**Chemical Equilibrium** Name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*AP Chemistry Lecture Outline*

Chemical equilibrium is reached when the concentrations of reactants and products cease changing with time. **reactants** **products**

 -- system must be closed

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For the reaction A B:

 -- Eq. can be reached starting with…

law of mass action: expresses the relationship between amounts of R and P in any reaction

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For the equilibrium system aA + bB pP + qQ the law of mass action says that an equilibrium constant K is given by:

When amts. are given in terms

of concentration (i.e., molarity):

 For a gaseous system:

 where PX is the partial pressure of X at eq., and Kp is the pressure eq. constant

The relationship between Kc and Kp is given by...

EX. For the gaseous reaction 2 NO + O2 2 NO2

1. write the Kc and Kp expressions
2. find Kp at T = 750oC, if Kc = 2.19 x 10–3.

A few notes about K:

-- it depends only on the reaction stoichiometry, not its mechanism

 -- it is independent of initial concentrations

 -- it is unaffected by other substances, as long as they don’t react with R or P

 -- it varies with temperature

 -- it is written without units

 -- it NEVER includes pure solids or pure liquids

EX. Write expressions for Kc and Kp.

CO2(g) + H2(g) CO(g) + H2O(l)

SnO2(s) + 2 CO(g) Sn(s) + 2 CO2(g)

EX. Write the Kc expression for each reaction.

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 N2 + 3 H2 2 NH3 2 SO3 2 SO2 + O2

EX. Based on CaCO3(s) CaO(s) + CO2(g), which of the following can attain

 equilibrium? Start with...

 (a) ...pure CaCO3

(b) ...CaO and some CO2 at P > Kp

(c) ...CaCO3 and some CO2 at P > Kp

(d) ...CaCO3 and CaO

***The Magnitude of the Equilibrium Constant***

 If K >> 1...

 If K << 1...

 The K for the forward and reverse reactions are NOT the same.

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 -- You must write out the equation and specify the temperature when reporting a K.

**Calculating Equilibrium Constants**

(1) If the concentrations of all substances at equilibrium are known, plug and chug.

EX. Find Kc @ 472oC for N2(g) + 3 H2(g) 2 NH3(g)

 At equilibruim @ 472oC, [NH3] = 0.00272 M, [N2] = 0.0402 M, [H2] = 0.1207 M.

(2) If you know the concentrations of only some substances at equilibrium, make a chart and

 use reaction stoichiometry to figure out the other concentrations at equilibrium. THEN

 plug and chug.

EX. At 1000 K, the amounts shown below are known. Find Kc @ 1000 K.

2 SO3(g) 2 SO2(g) + O2(g)

 initial **6.09 x 10–3 M 0 M 0 M**

 

 at eq. **2.44 x 10–3 M**

By knowing K, we can...

 (1)

 (2)

 reaction quotient, Q: what you get when you plug the R and P amts. ***at any given time***

 into the eq.-constant expression

 If Q > K...

 If Q < K...

 If Q = K...

EX. For H2(g) + I2(g) 2 HI(g), Kc = 51 at a temp. of 488oC. If you start

 with 0.020 mol HI, 0.010 mol H2, and 0.030 mol I2 in a 2.0-L container, which way

 will the reaction proceed?

EX. For PCl5(g) PCl3(g) + Cl2(g), Kp = 0.497 at 500 K. At equilibrium, the

 partial pressures of PCl5 and PCl3 are 0.860 atm and 0.350 atm, respectively. Find

 the partial pressure of Cl2.

EX., cont. For the reaction in the previous problem, if a gas cylinder at 500 K is charged

 with PCl5 at 1.66 atm, find the partial pressures of all three substances at

 equilibrium.

 PCl5(g) PCl3(g) + Cl2(g)

 Initial **1.66 atm 0 atm 0 atm**

 

 at eq.

Le Chatelier’s Principle: “If a system at equilibrium is disturbed by a change in temperature,

 pressure, or concentration of a component, the system will shift its

 equilibrium position to counteract the effect of the disturbance.”

 (A) *change in concentration*

 N2(g) + 3 H2(g) 2 NH3(g)

 H2

 Diagram shows what happens

 NH3

 when we add H2 to an equilibrium

 system...

 N2

 Suppose we remove NH3...

 (B) *change in pressure – for gaseous equilibrium systems only*

 2 NO2(g) N2O4(g)

 If we increase pressure, the system “wants” to...

 If we decrease pressure, the system “wants” to...

 For H2(g) + I2(g) 2 HI(g), pressure changes result in...

 More specifically, if the partial pressures are affected, then there will be shifting.

 Otherwise...no.

 e.g., 2 SO2(g) + O2(g) 2 SO3(g)

 If we add neon into reaction vessel...

 As long as temperature doesn’t change, K is...

 (C) *changes in temperature*

 These always result in...

