

## Chem 103

Lecture 2a  
Chemical Equilibrium 3

### Last time: we discussed...

- 1. Properties of equilibria
- 2. Manipulation of K equations
- 3. Sample Problems
- 4.  $K_p$  expression and value vs  $K_c$  expression and value
- 5. The "meaning" of K

### Today

- ICE method of calculating equilibrium values given certain initial conditions.
- Reaction Quotient, Q
- Using Q to predict favored direction of reaction
- Special types of equilibria and their K's.
- Sample Calculations.

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

Sample problem:

If  $A \rightleftharpoons B$  and  $K = 2.00$

Initially we have  $[A] = 0.300M$ ,  $[B] = 0.000M$

At equilibrium, what are the final values of  $[A]$  and  $[B]$ ?

(Remember: K is independent of initial conditions)

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

Solution: (using the **ICE method**)

A  $\rightleftharpoons$  B

**I**nitial 0.300M 0.000 M

**C**hange -x +x

**E**quil. 0.300-x x

At equil:  $K = 2.00 = [B]/[A] = x/(0.300M-x)$

Solve for x :  $0.600M - 2.00x = x$

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

And  $[A] = 0.300 M - (0.200 M) = 0.100M$

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

As a final check, verify that the values of  $[A]_{\text{eq}}$  and  $[B]_{\text{eq}}$  yield the correct value of K:

$$K = [B]_{\text{eq}} / [A]_{\text{eq}} = 0.200/0.100 = 2.00$$

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.

For example:

Write Q for:  $A \rightleftharpoons 2B$

$$Q = \frac{[B]_{\text{initial}}^2}{[A]_{\text{initial}}} = \text{a variable}$$

In contrast, K's expression is:

$$K = \frac{[B]_{\text{final}}^2}{[A]_{\text{final}}} = \text{a constant}$$

## Using reaction quotient, Q

Again: Q *expression* looks like K *in form* but value of Q depends on initial conditions.

**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

In the previous example:

$A \rightleftharpoons B$  K = 2.00

Actual concentrations:

[B] = 0 and [A] = 0.300M

$$Q = \frac{[B]}{[A]} = \frac{0}{.300} = 0$$

Compare Q to K:  $Q = 0 < K = 2.00$

Therefore the reverse reaction ( $\leftarrow$ ) is favored: [B] will INcrease and [A] will DEcrease until Q=K.

## Predicting direction of reaction

Another scenario:

$C \rightleftharpoons 2D$  K =  $3.0 \times 10^{-3}$

Initial concentrations:

[C] =  $5.0 \times 10^{-4}$ M and [D] =  $2.0 \times 10^{-2}$ M

First, get Q:

$$Q = \frac{[D]^2}{[C]} = \frac{(2.0 \times 10^{-2})^2}{5.0 \times 10^{-4}} = 0.80$$

Compare Q to K:  $Q = 0.80 > K = 3.0 \times 10^{-3}$

Therefore the reverse reaction ( $\rightleftharpoons$ ) is favored:

[D] will DEcrease and [C] will increase until Q=K.

## Predicting direction of reaction

Another scenario:

$C \rightleftharpoons 2D$  K =  $3.0 \times 10^{-3}$

Actual concentrations:

[C] = 1.0 M and [D] =  $5.5 \times 10^{-2}$  M

Frst, get Q:

$$Q = \frac{[D]^2}{[C]} = \frac{(5.5 \times 10^{-2})^2}{1.0} = 3.0 \times 10^{-3}$$

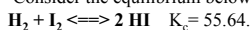
Compare Q to K:  $Q = 3.0 \times 10^{-3} = K = 3.0 \times 10^{-3}$

Therefore neither direction is favored.

The system is ALREADY AT EQUILIBRIUM!

### 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?

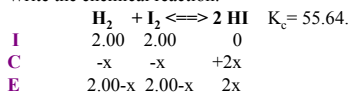
Solution: first, let's get  $[\text{H}_2]$  and  $[\text{I}_2]$ :

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

### 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 :  $x = 1.57_7 \text{ M}$

And so:  $[\text{H}_2] = 2.00 - 1.57_7 = 0.42 \text{ M} = [\text{I}_2]$ ;  $[\text{HI}] = 3.15 \text{ M}$

### Some special types of K

(a)  $\text{Ca}^{2+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Ca}(\text{NH}_3)_6]^{2+}(\text{aq})$   
 $\Rightarrow K = \frac{[\text{Ca}(\text{NH}_3)_6^{2+}]}{[\text{Ca}^{2+}][\text{NH}_3]^6}$   
 ( $K_c$  is known as formation constant, " $K_f$ ")

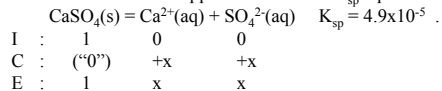
(b)  $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad \Rightarrow K = [\text{Ag}^+][\text{Cl}^-]$   
 (known as *solubility product*, " $K_{sp}$ ")

(c)  $\text{HAc}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{Ac}^-(\text{aq}) \quad \Rightarrow K = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}$   
 (known as *weak acid ionization const.*, " $K_a$ ")

### Sample solubility problem #1

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

Solution: Use the ICE approach: Write the  $K_{sp}$  equilibrium:



(note: above, we let  $x = [\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$ , and  $\text{CaSO}_4(\text{s}) = 1$ )

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]/1 = (x)(x) = x^2 = 4.9 \times 10^{-5}$$

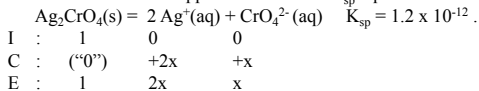
Take square root of both sides:

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

### Sample solubility problem #2

Silver chromate,  $\text{Ag}_2\text{CrO}_4$ , a sparingly soluble compound, has a *solubility product*,  $K_{sp}$ , of  $1.2 \times 10^{-12}$ . What is the *molar solubility* of  $\text{Ag}_2\text{CrO}_4$ ?

Solution: Use the ICE approach: Write the  $K_{sp}$  equilibrium:



(note: above, we let  $x = [\text{CrO}_4^{2-}]$  and so  $[\text{Ag}^+] = 2x$ )

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]/1 = (2x)^2(x) = 4x^3 = 1.2 \times 10^{-12}$$

Or,  $x^3 = 3.0 \times 10^{-13}$  Take cube root of both sides:

$$\Rightarrow x = 6.7 \times 10^{-5} \text{ M} = [\text{CrO}_4^{2-}] \Rightarrow [\text{Ag}^+] = 2x = 1.3 \times 10^{-4} \text{ M}$$