Minimum and Maximum Boiling Azeotropes: The Gibbs-Konovalov Theorem

Chemistry CHEM 213W

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As we discussed in class, a system where the temperature-composition phase diagram has a minimum or maximum for some composition is called an azeotrope. Here we will show that the composition of the vapor and liquid phases of azeotropes must be the same. This result is called the Gibbs-Konovalov theorem, and is an sophisticated exercise in Maxwell relations, equilibrium conditions, and partial molar quantities.

For what follow, we will call the two components 1 and 2. Quantities pertaining to the two phases will be distinguished by having a prime in the case of the vapor. Finally, the mole fraction of 1 in the liquid and vapor phases are x_1 and y_1, respectively.

The phase rule tells us that a two-phase, binary mixture has $F = 2 + 2 - 2 = 2$ degrees of freedom. One will be taken to be the pressure, which is held fixed. The other will be some convenient concentration variable. In general, the chemical potentials in either phase can be viewed as functions of T,P, and a mole fraction (e.g., x_1 or y_1). Hence, for arbitrary changes of state:

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,x_1} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_i}{\partial x_1}\right)_{P,T} dx_1. \tag{1}$$

The first two partial derivatives may be rewritten by using Maxwell relations obtained from the Gibbs free energy (recall, $dG = -SdT + VdP + \sum \mu_i dN_i$). Thus,

$$d\mu_i = -\bar{S}_i dT + \bar{V}_i dP + \left(\frac{\partial \mu_i}{\partial x_1}\right)_{P,T} dx_1, \tag{2}$$

where

$$\bar{S}_i \equiv \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_{j\neq i}},$$

and

$$\bar{V}_i \equiv \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

are the partial molar entropies and volumes, respectively.

Equation (2) must hold for either component in either phase (in the vapor phase, just add primes to all quantities and change x_1 to y_1). Moreover, for changes in state along the

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coexistence curve,

$$d\mu_i = d\mu_i' \quad i = 1, 2. \tag{3}$$

If we use Eq. (2) in (3), two equations relating changes in T, P, x_1 and y_1 are obtained. In addition, for the case at hand $dP = 0$, and thus, we find that

$$-(\bar{S}_i - \bar{S}_i')dT + \left(\frac{\partial \mu_i}{\partial x_1}\right)_{T,P} dx_1 = \left(\frac{\partial \mu_i'}{\partial y_1}\right)_{T,P} dy_1, \quad i = 1, 2. \tag{4}$$

Next, we divide through by dx_1, multiply the equation for component 1 by x_1, the equation for component 2 by x_2 and add the results. This gives

$$-[x_1(\bar{S}_1 - \bar{S}_1') + x_2(\bar{S}_2 - \bar{S}_2')]\left(\frac{\partial T}{\partial x_1}\right)_{P,coex} + x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \mu_2}{\partial x_1}\right)_{T,P}$$

$$= \left[x_1\left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P} + x_2\left(\frac{\partial \mu_2'}{\partial y_1}\right)_{T,P}\right]\left(\frac{\partial y_1}{\partial x_1}\right)_{P,coex}. \tag{5}$$

The changes in the chemical potentials at constant T and P are not independent, but are related through the Gibbs-Duhem equations,

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{6a}$$

and

$$y_1 d\mu_1' + y_2 d\mu_2' = 0. \tag{6b}$$

Dividing Eqs. (6a) and (6b) by dx_1 and dy_2, respectively, and using the results in Eq. (5) shows that

$$-[x_1(\bar{S}_1 - \bar{S}_1') + x_2(\bar{S}_2 - \bar{S}_2')]\left(\frac{\partial T}{\partial x_1}\right)_{P,coex} = \left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P}\left(\frac{\partial y_1}{\partial x_1}\right)_{coex}\left[x_1 - \frac{x_2 y_1}{y_2}\right] \tag{7}$$

$$= \left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P}\left(\frac{\partial y_1}{\partial x_1}\right)_{coex}\frac{(x_1 - y_1)}{y_2}, \tag{8}$$

where the last equality is obtained by noting that the sum of the mole fractions in either phase is unity.

The left hand side of the equation vanishes at a minimum or maximum of the T-X phase diagram; hence, one of the factors on the right hand side must be zero. Thermodynamic stability requirements (i.e., G is a minimum) can be used to show that

$$\left(\frac{\partial \mu_1'}{\partial x_1}\right)_{T,P} > 0.$$

It is also easy to show, using the definitions of the mole fractions and the fact that the total number of moles of each type is constant, that

$$\left(\frac{\partial y_1}{\partial x_1}\right)_{coex} \neq 0.$$

Hence, at an azeotropic point, $x_1 = y_1$; i.e., the compositions of the liquid and vapor phases are the same. This is called the Gibbs-Konovalov theorem. Note that the derivation did not require any specific properties of liquids or gases and our result will hold for any two-phase coexistence in binary mixtures.

Finally, note that essentially the same manipulations can be used to show that

$$\left(\frac{\partial P}{\partial x_1}\right)_{T,coex} = \frac{\left(\frac{\partial \mu_1'}{\partial y_1}\right)_{T,P} \left(\frac{\partial y_1}{\partial x_1}\right)_{coex} (x_1 - y_1)}{y_2[x_1(\bar{V}_1 - \bar{V}_1') + x_2(\bar{V}_2 - \bar{V}_2')]} \ .$$

Hence, the P-X phase diagram will also have a minimum or maximum at the azeotropic composition.