American Chemical Society

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USNCO Coaching Session National Exam Preparation Tutorial Notes: Equilibrium

Latha Nair

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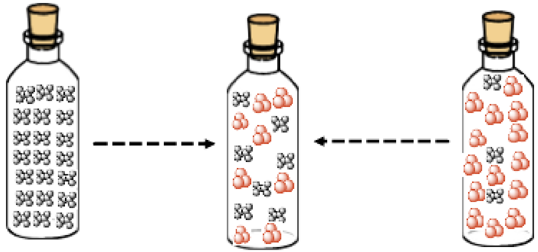
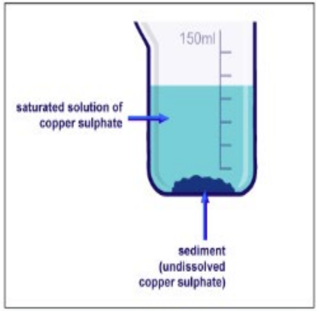
Equilibrium



$$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

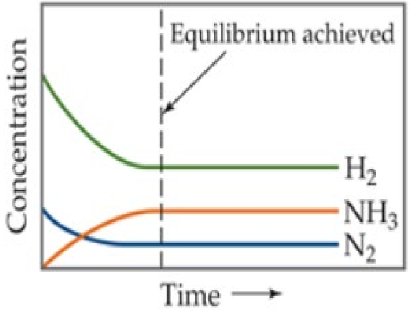
Chemical

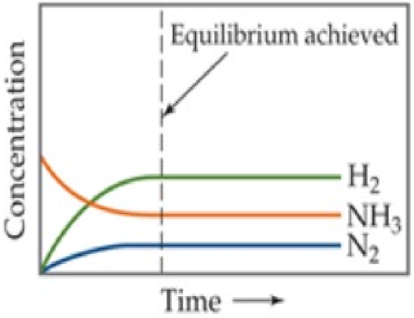


Physical

Equilibrium: Haber Process

$$N_{2\,(g)} + 3H_{2\,(g)} \longleftrightarrow 2NH_{3\,(g)}$$



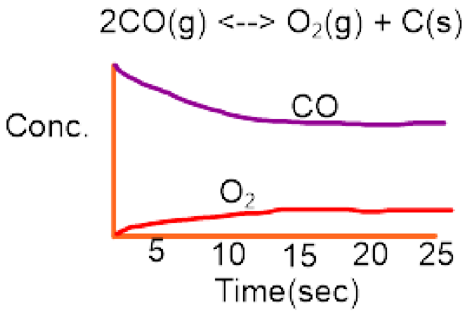


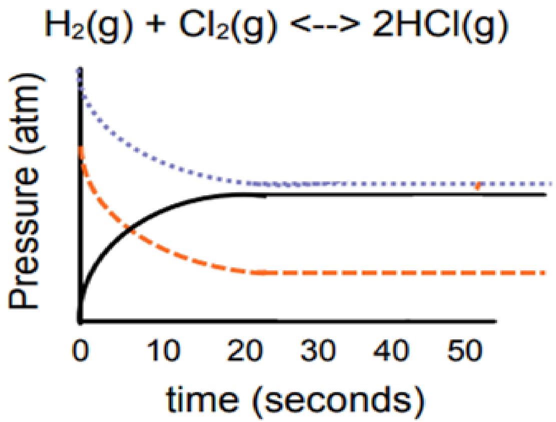
- Equilibrium can be achieved regardless we start with reactants or products as long as there is sufficient material for both the process going

