**University of Washington**
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## Lecture 10.1 7/13/11

### A. Free Energy and Changes in Composition: The Chemical Potential

- We have thus far considered free energy changes in single component systems, i.e. free energy changes accompanying a changes in pressure of an ideal gas. But many chemical and biochemical systems are naturally composed of a number of components and the composition of such systems may change as a result of chemical reactions, physical transport, etc. In such cases we must consider how the free energy changes when compositions changes. Consider the reaction $n_A A \rightarrow n_B B$ . The free energy change is given by
$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_B} dP - \left(\frac{\partial G}{\partial T}\right)_{P,n_A,n_B} dT + \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{P,T,n_A} dn_B$$
$$= VdP - SdT + \mu_A dn_A + \mu_B dn_B$$
- In general $dG = VdP - SdT + \sum_i \mu_i dn_i$
- The terms $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$ are called a chemical potentials.
- The chemical potential of a pure substance is simply the molar Gibbs energy. For a pure substance: $\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T} = \frac{G}{n} = \overline{G}$
- We can relate partial molar quantities using the same derivative equations that we used for thermodynamic state functions. Again for a pure substance: $\left(\frac{\partial \overline{G}}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_{T\,i} = \frac{V}{n} = \overline{V}$ .
- Similarly we have $\left(\frac{\partial \overline{G}}{\partial T}\right)_P = \left(\frac{\partial \mu}{\partial T}\right)_P = -\frac{S}{n} = \overline{S}$
- And the chemical potential is an exact differential so that
$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_P dT + \left(\frac{\partial \mu}{\partial P}\right)_T dP = -\overline{S}dT + \overline{V}dP$$
- This equation gives us a method for calculating the chemical potential of a one component ideal gas. Suppose the temperature is a constant, i.e. dT=0. Then:

$$d\mu = -\bar{S}dT + \bar{V}dP = \bar{V}dP$$

$$\therefore \int_{\mu^0}^{\mu_i} d\mu = \mu - \mu^0 = \int_{P^0}^{P} \bar{V}dP = \int_{P^0}^{P} \frac{V}{n}dP = RT\int_{P^0}^{P}\frac{dP}{P} = RT\ln\left(\frac{P}{P^0}\right)$$

$$\therefore \mu = \mu^0 + RT\ln\left(\frac{P}{P^0}\right)$$

- $\mu^0$ is the chemical potential of a standard reference state for the gas which is characterized by the pressure $P^0$ , which is frequently taken to be 1 bar.

## B. Chemical Potential in a Mixture

- So far the chemical potential just seems to be an alternative notation for performing molar Gibbs energy calculations. The real utility of the chemical potential is in describing thermodynamic properties of a mixture. Consider a mixture of ideal gases which satisfies: $PV = \sum_i n_i RT$ . Here we define the partial pressures P$_i$

  $P = \sum_i P_i = \sum_i \chi_i P$ where the mole fraction $\chi_i = \frac{n_i}{\sum_i n_i} = \frac{n_i}{n}$

- For the ith component of an ideal gas mixture we define the chemicakl potential as $d\mu_i = -\bar{S}_i dT + \bar{V}_i dP$ . We calculate this chemical potential at constant T, i.e. dT=0:

$$\mu_i - \mu_i^0 = \int_{P^0}^{P_i} \bar{V}_i dP = \int_{P^0}^{P_i} \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} dP = \int_{P^0}^{P_i} \frac{RT}{P}\left(\frac{\partial n}{\partial n_i}\right)_{T,P,n_j} dP = RT\ln\left(\frac{P_i}{P^0}\right)$$

$$\therefore \mu_i = \mu_i^0 + RT\ln\left(\frac{P_i}{P^0}\right)$$

## C. Criteria for Equilibrium

- The chemical potential is used to express criteria for equilibrium. A very simple example is a single component system containing two phases α and β. At constant pressure and temperature and with the system closed:

