Oct. 25 2002: Lecture 20:

The Chemical Potential

Last Time

Internal Degrees of Freedom

At constant P, T: G, which represents the internal degrees of freedom, is minimized.

The Chemical Potential μ_i

The Chemical Potential in a Closed System

It was demonstrated that a system that can exchange energy and volume with a reservoir is in equilibrium with the reservoir when the pressure is the same in the system as in the reservoir. This idea can be extended to a complicated set of many interacting subsystems to arrive at the conclusion that pressure and temperature must be uniform at equilibrium.

Recall the method that was used to demonstrate the uniformity of P and T: from a conservation principle (i.e., constant internal energy and constant volume) for an extensive variable, and with a maximal principle for entropy (i.e., $dS_{\text{universe}} = 0$) it followed that the intensive variables associated with the conserved quantities must be equal at equilibrium.

At constant temperature and pressure, the Gibbs free energy of the system is minimized at equilibrium–this is another extremal principle With another conservation principle, another equality can be derived. For a closed system, the total number or atoms or molecules of a particular type is conserved; this is an additional constraint for each species in the f possible phases:

$$\begin{aligned} {N_A}^{\text{total}} = \text{constant} =& N_A^\alpha + N_A^\beta + \ldots + N_A^i + \ldots N_A^f \\ d{N_A}^{\text{total}} = 0 =& dN_A^\alpha + dN_A^\beta + \ldots + dN_A^i + \ldots dN_A^f \\ dN_A^f =& -\left(dN_A^\alpha + dN_A^\beta + \ldots + dN_A^i + \ldots dN_A^{f-1}\right) \end{aligned} \tag{20-1}$$

where the equations are written out for the A-type atoms.

Using a similar expression for each of the C-conserved species and putting this into the expression for dG:

$$dG = -SdT + VdP + \sum_{i=1}^{f-1}\sum_{j=1}^{C}\left(\mu_j^i - \mu_j^f\right) dN_j^i \tag{20-2}$$

Because G is minimized at equilibrium at constant P and T, it follows that if any species j can be exchanged between the i-phase and the f-phase (i.e., one can consider *virtual changes* with nonzero values of $dN_i^j = -dN_i^f$) then it follows from Equation 21-2 that $\mu_j^i = \mu_j^f$ at equilibrium.

To see this consider three different cases:

$\mu_j^i > \mu_j^f$ Species can flow from the i-phase into the f-phase ($dN_i^j < 0$) and the Gibbs free energy can be decreased at constant P and T ($(dG)_{P,T} < 0$).

$\mu_j^i < \mu_j^f$ Species can flow from the f-phase into the i-phase ($dN_i^j > 0$) and the Gibbs free energy can be decreased at constant P and T ($(dG)_{P,T} < 0$).

$\mu_j^i = \mu_j^f$ Any direction of flow of species ($dN_i^j \geq 0$ or $dN_i^j < 0$) will not decrease G ($(dG)_{P,T} = 0$).

In other words, a chemical species could be spontaneously transported from a phase of larger chemical potential to one of lower chemical potential.

At equilibrium, the chemical potential of any transportable species,

$$\mu_i \equiv \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j \neq N_i} = \left(\frac{\partial \overline{G}}{\partial X_i}\right)_{P,T,X_j \neq X_i} \tag{20-3}$$

must be uniform throughout the system.[19]

Application to Mixtures of Ideal Gases

It has been shown that if several phases are in equilibrium with each other, then the chemical potential of any chemical species will be the same in each phase. Therefore, if we can calculate the chemical potential in *some* phase we know its value in *any other* phase that is in equilibrium with it. A clever approach would be to determine the chemical potential in the phase where it is most simple to calculate. It is particularly simple to calculate the chemical potential in an ideal gas mixture. In this manner, the determination of chemical potential in any phase can be determined by finding the ideal gas mixture that is equilibrium with it.

We begin by applying the condition that applies for equilibrium to a a single phase mixture of ideal gases at constant pressure and temperature.