Chemical Equilibrium

Equilibrium @ 15 sec
22 sec

Equilibrium @





Equilibrium constant and Expressions

$$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

Rate of forward reaction = Rate of reverse reaction

$k_f\,[N_2O_4] = k_r\,[NO_2]^2$; Re writing this,

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

For a general Reaction,

$$aA + bB \rightleftharpoons cC + dD$$

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

Equilibrium constant and Expressions

Pure solids and liquids are not included in equilibrium expressions

The equilibrium constant for the reaction

$(CH_3)_4Sn_{(s)} \rightleftharpoons (CH_3)_4Sn\ (g)$

$$\frac{[(CH_3)_4Sn_{(g)}]}{1}$$

Kp vs Kc

- Equilibrium constant in terms of pressure is Kp

$$aA + bB \rightleftharpoons cC + dD$$

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

Kp vs Kc

$$CH_4(g) + 2O_2(g) \leftrightarrow CO_2(g) + 2H_2O(g)$$

$$Kp = \frac{(P_{CO2})(P_{H2O})^2}{(P_{CH4})(P_{O2})^2} \qquad Kc = \frac{[CO_2][H_2O]^2}{[CH_4][O_2]^2}$$

Kp vs Kc

We can derive the relationship between Kp and Kc using ideal gas law. (PV=nRT; P=nRT/V. n/V =M)

$$K_p = K_c\,(RT)^{\Delta mol}$$

Gaseous Equilibria

Example:

Calculate Kc for the reaction below @ 10 C:

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g) \quad Kp = 0.045$$

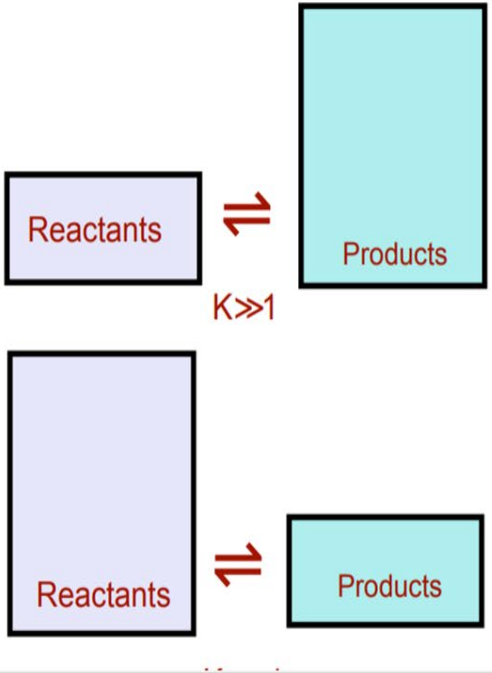
$$Kc = Kp / (RT)^{\Delta mol}$$

$$Kc = 0.045 / (23.2)^{-2}$$

$$Kc = 24.2$$

Note: If the change in moles is zero = Kp = Kc. This will occur when there are equal numbers of gaseous moles of product and reactant.

What Does the Value of *K* Mean?



If *K*>>1, the reaction is *product-favored*; product predominates at equilibrium.

If *K*<<1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

Direction of Reaction

The direction from which equilibrium is achieved (starting with all products or all reactants) doesn't matter.

It is only a convention that we calculate K by dividing the concentrations of products over reactants, since the reaction proceeds both ways.

Unless specified, read the equation left to right (Left -reactants, right -products).

This convention makes it easy to understand the meaning of K_{eq} .

Direction of Reaction

The equilibrium constant for a reaction is specific to how the reaction is written.

If a reaction is reversed, the new K value will be the inverse of the original K value.

$$CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) \quad K_{eq} = 6 \times 10^{-9}$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \quad K_{eq} = 2 \times 10^{8}$$

The Equilibrium Constant

The equilibrium constant for a reaction is specific to how the reaction is written.

If the coefficients of a reaction are changed, the exponents of each substance will change in the expression thereby exponentially changing K.

$$CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$Keq = 6 \times 10^{-9}$$

$$1/2CaCO_3(s) \rightarrow 1/2Ca^{2+}(aq) + 1/2CO_3^{2-}(aq)$$

$$Keq = (6 \times 10^{-9})^{1/2}$$

$$Keq = 8 \times 10^{-5}$$

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The Equilibrium Constant

If reactions are added together, the equilibrium constants are multiplied.

