Enthalpy Values for Hypothetical Fluids from Vapor-Liquid Equilibrium Data

J. REED WELKER, S. DEAN LARSON, DWIGHT S. HOFFMAN
University of Idaho, Moscow, Idaho

and JAMES H. WEBER
University of Nebraska, Lincoln, Nebraska

To make complete design calculations on a distillation column, absorber, stripper, or similar type of equipment, not only are vapor-liquid equilibrium data necessary, but enthalpy data for mixtures are necessary as well. In many instances conditions of constant molal vapor flow and constant molal liquid flow can not be assumed. Also frequently when tray to tray material and energy balance calculations are attempted, it becomes evident the available equilibrium and thermal data are not consistent. This of course means that either or both types of data are not correct because thermodynamically, the aforementioned situation can not exist. Hence the purpose of this work is to present enthalpy values which are thermodynamically consistent with the vaporization equilibrium constants presented previously (*7*, *8*).

Of these two types of data, equilibrium and enthalpy, necessary for rigorous tray-to-tray calculation considerably greater effort has been expended gathering, interpreting, and predicting vapor-liquid equilibrium data than enthalpy data. Only in recent years has the need for enthalpy data become pressing. This has been brought about chiefly by the use of low-temperature and high-pressure operating conditions. Concurrently the number of attempts to calculate and correlate enthalpy values for mixtures has increased. Some of the more recent work has been done by Papadopoulos, Pigford, and Friend (*11*); Edmister and Canjar (*5*); Canjar and Peterka (*3*); Edmister (*4*); Peters (*12*); Sage and Lacey (*13*); and Weber et al. (*6*, *9*, *14*, *15*, *16*). Experimental enthalpy data on mixtures are extremely limited.

Many energy balance calculations require a knowledge of both liquid and vapor phase enthalpies of mixtures. The latter can frequently be calculated from an equation of state. In reality the isothermal effect of pressure on enthalpy is calculated, and this with enthalpy values for the pure substances in the ideal gas state makes possible the evaluation of enthalpy values for the mixture in the vapor phase.

To complete the calculation liquid-phase values are necessary. One approach to the determination of the liquid-phase enthalpy values is to calculate the value of the latent heat effect which exists between the saturated phases and obtain the enthalpy value for the liquid phase by difference. In the case of mixtures three latent heat effects may be considered: the isobaric integral, isothermal integral, or the differential. Edmister (*4*) and Peters (*12*) calculated isobaric integral heats of vaporization by approximate methods, while Weber et al. (*6*, *9*, *14*, *15*, *16*) calculated differential heat effects rigorously.

Since enthalpy is a point function, changes in this property in going from a saturated vapor to a saturated liquid can be evaluated along any convenient path. One path which could be used to evaluate the isobaric integral heat of condensation might be as follows (for the purpose of illustration a binary mixture will be used):

Step 1. Separate at the dew-point temperature the saturated vapor mixture into the pure components.

Step 2. Condense the heavier component at the dew-point temperature of the mixture.

Step 3. Cool the heavier component now in the liquid state to the bubble-point temperature.

Step 4. Cool the lighter component in the vapor state to the bubble-point temperature.

Step 5. Condense the lighter component to a liquid at the bubble-point conditions.

Step 6. Isothermally mix the two components.

In the process the pressure is constant, the initial and final compositions are identical, but the temperature has changed from the dew-point temperature of the mixture to its bubble-point temperature.

Steps 1 and 6 are fundamentally the same type, and the heat of mixing involved can be calculated through the activity coefficient by the relationship

$$\left[\frac{\partial \ln \gamma}{\delta\left(\frac{1}{T}\right)}\right]_P = \frac{\Delta H_{\text{mixing}}}{R} = \frac{\overline{H} - H^\circ}{R} \tag{1}$$

Equation (1) can be applied to either the liquid or the vapor phase, and the activity coefficients represent deviations from the Lewis and Randall rule. Steps 3 and 4 are basically similar and involve the evaluation of enthalpy changes for sensible heat effects. Heat capacities of the real, pure fluids are required in both cases.

