# ISOBARIC INTEGRAL HEAT OF VAPORIZATION of Hydrocarbon Mixtures from Vapor-liquid *K* Values

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The isobaric integral heat of vaporization is the difference between the enthalpy values for a given mixture at its dew and bubble points taken at the same pressure but different temperatures. In terms of partial enthalpies

$$\Delta H_V = (H^V - H^L)_P = \Sigma z \overline{\Delta H}_V = (\Sigma y \overline{H}^V)_2 - (\Sigma x \overline{H}^L)_1 \qquad (1)$$

where $H$ is enthalpy of the mixture, $\overline{H}$ is the partial enthalpy of a component of the mixture, superscript $V$ or $L$ designates the phase (vapor or liquid), subscript $V$ (after $\Delta H$) designates heat of vaporization, subscripts 1 and 2 designate the temperatures of the bubble and dew points, respectively, and $x$, $y$, and $z$ are mole fractions for liquids, vapors, and mixtures in general [all numerically the same in Equation (1)]. In terms of partial enthalpies referred to ideal-gas-state values,

$$\Sigma z \overline{\Delta H}_V = \Sigma z(\overline{\Delta H}^V_2 - \overline{\Delta H}^L_1) + \Sigma z \Delta H^\circ \qquad (2)$$

where $\overline{\Delta H} = \overline{H} - H^\circ$, $H^\circ$ is the enthalpy of a component of a mixture in the ideal gas state, and $\Delta H^\circ = H^\circ_2 - H^\circ_1$.

The summations of Equation (2) are illustrated in Figure 1, where $T_1$ is the bubble-point temperature and $T_2$ the dew-point temperature.

The partial-enthalpy differences, $\overline{\Delta H}^V_2$ and $\overline{\Delta H}^L_1$, are related to the fugacity coefficients as are the vapor-liquid equilibria $K$ values. An equation for $\Sigma z \overline{\Delta H}_V$ in terms of the temperatures and $K$ values at the bubble and dew points is derived below.

From the definition of fugacity $f$, the following equation has been obtained and appears in thermodynamic texts:

$$\overline{\Delta H} = \overline{H} - H^\circ = -RT^2 \left(\frac{\delta \ln f}{\delta T}\right)_{P,\,N} \qquad (3)$$

where subscript $N$ means at constant composition and $P$ at constant pressure. Equation (3) is general and applies to either a liquid or vapor phase. This differential form can be approximated by a difference form by integrating with a constant value of $\overline{\Delta H}$ for a small temperature interval. If at the same time fugacity is divided by mole fraction to give fugacity coefficient,

$$\overline{\Delta H} = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{(f/z)_1}{(f/z)_2} \qquad (4)$$

Equation (4) may be applied to a component of any phase, whether it be a liquid or vapor, at constant pressure and composition, so long as $\overline{\Delta H}$ is assumed constant. Figure 1*A* shows graphically the partial enthalpies of propane in a liquid and vapor of fixed composition as given by mole average boiling point at 300 lb./sq. in. abs. compared to the ideal-gas-state values. Points $1^L$ and $2^V$ represent the bubble and dew points of a certain mixture that is considered later in an illustrative example. In the application of Equation (4) to propane vapor from $1^V$ to $2^L$, it is assumed that $\overline{\Delta H}^V$ remains constant at $\overline{\Delta H}^V_2$ even though it obviously is greater at $\overline{\Delta H}^V_1$. Correspondingly it is assumed that $\overline{\Delta H}^L$ remains constant at $\overline{\Delta H}^L_1$ when Equation (4) is applied to the liquid from $1^L$ to $2^L$.

Figure 1*B* shows how the fugacity of propane in the liquid and vapor at two compositions and at 300 lb./sq. in. abs. does vary with temperature. Applying Equation (4) to any component of a mixture, as required in Equation (2), gives

$$\overline{\Delta H}^V_2 - \overline{\Delta H}^L_1 = \frac{RT_1T_2}{T_2 - T_1} \left[\ln \frac{(f^V/y)_1}{(f^V/y)_2} - \ln \frac{(f^L/x)_1}{(f^V/x)_2}\right]_P \qquad (5)$$

