Physical Chemistry

Lecture 20

The Chemical Potential and Activity

Chemical potential

- The chemical potential is a real molar energy
- Describes the molar energy needed for a system to exist at certain conditions
- Like describing the mechanical potential energy of a ball perched on a hill

Differential of the chemical potential

- The chemical potential depends on any two other state variables, e.g. T and P

$$d\mu^{\alpha} = - S_m^{\alpha} dT + V_m^{\alpha} dP$$

- Relate $\mu(T,P)$ to $\mu^{\theta}(T)$ by integration

$$\mu(T,P) = \mu^{\theta}(T) + \int_{P^{\theta}}^{P} V_m dP$$

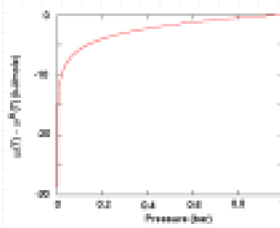
- Example: ideal gas

$$\mu_{ideal}(T,P) = \mu^{\theta}(T) + \int_{P^{\theta}}^{P} \frac{RT}{P} dP$$

$$= \mu^{\theta}(T) + RT \ln \frac{P}{P^{\theta}}$$

Chemical potential of an ideal gas

- The chemical potential depends on P



Chemical potential of a real gas at P and T

- Standard state of a gas is an ideal gas

$$\mu(T,P) = \mu^{\theta}(T) + \int_{P^{\theta}}^{P} V_m dP$$

$$= \mu^{\theta}(T) + \int_{P^{\theta}}^{0} \frac{RT}{P} dP + \int_{0}^{P} V_m dP$$

$$= \mu^{\theta}(T) + RT \ln \frac{P}{P^{\theta}} + \int_{0}^{P} \left(V_m - \frac{RT}{P} \right) dP$$

$$= \mu_{ideal}(T,P) + \int_{0}^{P} \left(V_m - \frac{RT}{P} \right) dP$$

$\Leftarrow$ Correction for nonideality

Activity

- The chemical potential is referenced to some standard state

$$\mu = \mu^{\theta} + \Delta\mu$$

- Define the difference in terms of the logarithm of some function of state variables – the activity

$$\boxed{\mu(T,a) = \mu^{\theta}(T) + RT \ln a}$$

- The activity is a measure of how far the state of the system is from the standard state
  - $a = 1 \Rightarrow$ standard state
  - $a \neq 1 \Rightarrow$ away from the standard state

Activity of an ideal gas at P

- Comparison of definition with the chemical potential of an ideal gas

$$\mu_{ideal}(T,P) = \mu^{\theta}(T) + RT\ln\frac{P}{P^{\theta}}$$

$$\mu(T,a) = \mu^{\theta}(T) + RT\ln a$$

- Activity

$$\boxed{a_{ideal} = \frac{P}{P^{\theta}}}$$

Activity of a real gas

- Insert a parameter, γ, the activity coefficient, that determines how far the system is from ideality

$$RT\ln a_{real} = RT\ln(\gamma\, a_{ideal}) = RT\ln a_{ideal} + RT\ln\gamma$$

- Implies the chemical potential of a gas has two components to the energy

$$\mu(T,a) = \mu_{ideal}(T,a) + RT\ln\gamma = \mu^{\theta}(T) + RT\ln\left(\frac{P}{P^{\theta}}\right) + RT\ln\gamma$$

Summary

- The chemical potential determines phase equilibrium at P and T
- The criterion for equilibrium between phases
  - $\mu^{\alpha} = \mu^{\beta}$
- Applies to a wide variety of situations
  - Liquid-vapor equilibrium
  - Solid-liquid equilibrium
  - Solid-vapor equilibrium
  - Bubbles and a bulk phase
  - Surface phase equilibrium
  - Solid-solid transition