 For exothermic reactions: R P (H is \_\_\_\_)

 -- as T increases...

 -- as T decreases...

 For endothermic reactions: R P (H is \_\_\_\_)

 -- as T increases...

 -- as T decreases...

EX. For PCl5(g) PCl3(g) + Cl2(g), Ho = 87.9 kJ. Predict shifts for...

 (a) adding Cl2

 (b) increasing temperature

 (c) decreasing volume

 (d) adding PCl5

EX. Using standard molar enthalpies, predict the eq. shifts and changes in K with

 changes in temperature for 2 POCl3(g) 2 PCl3(g) + O2(g)

 Hfo (kJ/mol) –542.2 –288.1 0

**Effect of a Catalyst**

 -- the forward and reverse reaction rates are both increased

 --

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***Acids and Bases: Introductory Concepts***

 Arrhenius ...acids increase the \_\_\_\_\_\_ when dissolved in H2O.

 ...bases increase the \_\_\_\_\_\_when dissolved in H2O.

 e.g., HCl and NaOH

 --

 Bronsted-Lowry acids:

 Bronsted-Lowry bases:

 -- H+ and H3O+ are used interchangeably

 -- B-L concept is NOT limited to aqueous solutions

Arrhenius and Bronsted-Lowry definitions overlap, in many cases.

NH3(aq) + H2O(l) NH4+(aq) + OH–(aq)

 One substance can’t be a Bronsted-Lowry acid unless...

 -- the acid must be able to lose H+

 -- the base must have a nonbonding pair of e– that can bind with the H+

Amphoteric substances can be acids or bases, depending on the reaction conditions.

 HCl(aq) + H2O(l)

 NH3(aq) + H2O(l)

 -- In acid-base equilibria, protons are donated in forward and reverse reactions.

 -- The two substances in a conjugate acid-base pair differ by a H+...

EX. HNO2(aq) + H2O(l) NO2–(aq) + H3O+(aq)

 -- Strong acids / bases easily / \_\_\_\_\_\_\_\_\_\_\_ H+.

 -- Weak acids / bases do NOT easily / \_\_\_\_\_\_\_\_\_\_\_ H+.

 --

 In every acid-base reaction, the position of equilibrium favors the

 transfer of protons from the stronger acid to the stronger base.

**The Autoionization of Water**

In water, we constantly have (a little)... H2O(l) + H2O(l) H3O+(aq) + OH–(aq)

Thus (@ 25oC), the eq. const. for water is:

 This equation is taken to be valid for pure water and for dilute aqueous solutions, @ 25oC.

 [ H+ ] > [ OH– ] [ H+ ] < [ OH– ] [ H+ ] = [ OH– ]

 \_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_

EX. At 25oC, calculate the hydrogen ion concentration if the hydroxide ion concentration

is 2.7 x 10–4 M. Is this solution an acid or a base?

**The pH Scale**

 Definition of pH... **0 ACID 7 BASE 14**

 --

A change of 1 pH unit means that [H+] (and [OH–]) has changed by a factor of \_\_\_\_\_.

EX. A solution with pH 2 is how many times more acidic than one with pH 5?

Especially in biochemical reactions, the rate law is often dependent on the hydrogen ion concentration. If the rate is 1st order in [H+], then doubling [H+] would double the rate.

 -- Human blood pH is between 7.35 and 7.45.

\*\* Significant figures rule for logarithms:

EX. Find the pH if the hydronium ion concentration is 5.2 x 10–9 M.

EX. Find the pH if the hydroxide ion concentration is 3.9 x 10–10 M.

 Other equations:

EX. Find [H+] if the pH = 5.22.

**Measuring pH**

 pH meter

 acid-base indicators:

 e.g.,

 pH paper is paper impregnated with mixtures of various indicators.

**Strong Acids and Bases**

 -- these are strong electrolytes that exist entirely as ions in aqueous solution

 -- memorize the names and formulas of the seven strong acids...

 ...and the eight strong, hydroxide bases...

Strong electrolytes are often written using a one-sided arrow.

 e.g., HNO3(aq) H+(aq) + NO3–(aq)

EX. Find the pH of a 0.012 M perchloric acid solution.

EX. If a nitric acid solution has pH = 2.66, find the solution’s concentration.

\*\* NOTE: Ca(OH)2, Sr(OH)2, and Ba(OH)2 are strong electrolytes, but have limited solubilities. This means that if you put a big chunk of any of these into water, little of the chunk will dissolve, BUT the little that does dissolve will float around as X2+(aq) and

 OH–(aq), NOT as X(OH)2(aq).

EX. Find the pH of a 0.0034 M solution of calcium hydroxide.

Metal oxides, hydrides, and nitrides (containing O2–, H–, and N3–, respectively) also react with water to produce strongly basic solutions.

 e.g., --

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