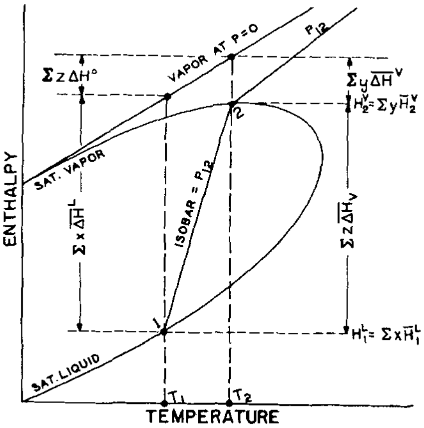


FIG. 1. ENTHALPY-TEMPERATURE DIAGRAM FOR MIXTURE ILLUSTRATING ISOBARIC INTEGRAL HEAT OF VAPORIZATION.

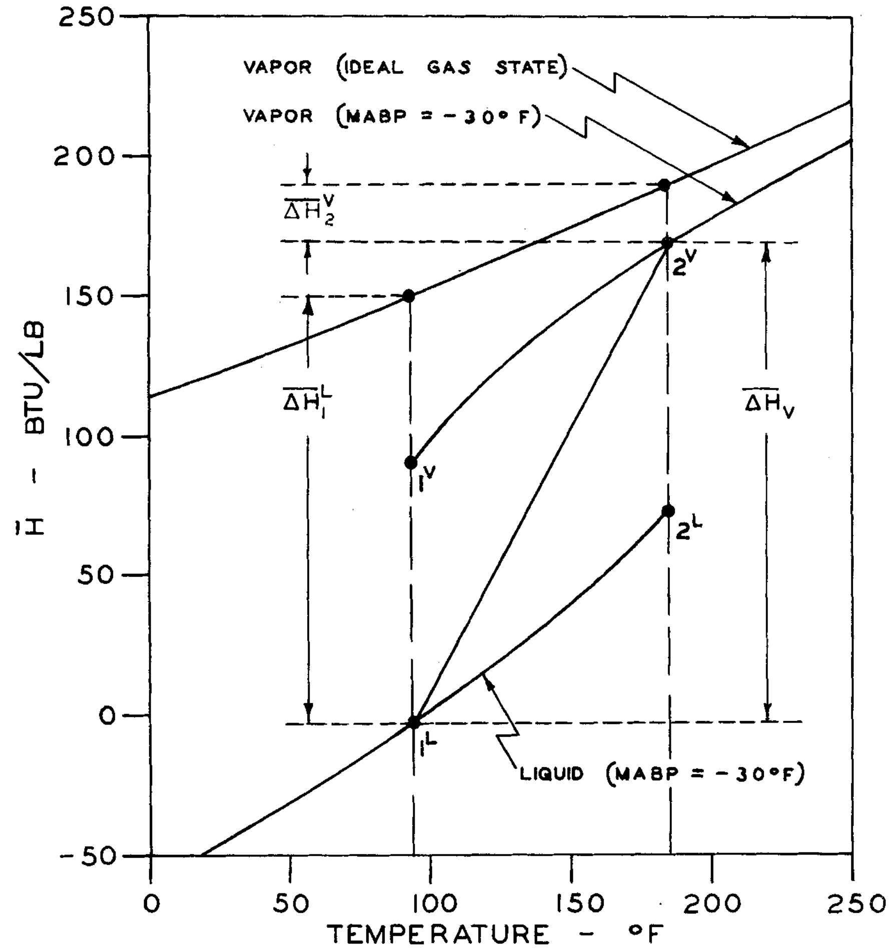
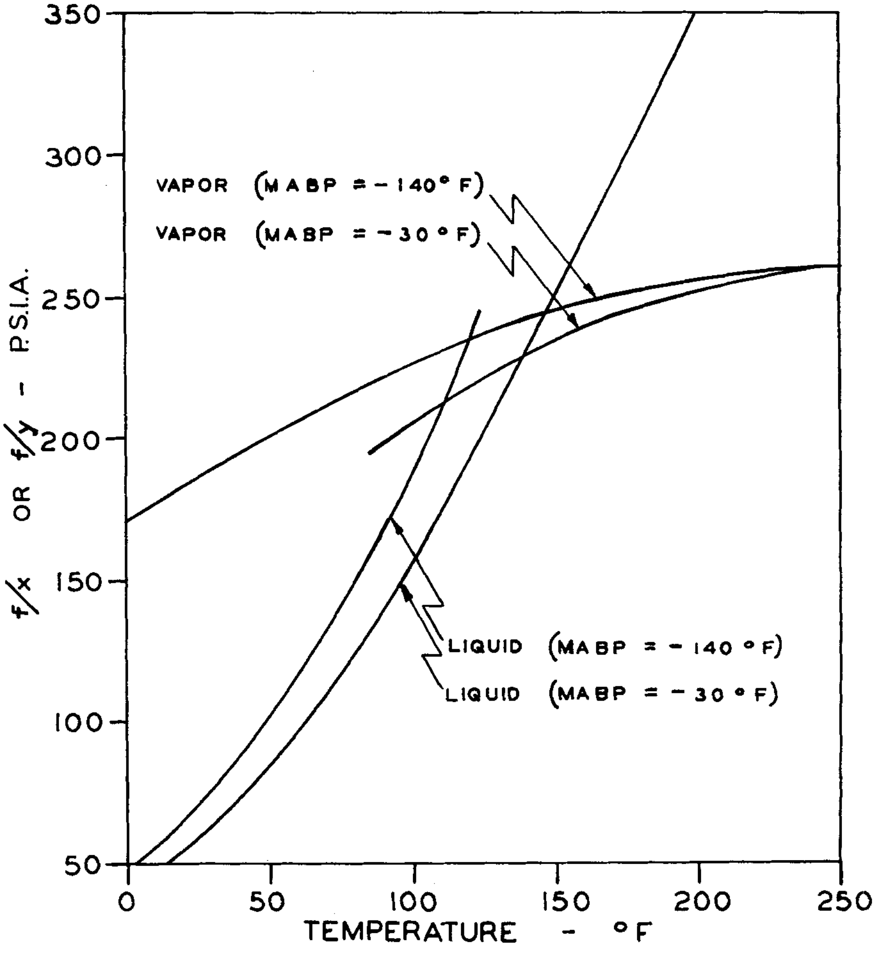


