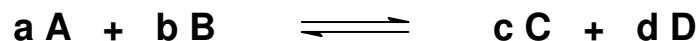


## Chemical Equilibrium - Chapter 15

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### 1. Dynamic Equilibrium



#### *At Equilibrium:*

Reaction is proceeding in both directions at the same rate.  
There is no net change in concentrations of reactants and Products.

### 2. Equilibrium Constant Expression

(a) Mass action expression:  $Q =$  "reaction quotient"

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where,  $[A]$ ,  $[B]$ , etc. are "non-equilibrium" concentrations

(b) *At Equilibrium:*

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where,  $K_c =$  "equilibrium constant"  
 $[A]$ ,  $[B]$ , etc. are the equilibrium concentrations!

(c) Magnitude of  $K$

$$K \approx [\text{products}] / [\text{reactants}]$$

if  $K$  is very large: mostly products at equilibrium

if  $K$  is very small: mostly reactants at equilibrium

if  $K \approx 1$ : roughly equal conc's of reactants and products

- (d) Manipulating equilibrium constant expressions  
 reverse equation  $\longrightarrow$  invert  $K_C$   
 multiply equation by coefficient "n"  $\longrightarrow$   $(K_C)^n$   
 add two equations  $\longrightarrow$  multiply their  $K_C$ 's
- (e) Relationship between Q and K

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

if  $Q > K$

conc of products are too large  
 reaction shifts in reverse to reach equilibrium

if  $Q < K$

conc of reactants are too large  
 reaction shifts forward to reach equilibrium

### 3. Equilibrium Constants for Gas Phase Reactions

- (a) since  $P \propto$  molar conc, the equilibrium constant can be expressed in terms of partial pressures (in atm):

$$K_p = \frac{(P_c)^c (P_d)^d}{(P_a)^a (P_b)^b}$$

- (b) relationship of  $K_C$  and  $K_p$

based on ideal gas law . . . .

$$K_p = K_C (RT)^{\Delta n}$$

$\Delta n$  = moles gaseous products - moles gaseous reactants

$R = 0.0821 \text{ L atm / mole K}$

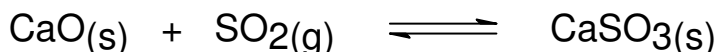
#### 4. Heterogeneous Equilibria

concentrations of pure liquids and solids are effectively constants,  $\therefore$  they do not appear in K expressions

for example:



$$K_c = [\text{NH}_4^+] [\text{OH}^-] / [\text{NH}_3]$$



$$K_p = 1 / P_{\text{SO}_2}$$

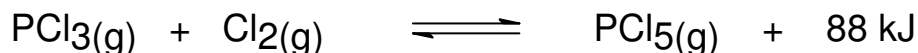
#### 5. Le Châtelier's Principle

***"When a system at equilibrium is subjected to an external stress, the system will shift in a direction to counteract the stress and achieve a new equilibrium state."***

Common factors ("external stresses") to consider:

- addition or removal of some reactant or product
- change in volume (important for gaseous reactions)
- change in temperature
- addition of a catalyst

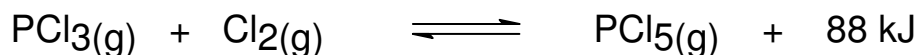
Example -- consider a series of possible changes to the following equilibrium reaction:



( this reaction is exothermic:  $\Delta H^\circ = - 88 \text{ kJ}$  )

What happens to  $[\text{Cl}_2]$  if

- (a) some  $\text{PCl}_3$  is added?  
the "stress" is more  $\text{PCl}_3$   
system needs to remove  $\text{PCl}_3$   
 $\therefore$  reaction shifts forward and  $[\text{Cl}_2]$  decreases



- (b) some  $\text{PCl}_5$  is added?  
the "stress" is more  $\text{PCl}_5$   
system needs to remove  $\text{PCl}_5$   
 $\therefore$  reaction shifts in reverse and  $[\text{Cl}_2]$  increases
- (c) the temp is increased? (this requires a  $\Delta H^\circ$  value)  
the "stress" is added heat  
the system needs to remove heat  
since the reaction is exothermic, heat is a "product"  
adding a "product" causes reaction to shift in reverse  
 $\therefore$   $[\text{Cl}_2]$  increases
- (d) the volume is increased? (or pressure is decreased)  
the "stress" is more space for gas molecules  
system tries to produce more gas to fill the space  
reaction shifts in direction of more moles of gas  
in this case, it shifts in reverse  
(2 mol gaseous reactants vs 1 mol gaseous product)  
 $\therefore$   $[\text{Cl}_2]$  increases
- (e) a catalyst is added?  
Addition of a catalyst does not affect the position of equilibrium.  $\therefore$  There is no change in any of the equilibrium concentrations. The catalyst merely lowers the time needed to attain equilibrium.

## 6. Equilibrium Calculations

Two basic types of problems:

- (a) Given the equilibrium concentrations (or partial pressures), determine  $K_C$  (or  $K_P$ ).

General Method:

Put conc values into K expression!

or, if necessary, set up a "concentration table" based on reaction stoichiometry, e.g.



In an experiment, 0.20 mol of  $\text{PCl}_3$  and 0.10 mol  $\text{Cl}_2$  were placed in a 1.00 L container. After the reaction had come to equilibrium, the concentration of  $\text{PCl}_3$  was found to be 0.12 mole/L. Determine the  $K_C$  value.

- (b) Given K and one or more initial concentrations, determine the equilibrium concentrations

General Method:

Set up a "concentration table" based on an unknown "x" -- usually one of the equilibrium concentrations or a change in a conc.

Express all equilibrium concentrations in terms of "x" and initial values

Insert these equilibrium values (in terms of "x") into the proper equation for K, and

If possible, solve directly for "x" using simple math

**No need for quadratic formula on Exams !**

(but necessary in some homework problems)

Otherwise make a **chemically reasonable approximation !**