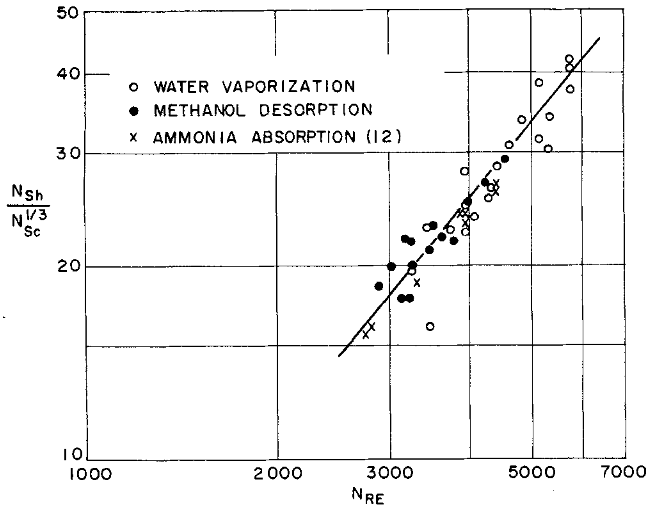

Fig. 3. Correlating of vaporization, absorption and desorption data.

determined from the gain in weight of drying tubes associated with a measured volume of gas sample. In the methanol desorption runs, the methanol concentration of the inlet liquid and outlet gas streams was determined chromatographically. The relative response of a thermal conductivity detector with the solvent water as a reference substance was used for the liquid samples. A flame ionization detector was used for the gas samples, and secondary butanol was added to the gas samples as a reference substance. Carbowax 1500 columns were used for both the liquid and gas samples.

The results of the vaporization and desorption experiments are shown in Figure 2. The water vaporization coefficients are higher than the methanol desorption coefficients. When allowance is made, however, for the different gas phase diffusivities of water and methanol, the data for the two systems agree well as shown in Figure 3. Since in both systems, solute concentrations in the gas phase are very low, gas phase diffusivity is the only gas phase property which is significantly different. Data for ammonia absorption into water (*12*) in a short wetted wall column are also shown in Figure 3 to agree well with the water vapor and methanol data. Use of the ratio $(Sh)/(Sc)^{1/3}$ in this case is equivalent to a 2/3 power adjustment of the gas phase diffusivity as suggested by the Chilton-Colburn correlation (*2*).

The agreement between the data on absorption and desorption of highly soluble gases and vaporization shown in Figure 3 indicates the similarity of these processes; the agreement tends to substantiate the suggestion that the discrepancies observed in packed tower data are in fact the result of liquid phase resistance due to elements of the liquid surface having a wide distribution of lifetimes.

NOTATION

d = short wetted wall column diameter
D = diffusivity of solute in gas phase
G = gas mass velocity, lb./hr.-sq.ft.
H_G = height of a transfer unit (gas phase), ft.
k_G = gas phase coefficient, lb. moles/hr.-sq.ft.-atm.
N_{Re} = Reynolds number, dG/μ
N_{Sc} = Schmidt number, $\mu/\rho D$
N_{Sh} = Sherwood number, $k_G\ RTd/D$
R = gas constant
T = temperature
μ = viscosity
ρ = density

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A Thermodynamic Relationship between Integral Heat of Vaporization and Isobaric Equilibrium Vapor-Liquid Compositions

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A rigorous thermodynamic equation relating the phase composition and the phase enthalpy difference for an isobaric, multicomponent vapor-liquid equilibrium system was recently proposed by me (*1*). That equation establishes a useful relationship in estimating the enthalpy-composition space between the two saturated phases for the design of distillation equipment. This paper shows an analogous derivation that results in an equation containing the commonly used integral heat of vaporization instead of the phase enthalpy difference.

The integral heat of vaporization is defined by Equation (1); the right side of which consists of three groups.

$$\lambda_x = H^V{}_{xd} - H^L{}_{xb} = [H^V{}_{xd} - H^*{}_{xd}] + [H^*{}_{xd} - H^*{}_{xb}] + [H^*{}_{xb} - H^L{}_{xb}] \quad (1)$$

These groups indicate molar enthalpies required in vaporizing the liquid to an ideal gas at T_{xb}, heating the ideal gas from T_{xb} to T_{xd} and compressing the ideal gas to the pressure of the equilibrium system at T_{xd}.

By following the known thermodynamic relationships between fugacities of components in a mixture and its enthalpy relative to the corresponding ideal gas, Equations (2) and (3) describe the saturated vapor and liquid phases having the same composition, x, at a constant pressure.

$$H^*{}_{xd} - H^V{}_{xd} = RT^2{}_{xd} \sum_i x_i \,[d \ln f^V{}_{xi}/dT_{xd}] \quad (2)$$

$$H^*{}_{xb} - H^L{}_{xb} = RT^2{}_{xb} \sum_i x_i \,[d \ln f^L{}_{xi}/dT_{xb}] \quad (3)$$

Since the saturated vapor phase in equilibrium with the liquid phase of x has a composition y at a constant pressure, $T_{xb} = T_{yd}$ and $f^L{}_{xi} = f^V{}_{yi}$. With these substitutions (3) can be transformed into Equation (4).

$$H^*{}_{xb} - H^L{}_{xb} = RT^2{}_{yd} \sum_i x_i \,[d \ln f^V{}_{yi}/dT_{yd}] \quad (4)$$

By combining Equations (1), (2), and (4) we obtain the aimed relationship as in Equation (5).

$$\lambda_x = RT^2{}_{yd} \sum_i x_i \,[d \ln f^V{}_{yi}/dT_{yd}] - RT^2{}_{xd} \sum_i x_i \,[d \ln f^V{}_{xi}/dT_{xd}] + [H^*{}_{xd} - H^*{}_{xb}] \quad (5)$$

The difference is that one has to obtain derivatives at two composition points in Equation (5) instead of at only one point in the previous equation (*1*). This is indicated in Figure 1. However, both equations require only a complete set of x-y-T at a constant pressure and an equation of state of vapor.

