

EQUILIBRIUM

Chapter 13

Homework

- Read Chapter 13 look at the problems
- Do the AP practice test on page AP-13 A-D
- (it is in between numbered pages 547-548)

AP Test

- Historically, the first question on the free response has ALWAYS been an equilibrium question.
- The new style of test no longer requires that, however, I would be surprised if they didn't have one on the test.

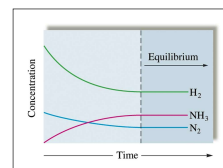
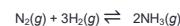
Equilibrium

- A state when two competing reactions are canceling each other out.
- $\text{H}_3\text{O}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{H}_2\text{O}$
- You reach equilibrium when the **rate of forward reaction** is equal to the **rate of backwards reaction**.
- This does NOT mean the concentration of products and reactants are equal.
- The above reaction is at equilibrium when $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mol/L}$. In 1 L of water there are 55 moles.

Macro Micro

- Macroscopically, anything that is in equilibrium is stable. Meaning the concentrations of the different substances are not changing.
- Law of mass action- when the ratio of product to reactant is a constant value the system is at equilibrium
- Microscopically, atoms and molecules are constantly reacting in both reactions

Changes in Concentration



Equilibrium expression and constant

- K is calculated from EQUILIBRIUM CONCENTRATIONS! Its values may only be calculated experimentally.
- $aA + bB \rightleftharpoons cC + dD$
- equilibrium constant = equilibrium expression
- $$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
- [] means concentration in M

Determine the equilibrium expression

- For the following:
- $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$
- $\text{HCN}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CN}^-(\text{aq})$

K values, K is always positive

- Intermediate K . $0.00001 < K < 10000$
- Significant concentrations of all substances are present.
- Very Large K . $K \gg 1$
- The product concentration is very large with virtually no reactant concentration (the reaction has gone to completion).
- Very Small K . $K \ll 1$
- The reactant concentration is very large with virtually no product concentration.

Types of K

- K_c = equilibrium constant in terms of concentration. This is implied if K is written
- K_p = equilibrium concentration in terms of pressure.
- K_a = acid dissociation constant
- K_b = base dissociation constant
- K_w = ion-product constant for water
- These are listed on your equation sheet

Actual equation sheet

EQUILIBRIUM

$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$, where $aA + bB \rightleftharpoons cC + dD$

$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$

$K_a = \frac{[H^+][A^-]}{[HA]}$

$K_b = \frac{[OH^-][HB^+]}{[B]}$

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

$= K_a \times K_b$

$pH = -\log[H^+]$, $pOH = -\log[OH^-]$

$14 = pH + pOH$

$pH = pK_a + \log \frac{[A^-]}{[HA]}$

$pK = -\log K$, $pK_c = -\log K_c$

Equilibrium Constants

- K_c (molar concentrations)
- K_p (gas pressures)
- K_a (weak acid)
- K_b (weak base)
- K_w (water)

K problem

- The following equilibrium concentrations were observed for the Haber process at 127°C.
- $[NH_3] = 3.1 \times 10^{-2}$ M, $[N_2] = 8.5 \times 10^{-1}$ M, $[H_2] = 3.1 \times 10^{-3}$ M
- Forward Reaction.
- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- Reverse Reaction.
- $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
- Multiply by Factor n.
- $1/2N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g)$
- K is unitless

Summary

- For forward reaction $jA + kB \rightleftharpoons lC + mD$,
 $K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$
- For reverse reaction $jA + kB \rightleftharpoons lC + mD$,
 $K' = K^{-1} = \frac{[A]^j [B]^k}{[C]^l [D]^m}$
- For reaction $njA + nkB \rightleftharpoons nlC + nmD$
 $K'' = K^n = \frac{[C]^{nl} [D]^{nm}}{[A]^{nj} [B]^{nk}}$
- For an overall reaction of two or more steps,
 $K_{overall} = K_1 \times K_2 \times K_3 \times \dots$

Equilibrium of Gases.

