Chemical Reactions and Chemical Equilibria

- Chemical reactions will be considered from the perspective of a thermodynamic path.
- A reaction will be proceed until no further macroscopic change is observed, at which point equilibrium has been attained.
- Notation must be carefully considered.
- Consider the oxidation of ethanol to carbon dioxide and water:

$$C_2H_5OH(l) \ + \ 3O_2(g) \rightleftharpoons 2CO_2(g) + 3H_2O(l)$$

  - The equation is balanced
  - Any factor could multiply all the stoichiometric coefficients and still leave a balanced equation.
  - If the multiplying factor is a negative number, the roles of reactants and products will be reversed.
  - All calculations must be consistent with the direction in which the equation is written.
  - The double arrow $\rightleftharpoons$ indicates the attainment of equilibrium.

- The phase of each species must be specified.
  - (g) denotes the gas phase
  - (l) denotes the liquid phase
  - (s) denotes the solid phase
  - (aq) denotes an aqueous solution.

    $$NaCl(s) \rightleftharpoons Na^{+}(aq) + Cl^{-}(aq)$$

    describes a saturated aqueous NaCl solution.
- In order to describe a reaction path in a thermodynamic sense, consider a chemical reaction in the general form:

  $$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

  where α, β, γ and δ are the stoichiometric coefficients.
- Consider the initial condition at a given T and P with $n_A^\circ, n_B^\circ, n_C^\circ$ and n_D° as the initial amounts of A, B, C, and D.
  - Let the reaction ensue.
  - Some time later find n_A, n_B, n_C and n_D as the amounts of A, B, C, and D present.

- Define ξ as the extent of reaction such that:

$$\frac{n_A^\circ - n_A}{\alpha} = \frac{n_B^\circ - n_B}{\beta} = \frac{n_C - n_C^\circ}{\gamma} = \frac{n_D - n_D^\circ}{\delta} = \xi$$

  - Note that ξ has units of moles.
  - ξ is also known as the degree of advancement or the reaction progress variable.

- The differential degree of advancement is:

$$d\xi = -\frac{dn_A}{\alpha} = -\frac{dn_B}{\beta} = \frac{dn_C}{\gamma} = \frac{dn_D}{\delta}$$

  - Positive values of $d\xi$ correspond to the disappearance of reactants (dn_A and dn_B are negative) and the appearance of products (dn_C and dn_D are positive).
  - The initial value of ξ is always zero and can either decrease or increase as the reaction proceeds.
  - ξ is an extensive variable used to describe reaction path.

Energy and Entropy Changes in Chemical Reactions

- Consider first entropy and the following reaction with reactants in stoichiometric proportions:

$$\frac{1}{2}H_2(g) \ + \ \frac{1}{2}F_2(g) \ \rightarrow \ HF(g)$$

  carried out at constant T and P.

  - "$\rightarrow$" means that the reaction goes stoichiometrically completely to products.

- The initial entropy is that of the isolated reactants:

$$S(\text{isolated reactants}) \ =$$

$$\left(\frac{1}{2}\ \text{mol}\right)\overline{S}(H_2(g)) \ + \ \left(\frac{1}{2}\ \text{mol}\right)\overline{S}(F_2(g))$$

- Now allow the reactants to mix, but not react:

$$S(\text{mixed reactants}) = S(\text{isolated reactants}) + \Delta S_{mix}$$

- Now allow reaction to go to completion:

$$S(\text{isolated product}) = (1\text{mol})\,\overline{S}(HF(g))$$

- The molar entropy change associated with the reactions $\Delta_r \overline{S}$ may be written:

$$\Delta_r \overline{S} =$$

$$\sum_{products} \nu_i \overline{S}(\text{product i}) - \sum_{reactants} \nu_i \overline{S}(\text{reactant i})$$

where the ν_i are the dimensionless stoichiometric coefficients.

- In this case complete conversion of reactants to products corresponds to ξ=1 mol.
- Note that the entropy of mixing does not contribute to $\Delta_r \overline{S}$.
  - The role of mixing will be considered separately later.
- Now consider the enthalpy changes ($\Delta_r H$).
- A particularly convenient thermodynamic path to consider is one in which the bonds in the reactants are broken, then the bonds in the product molecules are formed.
  - This would permit the calculation of $\Delta_r \overline{H}$ to be determined from bond energies.

  - But bond energies can be difficult to determine, especially in polyatomics.
  - Real reactions do not follow this type of path.
- All alternate but useful path is one in which the compounds of interest are formed from compounds for which the bond energies are known or are easily determined.
  - One example of this is the formation of compounds from elements in their common stable standard state.
- Consider:

$$2CO(g) \ + \ O_2(g) \ \rightarrow \ 2CO_2(g)$$

  - The carbon containing compounds can be formed from elemental carbon and oxygen.

$$2C(\text{graphite}) \ + \ O_2(g) \ \rightarrow \ 2CO(g)$$

$$C(\text{graphite}) \ + \ O_2(g) \ \rightarrow \ CO_2(g)$$

  The energies association with these reactions may be determined by calorimetry and are known as the standard enthalpies of formation.

- In this case the standard enthalpy of formation coincides with the standard enthalpy of combustion.
- These and other named enthapies and reference states are discussed in your text.

Chemical Reaction Equilibria

- Consider the schematic chemical reaction:

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

where with initial state n_A°, n_B°,n_C°, and n_D° moles of compound isolated from one another.