Steps 2 and 5 represent condensation processes, and the presentation of a method to evaluate the enthalpy changes in these steps is the purpose of this paper. The two components of the mixture present somewhat different problems. If a saturated vapor mixture is separated under isothermal and isobaric conditions into its components, the heavier component will be in the so-called hypothetical vapor state (that is the system pressure is greater than

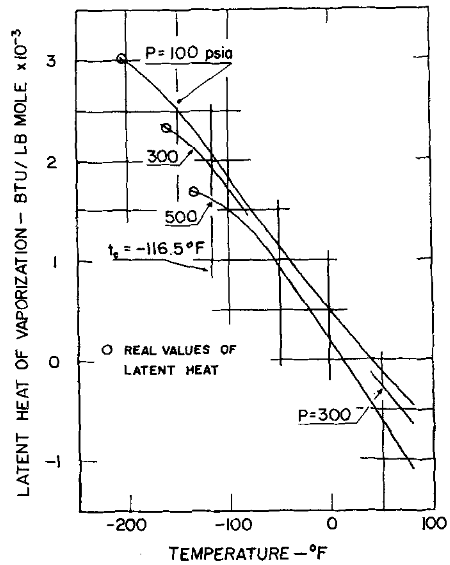

Fig. 1. Enthalpy differences and latent heat values for methane.

the vapor pressure of the substance at the given temperature). The conditions of temperature and pressure are such that the pure heavier component would exist only as a liquid. On the other hand the lighter component will exist as a real vapor but only as hypothetical liquid, the system pressure being less than the vapor pressure of the substance at the temperature involved. Or the temperature may be greater than the critical temperature of the lighter component.

In step 2 the heavier component is condensed from a hypothetical vapor to a real liquid, both of these fluids being at the dew-point temperature and pressure. In step 5 the lighter component is condensed from a real vapor to a hypothetical liquid. Both of these fluids are at the bubble-point temperature and pressure.

Rigorous thermodynamic relationships are available to evaluate the heat effects involved in steps 2 and 5. From the definition of fugacity and the selection of the standard state (that is the pure substance in a given state, liquid or vapor, at the temperature and pressure of the system) the following expressions can be written:

$$\left[\frac{\partial \ln f^\circ_L}{\partial\left(\frac{1}{T}\right)}\right]_P = \frac{-(H^* - H^\circ_L)}{R} \qquad (2)$$

Similarly for the vapor phase

$$\left[\frac{\partial \ln f^\circ_v}{\partial\left(\frac{1}{T}\right)}\right]_P = \frac{-(\mathrm{H}^* - \mathrm{H}^\circ_v)}{R} \qquad (3)$$

If Equations (2) and (3) are combined, the result is

$$\left[\frac{\partial \ln \frac{f^\circ_L}{f^\circ_v}}{\partial\left(\frac{1}{T}\right)}\right]_P = \frac{-(H^\circ_v - H^\circ_L)}{R} \qquad (4)$$

or

$$\left[\frac{\partial \ln K}{\partial\left(\frac{1}{T}\right)}\right]_P = -\frac{(H^\circ_v - H^\circ_L)}{R} = -\frac{\Delta H}{R} \qquad (4a)$$

The difficulty in the application of Equation (4) or (4*a*) arises in the evaluation of f°_v for a hypothetical vapor in the case of the heavier component and f°_L for a hypothetical liquid in the case of the lighter component. In previous papers (7, 8) a method using the van Laar equation was presented for the evaluation of f°_L and f°_v for substances under the conditions mentioned. For a number of hydrocarbons, vaporization equilibrium constants, using these fugacity values, were also presented. The K values so obtained were also generalized by a correlation of the Z factor (Pv/KP). Provided the K's are thermodynamically correct they can be used in Equation (4*a*) to calculate the quantity $(H^\circ_v - H^\circ_L)$.

Hence the K's, at constant pressure conditions, presented previously or obtained from the generalized Z correlations were fitted to a polynomial of the form

$$\ln K = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} \qquad (5)$$

If Equation (5) is differentiated and substituted into (4*a*), the result is

$$B + \frac{2C}{T} + \frac{3D}{T^2} = -\frac{(H^\circ_v - H^\circ_L)}{R} \qquad (6)$$

Since the latent heat of vaporization is known at the saturation temperature T_s, B may be expressed in terms of the known value of the latent heat, C and D, and T_s. The relationship for B may be substituted into Equation (5), and a relationship between ln K, A, C, and D obtained:

$$\ln K + \frac{\Delta H_{\mathrm{vap}}}{RT} = A + C\left(\frac{1}{T^2} - \frac{2}{T_sT}\right) + D\left(\frac{1}{T^3} - \frac{3}{T_s^2T}\right) \qquad (7)$$

The constants A, C, and D can be determined by the method of least squares.

