CHEMICAL ENGINEERING THERMODYNAMICS II (0905322)

11 -Equilibrium and Chemical Reactions

ALI KH. AL-MATAR (aalmatar@ju.edu.jo)

Chemical Engineering Department
University of Jordan’
Amman 11942, Jordan

Outline

- Spontaneous Chemical Reactions
- Exergonic and Endergonic Reactions
- Ideal Gas Equilibrium
- Reaction Quotient
- Equilibrium Constant
- Activity: Different Views Same Quantity
- The Relation Between Equilibrium Constants
- What Affects the Equilibrium Constant?
- Effect of Temperature:van’t Hoff’s Equation

Spontaneous Chemical Reactions

- **The Gibbs energy minimum**
  - **Reaction Gibbs energy,** the slope of the graph of the Gibbs energy plotted against the extent of reaction: $\Delta_r G = (\partial G/\partial \xi)_{p,T}$.
  - **Relation of $\Delta_r G$ to the chemical potentials** of the species in the reaction

$$A \rightarrow B,\ \Delta_r G = \mu_B - \mu_A.$$

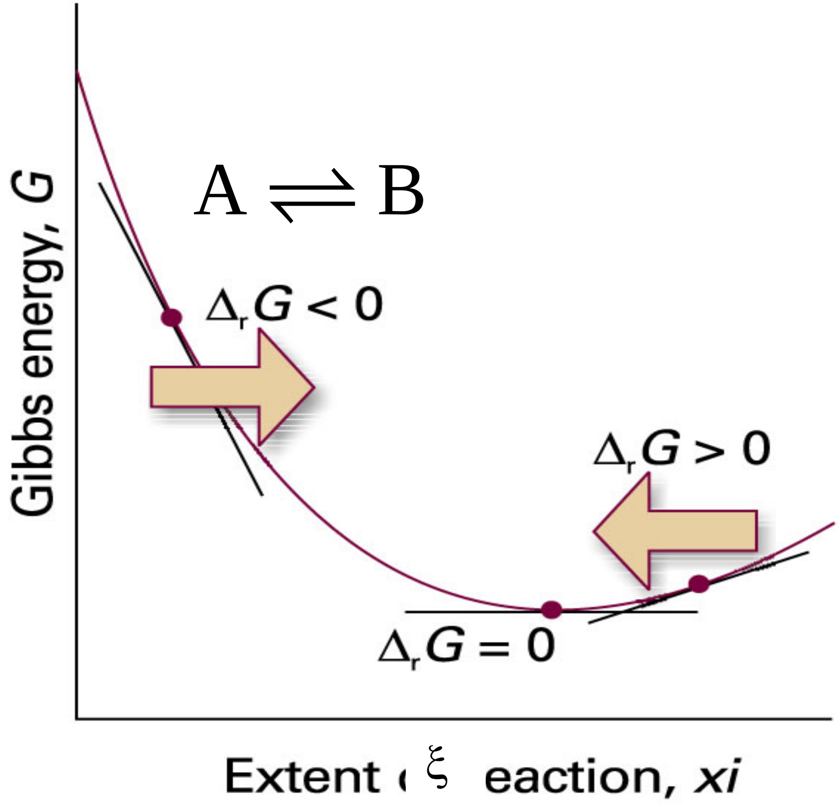

Fig. 7.1 As the reaction advances (represented by motion from left to right along the horizontal axis) the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope, at the foot of the valley.

Exergonic and Endergonic Reactions

- Reaction is at equilibrium when, $\Delta_r G = 0$.
- **Exergonic reaction**
  - $\Delta_r G < 0$,
  - Forward reaction is spontaneous.
  - Can be used to drive another process.
- **Endergonic reaction**
  - $\Delta_r G > 0$.
  - Reverse reaction is spontaneous.

Subject to the assumption of constant temperature and pressure

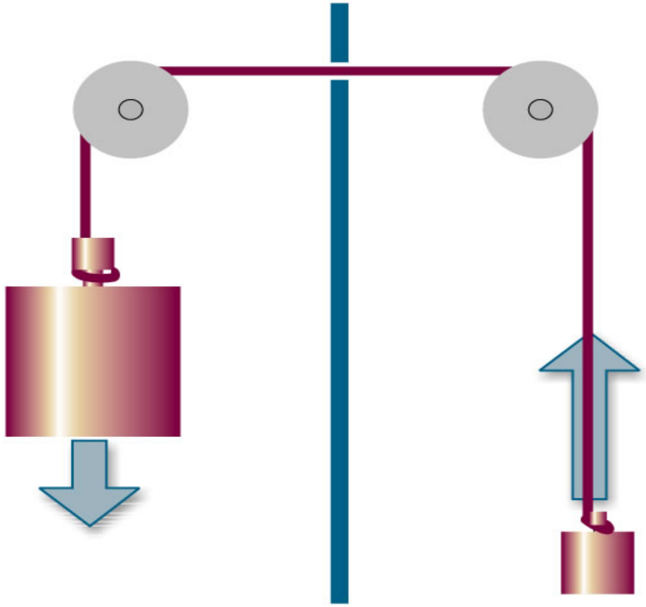

Fig. 7.2 If two weights are coupled as shown here, then the heavier weight will move the lighter weight in its non-spontaneous direction: overall, the process is still spontaneous. The weights are the analogues of two chemical reactions: a reaction with a large negative ΔG can force another reaction with a less ΔG to run in its non-spontaneous direction.