To apply equilibrium condition:

$$\sum_{i=1}^{C} \mu_i dN_i = 0 \tag{20-4}$$

to an ideal gas, an expression for the Gibbs free energy associated with each component is calculated. For an ideal gas, U is a function of T only. And since $H = U + PV = U + NRT$, H is a function of T only. μ_i is the Gibbs free energy per mole of species i (this will be shown to be true later), so we need to find an expression for:

$$\overline{G_i} = \overline{H_i} - T\overline{S_i} \tag{20-5}$$

[19] For the partial derivative with respect to X_i in Equation 21-3, there is a constraint between the variables $\sum X_i = 1$, that must be considered when taking the derivative of the molar free energy. Later, we will derive an important graphical construction for the determination of μ_i from curves of $\overline{G}$.

for each deal gaseous species i that comprises and ideal gas mixture at constant pressure, P and temperature, T.

To find a model for the chemical potential in an ideal gas mixture[20], one might imagine that the system is in contact with C pistons and each of the pistons only interacts with one gas. The total pressure is the sum of the partial pressures on each of the pistons. Or, one might associate a sub-volume V_i with each of the C components.

For an ideal gas,

$$\begin{aligned} T d\overline{S_i} &= d\overline{U_i} + P d\overline{V_i} \\ d\overline{S_i} &= \overline{C_{V,i}} \frac{dT}{T} + R \frac{d\overline{V_i}}{\overline{V_i}} \end{aligned} \tag{20-6}$$

Because the individual volumes associated with each gas species are the "internal degrees of freedom" which may adjust themselves so that the system attains equilibrium, an expression for the the molar entropy can be calculated for any ideal gas species occupying volume V_i at some temperature T by integrating that volume from some reference state.

It will be useful to introduce a particular reference state, $\overline{V_i}^{\text{ref}}$, which is the volume that a mole of isolated gas would occupy at some temperature T and some reference pressure P^{ref}[21]

Therefore changing the state of each of species i from its reference state to any molar volume $\overline{V_i}$ at constant temperature can be calculated by integrating Equation Addendum-1 along an isotherm:

[20] That is a system of particles that occupy a neglible volume and are non-interacting. Each particle is identified with a chemical species. If the species are assumed to react, then the combinations of particles to form another vary according to the stoicheometric coefficients of a chemical reaction of the form $rR + qQ \rightleftharpoons bB + aA$

[21] All the chemical species i should use the same reference pressure so the subscript can be dropped. Whenever a subscript appears below, it will refer to a partial pressure, i.e., $\sum_i P_i = P^{\text{total}}$

$$\begin{aligned}\overline{S_i}(\overline{V_i}) - \overline{S_i}(\overline{V_i}^{\text{ref}}) &= R\int_{\overline{V_i}^{\text{ref}}}^{\overline{V_i}} \frac{dV}{V} \\ \overline{S_i}(\overline{V_i}) - \overline{S_i}(\overline{V_i}^{\text{ref}}) &= R\log\frac{\overline{V_i}}{\overline{V_i}^{\text{ref}}}\end{aligned} \tag{20-7}$$

And because

$$\begin{aligned}P_i\overline{V_i} &= P^{\text{ref}}\overline{V_i}^{\text{ref}} \\ \frac{\overline{V_i}}{\overline{V_i}^{\text{ref}}} &= \frac{P^{\text{ref}}}{P_i}\end{aligned} \tag{20-8}$$

therefore

$$\Delta\overline{G_i}(\overline{V_i},\overline{V_i}^{\text{ref}},T) = \Delta\overline{H_i}(T) - RT\log\frac{\overline{V_i}}{\overline{V_i}^{\text{ref}}} \tag{20-9}$$