FIG. 1A. TYPICAL VALUES OF *H* FOR PROPANE AT 300 LB./SQ. IN. ABS.

FIG. 1B. TYPICAL VALUE OF FUGACITY FOR PROPANE AT 300 LB./SQ. IN. ABS.



where, as before, $x$ and $y$ are numerically the same.

The equilibrium vapor and liquid phases at $T_1$ and $T_2$ will now be considered so that the $K$ values may be introduced into Equation (5). If the composition of the liquid which would be in equilibrium with the dew-point vapor is denoted by $x^*$ and the composition of the vapor which would be in equilibrium with the bubble-point liquid is denoted by $y^*$, the definition of $K$ gives

$$K_2 = \frac{(f^L/x^*)_2}{(f^V/y)_2} \text{ at } T_2 \qquad (6a)$$

$$K_1 = \frac{(f^L/x)_1}{(f^V/y^*)_1} \text{ at } T_1 \qquad (6b)$$

Combining Equations (5) and (6) gives for any one component:

$$\overline{\Delta H}_2^V - \overline{\Delta H}_1^L = \frac{RT_1T_2}{T_2-T_1}\left[\ln\frac{K_2}{K_1} + \ln\frac{(f^V/y)_1}{(f^V/y^*)_1} + \ln\frac{(f^L/x)_2}{(f^L/x^*)_2}\right]_P \qquad (7)$$

Summing for all components according to Equation (2) gives

$$\Sigma z\overline{\Delta H}_V = \frac{RT_1T_2}{T_2-T_1}\left[\Sigma z\ln\frac{K_2}{K_1} + \Sigma y\ln\frac{(f^V/y)_1}{(f^V/y^*)_1} + \Sigma x\ln\frac{(f^L/x)_2}{(f^L/x^*)_2}\right]_P + \Sigma z\,\Delta H^\circ \qquad (8)$$

The second and third terms in the bracket of Equation (8) will next be examined from the point of view of the Gibbs-Duhem equation for changes in composition at constant temperature and pressure. In terms of fugacities this equation is

