

Chemical potential forms allowed by Gibbs-Duhem

Jian Qin
March 7, 2017

1.1 Solution thermodynamics.

The free energy of mixtures is typically decomposed as a summation

$$g^{\text{ideal}} + g^{\text{ex}} = \sum_i^c x_i (g_i + \ln(x_i)) + g^{\text{ex}},$$

in which x_i is the molar fraction, $g_i = g_i(T, P)$ is the free energy density of species i , $x_i \ln(x_i)$ is the mixing entropy contribution to free energy, and $g^{\text{ex}} = g^{\text{ex}}(x_1, x_2, \dots, x_c; T, P)$ is the excess free energy density.

The ideal mixing term g^{ideal} results in a chemical potential

$$\begin{aligned} \mu_i^{\text{ideal}} &= \left(\frac{\partial n g^{\text{ideal}}}{\partial n_i} \right)_{j \neq i} = g^{\text{ideal}} + n \left(\frac{\partial g^{\text{ideal}}}{\partial n_i} \right)_{j \neq i} \\ &= \sum_j^c x_j (g_j + \ln(x_j)) + (1 - x_i)(g_i + 1 + \ln(x_i)) - \sum_{j \neq i}^c x_j (g_j + 1 + \ln(x_j)) \\ &= g_i(T, P) + \ln(x_i). \end{aligned}$$

Here g_i is the chemical potential of species i . For ideal mixture of *ideal* gases, this results in

$$\mu_i^{\text{ideal}} = g_i^{(\text{v})}(T, P_0) + \ln(y_i P / P_0).$$

Here y_i represents the molar fraction of species i in gaseous phase, and $g_i^{(\text{v})}(T, P_0)$ is the chemical potential of pure vapor at $P_0 = 1$ atm. (Note that the notation $g_i^{(\text{v})}(T, P_0)$ is redundant as g_i does not depend on pressure for ideal gas.)

The excess free energy gives rise to an excess chemical μ_i^{ex} , which may takes arbitrary form as derived from g^{ex} . The simplest form of g^{ex} is the Flory-Huggins type free energy density, Ax_1x_2 , etc. The activity or fugacity coefficients are introduced, formally, such that

$$\mu_i = g_i(T, P) + \ln(x_i) + \mu_i^{\text{ex}} = g_i(T, P) + \ln(\gamma_i x_i),$$

where the activity coefficients are defined by $\gamma_i = \exp(\mu_i^{\text{ex}})$. The activity coefficients are constrained by the Gibbs-Duhem relation (the ideal mixing parts satisfy Gibbs-Duhem relation spontaneously)

$$\sum_i x_i d\mu_i^{\text{ex}} = \sum_i x_i d\ln(\gamma_i) = 0.$$

1.2 Vapor/Liquid/Equilibrium.

The chemical potentials of vapor and liquid phases are equal at the VLE. It implies that, for pure substance ($x_i = y_i = 1$), at the saturation temperature and pressure,

$$\mu_i^{(l)} = \mu_i^{(\text{v})} \quad (\text{ideal mixture}) \quad \rightarrow \quad g_i^{(l)}(T, P^{\text{sat}}(T)) = g_i^{(\text{v})}(T, P_0) + \ln(P^{\text{sat}}/P_0).$$

This is just the chemical potential at the saturation condition. For convenience, it is defined as

$$\Gamma_i(T) = g_i(T, P^{\text{sat}}(T)).$$

Using this notation, the vapor phase chemical potential at arbitrary pressure may be denoted

$$\mu_i^{(\text{v})} = \Gamma_i(T) + \ln(y_i P / P^{\text{sat}}(T)).$$

The liquid phase chemical potential is written

$$\mu_i^{(l)} = \Gamma_i(T) + (g_i(T, P) - \Gamma_i(T)) + \ln(x_i).$$

The correction accounts for the departure from the saturation pressure, and may be calculated by using

$$\begin{aligned} g_i(T, P) - \Gamma_i(T) &= \int_{P^{\text{sat}}}^P dp V(T, p) \\ &\simeq v^{(l), \text{sat}}(T)(P - P^{\text{sat}}(T)). \end{aligned}$$

