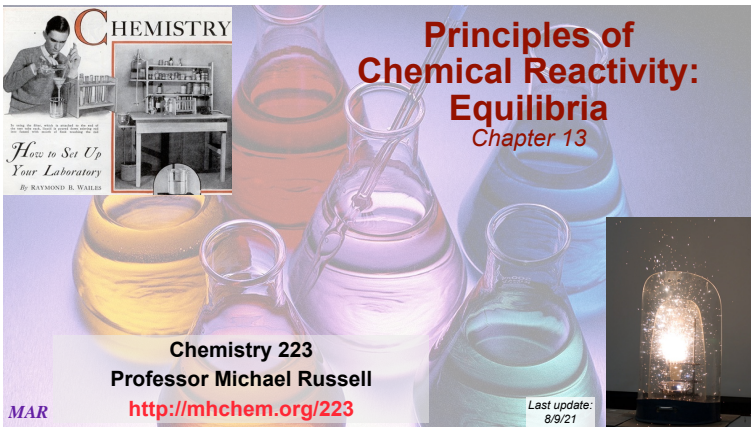

Principles of Chemical Reactivity: Equilibria

Chapter 13

Chemistry 223
Professor Michael Russell
http://mhchem.org/223

Last update: 8/9/21

MAR

CHEMICAL EQUILIBRIUM

⇌ = Bi-directional arrow

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Properties of an Equilibrium

Equilibrium systems are

- **DYNAMIC (in constant motion)**
- **REVERSIBLE**
- **can be approached from either direction**

Pink to blue

$Co(H_2O)_6Cl_2 + 2\ Cl^{-1} \text{ ---> } Co(H_2O)_2Cl_4^{2-} + 4\ H_2O$

Blue to pink

$Co(H_2O)_2Cl_4^{2-} + 4\ H_2O \text{ ---> } Co(H_2O)_6Cl_2 + 2\ Cl^{-1}$

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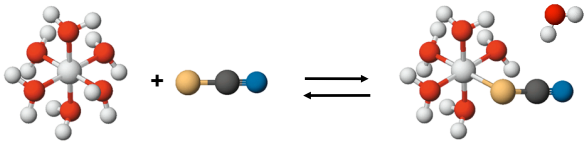
Chemical Equilibrium

$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$



$Fe(H_2O)_6^{3+} + SCN^- \rightleftharpoons Fe(SCN)(H_2O)_5^{2+} + H_2O$

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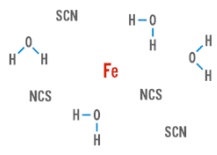
Chemical Equilibrium

$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$



After a period of time, the concentrations of reactants and products are constant.

The forward and reverse reactions continue after equilibrium is attained.

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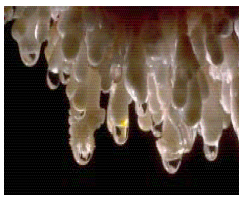
Phase changes:

$H_2O(s) \rightleftharpoons H_2O(liq)$

Examples of Chemical Equilibria



Formation of stalactites and stalagmites:

$CaCO_3(s) + H_2O(liq) + CO_2(g) \rightleftharpoons$

$Ca^{2+}(aq) + 2\ HCO_3^-(aq)$

The Equilibrium Constant

For any type of chemical equilibrium of the type

a A + b B ⇌ c C + d D

the following is a CONSTANT (at a *given T*)

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

conc. of products

conc. of reactants

equilibrium constant

If K is known, we can predict concentrations of products or reactants.

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The Equilibrium Constant: Example

Equilibrium constants, K, come from *kinetic rate constants, k*

Example: **For 2 $NO_{2(g)}$ ⇌ $N_2O_{4(g)}$,**

$rate_f = k_f[NO_2]^2$

$rate_r = k_r[N_2O_4]$

When rates equal, $rate_f = rate_r$, and

$k_f[NO_2]^2 = k_r[N_2O_4]$

$[N_2O_4]/[NO_2]^2 = k_f/k_r = K$ ***(equilibrium)***

Product of two constants (k_f & k_r) is itself a constant (K)!