TABLE 1.—SOLUTION OF ISOBARIC HEAT OF VAPORIZATION EXAMPLE BY *K*-VALUE METHOD

| Component | Moles | *K* values at 300 lb./sq. in. abs. At. D. P. 185° F. | At B.P. 95° F. | Ratio | $\frac{RT_1T_2}{T_2-T_1}\ln\frac{K_2}{K_1}$ | $H°$ M B.t.u./lb. mole | | | $\overline{\Delta H}_V$ | $(\overline{\Delta H}_V)$ (moles) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $K_2$ | $K_1$ | $K_2/K_1$ | M B.t.u./lb. mole | 185° F. | 95° F. | $\Delta H°$ | M B.t.u./lb. mole | M B.t.u./100 moles mixture |
| $C_1$ | 5 | 8.48 | 7.76 | 1.093 | 0.70 | 5.266 | 4.466 | 0.800 | 1.500 | 7.5 |
| $C_2$ | 15 | 2.94 | 1.86 | 1.581 | 3.62 | 6.593 | 5.367 | 1.266 | 4.886 | 72.7 |
| $C_3$ | 30 | 1.36 | 0.695 | 1.956 | 5.37 | 8.375 | 6.643 | 1.732 | 7.102 | 213.1 |
| $nC_4$ | 50 | 0.685 | 0.258 | 2.655 | 7.75 | 11.073 | 8.783 | 2.290 | 10.040 | 502.0 |
| | 100 | | | | | | | | | 795.3 |

$$\Sigma\, z\, d \ln f = 0 \qquad (9)$$

Since the sum of the *z*'s is unity,

$$\Sigma\, z\, d \ln (f/z) = 0 \qquad (10)$$

For small changes in composition the differential form is approximated by the difference form,

$$\Sigma\, z \ln \frac{(f/z)'}{(f/z)''} = 0. \qquad (11)$$

where the prime and double prime designate two different compositions for the same phase, temperature, and pressure. This equation may be applied to either vapor or liquid phases.

Assuming the approximate form of the Gibbs-Duhem relationship with the composition factor of the logarithm taken at one end of the interval, the second and third summations in the brackets of Equation (8) are zero, or

$$\Sigma y \ln \frac{(f^V/y)_1}{(f^V/y^*)_1} = 0 \qquad (12a)$$

$$\Sigma x \ln \frac{(f^L/x)_2}{(f^L/x^*)_2} = 0 \qquad (12b)$$

Equation (8) now becomes by combination with Equation (12)

$$\Delta H_V = \Sigma z \left[\frac{RT_1T_2}{T_2 - T_1} \ln \frac{K_2}{K_1}\right] + \Sigma z\, \Delta H° \qquad (13)$$

Equation (13) gives the isobaric integral heat of vaporization of a mixture. The term in brackets of Equation (13) is the same as Dodge's(*2*, Equation IV-208, page 142) which was derived for ideal solutions with the assumption that $\overline{\Delta H}$ was independent of temperature. As shown above, it is not necessary to restrict this equation to ideal solutions, but it is necessary to assume that $\overline{\Delta H}$ is independent of temperature for the bubble- to dew-point interval. Also it has been necessary to assume that the changes in composition in going from the bubble-point liquid to its equilibrium vapor and from the dew-point vapor to its equilibrium liquid are such that the Gibbs-Duhem equation can be applied in an approximate form.

Equation (13) has been derived primarily for application to multicomponent hydrocarbon mixtures, particularly for cases in which composition effects on vapor-liquid *K* values are represented satisfactorily by average boiling points of the equilibrium phases. Figure 2 has been prepared to aid in the evaluation of the bracketed term in Equation (13). Liquid-bubble-point temperature, $\Delta T$, and $K_2/K_1$ are required, and the dashed lines and arrows illustrate the way the chart is read. A typical example follows:

## ILLUSTRATIVE EXAMPLE

Find the heat required to vaporize a mixture of 5 moles methane, 15 moles ethane, 30 moles propane, and 50 moles *n*-butane from bubble to dew points at 300 lb./sq. in.

The *K* values were found from De Priester's *P-T-C* charts(*1*), and the bubble and dew points computed as 95° and 185°F. by conventional methods.

Table 1 gives the solution by the *K*-value method [Equation (13)], and Table 2 gives the solution by the partial-enthalpy method(*3*). The results are compared in Table 3.