$$dG = \mu_\alpha dn_\alpha + \mu_\beta dn_\beta$$

- If we convert β to α we must conserve mass so $dn_\alpha = -dn_\beta$ so that

  $dG = \mu_\alpha dn_\alpha + \mu_\beta dn_\beta = \left(\mu_\alpha - \mu_\beta\right) dn_\alpha$. The direction of the phase change is dictated by the difference $\mu_\alpha - \mu_\beta$. If $\mu_\alpha > \mu_\beta$ then dG>0. If $\mu_\alpha < \mu_\beta$ then dG<0. Clearly the direction of phase change in this closed system is designated by “transport” into the phase with lowest chemical potential. However if $\mu_\alpha - \mu_\beta = 0$ i.e. the chemical potentials are equal, then dG=0 and the system is at equilibrium.

- The criterion for equilibrium in a reacting mixture is somewhat more involved. Assume a chemical reaction $\nu_1 X_1 + \nu_2 X_2 + \dots \nu_{j-1} X_{j-1} \rightarrow \nu_j X_j + \dots \nu_{n-1} X_{n-1} + \nu_n X_n$ where $\nu_i$ are stoichiometric coefficients. We can represent this reaction as an algebraic equation $\sum_{i=1}^{n} \nu_i X_i = 0$ where $\nu_i < 0$ for reactants (i.e. i<j) and $\nu_i > 0$ for productions (i.e. $i \geq j$).
- Now we define the reaction coordinate $\xi$ which varies between 0 and 1 such that $dn_i = \nu_i d\xi$. Then for dT=dP=0

$$dG = \sum_{i=1}^{n} \mu_i dn_i = \sum_{i=1}^{n} \mu_i \nu_i d\xi = d\xi \sum_{i=1}^{n} \mu_i \nu_i$$

$$\therefore \left( \frac{\partial G}{\partial \xi} \right)_{P,T} = \sum_{i=1}^{n} \mu_i \nu_i$$

- At equilibrium $\left( \frac{\partial G}{\partial \xi} \right)_{P,T} = \sum_{i=1}^{n} \mu_i \nu_i = 0$ and the criterion for equilibrium in a reacting mixture is: $\sum_{i=1}^{n} \mu_i \nu_i = 0$. If $\sum_{i=1}^{n} \mu_i \nu_i \neq 0$ the reacting mixture is not at equilibrium.
- If we use our expression for the chemical potential for components of an ideal gas mixture:

$$\Delta G = \sum_{i=1}^{n} \nu_i \mu_i = \sum_{i=1}^{n} \nu_i \left( \mu_i^0 + RT \ln\left( \frac{P_i}{P^0} \right) \right)$$

$$= \sum_{i=1}^{n} \nu_i \mu_i^0 + RT \sum_{i=1}^{n} \nu_i \ln\left( \frac{P_i}{P^0} \right) = \Delta G^0 + RT \sum_{i=1}^{n} \ln\left( \frac{P_i}{P^0} \right)^{\nu_i}$$

$$= \Delta G^0 + RT \ln \prod_{i=1}^{n} \left( \frac{P_i}{P^0} \right)^{\nu_i}$$

- If the system is at equilibrium

$$\Delta G = \left( \frac{\partial G}{\partial \xi} \right)_{P,T} = 0 = \Delta G^0 + RT \ln \prod_{i=1}^{n} \left( \frac{P_{i,eq}}{P^0} \right)^{\nu_i}$$

$$\therefore \Delta G^0 = -RT \ln \prod_{i=1}^{n} \left( \frac{P_{i,eq}}{P^0} \right)^{\nu_i} = -RT \ln K_P$$

where the equilibrium constant $K_P = \prod_{i=1}^{n} \left( \frac{P_{i,eq}}{P^0} \right)^{\nu_i}$.

- If the system is not at equilibrium:

$$\Delta G = \left( \frac{\partial G}{\partial \xi} \right)_{P,T} = \Delta G^0 + RT \ln \prod_{i=1}^{n} \left( \frac{P_i}{P^0} \right)^{\nu_i} = \Delta G^0 + RT \ln Q_P$$

Note: Q is a dimensionless quantity called the reaction quotient. K is also dimensionless.