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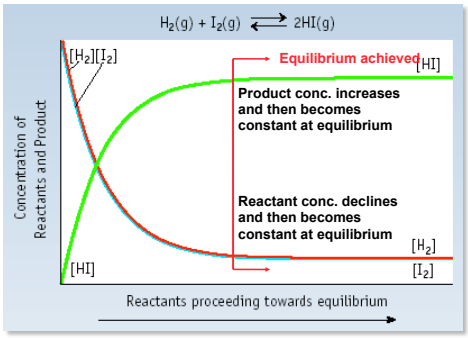
The Equilibrium Constant: Example



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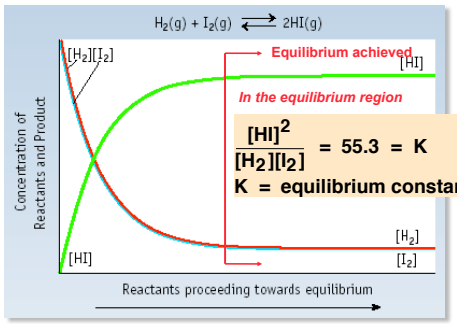
The Equilibrium Constant: Example



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Determining K

2 NOCl(g) ⇌ 2 NO(g) + Cl_2(g)

Place 2.00 mol of NOCl is a 1.00 L flask. At equilibrium you find 0.66 mol/L of NO. Calculate K.

Solution

Set of a table of concentrations (ICE)

	[NOCl]	[NO]	[Cl_2]
Initial	2.00	0	0
Change			
Equilibrium		0.66	

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Determining K

2 NOCl(g) ⇌ 2 NO(g) + Cl_2(g)

Place 2.00 mol of NOCl is a 1.00 L flask. At equilibrium you find 0.66 mol/L of NO. Calculate K.

Solution

Set of a table of concentrations (ICE)

	[NOCl]	[NO]	[Cl_2]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

How to remember ICE:

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Determining K

2 NOCl(g) ⇌ 2 NO(g) + Cl_2(g)

	[NOCl]	[NO]	[Cl_2]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080$$

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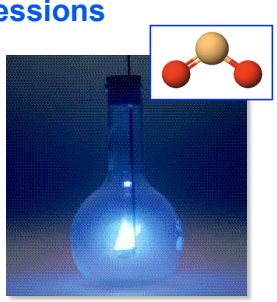
Writing and Manipulating K Expressions

Solids and liquids *NEVER* appear in equilibrium expressions.

S(s) + O_2(g) ⇌ SO_2(g)



$$K = \frac{[SO_2]}{[O_2]}$$

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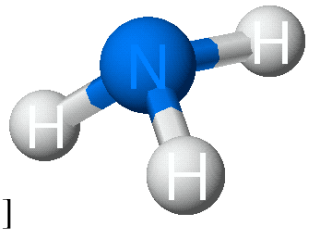
Writing and Manipulating K Expressions

Solids and liquids *NEVER* appear in equilibrium expressions.

NH_3(aq) + H_2O(liq) ⇌ NH_4^+(aq) + OH^-(aq)



$$K = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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Writing and Manipulating K Expressions

Adding equations for reactions

S(s) + O_2(g) ⇌ SO_2(g) $K_1 = [SO_2] / [O_2]$

SO_2(g) + 1/2 O_2(g) ⇌ SO_3(g)

$K_2 = [SO_3] / [SO_2][O_2]^{1/2}$

NET EQUATION

S(s) + 3/2 O_2(g) ⇌ SO_3(g)

$$K_{net} = \frac{[SO_3]}{[O_2]^{3/2}} = K_1 \bullet K_2$$

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Writing and Manipulating K Expressions

Changing coefficients

S(s) + 3/2 O_2(g) ⇌ SO_3(g) $\quad K_{old} = \frac{[SO_3]}{[O_2]^{3/2}}$

2 S(s) + 3 O_2(g) ⇌ 2 SO_3(g)

$$K_{new} = \frac{[SO_3]^2}{[O_2]^3}$$

$$K_{new} = \frac{[SO_3]^2}{[O_2]^3} = (K_{old})^2$$

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Writing and Manipulating K Expressions

Changing direction

S(s) + O_2(g) ⇌ SO_2(g) $\quad K = \frac{[SO_2]}{[O_2]}$

SO_2(g) ⇌ S(s) + O_2(g) $\quad K_{new} = \frac{[O_2]}{[SO_2]}$

and: $K_{new} = \frac{[O_2]}{[SO_2]} = \frac{1}{K_{old}}$

See Manipulating Equilibrium Constant Expressions

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Kp Expressions

We have been writing K in terms of M (mol/L), designated by K_c

Equilibrium constants expressed in terms of gases designated K_p where all pressures in atm *(760 mm Hg = 1 atm)*

For: **$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$**

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad K_p = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}$$

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Converting K_c Into K_p

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

T = Temperature (K)

R = 0.082057 L atm mol^{-1} K^{-1}

Δn = change in moles of gas

Example:

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

$\Delta n = 2 - 4 = -2$

see: Types of Equilibrium Constants

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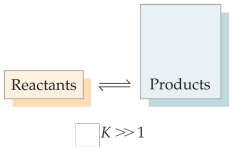
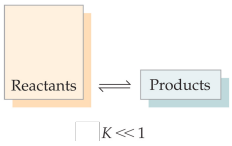
The Meaning of K



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



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

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The Meaning of K

Can tell if a reaction is product-favored or reactant-favored.