Ideal Gas Equilibrium

- For an ideal gas

$$\mu = \mu^{\circ} + RT\,\ln\frac{P}{P^{\circ}} = \mu^{\circ} + RT\,\ln p$$

- The Gibbs energy of the reaction becomes

$$\Delta_r G = \mu_B - \mu_A = \left(\mu_B^{\circ} + RT\,\ln p_B\right) - \left(\mu_A^{\circ} + RT\,\ln p_A\right)$$

$$= \Delta_r G^{\circ} + RT\,\ln\frac{p_B}{p_A} = \Delta_r G^{\circ} + RT\,\ln Q$$

- At equilibrium $\Delta_r G = 0$, from which

$$RT\,\ln K = RT\,\ln\left(\frac{p_B}{p_A}\right)_{\text{Equilibrium}} = -\Delta_r G^{\circ}$$

K is the equilibrium constant

Reaction Quotient

- Reaction quotient,

$$Q = \prod_J a_J^{\nu_J}$$

Derive

- General expression for $\Delta_r G$ at an arbitrary stage of the reaction,

$$\Delta_r G = \Delta_r G^{\circ} + RT \ln Q$$

- Thermodynamic equilibrium constant**,** an equilibrium constant K expressed in terms of activities (or fugacities)

$$Q = \left(\prod_J a_J^{\nu_J} \right)_{\text{equilibrium}}$$

Equilibrium Constant

- Standard reaction Gibbs energy

$$\Delta_r G = \sum_{\text{Products}} \nu \Delta_f G^\circ - \sum_{\text{Reactants}} \nu \Delta_f G^\circ = \sum_J \nu_J \left(\Delta_f G^\circ\right)_J$$

- Equilibrium constant**,** *K*, in terms of $\Delta_r G^\circ$,

$$\Delta_r G^\circ = -RT \ln K$$

Activity: Different Views Same Quantity

- Remember that activity can be defined in may forms:
  - Mole fractions

$$a_J = x_J \gamma_J$$

  - Molality (common for electrolytes)

$$a_J = \frac{b_J}{b^{\circ}} \gamma_J = b_J \gamma_J$$

$$b^{\circ} = 1 \text{ mol/kg}$$

  - Partial pressures

$$a_J = \frac{P_J}{P^{\circ}} \gamma_J = P_J \gamma_J$$

$$P^{\circ} = 1 \text{ bar}$$

  - Concentration

$$a_J = \frac{C_J}{C^{\circ}} \gamma_J = C_J \gamma_J$$

$$C^{\circ} = 1 \text{ mol/dm}^3$$

The Relation Between Equilibrium Constants

- **Activity coefficients must be evaluated at the equilibrium composition of the reaction mixture.**
- For example in molality terms

$$A + B \rightleftharpoons C + D$$

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\left(\frac{b}{b^{\circ}}\gamma\right)_C \left(\frac{b}{b^{\circ}}\gamma\right)_D}{\left(\frac{b}{b^{\circ}}\gamma\right)_A \left(\frac{b}{b^{\circ}}\gamma\right)_B} = \frac{b_C b_D}{b_A b_B}\frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} = K_b K_\gamma$$

What Affects the Equilibrium Constant?

- **Le Chatelier's principle: a system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.**
- The value of $\Delta_r G^\circ$ and hence of K is **independent** of the **pressure** at which equilibrium is established

$$\left(\frac{\partial K}{\partial p}\right)_T = 0$$

  - Does not necessarily imply that the reaction mixture composition is independent of pressure!
- The equilibrium constant is **not affected** by the presence of a **catalyst or an enzyme** (a biological catalyst).
  - Catalysts affect the rates of reaction but not their equilibrium composition.

Effect of Temperature: van’t Hoff’s Equation

- Le Chatelier’s principle for the effect of temperature:
  - increased temperature favors the reactants in exothermic reactions.
  - increased temperature favors the products in endothermic reactions.
- The van’t Hoff equation is an expression for the slope of a plot of the equilibrium constant as a function of temperature

$$\frac{d\ln K}{dT} = \frac{\Delta_r H^{\circ}}{RT^2}$$

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^{\circ}}{R}$$

Beyond van’t Hoff

- The overall temperature influence on the equilibrium constant can be written as a product of three terms

$$K = K_0 K_1 K_2$$

$$K_0 = \exp\left(-\frac{\Delta_r G_0^{\circ}}{RT_0}\right)$$

$$K_1 = \exp\left[\frac{\Delta_r H_0^{\circ}}{RT_0}\left(1 - \frac{T_0}{T}\right)\right]$$

$$K_2 = \exp\left[-\frac{1}{T}\int_{T_0}^{T}\frac{\Delta_r C_P^{\circ}}{R}dT + \int_{T_0}^{T}\frac{\Delta_r C_P^{\circ}}{R}\frac{1}{T}dT\right]$$

