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:

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

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

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.

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

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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

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

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

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

Table 1. Comparison of Equation (2) with Equation (1) and Data

	Analytical expressions		f(data plots)	
Velocity, N_{Re}	f(Ergun), Equation (1)	f(this work), Equation (2)	Ergun (*1, 2*)	Tallmadge (*3*)
10^0	152	154	~150	—
10^1	16.8	17.9	16 to 18	—
10^2	3.25	3.44	3.0 to 3.8	—
10^3	1.90	1.48	1.5 to 1.9	—
$3 \cdot 10^3$	1.80	1.06	—	1.1 to 1.3
10^4	1.77	0.92	—	0.8 to 1.0
$6 \cdot 10^4$	1.76	0.67	—	0.6 to 0.7
10^5	1.75	0.62	—	—

of N_{Re} by extension of the Blake-Kozeny equation to N_{Re} of 10^5. Noting that the data have been described by Tallmadge (*3*) as the smooth function $f = 5.28\ N_{Re}^{-0.19}$, we obtain the following desired result:

$$f = \frac{150}{N_{Re}} + \frac{a}{N_{Re}^{b}} = \frac{150}{N_{Re}} + \frac{4.2}{N_{Re}^{1/6}} \tag{2}$$

Here, Equation (2) is valid for $10^{-1} < N_{Re} < 10^5$ (see Table 1).

Other parameters might be used in Equation (2), but it was found that the deviations between data and the values predicted by Equation (2) are larger with $b = 1/5$. With $b = 1/7$, agreement is intermediate to that for 1/5 and 1/6. Thus b was chosen as 1/6. The parameter a was then determined by averaging local a values over the N_{Re} range of the Wentz and Thodos data (2,500 to 65,000).

The high N_{Re} data of Wentz and Thodos were taken over a wide range of porosity (35 to 88%) by using extended beds as well as closely packed beds of spheres. Thus, Equation (2) has been tested for wide ranges of both porosity and Reynolds number. Equation (2) is also an improvement because it includes the small but noticeable effect of N_{Re} in the turbulent region; no such behavior was included in Equation (1).

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Single- and Two-Phase Film Flow on Near Horizontal Planes

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The quest for more efficient three-phase heat exchangers for water desalination plants has led to the study of two-phase, liquid-liquid, films flowing concurrently down an inclined plane (*1, 2*). It was, however, experimentally found (*3*) that two-phase flow on a negatively inclined plane with a very thin layer of the lighter upper liquid phase is advantageous, since unlike the flow down a positively inclined plane, the upper film remains unbroken, at identical flow rates.

An analytical solution for two-dimensional flow of films of decreasing thickness on a horizontal plane was given by Nedderman (*4*), including a numerical solution for the case of flow down a plane with a slight positive inclination. The solution is based on the experimentally established (*5*) existence of a parabolic velocity profile in such films.

Analytical integral type of solutions are presented here for single-phase laminar flow of films of varying thickness on near horizontal planes with positive and negative inclinations (Figure 1). These solutions are then extended for the practically interesting case of two-phase, liquid-liquid concurrent flow on a negatively inclined plane with a very thin upper film.

SINGLE-PHASE FLOW

It is assumed that the flow is stable and fully developed and that semiparabolic velocity profile prevails throughout. It is further assumed that the x directed motion is dominating the flow phenomenon, and that the large interfacial radius of curvature allows neglect of surface tension forces. Viscous momentum transfer in the flow direction is neglected.

With reference to Figure 1, the governing equations of motion thus reduce to

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu\frac{\partial^2 u}{\partial y^2} + f \tag{1}$$

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