscripts**

$^+$ = a gaseous state approaching ideal-solution behavior
$^\circ$ = the reference state, saturated liquid at 77°F.
$i$ = pure component $i$
1 = state at the entrance to the calorimeter. Subscripts 1 and 2 also indicate components 1 and 2.

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*Presented at A.I.Ch.E. New Orleans meeting*