Can be written by changing variables from V to P:

$$\begin{aligned}\overline{G_i}(P_i,P^{\text{ref}},T) =& \overline{G_{i\circ}}(T) + RT\log\frac{P_i}{P^{\text{ref}}} \\ G_i(P_i,P^{\text{ref}},T) =& N_i\overline{G_{i\circ}}(T) + N_iRT\log\frac{P_i}{P^{\text{ref}}} \\ =& N_i\overline{G_{i\circ}}(T) + N_iRT\log\frac{P_iP^{\text{total}}}{P^{\text{total}}P^{\text{ref}}} \\ =& N_i\overline{G_{i\circ}}(T) + N_iRT\log\frac{P^{\text{total}}}{P^{\text{ref}}} + N_iRT\log X_i\end{aligned} \tag{20-10}$$

$$G(P^{\text{total}},T,N_i) = \sum_{i=1}^{C}\overline{G_i} = = \sum_{i=1}^{C}\left(N_i\overline{G_{i\circ}}(T) + N_iRT\log\frac{P^{\text{total}}}{P^{\text{ref}}} + N_iRT\log X_i\right)$$

where in an ideal gas, the ratio of partial pressure to the total pressure $P_i/P^{\text{total}} = X_i$.

if we take P^{ref} to be some convenient standard state (i.e. STP) then $P_i/P^{\text{ref}} = P_i/1\text{atm} \equiv P_i^{\text{atm}}$ is the partial pressure of the gaseous species i with respect to one atmosphere. P_i^{atm} is the *numerical* value of the partial pressure of the ith species, but it is really unitless.

Typically, a standard is adopted where all pressure measurements are assumed to be in atmospheres and thus the $\log P_i/P^{\text{ref}}$ term is written as $\log P_i$ where it is understood that P_i is exactly the numerical value of the unitless P_i^{atm} and there is no difficulty in carrying around units like log(atmospheres). **We will adopt this standard below.**

From these considerations derives an expression for the chemical potentials of ideal gases in a mixture:

$$\begin{aligned} \mu_i(P_i, T) =& \mu_{i\circ}(T) + RT \log P_i \\ \mu_i(X_i, P^{\text{total}}, T) =& \mu_{i\circ} + RT \log P^{\text{total}} + RT \log X_i \end{aligned} \tag{20-11}$$

Compare this to $\overline{G} = \mu = \overline{H} - T\overline{S}$

$$\begin{aligned} \overline{S_i} = -R \log P_i =& - R \log P^{\text{total}} - R \log X_i \\ \overline{G_{i\circ}}(T) =& \mu_{i\circ}(T) = \overline{H_{i\circ}}(T) \end{aligned} \tag{20-12}$$

for an ideal gas mixture.

Models for Chemical Potentials in Solutions

The are various models for the chemical potential in a solution; the simplest is the ideal gas.[22]

[22] An ideal single gas: $\mu(P,T) = \mu_\circ(T) + RT \log P/P_\circ$. Note, you will often see formulae like $\mu = \mu_\circ + RT \log P$, you know that P cannot have units–so a convenient $P_\circ = 1$ has been picked.

The following are definitions that will be used when we discuss solution behavior, but are useful to introduce in the context of ideal gases.

An Ideal Gas Mixture

$$\begin{aligned} \mu_i(P_i, T) &= \mu_{i\circ}(T) + RT \log \frac{P_i}{P_\circ} \\ \mu_i(X_i, T) &= \mu_{i\circ}(T) + RT \log X_i \end{aligned} \tag{20-13}$$

An Ideal Solution In an "ideal solution," the system is made slightly more complicated by allowing chemical potential to become a function of pressure.

$$\mu_i(X_i, P, T) = \mu_{i\circ}(P, T) + RT \log X_i \tag{20-14}$$

A General Solution In the general case, a new term (the activity a_i) is introduced to generalize the dependence on concentration:

$$\mu_i(X_i, P, T) = \mu_{i\circ}(P, T) + RT \log a_i \tag{20-15}$$

a_i is called the "activity of species i"—it is a "generalized composition." Factoring out the X_i:

$$a_i = \gamma_i X_i \tag{20-16}$$

γ_i is called an activity coefficient. In the most general case, it could also be a function of c_i, but limiting cases where it is independent of c_i will be discussed later.

Equilibrium Compositions in an Ideal Reacting Gas Mixture

The simple expression for the chemical potentials in an ideal gas can be put into the equilibrium condition:

$$\sum_{i=1}^{C} \mu_i dN_i = 0 \tag{20-17}$$

and equilibrium amounts of material can be calculated.