By this procedure a polynominal of the form of Equation (5) was found to fit the K data well. In most cases the maximum difference between the curve fit value of K and the original input value of K was less than 3% and seldom greater than 5%.

To illustrate some of the results obtained by the application of Equation (6) values of the enthalpy differences between the vapor and liquid states for methane and ethane over the pressure range 100 to 500 lb./sq. in. abs. are shown in Figures 1 and 2, respectively. In the case of

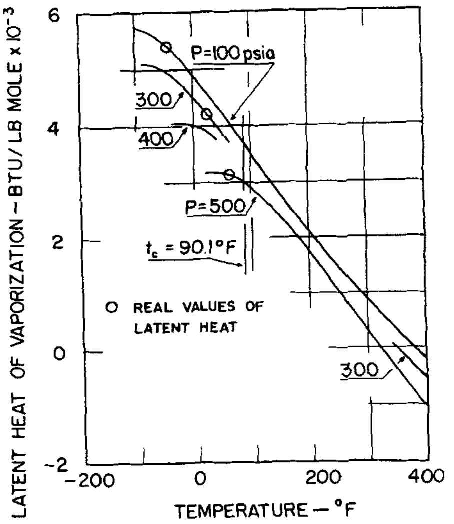

Fig. 2. Enthalpy differences and latent heat values for ethane.

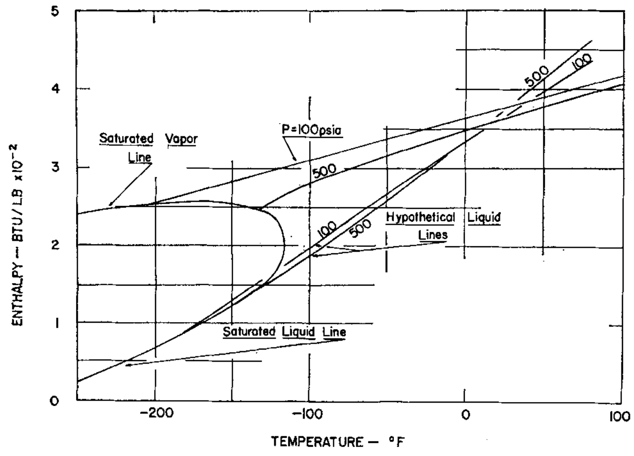

Fig. 3. Enthalpy temperature diagram for methane.

methane the values represent the heat effects when the real vapor is condensed to a hypothetical liquid, while in the case of ethane a complete range of values is given, that is for the hypothetical vapor to the real liquid and for the real vapor to the hypothetical liquid. For both substances actual latent heats of vaporization values are shown.

One interesting feature of the values shown in Figures 1 and 2 is enthalpy differences between the hypothetical liquid phase and the real vapor phase become negative in sign at temperatures considerably above the critical temperature. The negative differences are of course brought about by the fact that the equilibrium constant at a given pressure goes through a maximum value and then decreases. The sign of slope of the K curve on a plot of ln K vs. $1/T$ changes from negative to positive in this temperature range.

This does not mean the enthalpy, or more accurately the partial enthalpy, of the component in the liquid phase of mixture is greater than its enthalpy in the vapor phase of the mixture. At the conditions under consideration the concentration of the lighter component in a two-component system would be very low, and there would be a marked deviation from ideal behavior for this component, hence a relatively large heat of mixing.

The calculated enthalpy differences can be used to calculate enthalpy values for hypothetical fluids. To show how these values fit with the enthalpy data for the pure substances in the real state enthalpy vs. temperature diagrams for methane and ethane are included as Figures 3 and 4. The data of Matthews and Hurd (*10*) and Barkelew et al. (*1*) were used for methane and ethane, respectively, on these figures. The hypothetical liquid phase enthalpy values were obtained by subtracting the enthalpy differences, at a given temperature and pressure, from the enthalpy of the real vapor. They extend to the right of the portion of the two-phase envelope representing the saturated liquid phase.

