

Lecture ~~32~~ 2 (class 1)
Equilibrium Concepts

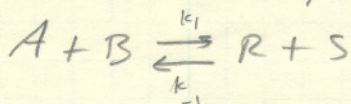
1. Why study equilibrium
 - a. difference between kinetics and equilibrium
 - b. limiting case - long time
 - c. may not know kinetics
 - d. turbulence hinders use of kinetics
2. Definitions
 - a. kinetic definition
 - b. thermodynamic definitions
3. Example of using K_{eq}
4. K_{eq} at different temperatures
5. Discuss possible projects

- handout on STANJAN

Definitions

A. kinetic

- For simple elementary, reversible reactions



$$r_{R \text{ forward}} = k_1 C_A C_B$$

$$r_{R \text{ backward}} = k_{-1} C_R C_S$$

At equilibrium, no net rate of formation

$$r_{R \text{ forward}} = r_{R \text{ backward}}$$

or

$$k_1 C_A C_B = k_{-1} C_R C_S$$

$$K_{eq} = \frac{k_1}{k_{-1}} \left[\frac{C_R C_S}{C_A C_B} \right] \text{ at equilibrium}$$

Caution: This only works when

(1) elementary reaction

(2) rate constants (k_1 , etc.) are known

Definitions

B. Thermodynamic

$$\Delta G_{\text{reaction}}^{\circ} = -RT \ln K_{eq}$$

a. the $^{\circ}$ refers to standard pressure, and the T ; ΔG° must agree

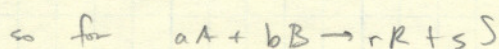
b. $G = H - TS$

$$dG = -SdT + VdP$$

c. $K_{eq} = \prod (a_i)^{\alpha_i}$

d. Tables of ΔG_f° at 25°C

$$\Delta G_{\text{react}}^{\circ} = \sum \alpha_i (\Delta G_i^{\circ})_f$$



$$\Delta G_{\text{react}}^{\circ} = r(\Delta G_R^{\circ})_f + s(\Delta G_S^{\circ})_f - a(\Delta G_A^{\circ})_f - b(\Delta G_B^{\circ})_f$$

e. $a_i = \frac{f_i}{f_i^{\circ}}$

f_i = fugacity of species i

f_i° = standard state fugacity = 1 (unit) of pressure for gases

$f_i = y_i \cdot \underset{\substack{\uparrow \\ \text{fugacity coefficient}}}{\nu_i} P_{\text{tot}}$ (for gases)

most combustion-related equilibrium codes assume ideal gas, ideal solution,

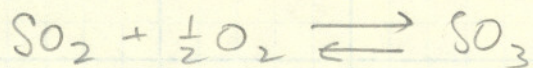
so

$$f_i = P_i = y_i P_{\text{tot}}$$

f. $K_{eq} = \frac{k_y k_{\nu} k_{P_{\text{tot}}}}{k_{f^{\circ}}} = k_y k_{P_{\text{tot}}} = k_{P_i} = \frac{k_{a_i}}{k_T}$

$$P_i = \frac{c_i}{RT}$$

Example



$$K_{eq} = 8.5 \text{ @ } 610^\circ\text{C}$$

feed = 12 mole % SO_2

8 % O_2

80 % N_2

Pressure = 1 atm

What is equilibrium mixture?

A. Mole Balance

	SO_2	O_2	N_2	SO_3	total
initially	12	8	80	0	100
finally	$12-x$	$8-\frac{1}{2}x$	80	x	$100-\frac{1}{2}x$

$x = \text{moles of } \text{SO}_3 \text{ formed}$

B. Mole fractions

$$y_{\text{SO}_2} = \frac{12-x}{100-\frac{1}{2}x}$$

$$y_{\text{SO}_3} = \frac{x}{100-\frac{1}{2}x}, \quad y_{\text{O}_2} = \frac{8-\frac{1}{2}x}{100-\frac{1}{2}x}$$

C. Equilibrium

$$K_{eq} = 8.5 = \frac{y_{\text{SO}_3}}{y_{\text{SO}_2} y_{\text{O}_2}^{1/2}} = \frac{\frac{x}{100-\frac{1}{2}x}}{\left(\frac{12-x}{100-\frac{1}{2}x}\right) \left(\frac{8-\frac{1}{2}x}{100-\frac{1}{2}x}\right)^{1/2}} = \frac{x (100-\frac{1}{2}x)^{1/2}}{(12-x)(8-\frac{1}{2}x)^{1/2}}$$

$$\text{solve for } x \Rightarrow x = 7.67$$

$$y_{\text{SO}_3} = 0.0797$$

$$y_{\text{SO}_2} = 0.0451$$

$$y_{\text{O}_2} = 0.0433$$

$$y_{\text{N}_2} = 0.832$$

What % of incoming SO_2 is converted?

$$\text{initial} \rightarrow \frac{x}{12} \times 100 = 63.9\%$$

of moles

Repeat previous example for 100 atm!

$$K_{eq} = K_y K_{\pi} = \frac{y_{SO_3}}{y_{SO_2} y_{O_2}^{1/2}} \pi^{1-1-\frac{1}{2}} = 8.5$$

$$\frac{y_{SO_3}}{y_{SO_2} y_{O_2}^{1/2}} = \frac{8.5}{100^{0.5}} = 85 = \frac{x(100 - \frac{1}{2}x)^{1/2}}{(12-x)(8 - \frac{1}{2}x)^{1/2}}$$

$$x = 11.18$$

$$y_{SO_3} = 0.1184$$

$$y_{SO_2} = 0.0087$$

$$y_{O_2} = 0.0255$$

$$y_{N_2} = 0.8474$$

$$\% \text{ Conversion} = \frac{x}{12} \times 100 = 93.1\% !!$$

High pressure favors lower number of moles (Le Chatlier)

Ideas for Equilibrium Projects

1. Generate program / spreadsheet to make species "cards" for oil, coal, air, etc. based on wt%.
2. Examine $P;T$ effects for different systems $\left\{ \begin{array}{l} - \text{water-gas shift} \\ - \text{sulfation} \\ - \text{CO combustion} \end{array} \right.$
3. Explore boundaries of $C(s)$ envelope and compare with sooting thresholds
4. Explore NO_x / SO_x equilibrium and compare w/data from Comb. systems.
5. Figure out what the rocket stuff means
6. Code development
 - get them all to work on all machines (PC version?)
 - better user interfaces
 - updated copies
 - get Super Burn to work right
7. Check codes vs. simple system K_{eq} approach