For: $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 3.5 \times 10^8$$

Conc. of products is much greater than that of reactants at equilibrium.

The reaction is strongly product-favored.

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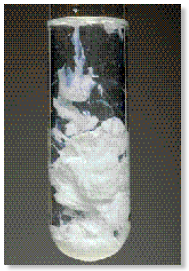
The Meaning of K

For: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_c = [Ag^+]\,[Cl^-] = 1.8 \times 10^{-5}$

Conc. of products is much less than that of reactants at equilibrium.

The reaction is strongly reactant-favored.



The reverse reaction

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

*is **product-favored,***

K_{rev} = *1/1.8 x 10^{-5}* = 5.6 x 10^4

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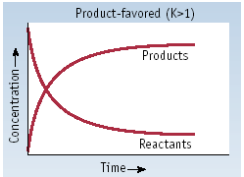
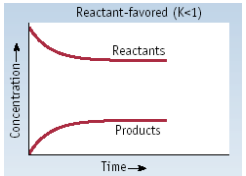
Product- or Reactant Favored



Product-favored
K > 1



Reactant-favored
K < 1

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The Reaction Quotient, Q

All reacting chemical systems can be characterized by their REACTION QUOTIENT, Q.

For: **a A + b B ⇌ c C + d D**

Under Any Reaction Conditions

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

(Product concentrations / Reactant concentrations)

If Q = K, then system is at equilibrium.

If Q ≠ K, then system is not at equilibrium

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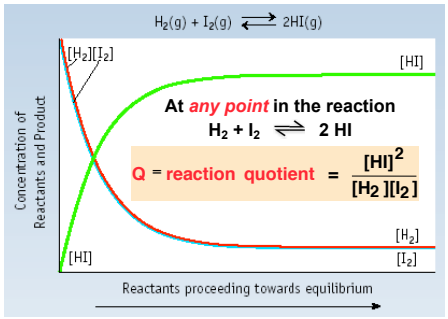
The Reaction Quotient, Q



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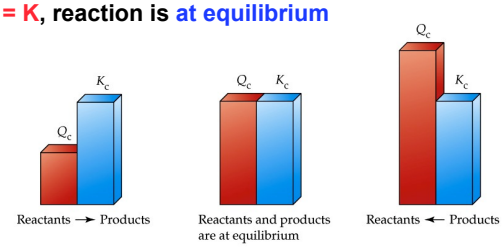
The Reaction Quotient, Q

Comparing Q and K:

Q < K, reaction shifts to the products (right)

Q > K, reaction shifts to the reactants (left)

Q = K, reaction is at equilibrium



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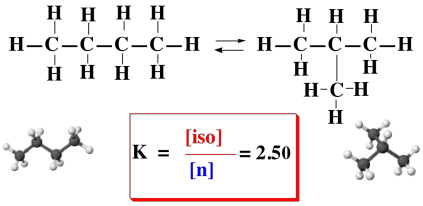
The Reaction Quotient, Q

We can use Q to tell if a reaction is at equilibrium. If not at equilibrium, we can predict which way the reaction will move to approach equilibrium.

n-butane ⇌ **iso-butane**



$$K = \frac{[iso]}{[n]} = 2.50$$

see Understanding K and Q Handout

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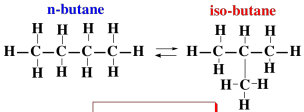
The Reaction Quotient, Q

n-butane ⇌ **iso-butane**



$$K = \frac{[iso]}{[n]} = 2.50$$

If [iso] = 0.35 M and [n] = 0.15 M, are you at equilibrium?

Which way does the reaction "shift" to approach equilibrium?

$$Q = \frac{\text{conc. of iso}}{\text{conc. of n}} = \frac{0.35}{0.15} = 2.3$$

To [iso]! Q = 2.3, Q < K, reaction will shift to "right" (product side, or [iso])

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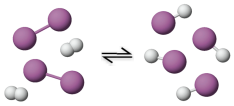
Typical Calculations

$H_2(g)$ + $I_2(g)$ ⇌ 2 HI(g)

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 55.3$$



Place 1.00 mol each of H_2 and I_2 in a 1.00 L flask. Calc. equilibrium concentrations.

