Lecture ~~3~~ ~~1~~ 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

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R + S$$

$$r_{R_{forward}} = k_1 C_A C_B$$

$$r_{R_{backward}} = k_{-1} C_R C_S$$

At equilibrium, no net rate of formation

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

or

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

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

<u>Caution</u>: This only works when
(1) elementary reaction
(2) rate constants (k_1, etc.) are known

Definitions

B. Thermodynamic

$$\Delta G^\circ_{reaction} = -RT \ln K_{eq}$$

a. the ° 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

$$\Delta G^\circ_{react} = \sum \alpha_i (\Delta G^\circ_i)_f$$

so for $aA + bB \rightarrow rR + sS$

$$\Delta G^\circ_{react} = r(\Delta G^\circ_R)_f + s(\Delta G^\circ_S)_f - a(\Delta G^\circ_A)_f - b(\Delta G^\circ_B)_f$$

e. $a_i = \dfrac{f_i}{f_i^\circ}$ f_i = fugacity of species i

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

$$f_i = y_i \, \nu_i \, P_{tot} \quad \text{(for gases)}$$

(ν_i = fugacity coefficient)

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

so

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

f. $$K_{eq} = \frac{K_y K_\nu K_{P_{tot}}}{K_{f^\circ}} = K_y K_{P_{tot}} = K_{P_i} = \frac{K_{c_i}}{K_T}$$

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

Example

$$SO_2 + \tfrac{1}{2}O_2 \rightleftarrows SO_3$$

$$K_{eq} = 8.5 \quad @ \ 610°C$$

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 = moles of SO_3 formed

B. Mole fractions

$$y_{SO_2} = \frac{12-x}{100-\frac{1}{2}x}, \quad y_{SO_3} = \frac{x}{100-\frac{1}{2}x}, \quad y_{O_2} = \frac{8-\frac{1}{2}x}{100-\frac{1}{2}x}$$

C. Equilibrium

$$K_{eq} = 8.5 = \frac{y_{SO_3}}{y_{SO_2}\, y_{O_2}^{1/2}} = \frac{\frac{x}{100-\frac{1}{2}x}}{\left(\frac{12-x}{100-\frac{1}{2}x}\right)\left(\frac{8-\frac{1}{2}x}{100-\frac{1}{2}x}\right)^{1/2}} = \frac{x\,(100-\frac{1}{2}x)^{1/2}}{(12-x)(8-\frac{1}{2}x)^{1/2}}$$

solve for $x \Rightarrow x = 7.67$

$y_{SO_3} = 0.0797$
$y_{SO_2} = 0.0451$
$y_{O_2} = 0.0433$
$y_{N_2} = 0.832$

What % of incoming SO_2 is converted?

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

(12 = initial # of moles)

Repeat previous example for 100 atm!

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

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

$$x = 11.18$$

$y_{SO_3} = 0.1184$

$y_{SO_2} = 0.0087$

$y_{O_2} = 0.0255$

$y_{N_2} = 0.8474$

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

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 { - water-gas shift - sulfation - CO combustion

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