- $PV = nRT$ or $P = (n/V)RT$
- n/V is mol/L, or a concentration.
- Concentration of a gas is $C = P/RT$
- Therefore you can determine the K of a gas from its pressure and temperature

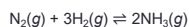
Problem

- $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$
- The reaction for the formation of nitrosyl chloride was studied at 25°C. The pressures at equilibrium were found to be
- $P_{NOCl} = 1.2$ atm
- $P_{NO} = 5.0 \times 10^{-2}$ atm
- $P_{Cl_2} = 3.0 \times 10^{-1}$ atm
- Calculate the value of K for the reaction at 25°C.
- $PV = nRT$ $R = .0821 \text{ atm L / mol K}$

K_p

- Since we are always dividing by the **pressure** value by RT, there has to be a way to cancel that out.
- K_p is a value that looks at the pressure of the gases involved instead the concentrations
- To convert K_p to K
- K may be written K_c , or K with respect to conc.
- $K_p = K_c (RT)^{\Delta n}$
- Where $\Delta n = \Sigma$ coefficients of products
- $\quad \quad \quad - \Sigma$ coefficients of reactants
- **This equation was removed from the equation sheet**

Example of K_p and K_c



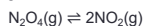
$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} \quad K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Same Problem

- $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$
- The reaction for the formation of nitrosyl chloride was studied at 25°C. The pressures at equilibrium were found to be
- $P_{NOCl} = 1.2$ atm
- $P_{NO} = 5.0 \times 10^{-2}$ atm
- $P_{Cl_2} = 3.0 \times 10^{-1}$ atm
- Calculate the value of K_p for the reaction at 25°C, and then convert that K_p to K.

Pressure Problem

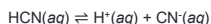
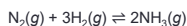
- Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions. In the gas phase it decomposes to gaseous nitrogen dioxide:



- Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of $\text{NO}_2(\text{g})$.

Homogeneous Equilibria

- Homogeneous equilibria – involve the same phase:



Heterogeneous Equilibria

- Heterogeneous equilibria – involve more than one phase:



- The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.
- The concentrations of pure liquids and solids are constant.



$$K = [\text{O}_2]^3$$

Write the equilibrium expressions, K, for the following:

- The decomposition of solid phosphorus pentachloride to liquid phosphorus trichloride and chlorine gas.
- Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form solid green copper(II) sulfate.
- Small amounts of solid lead (II) iodide dissolve into ions.

Reaction Quotient, Q

- Q is obtained by applying the law of mass action to **INITIAL CONCENTRATIONS!**
- Q is useful in determining which direction a reaction must shift to establish equilibrium.
- Q uses the exact same equation as K!!!!
- K is calculated from *equilibrium* concentrations or pressures.
- Q is calculated from concentrations or pressures we have right now (most likely not equilibrium).

Reaction Quotient, Q, numerical value

- $K = Q$; The system is at equilibrium. No shift will occur.
- $K < Q$; The system shifts to the left.
 - Consuming products and forming reactants, until equilibrium is achieved.
- $K > Q$; The system shifts to the right.
 - Consuming reactants and forming products, to attain equilibrium.
 - Write K then Q, the greater/less than sign points the way the reaction proceeds to reach equilibrium!

Shift

- Shift Right
 - $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
 - Shift -2y | +y +y
- Shift Left
 - $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
 - Shift +2y | -y -y

K vs Q Problem

- For the synthesis of ammonia at 500° C, the equilibrium constant is 6.0×10^{-2} . Predict the direction in which the system will shift to reach equilibrium in each of the following cases:
 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - Conc. (M) $[\text{NH}_3]_0$ $[\text{N}_2]_0$ $[\text{H}_2]_0$
 - Trial 1 1.0×10^{-3} 1.0×10^{-5} 2.0×10^{-3}
 - Trial 2 2.0×10^{-3} 1.5×10^{-3} 3.54×10^{-1}
 - Trial 3 2.0×10^{-6} 5.0×10^{-1} 1.0×10^{-3}