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$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 55.3$

Step 1. Set up ICE table to define EQUILIBRIUM concentrations.

	$[H_2]$	$[I_2]$	$[HI]$
Initial			
Change			
Equilib			

where x is defined as am't of H_2 and I_2 consumed on approaching equilibrium.

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$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 55.3$

Step 2. Put equilibrium concentrations into K_c expression.

$$K_c = \frac{[2x]^2}{[1.00\text{-}x][1.00\text{-}x]} = 55.3$$

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$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 55.3$

Step 3. Solve K_c expression - take square root of both sides.

$$7.44 = \frac{2x}{1.00 - x}$$

7.44 (1.00 - x) = 2x

7.44 - 7.44x = 2x

x = 7.44 / 9.44 = 0.788

Therefore, at equilibrium

$[H_2] = [I_2] = 1.00 - x = 0.21$ M

$[HI] = 2x = 1.58$ M

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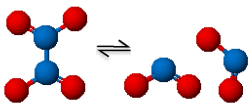
Nitrogen Dioxide Equilibrium

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$



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Nitrogen Dioxide Equilibrium

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.0059 \text{ at } 298 \text{ K}$$

If initial concentration of N_2O_4 is 0.50 M, what are the equilibrium concentrations?

Step 1. Set up an equilibrium table

	$[N_2O_4]$	$[NO_2]$
Initial	0.50	0
Change		
Equilib		

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Nitrogen Dioxide Equilibrium

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.0059 \text{ at } 298 \text{ K}$$

If initial concentration of N_2O_4 is 0.50 M, what are the equilibrium concentrations?

Step 1. Set up an equilibrium table

	$[N_2O_4]$	$[NO_2]$
Initial	0.50	0
Change	-x	+2x
Equilib	0.50 - x	2x

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Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

Step 2. Substitute into K_c expression and solve.

$$K_c = 0.0059 = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.50 - x)}$$

Rearrange: $0.0059\ (0.50 - x) = 4x^2$

$0.0029 - 0.0059x = 4x^2$

$4x^2 + 0.0059x - 0.0029 = 0$

This is a QUADRATIC EQUATION

$ax^2 + bx + c = 0$

$a = 4 \quad b = 0.0059 \quad c = -0.0029$

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Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

Solve the quadratic equation for x.

$ax^2 + bx + c = 0$

$a = 4 \quad b = 0.0059 \quad c = -0.0029$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.0059 \pm \sqrt{(0.0059)^2 - 4(4)(-0.0029)}}{2(4)}$$

$x = -0.00074 \pm 1/8(0.046)^{1/2} = -0.00074 \pm 0.027$

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Nitrogen Dioxide Equilibrium
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$$x = \frac{-0.0059 \pm \sqrt{(0.0059)^2 - 4(4)(-0.0029)}}{2(4)}$$

$x = -0.00074 \pm 1/8(0.046)^{1/2} = -0.00074 \pm 0.027$

$x = 0.026$ or -0.028

But a *negative* value is not reasonable.

***Conclusion:* x = 0.026**

$[N_2O_4] = 0.50 - x = 0.47\ M$

$[NO_2] = 2x = 0.052\ M$

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Le Chatelier's Principle

Temperature, catalysts, changes in volume, changes in pressure and changes in concentration affect equilibria.

The outcome is governed by LE CHATELIER'S PRINCIPLE

"...if a system at equilibrium is disturbed, the system tends to shift its equilibrium position to counter the effect of the disturbance."

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EQUILIBRIUM AND EXTERNAL EFFECTS

Temperature effects change the numeric value of K

Consider the fizz in a soft drink

$CO_2(g) + H_2O(liq) \rightleftharpoons CO_2(aq) + heat$

Decrease T. *What happens to equilibrium position? To value of K?*

K = $[CO_2]$ / P (CO_2)

K *increases* as T goes down because $[CO_2]$ increases *and* P(CO_2) decreases.

