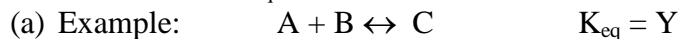


## AP Chemistry

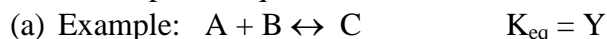
### Chapter 15 Outline

- a) Chemical equilibrium occurs when opposing reactions are proceeding at equal rates.
- i) The rate at which products are formed from the reactants equals the rate at which reactants are formed from the products.
- (1) No macroscopic changes (such as concentration changes) are observable, but the reaction DOES NOT stop!
  - (2) How fast a reaction reaches equilibrium is a matter of kinetics.
  - (3) Neither reactants nor products can escape the system.
    - (a) For forward reaction:  $R \rightarrow P$                        $\text{rate}_f = k_f[R]$
    - (b) For reverse reaction:  $P \rightarrow R$                        $\text{rate}_r = k_r[P]$
  - (4) At equilibrium,  $\text{rate}_f = \text{rate}_r$ ,
    - (a) so  $k_f[R] = k_r[P]$
    - (b) rearranged,  $\frac{[P]}{[R]} = \frac{k_f}{k_r} = \text{the equilibrium constant, } K \text{ (hint for a CALM problem!)}$
- b) The equilibrium constant
- (1) Equilibrium can be reached from either direction: starting with all reactants, starting with all products, or some of both products and reactants
  - ii) Law of Mass Action: for a generic reaction  $aA + bB \leftrightarrow cC + dD$ 
    - (1)  $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$      $K_c$ , because we're using molar concentrations
    - (2) in general,  $K = \text{products/reactants}$
    - (3) value of  $K$  depends on the on the particular reaction and the temperature; equilibrium constants are often typically recorded as dimensionless
    - (4) for gaseous systems,  $K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$      $K_p$ , because we're using partial pressures of each gas in atmospheres
    - (5)  $K_c$  and  $K_p$  are usually numerically different, but there is a relationship between them
      - (a)  $K_p = K_c (RT)^{\Delta n}$  where  $\Delta n = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants})$                       **KNOW AND BE ABLE TO USE THIS EQUATION!**
- c) Interpreting and working with equilibrium constants                      **KNOW THIS SECTION!**
- i) Value of  $K_{eq}$  gives information on system at equilibrium
- (1) If  $K_{eq} \gg 1$ : products predominate; equilibrium lies "to the right"
  - (2)  $K_{eq} \ll 1$ : reactants predominate; equilibrium lies "to the left"

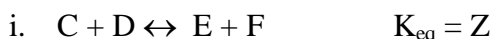
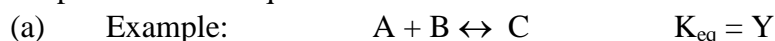
- ii) Equilibrium constant expressions can be manipulated in several ways  
 (1) If you write a reaction backwards, its  $K_{eq}$  value is equal to the reciprocal of the forward reaction  $K_{eq}$



- (2) If an equation is multiplied through by a constant value, the  $K_{eq}$  expression is raised to a power equal to that constant.



- (3) If two or more reactions are summed together, then the overall  $K_{eq}$  expression is the product of the equilibrium constants for the individual steps.



- d) Heterogeneous Equilibria = when substances are not all in the same phase  
 i) Whenever a pure solid or a pure liquid is included in a heterogeneous equilibrium, its concentration is not included in the  $K_{eq}$  expression.  
 ii) As long as the solid components of the heterogeneous equilibrium are present, the system will reach the same ratios!

- e) Calculation Equilibrium Constants *Be able to use the ICE strategy!*

- i) From the balanced equation, create a table: initial, change, equilibrium

i.  $A + 2B \leftrightarrow 3C$  if no products are initially present:

	A	B	C
I	[A]	[B]	0
C	-x	-2x	+3x
E	[A] - x	[B] - 2x	+3x

- ii) Use the given information and stoichiometric relationships to figure out the amount of change for each species and substitute into the  $K_{eq}$  expression

- f) Applications of Equilibrium Constants **KNOW AND BE ABLE TO DO THIS!**

- i) The Reaction Quotient, Q: Predicting the Direction of Reaction

- (1) Q: the ratio of products to reactants at this moment (not necessarily at equilibrium)

(a) Substitute “current” concentrations into the  $K_{eq}$  expression and evaluate

- (2) Compare Q to K to determine the direction of the reaction

(a) If  $Q = K$ , the reaction is already at equilibrium

(b) If  $Q > K$ , then there are too many products; products will react to form reactants, causing the reaction to move “to the left”

(c) If  $Q < K$ , then there are not enough products; reactants will form more products, causing the reaction to move “to the right”

(d) If both reactants and products are present initially, compare Q to  $K_{eq}$  to determine the signs when using the ICE approach

- g) LeChatelier's Principle: If a system at equilibrium is disturbed by a change in temperature, pressure, or concentration, the system will shift its equilibrium position so as to counteract the effect of the shift.
- i) Changing Concentrations:
- (1) Add reactant: forward reaction will proceed faster, making products; system will "shift right" to re-establish equilibrium
  - (2) Add product: reverse reaction will proceed faster, making reactants; system will "shift left"
  - (3) Remove reactant: forward reaction will slow down; reverse reaction will make more reactant; system will "shift left"
  - (4) Remove product: reverse reaction will slow down; forward reaction will make more product; system will "shift right"
- ii) Volume and Pressure Changes
- (1) Remember: fewer moles of gas  $\rightarrow$  reduced pressure
    - (a) If the pressure is increased (or volume is decreased), the system will shift towards the side with FEWER moles of gas
    - (b) If the pressure is decreased (or volume is increased), the system will shift toward the side with MORE moles of gas
- iii) Temperature changes: think about the energy change as if it were a chemical species
- (1) Endothermic: reactants + heat  $\leftrightarrow$  products
  - (2) Raising the temperature is like adding more reactants; system will shift right
  - (3) Lowering the temperature is like removing reactants; system will shift left
  - (4) Increasing T results in a larger  $K_{eq}$  value.
  - (5) Exothermic: reactants  $\leftrightarrow$  products + heat
    - (a) Raising the temperature is like adding more products; system will shift left
    - (b) Lowering the temperature is like removing products; system will shift right.
    - (c) Increasing T results in a smaller  $K_{eq}$  value.
- iv) Catalysts increase the rates of both the forward and reverse reactions.
- (1) Catalysts will NOT change the value of  $K_{eq}$  but will increase the rate at which equilibrium is achieved.