Heat Capacity of the Reaction Mixture

- The change of the heat capacity of the reaction mixture

$$\frac{\Delta_r C_P^\circ}{R} = \sum_j \nu_j C_{P,j}^\circ$$

- For a heat capacity model of the form

$$C_P^\circ = A + BT + CT^2 + DT^{-2}$$

- The third contribution can be written as

$$K_2 = \exp\left\{ \Delta A \left[\ln\tau - \left(\frac{\tau - 1}{\tau} \right) \right] + \frac{\Delta B}{2} T_0 \frac{(\tau-1)^2}{\tau} + \frac{\Delta C}{6} T_0^2 \frac{(\tau-1)^2(\tau+2)}{\tau} + \frac{\Delta D}{2T_0^2} \frac{(\tau-1)^2}{\tau^2} \right\}$$

$$\tau = T / T_0$$

Ellingham Diagram

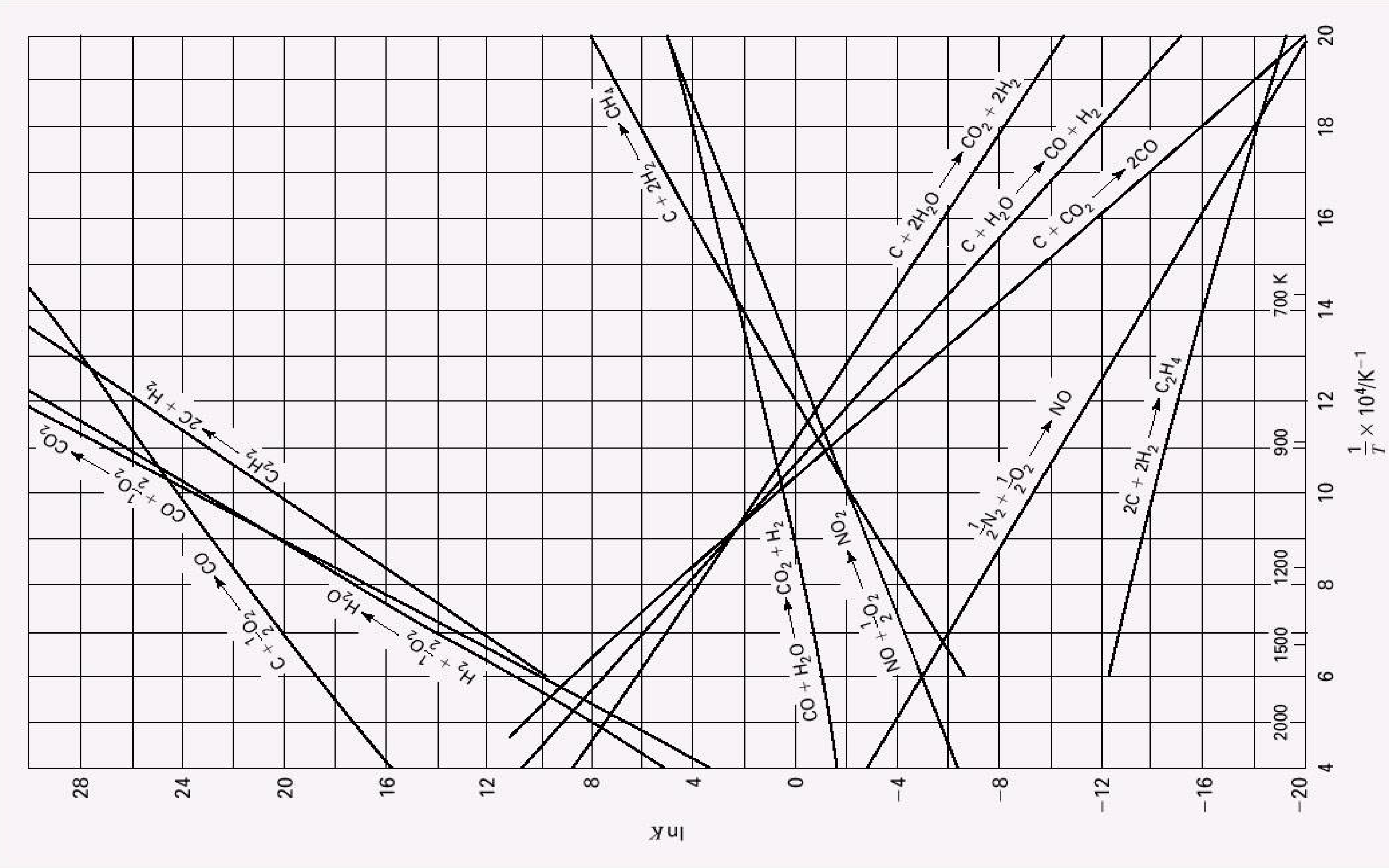

Figure 13.2: Equilibrium constants as a function of temperature.