This term is the Poynting correction factor. In ideal solutions, the equilibrium condition becomes

$$g_i(T, P) - \Gamma_i(T) = \ln(y_i P / (x_i P^{\text{sat}})).$$

In case the pressure is low, the term to the left-hand is small, and the Raoult's law is obtained

$$y_i P = x_i P^{\text{sat}}.$$

1.3 VLE for nonideal mixture of nonideal fluids.

The introduction of $\Gamma(T)$ for saturation chemical potential is still convenient. The contribution from the activity and fugacity coefficients γ_i and ϕ_i are merged with terms x_i and y_i , leaving the following

$$\begin{aligned} \mu_i^{(l)} &= \Gamma(T) + (g_i(T, P) - \Gamma_i(T)) + \ln(\gamma_i x_i) \\ \mu_i^{(v)} &= \Gamma(T) + \ln(\phi_i y_i P / P^{\text{sat}}(T)). \end{aligned}$$

The equilibrium condition becomes

$$\phi_i y_i P = \gamma_i x_i P_i^{\text{sat}} \exp(g_i(T, P) - \Gamma_i(T))$$

and simplies to

$$\phi_i y_i P = \gamma_i x_i P_i^{\text{sat}}$$

when the *Poynting correction factor is small*, or the difference between P and P^{sat} is small. The activity and fugacity coefficients mainly depend on compositions x_i and, in principle, also depend on P and T . They encoded all the excess term needed to correct the ideal mixing.

1.4 Azeotrope condition.

To consider when azeotrope emerges, we examine the variation of equilibrium condition. It is convenient to consider the logarithms of the VLE condition, or to consider the chemical potential identity directly, which yields

$$\ln(\phi_i y_i) + \ln(P / P_i^{\text{sat}}) = \ln(\gamma_i x_i) + g_i(T, P) - \Gamma_i(T).$$

The variation of the above with respect to the variation in composition dx_i is given by

$$d \ln(\phi_i y_i) = d \ln(\gamma_i x_i) + \left(\frac{\partial g_i(T, P)}{\partial P} - \frac{1}{P} \right) dP + \left(\frac{1}{P_i^{\text{sat}}} \frac{\partial P_i^{\text{sat}}}{\partial T} + \frac{\partial g_i(T, P)}{\partial T} - \frac{\partial \Gamma_i}{\partial T} \right) dT. \quad (*)$$

The above is the differential identity demanded by the VLE coexistence loci. The variations dP and dT are understood as the variation resulting from changes in composition x_i . *Caution*: the differentials of ϕ_i and γ_i in principle involves contributions coming from dP and dT , and are understood as given by

$$\begin{aligned} d \ln(\phi_i y_i) &= \sum_j^c \frac{\partial \ln(\phi_i y_i)}{\partial x_j} dx_j + \frac{\partial \ln(\phi_i y_i)}{\partial P} dP + \frac{\partial \ln(\phi_i y_i)}{\partial T} dT \\ d \ln(\gamma_i x_i) &= \sum_j^c \frac{\partial \ln(\gamma_i y_i)}{\partial x_j} dx_j + \frac{\partial \ln(\gamma_i x_i)}{\partial P} dP + \frac{\partial \ln(\gamma_i x_i)}{\partial T} dT. \end{aligned}$$

Now we multiply the Eqs. (*) for all $i = 1, 2, \dots, c$ by corresponding x_i and sum them up, and get

$$\sum_i^c \frac{x_i}{y_i} y_i d \ln(\phi_i y_i) = \sum_i^c x_i d \ln(\gamma_i x_i) + \left(\frac{\partial g_i(T, P)}{\partial P} - \frac{1}{P} \right) dP + \left(\frac{1}{P_i^{\text{sat}}} \frac{\partial P_i^{\text{sat}}}{\partial T} + \frac{\partial g_i(T, P)}{\partial T} - \frac{\partial \Gamma_i}{\partial T} \right) dT.$$

Necessary condition. The azeotrope is defined such that $y_i = x_i$. The Gibbs-Duhem relation for chemical potential, $\sum_i x_i d\mu_i = 0$, further demands that

$$\begin{aligned} \sum_i^c y_i d \ln(\phi_i y_i)|_{T, P} &= \sum_i^c y_i \left(\sum_j^c \frac{\partial \ln(\phi_i y_i)}{\partial y_j} dy_j \right) = 0 \\ \sum_i^c x_i d \ln(\gamma_i x_i)|_{T, P} &= \sum_i^c x_i \left(\sum_j^c \frac{\partial \ln(\gamma_i x_i)}{\partial x_j} dx_j \right) = 0. \end{aligned}$$

This leads to (Noting that $1/P$ really should be RT/P since RT factor in logarithm terms have all been neglected.)

