Note on a Proposal for Computing Heats of Vaporization

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It has been proposed (*1*) that integral heats of vaporization in multicomponent liquid-vapor systems be computed from constant pressure equilibrium composition/temperature data by a technique which relies on Gibbs-Duhem relations. The ethanol-water system has been treated as an example, by using a simplified form of a general equation:

$$\left[\frac{X_1}{Y_1}-\frac{X_2}{Y_2}\right]\frac{dY_1}{dT}=\frac{\Delta H}{RT^2} \qquad (1)$$

It seems to us that the proposed method of calculation has little practical use. The errors of the sample calculations are large compared with the errors of much simpler alternative calculations. Furthermore, a claim is made that one can (rigorously) compute heats of vaporization from constant pressure T-X data, when in fact such calculations must be based on knowledge or estimate of liquid heat of mixing effects.

The example of the ethanol-water system was based on vapor compositions values (Y) computed from T-X data by imposition of the thermodynamic consistency requirement:

$$\sum_{i=1}^{N} X_i \, d \ln \gamma_i = 0 \qquad (2)$$

It is well known that if constant-pressure equilibrium T-X-Y data satisfy Equation (2), the corresponding physical system exhibits negligible liquid heat of mixing effects. But if liquid heat of mixing effects are negligible, then the calculation of integral heats of vaporization is straightforward. For instance, in the ethanol-water example, the integral heat of vaporization may be computed as:

$$\Delta H = X_1 \Delta H_1 + X_2 \Delta H_2 + C_p (T_{dp} - T_{bp}) \qquad (3)$$

Values of the integral heat of vaporization computed in the simple fashion indicated are compared with experimental values in Table 1. Agreement is within 1%. By contrast, the corresponding calculations with the proposed method (*1*) result in scatter as great as 10%. Presumably the large errors of the proposed method are attributable to difficulties of measuring derivatives.

Evidently the only possible utility of the proposed method would be in cases involving significant liquid heat of mixing effects. But heat of mixing is generally small compared with heat of vaporization, and the proposed procedure is so inaccurate numerically that it would give little indication of possible liquid heat of mixing.

TABLE 1. INTEGRAL HEATS OF VAPORIZATION ETHANOL-WATER SYSTEM AT 1 ATM.

Weight fraction ethanol	Enthalpy differences between vapor and liquid, cal./g. Calculated ΔH	Experimental ΔH
0.0	540	540
0.1	514	518
0.2	484	487
0.3	451	454
0.4	417	418
0.5	382	382
0.6	347	345
0.7	310	308
0.8	275	272
0.9	239	237
1.0	204	204

NOTATION

C_p = specific heat of mixture in ideal gas state
ΔH = integral heat of vaporization of mixture
ΔH_1, ΔH_2 = heats of vaporization of pure components 1, 2
N = number of components
T = temperature
T_{dp} = dew point temperature
T_{bp} = bubble point temperature
X_i, X_1, X_2 = liquid mole fractions of components i, 1, 2
Y_1, Y_2 = vapor mole fractions of components 1, 2
γ_i = activity coefficient, component i

LITERATURE CITED

1. Tao, L. C., *AIChE J.*, **15**, 362 (1969).

Packed Bed Pressure Drop—An Extension to Higher Reynolds Numbers

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The Blake-Kozeny equation for low Reynolds numbers ($f = 150\ N_{Re}^{-1}$) was extended by Ergun (*1, 2*) to

$$f = \frac{150}{N_{Re}} + 1.75 \qquad (1)$$

Here, f and N_{Re} are defined for spheres by using the bed velocity and hydraulic radius as the characteristic velocity and length. Thus, $U_c = U_B = U_s/\epsilon$ and $L_c = V_B/A_c = r_H = D(1-\epsilon)/6\epsilon$. By dropping numerical constants, the definitions are

$$\frac{L_c U_c \rho}{\mu} = \frac{D_p U_s \rho}{\mu(1-\epsilon)} \equiv \frac{D_p G_s}{\mu(1-\epsilon)} \equiv N_{Re}$$

$$\frac{F_D/A_c}{\rho U_c^2} = \frac{(\Delta P/L)(V_B/A_c)}{\rho U_s^2/\epsilon^2} = \frac{\Delta P \rho D_p \epsilon^3}{G^2 L (1-\epsilon)} \equiv f$$

The first or laminar term in Equation (1) has been verified up to $N_{Re} \sim 10^1$ (say two cycles of $10^{-1} < N_{Re} < 10^1$). The Ergun equation extended the range to four cycles of about $10^{-1} < N_{Re} < 10^3$.

The Ergun equation, however, does not describe bed behavior in the high N_{Re} range, so a better wide-range expression is needed. The data of Wentz and Thodos (*4*) are useful because they extend the N_{Re} data range to about 10^5 (*3*). Accordingly, the Wentz-Thodos data are used here to develop an expression for a six cycle range