If we have a closed system (fixed number of moles of the independent species), then

$$\sum_{i=1}^{C} \mu_i dX_i = 0 \tag{20-18}$$

A Simple Example

Consider the gaseous reaction

Reaction:	H_2	$\frac{1}{2}O_2$	$\rightleftharpoons$	H_2O
Initial:	1	1	$\rightleftharpoons$	0
During Rx.:	$1-x$	$1-\frac{1}{2}x$	$\rightleftharpoons$	x

Therefore, $dX_{H_2} = -dX_{H_2O}$ and $dX_{O_2} = -\frac{1}{2}dX_{H_2O}$ (Every mole of hydrogen gas that appears is associated with the disappearance of one mole of water vapor; every mole of water vapar that appears is associated with the disappearance of one half a mole of oxygen gas).

Therefore, the condition for equilibrium (Equation Addendum-9) for an ideal gas mixture becomes:

$$0 = \begin{bmatrix} (\mu_{\circ(H_2)} + RT\log P_{H_2})dX_{H_2} + \\ (\mu_{\circ(O_2)} + RT\log P_{O_2})dX_{O_2} + \\ (\mu_{\circ(H_2O)} + RT\log P_{H_2O})dX_{H_2O} + \end{bmatrix} \tag{20-19}$$

which is possible only if

$$-(\mu_{\circ(\mathrm{H_2O})} - \mu_{\circ(\mathrm{H_2})} - \frac{1}{2}\mu_{\circ(\mathrm{O_2})}) = RT(\log P_{\mathrm{H_2O}} - \log P_{\mathrm{H_2}} - \frac{1}{2}\log P_{\mathrm{O_2}}) \tag{20-20}$$

$$\begin{aligned} \frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}} P_{\mathrm{O_2}}^{1/2}} &\equiv K_{eq} = e^{-\left(\frac{\Delta\overline{G_{rxn}}}{RT}\right)} \\ \frac{X_{\mathrm{H_2O}}}{X_{\mathrm{H_2}} X_{\mathrm{O_2}}^{1/2}} &= \sqrt{P^{\mathrm{total}}} K_{eq} = \sqrt{P^{\mathrm{total}}} e^{-\left(\frac{\Delta\overline{G_{rxn}}}{RT}\right)} \\ \Delta\overline{G_{rxn}} &\equiv (\mu_{\circ(\mathrm{H_2O})} - \mu_{\circ(\mathrm{H_2})} - \frac{1}{2}\mu_{\circ(\mathrm{O_2})}) \end{aligned} \tag{20-21}$$

In general for ideal gas mixture with reaction

$$\begin{aligned} p\mathrm{P} + q\mathrm{Q} &\rightleftharpoons r\mathrm{R} + m\mathrm{M} \\ \frac{P_{\mathrm{R}}^r P_{\mathrm{M}}^m}{P_{\mathrm{P}}^p P_{\mathrm{Q}}^q} &= e^{-\left(\frac{\Delta\overline{G_{rxn}}}{RT}\right)} = K_{eq}(T) \\ \frac{X_{\mathrm{R}}^r X_{\mathrm{M}}^m}{X_{\mathrm{P}}^p X_{\mathrm{Q}}^q} &= P_{\mathrm{total}}^{p+q-r-s} K_{eq}(T) \end{aligned} \tag{20-22}$$

where the molar free energy change of the reaction is:

and generalizing even more

$$\frac{a_{\mathrm{R}}^r a_{\mathrm{M}}^m}{a_{\mathrm{P}}^p a_{\mathrm{Q}}^q} = \frac{\gamma_{\mathrm{R}}^r \gamma_{\mathrm{M}}^m}{\gamma_{\mathrm{P}}^p \gamma_{\mathrm{Q}}^q} \frac{X_{\mathrm{R}}^r X_{\mathrm{M}}^m}{X_{\mathrm{P}}^p X_{\mathrm{Q}}^q} = e^{-\left(\frac{\Delta\overline{G_{rxn}}}{RT}\right)} \tag{20-23}$$

A Slightly More Complicated Worked Example

Let's consider a more complicated gaseous reaction:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{20-24}$$

Suppose we have a container at 1 atm and at 1000°C with initially two moles of water vapor and one mole of carbon dioxide.

