COMMUNICATIONS TO THE EDITOR

Clapeyron Equation of a Multicomponent Solution

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This communication is intended to clarify the relationship between a recently proposed (3), rigorous thermodynamic equation relating the equilibrium phase composition–phase enthalpy difference ΔH for an isobaric multicomponent system, and the Clapeyron equation. It also provides a rigorous and simple mathematical derivation of the Clapeyron equation for a multicomponent system.

The recently proposed equation (3) without the constraint of constant pressure is Equation (1) for a vapor-liquid equilibrium system:

$$\sum_i (x_i - y_i)\, d\ln f^V{}_{yi} = \sum_i (x_i - y_i)\, d\ln f^L{}_{xi} = \frac{\Delta H - \Delta H^*}{RT^2}\, dT + \frac{\Delta v}{RT}\, dP \qquad (1)$$

where

$$\Delta H = H_y{}^V - H_x{}^L$$

$$\Delta H^* = H_y{}^* - H_x{}^* = \sum_i y_i H_i{}^* - \sum_i x_i H_i{}^*$$

$$\Delta v = v_y{}^V - v_x{}^L$$

By imposing a constraint of constant phase composition, the following equations can be found in most thermodynamic textbooks (for example, *1*):

$$\left[d\ln f^V{}_{yi} = \frac{H_i{}^* - \overline{H}^L{}_{yi}}{RT^2}\, dT + \frac{\overline{v}^V{}_{yi}}{RT}\, dP \right]_y \qquad (2)$$

$$\left[d\ln f^L{}_{xi} = \frac{H_i{}^* - \overline{H}^L{}_{xi}}{RT^2}\, dT + \frac{\overline{v}^L{}_{xi}}{RT}\, dP \right]_x \qquad (3)$$

Combining Equations (1) and (2), and (1) and (3) result in Equations (4) and (5) as Clapeyron equations of a multicomponent system:

$$\left(\frac{\partial P}{\partial T}\right)_y = \frac{\Delta H + \Sigma (x_i - y_i)\overline{H}^V{}_{yi}}{T[\Delta v + \Sigma (x_i - y_i)\overline{v}^V{}_{yi}]} = \frac{\Sigma x_i \overline{H}^V{}_{yi} - H_x{}^L}{T[\Sigma x_i v^V{}_{yi} - v_x{}^L]} \qquad (4)$$

$$\left(\frac{\partial P}{\partial T}\right)_x = \frac{\Delta H + \Sigma (x_i - y_i)\overline{H}^L{}_{xi}}{T[\Delta v + \Sigma (x_i y_i)\overline{v}^L{}_{xi}]} = \frac{H_y{}^V - \Sigma y_i \overline{H}^L{}_{xi}}{T[v_y{}^V - \Sigma y_i \overline{v}^L{}_{xi}]} \qquad (5)$$

They agree with the Clapeyron equation for binary systems derived by Dodge (*1*), and for multicomponent systems by Hobson and Weber (*2*) without rigorous deviation. The sums of enthalpy terms in Equations (4) and (5) are respectively differential latent heat of condensation and differential latent heat of vaporization. From these equations, special cases of interest may be obtained for a multicomponent system. For example, at low pressures the vapor usually behaves as ideal gas so that the denominator of Equation (5) equals RT^2/P. This results in the following Clausius-Clapeyron equation.

$$\left[\frac{\partial \ln P}{\partial (1/T)} \right]_x = -\frac{H_y{}^V - \Sigma y_i \overline{H}^L{}_{xi}}{R} \qquad (6)$$

If the liquid solution is also ideal, the enthalpy sum will be $\Sigma y_i \Delta H_i$, an average latent heat of the vapor mixture, where ΔH_i is the latent heat of vaporization of pure component i.

Both Equations (1) and (4) can be used to estimate the enthalpy of a saturated liquid phase from the known enthalpy of the saturated vapor phase. Equation (1) was shown (3) to be superior to Equation (4) because of the following:

1. The use of a constant pressure constraint is more practical than that of a constant composition constraint so far as data requirement is concerned.
2. The use of a fugacity term eliminates the necessity of making many differential operations to obtain partial enthalpies and partial volumes of the vapor phase.

Besides estimating the enthalpy of a saturated phase, Equations (1), (4), and (5) can also be utilized to test data consistency or to estimate phase composition if enthalpy information of mixtures are available.

Finally, Equations (1), (4), and (5) are applicable to all types of phase equilibria involving solid, liquid, and vapor phases if one designates L and V as phases 1 and 2, with x and y as mol fractions in those phases respectively. Therefore, they may be useful in prediction and data testing of multicomponent systems with equilibrium phases other than the vapor-liquid equilibrium systems.

NOTATION

f = fugacity of a component in a mixture at the saturation T and P
H = molar enthalpy
P = total pressure of the system
R = gas constant
T = absolute temperature
v = molar volume
x = mole fraction of a saturated liquid
y = mole fraction of vapor in equilibrium with a liquid of x
Δ = difference between the saturated vapor and liquid

Subscript

x = with a composition of x
y = with a composition of y
i = identity of component in a mixture

Superscript

L = liquid phase
V = vapor phase
$*$ = as an ideal gas
$-$ = partial quantity

LITERATURE CITED

1. Dodge, B. F. "Chemical Engineering Thermodynamics," p. 124, 125, 134, McGraw-Hill, New York (1944).
2. Hobson, M. and J. H. Weber, *Petrol. Proc.*, 155 (1957).
3. Tao, L. C., *AIChE J.*, to be published.