$$\begin{aligned} &\left(\frac{\partial g_i(T, P)}{\partial P} - \frac{1}{P} + \sum_i^c x_i \frac{\partial \ln(\gamma_i x_i)}{\partial P} - \sum_i^c y_i \frac{\partial \ln(\phi_i y_i)}{\partial P} \right) dP + \\ &\left(\frac{1}{P_i^{\text{sat}}} \frac{\partial P_i^{\text{sat}}}{\partial T} + \frac{\partial g_i(T, P)}{\partial T} - \frac{\partial \Gamma_i}{\partial T} + \sum_i^c x_i \frac{\partial \ln(\gamma_i x_i)}{\partial T} - \sum_i^c y_i \frac{\partial \ln(\phi_i y_i)}{\partial T} \right) dT = 0. \end{aligned}$$

Noting that $g_i(T, P) + \ln(\gamma_i x_i)$ is the chemical potential of liquid, and $\Gamma_i(T) + \ln(\phi_i y_i P / P_i^{\text{sat}})$ is that of vapor, the above can be written

$$\left(v^{(l)} - v^{(v)} \right) dP - \left(s^{(l)} - s^{(v)} \right) dT = 0.$$

Neither coefficients vanish at the VLE except at the critical point. So at the isothermal condition, the azeotropy leads to vanishing dP with respect to changes in composition or, at the isobaric condition, leads to vanishing dT . So at the zeotrope, $T(x_i)$ is a local extremal for constant P , and $P(x_i)$ is a local extremal for constant T .

Sufficient condition. In case T or P is fixed, and P or T is a local extremal, so that $dT = 0$ and $dP = 0$, it is apparent that

$$\sum_i^c \frac{x_i}{y_i} y_i d \ln(\phi_i y_i) = \sum_i^c x_i d \ln(\gamma_i x_i) = 0.$$

The second equality is derived from the Gibbs-Duhem relation for liquid phase. To use the Gibbs-Duhem condition for vapor phase, we replace $\frac{x_c}{y_c} y_c d \ln(\phi_c y_c)$ by $-\sum_i^{c-1} \frac{x_c}{y_c} y_i d \ln(\phi_i y_i)$. Then we have

$$\sum_i^{c-1} \left(\frac{x_i}{y_i} - \frac{x_c}{y_c} \right) y_i d \ln(\phi_i y_i) = 0.$$

Since T or P is a local extremal with respect to arbitrary composition variation, the coefficients in the above all vanish, leaving

$$\frac{x_1}{y_1} = \frac{x_2}{y_2} = \dots = \frac{x_c}{y_c}.$$

This is an $c - 1$ dimensional linear system for $c - 1$ unknowns x_1, x_2, \dots, x_{c-1} at fixed y_i or vice versa. The unique solution is $x_1 = y_1, x_2 = y_2, \dots, x_c = y_c$. The argument for why $d \ln(\phi_i y_i) \neq 0$ is provided in the next section.

Therefore, being a local minimal in composition is the necessary and sufficient condition for azeotrope.

1.5 Derivation using chemical potential.

Chemical potentials μ_i depend on composition $\{x_i\}$, temperature T , and pressure P , generically: $\mu_i = \mu_i(x_i; T, P)$. Their differentials can be denoted

$$d\mu_i = d'\mu_i + \frac{\partial\mu_i}{\partial P}dP + \frac{\partial\mu_i}{\partial T}dT = d'\mu_i + \bar{V}_i dP - \bar{S}_i dT.$$

Here $d'\mu_i$ are differentials caused by composition variation at constant T and P . The Gibbs-Duhem relation is essentially $\sum_i^c x_i d'\mu_i = 0$.

The VLE is governed by equilibrium condition $\mu_i^{(v)} = \mu_i^{(l)}$. Equating the differentials along the coexisting loci gives $d\mu_i^{(v)} = d\mu_i^{(l)}$. To apply the Gibbs-Duhem condition, we multiply both sides by composition x_i in the liquid phase and sum over i . The result is

$$\sum_i^c \frac{x_i}{y_i} y_i d'\mu_i^{(v)} + \left(\sum_i^c x_i \bar{v}_i^{(v)} \right) dP - \left(\sum_i^c x_i \bar{s}_i^{(v)} \right) dT = \left(\sum_i^c x_i \bar{v}_i^{(l)} \right) dP - \left(\sum_i^c x_i \bar{s}_i^{(l)} \right) dT.$$