For low pressure systems, the vapor phase can be assumed as ideal or $f^V{}_{yi} = y_iP$ and $f^V{}_{xi} = x_iP$. Equation (5) can then be simplified to Equation (6) since the second sum in Equation (5) vanishes due to $\sum_i d\,x_i = 0$.

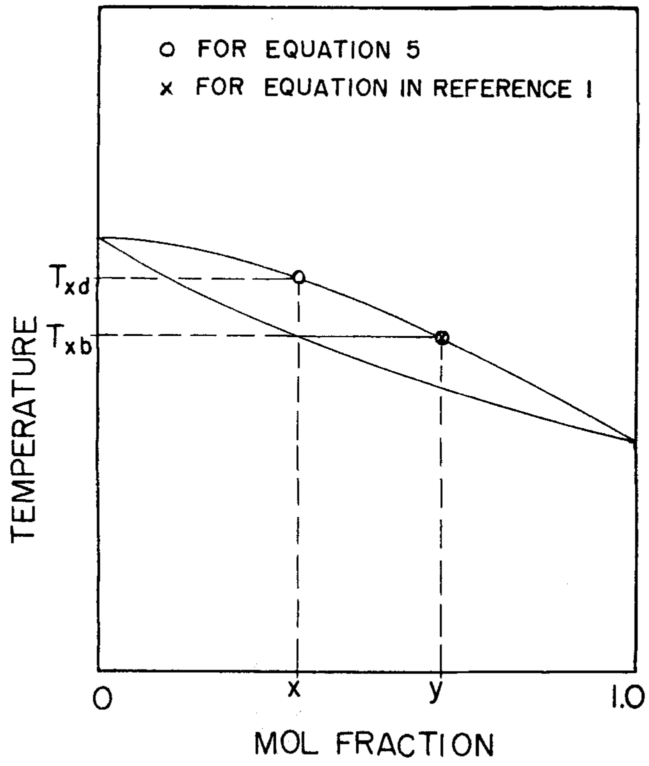

Fig. 1. Physical states of those points in two enthalpy equations.

$$\lambda_x = RT^2{}_{yd} \sum_i \left[\frac{x_i}{y_i} \frac{dy_i}{dT_{yd}} \right] + [H^*{}_{xd} - H^*{}_{xb}] \quad (6)$$

The first group on the right side represents the enthalpy difference which one obtains in the reference equation (*1*) and the last term compensates the temperature difference between the dew point and the bubble point of the vapor mixture with a composition x.

It is interesting to further develop the first sum in Equation (5) by using Equation (3), $f^L{}_{xi} = \gamma_i x_i \phi_i p_i{}^0 \exp\left[\int_{p_i{}^0}^{P} v_i{}^{L0} \; dp/RT\right]$, the Clapeyron equation and the conventional relationship of fugacity and enthalpy to result in Equation (7):

$$H^*{}_{xb} - H^L{}_{xb} = [\Sigma x_i H^{L0}{}_{ib} - H^L{}_{xb}] + \sum_i x_i \left[\int_P^{p_i{}^0} v_i{}^{L0}\, dp + \lambda_i{}^0 \,(RT_{xb}/p_i{}^0 \Delta v_i{}^0) + H^*{}_{ib} - H_{ib}{}^{V0} \right] \quad (7)$$

where $H_{ib}{}^{L0}$ is at P and $H_{ib}{}^{V0}$ at $p_i{}^0$. The right side interprets an equivalent process involving the isothermal enthalpy changes of separating pure liquid components from the liquid mixture (negative heat of mixing), changing pressure on liquid from P to $p_i{}^0$ for each component, evaporating each liquid to pure vapor at $p_i{}^0$ and expanding each real vapor to corresponding ideal gas. Therefore, Equation (7) proves that heat of mixing of a saturated liquid is included in both Equation (5) and the reference equation (*1*) as expected.

NOTATION

f = fugacity of a component in a mixture at the saturation T and P
H = molar enthalpy
p = pressure or vapor pressure
P = total pressure of the system
R = gas constant
T = absolute temperature
v = molar volume
x = mole fraction of either a liquid or a vapor
y = mole fraction of vapor in equilibrium with a liquid of x
γ = liquid phase activity coefficient
Δ = difference between the saturated vapor and liquid
λ = molar integral heat of vaporization
ϕ = fugacity coefficient of a pure component at its own vapor pressure

Subscript

x = with a composition of x
y = with a composition of y
b = bubble point or at the bubble point
d = dew point or at the dew point
i = identity of component in a mixture

Superscript

L = liquid phase
V = vapor phase
0 = in a pure state
$*$ = as an ideal gas

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