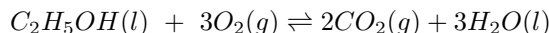
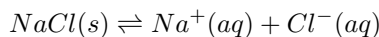


## Chemical Reactions and Chemical Equilibria

- 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:

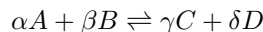


- The equation is balanced
  - Any factor could multiply all the stoichiometric coefficients and still leave a balanced equation.
  - If the multiplying factor is a negative number, the roles of reactants and products will be reversed.
  - All calculations must be consistent with the direction in which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



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:



where  $\alpha, \beta, \gamma$  and  $\delta$  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  $n_D^\circ$  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  $\xi$  as the extent of reaction such that:

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

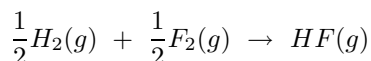
- Note that  $\xi$  has units of moles.
- $\xi$  is also known as the degree of advancement or the reaction progress variable.
- The differential degree of advancement is:

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

- 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  $\xi$  is always zero and can either decrease or increase as the reaction proceeds.
- $\xi$  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:



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:

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

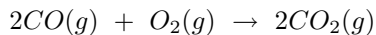
- The molar entropy change associated with the reactions  $\Delta_r \overline{S}$  may be written:

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

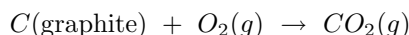
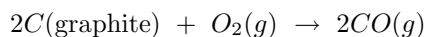
where the  $\nu_i$  are the dimensionless stoichiometric coefficients.

- In this case complete conversion of reactants to products corresponds to  $\xi=1$  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:



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

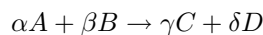


The energies associated with these reactions may be determined by calorimetry and are known as the standard enthalpies of formation.

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

### Chemical Reaction Equilibria

- Consider the schematic chemical reaction:



where with initial state  $n_A^\circ, n_B^\circ, n_C^\circ$ , and  $n_D^\circ$  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 becomes:

$$\begin{aligned} G(\text{poised to react}) &= G(\text{initial}) + \Delta G_{mix} \\ &= n_A^\circ \mu_A + n_B^\circ \mu_B + n_C^\circ \mu_C + n_D^\circ \mu_D \end{aligned}$$

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.
  - $f_A^\circ$  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 of the extent of reaction,  $\xi$
- 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  $\xi$  may be positive or negative.

- $\xi$  can increase from zero as reactants are consumed.
- $\xi$  can decrease from zero as products are consumed.
- The value of  $\xi$  (and its sign) are determined by the spontaneous direction of change of the reacting mixture such that  $G$  is minimized.

- At  $\xi_{eq}$ ,

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

- 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:

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

Because  $\xi$  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:

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

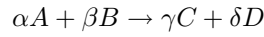
- Since for each component:

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

which gives:

$$\begin{aligned} & \gamma \mu_C^\circ + \delta \mu_D^\circ - \alpha \mu_A^\circ - \beta \mu_B^\circ \\ &= -RT \ln \left[ \frac{\left( \frac{f_C^{eq}}{f_C^\circ} \right)^\gamma \left( \frac{f_D^{eq}}{f_D^\circ} \right)^\delta}{\left( \frac{f_A^{eq}}{f_A^\circ} \right)^\alpha \left( \frac{f_B^{eq}}{f_B^\circ} \right)^\beta} \right] \end{aligned}$$

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



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

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