

## Chem 103

Lecture 1b  
Chemical Equilibrium 2

### Last time:

- 1. We went over the syllabus and policies
- 2. We started discussion of equilibrium by relating it to kinetics concepts
- 3. Equilibrium occurs after a "long" time!
- 4. K expression is based on a balanced reversible equation
- 5. Value of K can be determined experimentally.

### Some reminders

- Furlough Friday on June 25
- Valenzuela's calculator

### Chemical Equilibrium expression

If  $aA + bB \rightleftharpoons cC + dD$

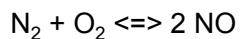
Then :  $K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$   
(remember : [prod]/[reactant])

Example:  $3A + 5B \rightleftharpoons C + 2D$

Then:  $K = \frac{[C][D]^2}{[A]^3[B]^5}$

### Determining value of K:

What is the *value* of K for



if  $[N_2]=0.20$ ,  $[O_2] = 1.2 \times 10^{-5}$  and  
 $[NO] = 0.10$  at equil.?

$$K = \frac{[NO]^2}{[N_2][O_2]} = \frac{.10^2}{(.20)(1.2 \times 10^{-5})} = 4.2 \times 10^3$$

### Chemical Equilibrium *properties*

- The expression is given above.  
It is based on stoichiometric coefficients.
- It applies only to equilibrium conditions.  
(concentration values at equilibrium)
- It is dimensionless (even though we use molarity(M)) in the expression.
- K value is independent of initial conditions.

### Other Equilibrium properties

Other properties:

If  $A \rightleftharpoons B$   $K = K_1$   
 then reversal:  $B \rightleftharpoons A$  has  $K = 1/K_1$

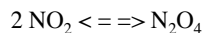
If  $A \rightleftharpoons B$   $K_1$   
 and  $B \rightleftharpoons C$   $K_2$   
 Then adding:  $A \rightleftharpoons C$  has  $K = K_1 K_2$

If  $A \rightleftharpoons B$   $K_1$   
 Then:  $2A \rightleftharpoons 2B$   $K = K_1^2$

For pure liquids, solids and solvents  
 Substitute molarity = 1 (i.e. activity = 1)

### Let's practice! Prob.#1

Given:  $K = 3.1$  for the following reaction:



If  $[\text{NO}_2] = 0.10 \text{ M}$  at equil, what is  $[\text{N}_2\text{O}_4]$ ?

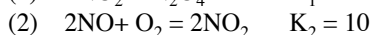
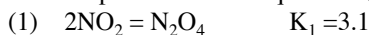
Solution:

$$K = [\text{N}_2\text{O}_4] / [\text{NO}_2]^2 \text{ or}$$

$$[\text{N}_2\text{O}_4] = K[\text{NO}_2]^2 = (3.1)(.10 \text{ M})^2 = 0.031 \text{ M}$$

### Let's practice! Prob.#2

Another problem: Have equations (1) & (2):



what is value of K for:

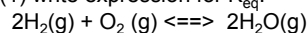


(You recognize this as (1) + (2), yes?)

(1) + (2) so  $K = K_1 K_2 = 3.1 (10) = 31$

### $K_c$ vs $K_p$

(1) write expression for  $K_{eq}$ :



Answer:  $K_c = [\text{H}_2\text{O}]^2 / [\text{H}_2]^2 [\text{O}_2]$  ( $K_c = K_{\text{concentration}}$ )

For equations involving gases,  $K_p$  is preferred  
 unless  $K_c$  is asked for. ( $K_p = K_{\text{partial pressure}}$ )

### Relationship between the values of $K_c$ and $K_p$

Note:  $p = (n/V)(RT) = MRT$

What is R=? Gas const. = 0.0821 atmL/molK

So, for  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$

$$K_p = P_{\text{H}_2\text{O}}^2 / P_{\text{H}_2}^2 P_{\text{O}_2}$$

e.g:  $P_{\text{H}_2} = (n_{\text{H}_2}/V)(RT) = M_{\text{H}_2}RT = [\text{H}_2]RT$

$$K_p = \frac{(M_{\text{H}_2\text{O}}RT)^2}{\{(M_{\text{H}_2}RT)^2 (M_{\text{O}_2}RT)\}} = \left\{ \frac{M_{\text{H}_2\text{O}}^2}{M_{\text{H}_2}^2 M_{\text{O}_2}} \right\} (RT)^{2-(2+1)}$$

$K_p = K_c(RT)^{-1}$  for this equation.

### Relationship between the values of $K_c$ and $K_p$

In general:

$$K_p = K_c(RT)^{\Delta n} \text{ where: } \Delta n = \Delta(\# \text{mol gases})$$

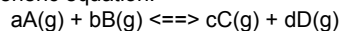
$$\Delta n = n_{\text{gas products}} - n_{\text{gas reactants}}$$

Note:  $p = (n/V)(RT) = MRT$

What is R=? Gas const. = 0.0821 atmL/molK

What is T=?  $T = 298\text{K}$  usually

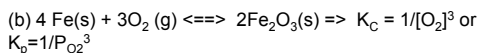
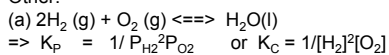
Generic equation:



Then:  $K_p = K_c(RT)^{\Delta n}$  where  $\Delta n = (c+d)-(a+b)$

Write  $K_c$  and  $K_p$  expressions for the following:

Other:



The “meaning” of K

Consider:  $\text{A} \rightleftharpoons \text{B}$

if  $K > 1$  that means  $K = [\text{B}]/[\text{A}] > 1$

i.e. since  $[\text{B}] > [\text{A}]$  therefore: B is favored.  
 “product-favored”

Example:  $K = 3.0 \times 10^{12} \gg 1$   
 means *product* strongly favored. Almost no reactant remains

The “meaning” of K

Consider:  $\text{A} \rightleftharpoons \text{B}$

if  $K < 1$  that means  $K = [\text{B}]/[\text{A}] < 1$

i.e. since  $[\text{B}] < [\text{A}]$  therefore: A is favored.  
 “reactant-favored”

Example:  $K = 2.0 \times 10^{-22}$   
 means *reactant* greatly favored. In this case, almost no reaction occurs.