- The initial Gibbs free energy is:

$$G(\text{initial}) = n_A^\circ \mu(A) + n_B^\circ \mu(B) + n_C^\circ \mu(C) + n_D^\circ \mu(D)$$

where

$$\mu(A) = \mu(\text{pure A}) = \mu^\circ(T) + RT \ln f(A)$$

- Now allow the species to mix but not yet react. The free energy become:

$$G(\text{poised to react}) = G(\text{initial}) + \Delta G_{mix}$$

$$= n_A^\circ \mu_A + n_B^\circ \mu_B + n_C^\circ \mu_C + n_D^\circ \mu_D$$

where

$$\mu_A = \mu_A(T) + RT\ln(f_A/f_A^\circ)$$

- Note that:
  - f_A is the fugacity of A in the mixture and depends on composition.
  - $f(A)$ is the fugacity of pure A.
  - f_A° is the fugacity of A in the reference state defining $\mu_A^\circ(T)$.
  - Instead of fugacity, partial pressure, activities, activity coefficients, mole fractions, etc. may be used.
- Once the reaction starts to progress, the Gibbs free energy must be expressed as a function as the extent of reaction, ξ
- For any composition:

  $$G = n_A\mu_A + n_B\mu_B + n_C\mu_C + n_D\mu_D$$

  where:
  - $n_A = n_A^\circ - \alpha\xi$
  - $n_B = n_B^\circ - \beta\xi$
  - $n_C = n_C^\circ + \gamma\xi$
  - $n_D = n_D^\circ + \delta\xi$

- Thus:

$$G(\xi) = n_A^\circ \mu_A + n_B^\circ \mu_B + n_C^\circ \mu_C + n_D^\circ \mu_D$$
$$+\xi(\gamma\mu_C + \delta\mu_D - \alpha\mu_A - \beta\mu_B)$$

- This may be interpreted as:

$$G(\xi) = G(\text{poised to react})$$
$$+G(\text{due to amount } \xi \text{ of reaction}).$$

  where ξ may be positive or negative.

- ξ can increase from zero as reactants are consumed.
- ξ can decrease from zero as products are consumed.
- The value of ξ (and its sign) are determined by the spontaneous direction of change of the reacting mixture such that G is minimized.
  - At ξ_{eq},

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$$

- At equilibrium:

$$dG = 0$$
$$VdP - SdT + \sum \mu_i dn_i = 0$$

  - But T and P are constant. Therefore:

$$\sum \mu_i dn_i = 0$$

- Recall:

$$d\xi = -\frac{dn_A}{\alpha} = -\frac{dn_B}{\beta} = \frac{dn_C}{\gamma} = \frac{dn_D}{\delta}$$

or:

$$dn_A = -\alpha d\xi$$

$$dn_B = -\beta d\xi$$

$$dn_C = \gamma d\xi$$

$$dn_D = \delta d\xi$$

Therefore:

$$\left(\sum_{products} \nu_i \mu_i - \sum_{reactants} \nu_i \mu_i \right) d\xi = 0$$

Because ξ is an independent variable,

$$\left(\sum_{products} \nu_i \mu_i - \sum_{reactants} \nu_i \mu_i \right) = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$$

- For the example under consideration:

$$\gamma \mu_C + \delta \mu_D - \alpha \mu_A - \beta \mu_B = 0$$

- Since for each component:

  $$\mu_i = \mu_i^\circ + RT \ln\left(\frac{f_i}{f_i^\circ}\right)$$

  which gives:

  $$\gamma\mu_C^\circ + \delta\mu_D^\circ - \alpha\mu_A^\circ - \beta\mu_B^\circ$$

  $$= -RT \ln\left[\frac{\left(\frac{f_C^{eq}}{f_C^\circ}\right)^\gamma \left(\frac{f_D^{eq}}{f_D^\circ}\right)^\delta}{\left(\frac{f_A^{eq}}{f_A^\circ}\right)^\alpha \left(\frac{f_B^{eq}}{f_B^\circ}\right)^\beta}\right]$$

- The standard Gibbs free energy of reaction is defined with respect to:

  $$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

  as

  $$\Delta_r \overline{G}^\circ = \gamma\mu_C^\circ + \delta\mu_D^\circ - \alpha\mu_A^\circ - \beta\mu_B^\circ$$

- Thus:

  $$-\frac{\Delta_r \overline{G}^\circ}{RT} = \ln\left[\frac{\left(\frac{f_C^{eq}}{f_C^\circ}\right)^\gamma \left(\frac{f_D^{eq}}{f_D^\circ}\right)^\delta}{\left(\frac{f_A^{eq}}{f_A^\circ}\right)^\alpha \left(\frac{f_B^{eq}}{f_B^\circ}\right)^\beta}\right]$$

- Define the thermodynamic reaction equilibrium coefficient as:

$$K_{eq}(T) = \left[\frac{\left(\frac{f_C^{eq}}{f_C^\circ}\right)^\gamma \left(\frac{f_D^{eq}}{f_D^\circ}\right)^\delta}{\left(\frac{f_A^{eq}}{f_A^\circ}\right)^\alpha \left(\frac{f_B^{eq}}{f_B^\circ}\right)^\beta} \right]$$

- In general form this becomes:

$$\Delta_r \overline{G}^\circ = \sum_{products} \nu_i \mu_i^\circ - \sum_{reactants} \nu_i \mu_i^\circ$$

and

$$K_{eq} = \frac{\prod_{products} \left(\frac{f_i^{eq}}{f_i^\circ}\right)^{\nu_i}}{\prod_{reactants} \left(\frac{f_i^{eq}}{f_i^\circ}\right)^{\nu_i}} = \exp\left(-\frac{\Delta_r \overline{G}^\circ}{RT}\right)$$