According to the Euler's theorem for extensive variables, the terms in brackets are recognized as molar volume and entropy of vapor and liquid phases respectively. So we further write

$$\sum_i^c \frac{x_i}{y_i} y_i d'\mu_i^{(v)} = \left(v^{(l)} - \sum_i^c x_i \bar{v}_i^{(v)} \right) dP - \left(s^{(l)} - \sum_i^c x_i \bar{s}_i^{(v)} \right) dT.$$

Necessity. At azeotrope, $x_i = y_i$. The left hand side of the above vanishes because of Gibbs-Duhem relation. The right hand side becomes

$$\left(v^{(l)} - v^{(v)} \right) dP - \left(s^{(l)} - s^{(v)} \right) dT = 0.$$

Following the same logic as before, P or T is local extremal for constant T or P . The above is essentially the Clausius-Clapeyron equation when applied to one-component system for which $x_i = y_i$ by definition.

Sufficiency. Demanding $dT = 0$ for arbitrary composition variation at fixed P or demanding $dP = 0$ for arbitrary composition variation at fixed T leads to

$$\sum_i^c \frac{x_i}{y_i} y_i d'\mu_i^{(v)} = \sum_i^{c-1} \left(\frac{x_i}{y_i} - \frac{x_c}{y_c} \right) y_i d'\mu_i^{(v)} = 0$$

for arbitrary variation $d'\mu_i^{(v)}$ resulting from composition change. As already discussed, the only solution is the azeotrope $x_i = y_i$ for $i = 1, 2, \dots, c$. So why does not $d'\mu_i^{(v)}$ vanish? It relates to $d'x_j$ (for $j = 1, 2, \dots, c-1$) through the Jacobian, $d'\mu_i^{(v)} = \frac{\partial\mu_i^{(v)}}{\partial x_j} d'x_j$. The stability condition requires the Jacobian to be positive-definite. So the only possibility is that all the coefficients, $\frac{x_i}{y_i} - \frac{x_c}{y_c}$, vanish.

The azeotrope condition simply states that when the composition difference vanishes, the coexistence loci are obtained by requiring variations related to dP , dT , and any other non-composition degree of freedom vanish. The azeotrope line or surface in the space (T, P, x_i) is stationary along the x_i axes.

(March 3, 2017)

1.6 Tangent rule in multi-component system.

The free energy density is determined by composition, $g = g(x_i)$. The composition relates to molarity via $x_i = n_i/n = n_i/\sum_i^c n_i$. The differential $\frac{\partial x_j}{\partial n_i} = (\delta_{i,j} - x_j)/n$. The chemical potential is thus given by

$$\begin{aligned}\mu_i &= \frac{\partial(n g)}{\partial n_i} = g - (\delta_{i,j} - x_j) \frac{\partial g}{\partial x_j} \\ &= (g - \mathbf{x} \cdot \nabla g) + \frac{\partial g}{\partial x_i}.\end{aligned}$$

The Euler's additivity relation is satisfied:

$$\mathbf{x} \cdot \boldsymbol{\mu} = \sum_i^c x_i \mu_i = (g - \mathbf{x} \cdot \nabla g) + \sum_i^c x_i \frac{\partial g}{\partial x_i} = g.$$

The Gibbs-Duhem relation is verified by first computing the differential at constant T and P ($d \rightarrow d'$),

$$d' \mu_i = d'(g - \mathbf{x} \cdot \nabla g) + d' \frac{\partial g}{\partial x_i}.$$

then computing the summation of composition-weighted variations

$$\begin{aligned}\sum_i^c x_i d' \mu_i &= d'(g - \mathbf{x} \cdot \nabla g) + \sum_i^c x_i d' \frac{\partial g}{\partial x_i} \\ &= d'g - \nabla g \cdot d\mathbf{x} - \mathbf{x} \cdot \nabla \nabla g \cdot d\mathbf{x} + \mathbf{x} \cdot \nabla \nabla g \cdot d\mathbf{x} \\ &= d'g - \nabla g \cdot d\mathbf{x} \\ &= 0.\end{aligned}$$

When variations in T and P are enabled,

$$\begin{aligned}d\mu_i &= d' \mu_i - \bar{s}_i dT + \bar{v}_i dP \\ \sum_i^c x_i d\mu_i &= 0 - s dT + v dP,\end{aligned}$$

which is the complete form of Gibbs-Duhem: The total differential $\mathbf{x} \cdot d\boldsymbol{\mu}$ is governed by dT and dP .

(March 7, 2017)