Many reactions occur as a series of steps. Consider the production of $Ag(NH_3)_2^+$

Step 1: $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ $K_{eq} = 1.8 \times 10^{-10}$

Step 2: $Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$ $K_f = 1.6 \times 10^8$

Overall

$AgCl(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+ + Cl^-(aq)$

$K_{eq} * K_f = K_{overall} = 0.028$

Applications

Coupling a non-favorable reaction with a small K value with one that is highly favorable with a large K value is a common way to drive a process towards product.

For example, $Co(OH)_3(s)$ is rather insoluble…

$Co(OH)_3$ --> $Co^{3+}(aq)$ + $3OH^{-}(aq)$ Ksp = 1.6×10^{-44}

But can be made more soluble by coupling it with a reaction that forms the complex $Co(NH_3)_6^{3+}(aq)$

Coupled Reaction

$Co(OH)_3$ + $6NH_3(aq)$ --> $Co(NH_3)_6^{3+}$ + $3OH^{-}$

$K_{overall} = 7.2 \times 10^{-13}$

Calculating K When Initial Reactant Concentrations are Known

Given the following reaction, what are the concentrations of all materials at equilibrium given a $[HCl]_{initial}$=0.5 M and $[HCl]_{eq}$=0.2 M? Given that HCl's coefficient is 2, then we know that 2x = 0.5 - 0.2 which equals 0.3. Since 2x = 0.3, x = 0.15, which is the amount gained for both H_2 and Cl_2.

	2HCl(g) -->	H_2(g) +	Cl_2(g)
Initial (I)	0.5	-	-
Change (C)	-0.3	+0.15	+0.15
Equilibrium (E)	0.2	0.15	0.15

K can then be calculated from the equilibrium concentrations.

Ice Tables

The equilibrium constant can be used to determine the concentrations of substances at equilibrium

Given that there are initially 0.2 atm of HCl, what would be the pressure of all gases at equilibrium given the reaction below:

$$2HCl(g) \longrightarrow H_2(g) + Cl_2(g) \quad K_p = 0.67$$

Initial (I)	0.2	-	-
Change(C)	-2x	+x	+x
Equilibrium(E)	0.2-2x	x	x

$$K_p = 0.67 = x^2 / (0.2-2x)^2$$

Take square root of both sides = 0.82 = x / 0.2 - 2x

Solve for x = 0.062 atm.

$$P_{HCl} = 0.12 \text{ atm} \quad P_{H2} = P_{Cl2} = 0.062 \text{ atm}$$

Tips for equilibrium problems.

There are three steps to solving a typical equilibrium problem.

- Step One: Write a balanced reaction, including states.
- Step Two: Write a proper ice table, being mindful of stoichiometrical coefficients.
- Step Three: Write a proper expression and solve for what is required.

Example: What would be the value of Kp for the reaction below where the initial pressure of methane and oxygen were 0.4 atm and the equilibrium pressure of carbon dioxide is 0.1 atm?

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

	$CH_4(g)$	$O_2(g)$	$CO_2(g)$	$H_2O(g)$
Initial (I)	0.4	0.4	-	-
Change (C)	-x	-2x	+x	+2x
Equil (E)	0.4-x	0.4-2x	x	2x

Since we are told that the equilibrium pressure of CO_2 is 0.1 atm which equals x, we can solve for the other values at equilibrium. The final pressures will be 0.3, 0.2, 0.1, and 0.2 respectively. Therefore, $Kp = (0.1)(0.2)^2/(0.3)(0.2)^2$ which equals 0.33.

Q and K

The reaction quotient, "Q", is the ratio of products to reactants at any stage in a reaction.

$$Q = \frac{[Products]^x}{[Reactants]^y}$$

The value of Q and its relation to K provides information as to which way a reaction will shift to reach equilibrium.