## DISCUSSION

It will be noted from examination of the values in Table 3 that the partial-heat-of-vaporization quantities for different components found from *K* values by Equation (13) differ from the values found from the more reliable partial-enthalpy values but that the totals are in agreement. Evidently

TABLE 2.—SOLUTION OF ISOBARIC INTEGRAL HEAT OF VAPORIZATION EXAMPLE BY PARTIAL-ENTHALPY METHOD

| Component | Moles | Partial enthalpies at 300 lb./sq. in. abs. M B.t.u./lb. mole* $\overline{H}^V$ at 185 | $\overline{H}^L$ at 95 | $\overline{\Delta H}_V$ | $(\overline{\Delta H}_V)$ (moles) M B.t.u./100 moles mixture |
|---|---|---|---|---|---|
| $C_1$ | 5 | 5.71 | 3.23 | 2.48 | 12.4 |
| $C_2$ | 15 | 6.37 | 0.96 | 5.40 | 81.1 |
| $C_3$ | 30 | 7.45 | —0.09 | 7.54 | 226.2 |
| $nC_4$ | 50 | 9.36 | —0.41 | 9.77 | 488.2 |
| | 100 | | | | 807.9 |

*Gas at O lb./sq. in. abs. and 0° R.

TABLE 3.—COMPARISON OF METHODS FOR ISOBARIC HEAT OF VAPORIZATION OF HYDROCARBON MIXTURES

| Component | $(\overline{\Delta H}_V)$ (moles), M B.t.u./100 moles mixture Via $\overline{H}$ values | Via *K* Values | % Dev. of $\overline{\Delta H}_V$ by *K*-value method |
|---|---|---|---|
| $C_1$ | 12.4 | 7.5 | —39.5 |
| $C_2$ | 81.1 | 72.7 | —10.4 |
| $C_3$ | 226.2 | 213.1 | —5.8 |
| $nC_4$ | 488.2 | 502.0 | +3.7 |
| Σ | 807.9 | 795.3 | —1.6 |