The enthalpies of hypothetical vapors were also calculated by the method described. It will be noted in Figure 4 the isobars cross the saturated vapor line and appear below it. In all cases the enthalpy values for the hypothetical fluids appear consistent with the enthalpy values for the real fluids. Also the enthalpy values presented are thermodynamically consistent with the vaporization equilibrium constants presented previously (*7, 8*). The necessary experimental data, heat capacities of liquid mixtures, and heats of mixing to check the enthalpy presented in this work are not available.

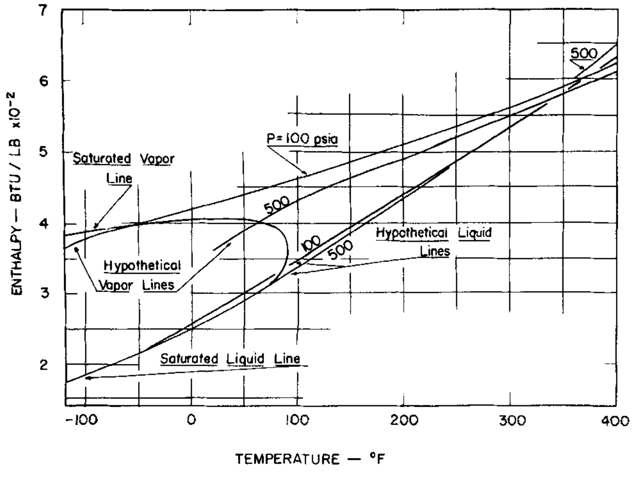

Fig. 4. Enthalpy temperature diagram for ethane.

NOTATION

A,B,C,D = empirical constants, Equation (6)
H = total enthalpy, B.t.u./lb. mole
$\overline{H}$ = partial enthalpy, B.t.u./lb. mole
K = equilibrium vaporization constant, $f°_L/f°_v$
P = total pressure, lb./sq. in.abs.
R = gas law constant, 1.987 B.t.u./lb. mole-°R.
T = absolute temperature, °R.
f = fugacity, lb./sq. in.
γ = activity coefficient, for example $\gamma_L = f_L/f°_L x$

Superscripts

° = standard state, temperature and pressure of system
$*$ = ideal gas state

Subscripts

L = liquid phase
s = saturation
v = vapor phase
vap = vaporization

LITERATURE CITED

1. Barkelew, C. H., J. L. Valentine, and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **43**, 25 (1947).
2. Brydon, J. W., N. Walen, and L. N. Canjar, *Chem. Eng. Progr Symposium Ser. No. 7*, **49**, p. 151 (1953).
3. Canjar, L. N., and V. J. Peterka, *A.I.Ch.E. Journal*, **2**, 243 (1956).
4. Edmister, W. C., *ibid.*, **1**, 38 (1955).
5. ———, and L. N. Canjar, *Chem. Eng. Progr. Symposium Ser. No. 7*, **49**, p. 73 (1953).
6. Hobson, M., and J. H. Weber, *Chem. Eng. Data. Ser.*, **2**, 7 (1957).
7. Hoffman, D. S., J. R. Welker, R. E. Felt, and J. H. Weber, *A.I.Ch.E. Journal*, **8**, 508 (1962).
8. —————, V. N. P. Rao, and J. H. Weber, paper submitted for publication in *A.I.Ch.E. Journal.*
9. Houser, C. G., and J. H. Weber, *Chem. Eng. Data. Ser.*, **6**, 510 (1961).
10. Matthews, C. S., and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **42**, 55 (1946).
11. Papadopoulos, A. R., R. L. Pigford, and L. Friend, *Chem. Eng. Progr. Symposium Ser. No. 7*, **49**, p. 93 (1953).
12. Peters, H. F., *Petrol. Refiner*, **28**, No. 5, p. 109 (1949).
13. Sage, B. H., and W. N. Lacey, "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," API (1950).
14. Stiehl, J. G., M. Hobson, and J. H. Weber, *A.I.Ch.E. Journal*, **2**, 389 (1956).
15. Vennix, A. J., and J. H. Weber, *J. Chem. Eng.*, **7**, 169 (1962).
16. Weber, J. H., *Chem. Eng. Data*, **4**, 301 (1959).

Manuscript received March 11, 1963; revision received November 7, 1963; paper accepted November 7, 1963. Paper presented at A.I.Ch.E. New Orleans meeting.