The Relationship Between Chemical Potentials, Fugacities, Activities, and Gibbs Free Energies
(with specific application to partial derivatives required in mass transport)

I. The Chemical Potential

The chemical potential of component α in phase ϕ, μ_α^ϕ, is defined as

$$\mu_\alpha^\phi \equiv \left(\frac{\partial N^\phi \underline{G}^\phi}{\partial N_\alpha^\phi} \right)_{T,P,N_{\beta \neq \alpha}} \tag{1}$$

where $\underline{G}^\phi$ is the molar Gibbs free energy of the mixture of phase ϕ, N^ϕ is the total number of moles in phase ϕ, and N_α^ϕ is the number of moles of component α in phase ϕ. As a result of this definition, the molar Gibbs free energy of the mixture is given by

$$\underline{G}^\phi = \sum_{\alpha=1}^{N_C} x_\alpha^\phi \mu_\alpha^\phi \tag{2}$$

One typically proceeds by writing the molar Gibbs free energy of the mixture as a sum of an ideal mixture (IM) component and an excess (XS) component,

$$\underline{G}^\phi = \underline{G}^{\phi,IM} + \underline{G}^{\phi,XS} \quad , \tag{3}$$

where the excess term, by definition, includes everything that isn't included in the ideal mixture. The molar Gibbs free energy of an ideal mixture is defined as

$$\underline{G}^{\phi,IM} \equiv RT \sum_{\alpha=1}^{N_C} x_\alpha^\phi \ln\left(x_\alpha^\phi\right). \tag{4}$$

As a consequence of this definition, the excess molar Gibbs free energy of a mixture must be

$$\underline{G}^{\phi,XS} = \underline{G}^\phi - \underline{G}^{\phi,IM} = \underline{G}^\phi - RT \sum_{\alpha=1}^{N_C} x_\alpha^\phi \ln\left(x_\alpha^\phi\right). \tag{5}$$

The definitions of the mixture properties also defined the partial molar Gibbs free energy of an ideal mixture as

$$\overline{G}_\alpha^{\phi,IM} \equiv \underline{G}_\alpha^\phi + RT \ln\left(x_\alpha^\phi\right), \tag{6}$$

where $\underline{G}_\alpha^\phi$ is the molar Gibbs free energy of component α in the pure state. The partial molar excess Gibbs free energy of a mixture is

$$\overline{G}_\alpha^{\phi,XS} \equiv \mu_\alpha^\phi - \underline{G}_\alpha^\phi - RT \ln\left(x_\alpha^\phi\right). \tag{7}$$

As a result of equations (6) and (7), we see that we have an expression for the chemical potential in terms of ideal mixture and excess terms, which is analogous to the expression for the molar Gibbs free energy of the mixture in equation (3), namely

$$\mu_\alpha^\phi = \overline{G}_\alpha^{\phi,IM} + \overline{G}_\alpha^{\phi,XS} = \underline{G}_\alpha^\phi + RT \ln\left(x_\alpha^\phi\right) + \overline{G}_\alpha^{\phi,XS}. \tag{8}$$

II. Fugacities

II.A. Fugacities of Pure Components

In phase ϕ of the pure component α, we define a fugacity, f_α^ϕ, as

$$f_\alpha^\phi \equiv P \exp\left(\frac{\underline{G}_\alpha^\phi - \underline{G}_\alpha^{IG}}{RT}\right), \tag{9}$$

where $\underline{G}_\alpha^{IG}$ is the molar Gibbs free energy of pure alpha as an ideal gas, where the pressure is equal to zero. When we have an equation of state, the evaluation of the pure component fugacity involves evaluating the following integral

$$f_\alpha^\phi \equiv P \exp\left(\frac{1}{RT}\int_0^P \left(\underline{V}_\alpha^\phi(P) - \frac{RT}{P}\right)dP\right). \tag{10}$$

We can also define a fugacity coefficient as

$$\varphi_\alpha^\phi \equiv \frac{f_\alpha^\phi}{P}, \tag{11}$$

II.B. Fugacities of Mixtures

We are interested in multi-component vapor-liquid equilibrium. In the multi-component case, the fugacity of component α in a mixture in phase ϕ, $\overline{f}_\alpha^\phi$, is defined as

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$$\bar{f}_\alpha^\phi \equiv x_\alpha^\phi P \exp\left(\frac{\mu_\alpha^\phi - \overline{G}_\alpha^{\phi,IGM}}{RT}\right) = x_\alpha^\phi P \exp\left(\frac{\overline{G}_\alpha^{\phi,XS}}{RT}\right). \tag{12}$$

where IGM indicates an ideal gas mixture. When we have an equation of state, the evaluation of the pure component fugacity involves evaluating the following integral

$$\bar{f}_\alpha^\phi \equiv P \exp\left(\frac{1}{RT}\int_0^P \left(\overline{V}_\alpha^\phi(P) - \overline{V}_\alpha^{\phi,IGM}(P)\right)dP\right). \tag{13}$$

We can also define a fugacity coefficient in a mixture as

$$\overline{\varphi}_\alpha^\phi \equiv \frac{\bar{f}_\alpha^\phi}{x_\alpha^\phi P}, \tag{14}$$

Using equation (6), we have a definition for the partial molar Gibbs free energy of component α in an ideal gas mixture

$$\overline{G}_\alpha^{\phi,IGM} \equiv \underline{G}_\alpha^{\phi,IG} + RT\ln\left(x_\alpha^\phi\right) \tag{15}$$

III. Activities

The activity of component α in a mixture in phase ϕ, a_α^ϕ, is defined as the ratio of the fugacity of component a in a mixture to that in the pure component, at the same T and P.

$$a_\alpha^\phi \equiv \frac{\bar{f}_\alpha^\phi}{f_\alpha^\phi} \tag{16}$$

We also can define an activity coefficient, γ_α^ϕ,

$$a_\alpha^\phi \equiv x_\alpha^\phi \gamma_\alpha^\phi \tag{17}$$

The activity is related to the chemical potential through the fugacities.

$$a_\alpha^\phi \equiv \frac{\bar{f}_\alpha^\phi}{f_\alpha^\phi} = \frac{x_\alpha^\phi P \exp\left(\dfrac{\mu_\alpha^\phi - \overline{G}_\alpha^{\phi,IGM}}{RT}\right)}{P \exp\left(\dfrac{\underline{G}_\alpha^\phi - \underline{G}_\alpha^{\phi,IG}}{RT}\right)}$$

$$= x_\alpha^\phi \exp\left(\frac{\mu_\alpha^\phi - \underline{G}_\alpha^{\phi,IG} - RT \ln\left(x_\alpha^\phi\right) - \underline{G}_\alpha^\phi + \underline{G}_\alpha^{\phi,IG}}{RT}\right) \qquad (18)$$

$$= \exp\left(\frac{\mu_\alpha^\phi - \underline{G}_\alpha^\phi}{RT}\right)$$

Or, alternatively,

$$\ln\left(a_\alpha^\phi\right) = \frac{\mu_\alpha^\phi - \underline{G}_\alpha^\phi}{RT} \qquad (19)$$

IV. Application in mass transport

In mass transport problems, one is concerned about gradients. From a fundamental non-equilibrium thermodynamics point of view, one is truly concerned with chemical potential gradients (as opposed to concentration or mole fraction gradients. The gradient of the chemical potential is related to the gradient of the activity in an *isothermal* system as follows:

$$\nabla \ln\left(a_\alpha^\phi\right) = \frac{1}{RT} \nabla \mu_\alpha^\phi \qquad (20)$$

The gradient of any pure component term is zero.