Q > K	Too many products	Reaction shifts left to reach equilibrium
Q < K	Too many reactants	Reaction shifts right to reach equilibrium
Q = K	At Equilibrium	No shift

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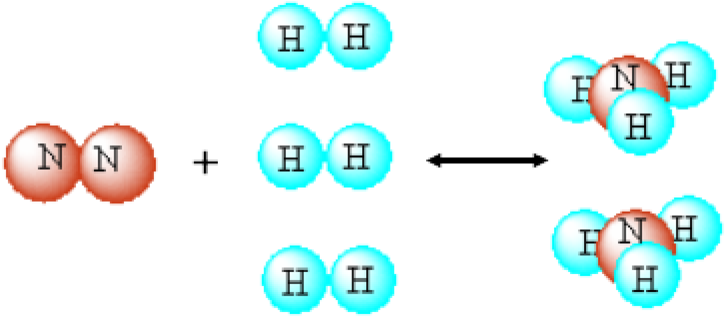
Le Châtelier's Principle

"If a system at equilibrium is disturbed by a change in temperature, change in pressure, or change in concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

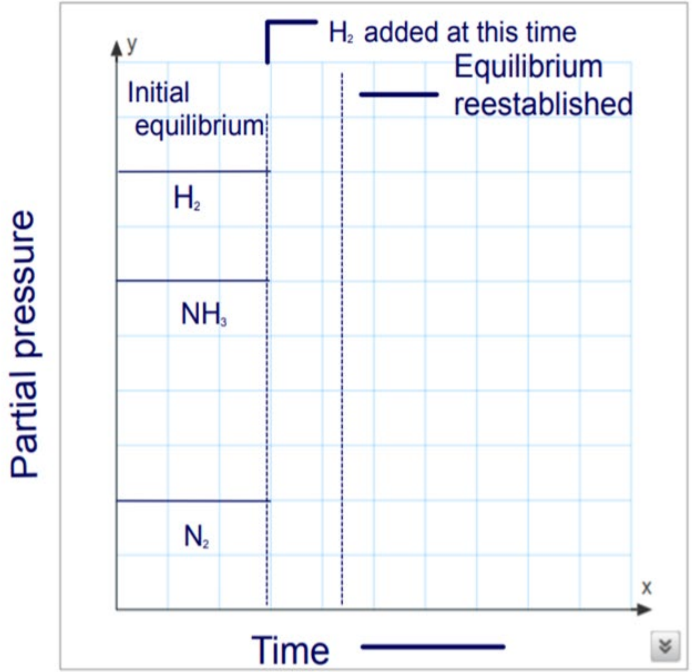
Henri Louis Le Châtelier

Le Châtelier's Principle

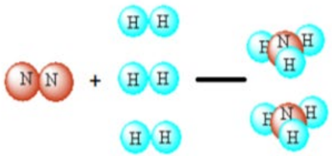


The Haber Process: Synthesis of ammonia from hydrogen and nitrogen

Le Châtelier's Principle



If we change the concentration:



Le Châtelier's Principle

If we change volume/pressure:

$$N_2 + 3H_2 \longleftrightarrow 2NH_3$$

If the volume is **increased**, it will reduce the pressure of the system, so the system will try to increase the pressure by producing more molecules.

The reaction will favor producing more molecules. The equilibrium will shift to the side with more moles - in this case - the left.

Le Châtelier's Principle

The Haber Process - Summary of pressure changes

$$N_{2\,(g)} + 3H_{2\,(g)} \longleftrightarrow 2NH_{3\,(g)}$$

Stress: Increasing pressure/ reducing volume
Effect: Equilibrium shifts to the right

Stress: Decreasing pressure/ increasing volume
Effect: Equilibrium shifts to the left

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Le Châtelier's Principle

If we change the Temperature:

If the temperature of the system is increased:

$PCl_5 \longleftrightarrow PCl_3 + Cl_2$ $\Delta H = 88$ KJ endothermic

Since the reaction is endothermic...view energy as a reactant

Energy + $PCl_5 \longleftrightarrow PCl_3 + Cl_2$

The system should accept (take in) the thermal energy supplied to favor the endothermic reaction, and the equilibrium will shift to the right (forward reaction).