The “meaning” of K

Consider:  $\text{A} \rightleftharpoons \text{B}$

if  $K \approx 1$  that means  $K = [\text{B}]/[\text{A}] \approx 1$

i.e. Reaction is “reversible”

Example:  $K = 2.0 \times 10^{-2}$   
 means *reactant* favored.

Ex#1: Solving for equil concs given the initial conditions

Sample problem:

If  $\text{A} \rightleftharpoons \text{B}$  and  $K = 2.00$

Initially we have  $[\text{A}] = 0.300\text{M}$ ,  $[\text{B}] = 0.000\text{M}$

At equilibrium  $K = 2.00 = [\text{B}]^2/[\text{A}]$

What are  $[\text{B}]_{\text{eq}}$  and  $[\text{A}]_{\text{eq}}$ ?

(Remember: K is independent of initial conditions)

Ex#1 Solving for  $[\text{A}]_{\text{equil}}$  etc.

Solution: (using the ICE method)

$\text{A} \rightleftharpoons \text{B}$

**I**nitial 0.300M 0.000

**C**hange -x +x

**E**quil. 0.300-x x

So  $K = 2.00 = [\text{B}]/[\text{A}] = x/(0.300\text{M}-x)$

Solve for x :  $0.600\text{M} - 2.00x = x$

$3x = 0.600\text{M} \Rightarrow x = 0.200\text{M} = [\text{B}]$

And  $[\text{A}] = 0.300\text{M} - (0.200\text{M}) = 0.100\text{M}$

Initial conditions important to determine favored *direction* of reaction.

In previous example: Initially no B but lots of A.

Thus forward reaction was favored to reach equilibrium.

Compare initial ratios of B to A with the ratio (K) at equilibrium.

We introduce Q as an aid. "Q" = "reaction quotient"

## The reaction quotient, Q

Q *expression* looks like K *in form* but values for *actual* initial concentrations not equilibrium concentrations.

**Compare Q with K** to determine which direction will be favored:

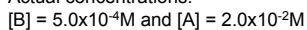
**If**            **then**  
 Q>K    reverse direction is favored  
 Q<K    forward direction is favored  
 Q=K    equilibrium condition prevails

## Predicting direction of reaction

Given:



Actual concentrations:



$$Q = \frac{[B]}{[A]} = \frac{5.0 \times 10^{-4}}{2.0 \times 10^{-2}} = 2.5 \times 10^{-2}$$

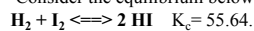
Compare Q to K:  $Q = 2.5 \times 10^{-2} > K = 3.0 \times 10^{-3}$

Therefore the reverse reaction is favored:

[B] will decrease and [A] will increase until Q=K.

## Problem solving: Back to ICE

Consider the equilibrium below



If a 0.500 L flask initially contains 1.00 mole each of  $\text{H}_2$  and  $\text{I}_2$  gas and no HI gas, what will be final concentrations of all three gaseous species at equilibrium?

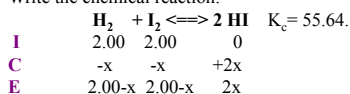
Solution: first, let's get  $[\text{H}_2]$  and  $[\text{I}_2]$ :

$$[\text{H}_2] = 1.00 \text{ mol} / 0.500 \text{ L} = 2.00 \text{ M} \quad \text{also} = [\text{I}_2]$$

## Using the ICE method...

Solution continuation:

Write the chemical reaction:



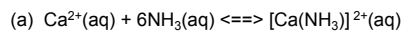
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(2.00-x)^2} = 55.64$$

Take square root of both sides:  $2x/(2.00-x) = \sqrt{55.64}$

Solve for x :  $x = 1.577 \text{ M}$

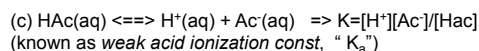
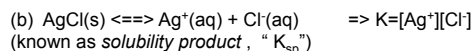
And so:  $[\text{H}_2] = 2.00 - 1.577 = 0.42 \text{ M} = [\text{I}_2]$ ;  $[\text{HI}] = 3.15 \text{ M}$

## Some special types of K



$$\Rightarrow K = \frac{[\text{Ca}(\text{NH}_3)_6]^{2+}}{[\text{Ca}^{2+}][\text{NH}_3]^6}$$

( $K_c$  is known as formation constant, " $K_f$ ")



### Sample solubility problem

Calcium sulfate,  $\text{CaSO}_4$ , a sparingly soluble compound, has a solubility product,  $K_{\text{sp}}$ , of  $4.9 \times 10^{-5}$ . What is the molar solubility of  $\text{CaSO}_4$ ?

Write the equilibrium:  $\text{CaSO}_4(\text{s}) = \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

Solution: Use the ICE approach:

$\text{CaSO}_4(\text{s}) = \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$   $K_{\text{sp}}$  of  $4.9 \times 10^{-5}$ .

ICE:  $\begin{array}{ccc} & 1 & \\ & x & \\ & x & \end{array}$

(note: above, we let  $x = [\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$ )

$K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (x)(x) = x^2 = 4.9 \times 10^{-5}$

$\Rightarrow x = 7.0 \times 10^{-3} \text{M} = [\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$ .