University of Washington
Department of Chemistry
Chemistry 452/456
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Lecture 13.1 7/28/14
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DeVoe: 9.3

A. How to Calculate the Chemical Potential of a Gas:

- Recall the definition of the chemical potential

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_P dT + \left(\frac{\partial \mu}{\partial P}\right)_T dP = -\bar{S}dT + \bar{V}dP$$

- 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:

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

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

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

- μ^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 of 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

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

- 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 for Reacting Systems.

- We have treated the criterion for equilibrium of two phases. The criterion for equilibrium in a reacting mixture is somewhat more involved. Assume a chemical reaction $\nu_1 X_1 + \nu_2 X_2 + \ldots \nu_{j-1} X_{j-1} \rightarrow \nu_j X_j + \ldots \nu_{n-1} X_{n-1} + \nu_n X_n$ where ν_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 ξ 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.