Le Châtelier's Principle

If we change the Temperature:

If the temperature of the system is lowered:

The system will restore equilibrium by producing energy hence resulting in a shift of the reaction back to the left.

Note: The only change that will affect the magnitude of the equilibrium constant is a change in the temperature!!

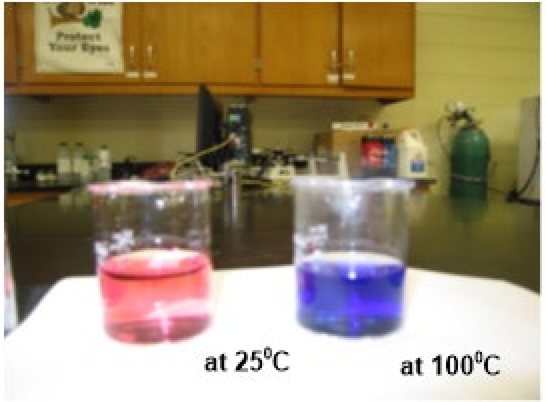
Le Châtelier’s Principle: Change of temperarture

Many ions containing transition metals produce colored solutions.

In the reaction below the cation, CoM(H2O)62+, yields a pink solution, while the anion CoCl42- produces a blue solution.

$$Co(H_2O)_6^{2+}(aq) + 4\,Cl(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6\,H2O\,(l) \quad \Delta H = (+)$$

Pink — blue



Acid Dissociation Constants, K_a

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons A^-\ (aq) + H_3O^+\ (aq)$$

For a generalized acid dissociation, the equilibrium expression is

$$K_c = K_a = \frac{[H_3O^+]\ [A^-]}{[HA]}$$

This equilibrium constant is called the acid-dissociation constant, Ka.

$$K_a = \frac{[H_3O^+]\ [A^-]}{[HA]}$$

Calculating K_a from the pH

The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

From this dissociation equation, write the K_a expression:

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

To calculate K_a, we need the equilibrium concentrations of all three species.

We know the concentration of HCOOH.
How do we determine the concentration of H_3O^+?

Calculating K_a from the pH

The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25°C is 2.38. Calculate K_a for formic acid at this temperature.

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

	[HCOOH], *M*	[HCOO⁻], *M*	$[H_3O^+]$, *M*
Initially	0.10	0	0
Change	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
At Equilibrium	$0.10 - 4.2 \times 10^{-3} \approx 0.10$	4.2×10^{-3}	4.2×10^{-3}

Calculating K_b from *pH*

What is the K_b of a 0.20 M solution of hydrazine H_2NNH_2 at 25°C that has a pH of 10.9?

First, we write the dissociation equation for hydrazine

$$H_2NNH_2(aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + H_2NNH_3^+(aq)$$

From the dissociation equation, we obtain the equilibrium constant expression:

$$K_b = \frac{[OH^-][H_2NNH_3^+]}{[H_2NNH_2]}$$

Calculating K_b from the pH

$$pOH = 14 - pH$$
$$pOH = 14 - 10.9$$
$$pOH = 3.1$$

$$3.1 = -\log [OH^-]$$

$$-3.1 = \log [OH^-]$$

$$10^{-3.1} = 10^{\log [OH^-]} = [OH^-]$$

$$7.94 \times 10^{-4} = [OH^-] = [H_2NNH_3^+]$$

Sample Questions

Equilibrium is 31-36 for all exams.

Samples : National 2019 #31 & 32

31. The molar solubility of PbF_2 is 2.1×10^{-3} mol L^{-1}. What is its K_{sp}?

(A) 4.4×10^{-6} **(B)** 8.8×10^{-6}

(C) 3.7×10^{-8} **(D)** 9.3×10^{-9}

32. What is the pH of a 0.10 M solution of ammonium acetate, $NH_4(CH_3COO)$? The K_a of NH_4^+ is 5.6×10^{-10} and the K_a of CH_3COOH is 1.8×10^{-5}.

(A) 2.87 **(B)** 5.13 **(C)** 7.00 **(D)** 8.87