Here are some questions that one might ask:

How many moles of oxygen gas will exist at equilibrium?

If the reaction is carried out at a different pressure, how will the concentration of carbon monoxide vary?

The first question may seem a little odd—there appears to be no oxygen in the reaction 20-24.

However, if reaction 20-24 is written as the sum of two reactions:

$$\begin{array}{ccccccl} CO & + & \frac{1}{2}O_2 & \rightleftharpoons & CO_2 & & \\ 0 \text{ mole} & + & 0 \text{ mole} & \rightleftharpoons & 1 \text{ mole} & & \text{initial} \\ 2Y & + & Y & \rightleftharpoons & 1-2Y & & \text{equilibrium} \end{array} \tag{20-25}$$

and

$$\begin{array}{ccccccl} H_2O & \rightleftharpoons & \frac{1}{2}O_2 & + & H_2 & & \\ 2 \text{ mole} & \rightleftharpoons & 0 \text{ mole} & + & 0 \text{ mole} & & \text{initial} \\ 2-2X & \rightleftharpoons & X & + & 2X & & \text{equilibrium} \end{array} \tag{20-26}$$

Then it is clear that oxygen plays a role in the reaction 20-24 as the there are two independent reactions contained in the three reactions 20-24, 20-25. and 20-26.

Furthermore, the sum of the standard free energies for the reaction will also add like the reactions and each of the reactions will have a standard reaction and the dependent reaction will be related to the others:

$$\begin{array}{ccccccc} H_2O & \rightleftharpoons & \frac{1}{2}O_2 & + & H_2 & -\Delta\overline{G^{rxn}_{H_2O}} \\ CO & + & \frac{1}{2}O_2 & \rightleftharpoons & CO_2 & \Delta\overline{G^{rxn}_{CO_2}} \\ \hline \end{array} \tag{20-27}$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \quad \Delta\overline{G^{rxn}_{CO_2}} - \Delta\overline{G^{rxn}_{H_2O}}$$

The total number of moles of ideal gas in the system at equilibrium will be $N^{\text{total}} = 3 + X + Y$. (n.b., the reaction 20-25 produces Y moles and the reaction 20-26 prooduces X moles in addition to the initial 3 moles.) Every independent reaction must be at equilibrium independently Therefore we can write the two equilibrium conditions for the reaction 20-25

$$\frac{\frac{1-2Y}{3+X+Y}}{\frac{2Y}{3+X+Y}\left(\frac{X+Y}{3+X+Y}\right)^{1/2}} = e^{-\left(\frac{\Delta\overline{G^{rxn}_{CO_2}}}{RT}\right)} \tag{20-28}$$

and for reaction 20-26,

$$\frac{\frac{2X}{3+X+Y}\left(\frac{X+Y}{3+X+Y}\right)^{1/2}}{\frac{2-2X}{3+X+Y}} = e^{-\left(\frac{-\Delta\overline{G^{rxn}_{H_2O}}}{RT}\right)} \tag{20-29}$$

so there are two independent equations and two unknowns, so it is now algebra to find X and Y and therefore the concentration of oxygen $(X+Y)/(3+X+Y)$.

To find how the concentration of carbon monoxide depends on pressure, rewrite Eq. 20-28 in terms of partial pressures:

$$\frac{\frac{P_{CO_2}}{P_{\text{total}}}}{\frac{P_{CO}}{P_{\text{total}}}\left(\frac{P_{O_2}}{P_{\text{total}}}\right)^{1/2}} = e^{-\left(\frac{\Delta\overline{G^{rxn}_{CO_2}}}{RT}\right)}$$

$$\frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}} = P^{1/2}{}_{\text{total}}\, e^{-\left(\frac{\Delta\overline{G^{rxn}_{CO_2}}}{RT}\right)} \tag{20-30}$$