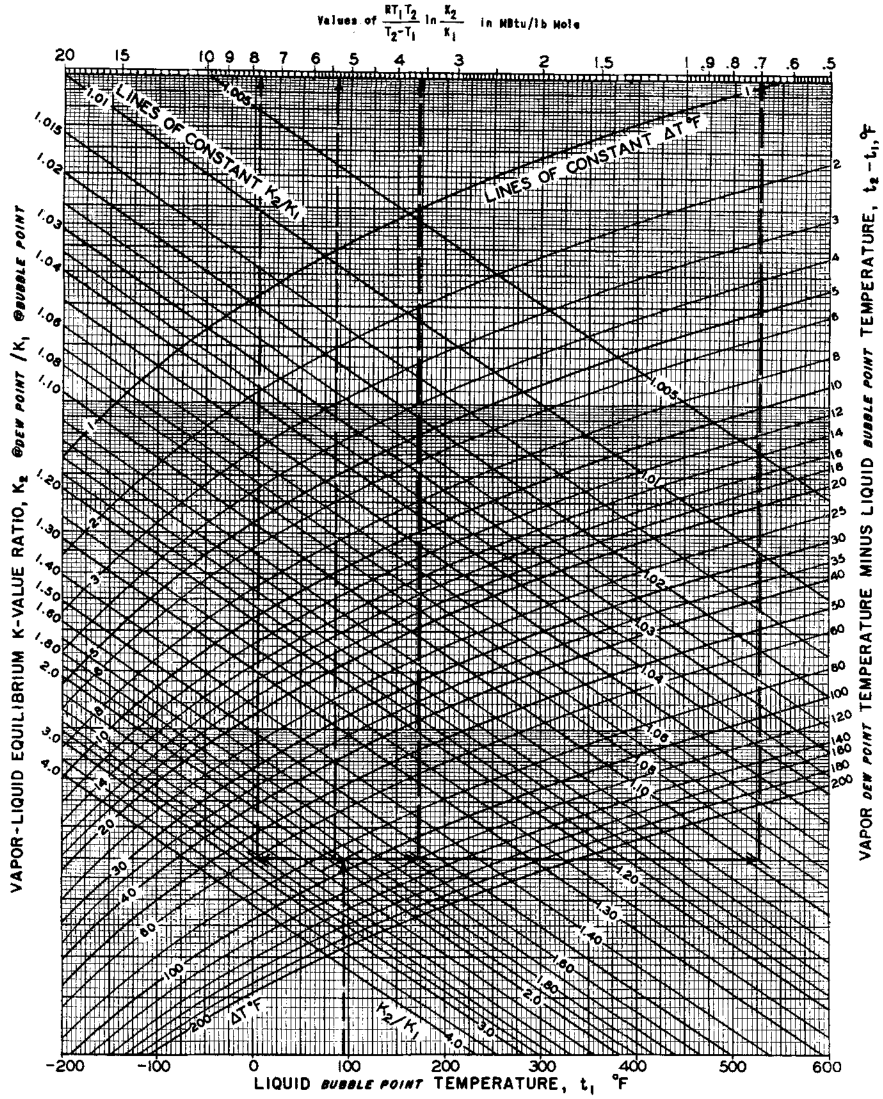


FIG. 2. ISOBARIC INTEGRAL HEAT OF VAPORIZATION OF MIXTURES FROM $K$ VALUES.

the values of ln $K_2/K_1$ for each component cannot be used to obtain accurate partial heats of vaporization or condensation, as the results are too high for high-boiling compounds and too low for lower boiling compounds. In getting the heat of vaporization for the whole mixture, however, these opposite deviations tend to compensate for each other.

Twelve sets of calculations were made on two other mixtures of light hydrocarbons at 400 and 600 lb./sq. in pressure. For each mixture and pressure $\Delta H$ values were found for complete vaporization, partial vaporization (i.e., vaporizing a portion of a mixture under steady-state conditions), and partial condensation.

The two partial cases were included to determine whether the difference in liquid (or vapor) boiling points for the same mixture showed the correct effect on heat of vaporization through the effects of average boiling point on $K$ values and the bubble and dew points.

These calculations showed that the isobaric heats of vaporization found by Equation (13) were consistently lower than the more precise values by an average of 3.7%. No effects of pressure, width of mixture (i.e., bubble- to dew-point temperature interval), or presence of large amounts of unvaporized liquid or uncondensed vapor were noted. This would indicate that the assumption of constant average $\overline{\Delta H}$ for the bubble- to dew-point temperature interval, made in obtaining Equation (4), is justified.

De Priester's *P-T-C—K*-value correlations, which were used in these calculations, have an average deviation of 6.4% from observed $K$ values. As the partial-enthalpy values used in the comparisons are of comparable accuracy, this evaluation of the proposed equation indicates that the $K$ and $\overline{H}$ values used are not consistent. The $\overline{\Delta H}$ values of Edmister and Canjar(*3*) may be 3 to 4% high, or the temperature coefficient of De Priester's (*1*) $K$ values may be low. Experimental vapor-liquid equilibria and isobaric integral heat of vaporization data, taken simultaneously, are required to establish which is the case.

## CONCLUSIONS

Equation (13) may be used to estimate the isobaric integral heat of vaporization of hydrocarbon mixtures from $K$ values. $K$ values cannot be used to obtain heats of solution of partial heats of vaporization for mixture components.

## NOTATION

$f$ = fugacity of a component of a mixture
$H$ = enthalpy of a mixture
$\overline{H}$ = partial enthalpy of a component of a mixture
$\Delta H_V$ = isobaric integral heat of vaporization
$\overline{\Delta H}$ = partial-enthalpy difference referred to ideal gas state, $\overline{H}$-$H°$
$\overline{\Delta H}_V$ = isobaric partial heat of vaporization
$\Delta H°$ = difference in ideal-gas-state enthalpy at $T_1$ and $T_2$
$R$ = gas constant
$T$ = absolute temperature, °R.
$x$ = mole fraction of a component of a liquid
$y$ = mole fraction of a component of a vapor
$z$ = mole fraction of a component in any mixture

### Superscripts

$V$ = vapor
$L$ = liquid
° = ideal gas state
* = equilibrium vapor at bubble point or equilibrium liquid at dew point on $y$ or $x$

### Subscripts

$N$ = constant composition on a partial derivative
$P$ = pressure
$V$ = vaporization change
1, 2 means at $T_1$ or $T_2$

## LITERATURE CITED

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3. Edmister, W. C., and L. N. Canjar, *Chem. Eng. Progr. Symposium Series* No. 7, 49, 73, 85 (1953).
4. Rossini, F. D., et al., *Am. Petroleum Inst. Research Project* 44.