Increase T. *Now what?*

Equilibrium shifts left *and* K *decreases.*

see: Le Chatelier's Guide

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Temperature Effects on Equilibrium

N_2O_4 (colorless) + heat $\rightleftharpoons$ 2 NO_2 (brown)

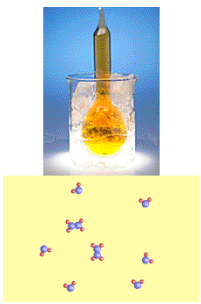
ΔH^o = + 57.2 kJ *(endothermic)*

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

K_c = 0.00077 at 273 K

K_c = 0.0059 at 298 K

K changes with temperature



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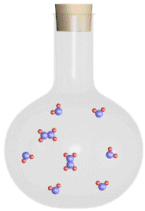
Volume & Pressure Effects on Equilibrium

N_2O_4 (colorless) + heat ⇌ 2 NO_2 (brown)

Volume and Pressure changes affect equilibrium

Larger volume / Less Pressure = more molecules

Smaller volume / Higher Pressure = fewer molecules



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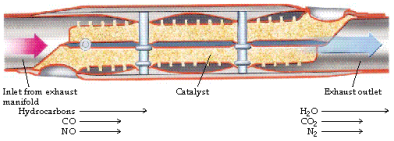
EQUILIBRIUM AND EXTERNAL EFFECTS

Add catalyst ---> no change in K

A catalyst only affects the *RATE* of approach to equilibrium.



Catalytic exhaust system

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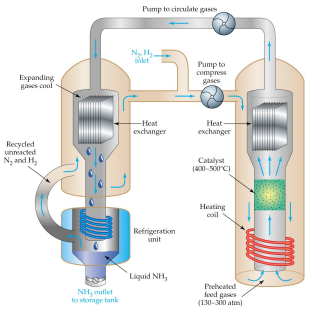

NH_3 Production

Catalyst for the Haber-Frisch reaction is mostly Fe with some KOH

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

K = 3.5×10^8 at 298 K

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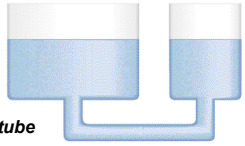
EQUILIBRIUM AND EXTERNAL EFFECTS

Concentration changes ---> no change in K - only the *position* of equilibrium changes.

We can use the "water U-tube" to demonstrate this phenomena (and connect to Haber-Frisch)

Haber-Frisch reaction:

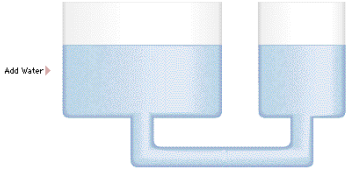
$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$



Water U-tube

MAR

Le Chatelier's Principle



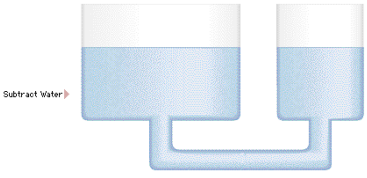
Adding a "reactant" to a chemical system.

Haber-Frisch reaction: adding N_2 or H_2, reaction moves to right

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

MAR

Le Chatelier's Principle



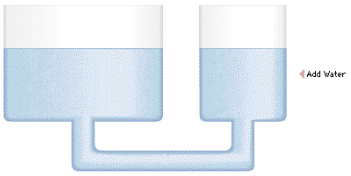
Removing a "reactant" from a chemical system.

Haber-Frisch reaction: removing N_2 or H_2, reaction moves to left

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

MAR

Le Chatelier's Principle



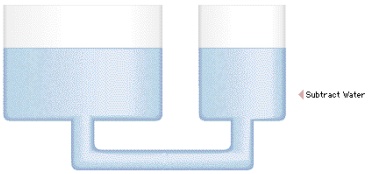
Adding a "product" to a chemical system.

Haber-Frisch reaction: adding NH_3, reaction moves to left

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

MAR

Le Chatelier's Principle

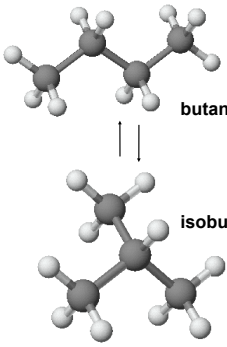


Removing a "product" from a chemical system.

Haber-Frisch reaction: removing NH_3, reaction moves to right

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

MAR



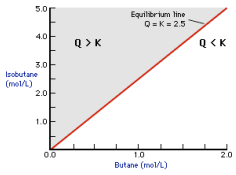
Butane-Isobutane Equilibrium

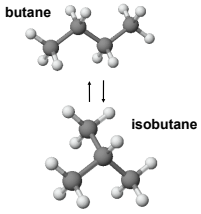
$$K = \frac{[\text{isobutane}]}{[\text{butane}]} = 2.50$$

MAR

Butane ⇌ Isobutane

Assume you are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane. When the system comes to equilibrium again, what are [iso] and [butane]? K = 2.50





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Butane ⇌ Isobutane

Assume you are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane. When the system comes to equilibrium again, what are [iso] and [butane]? K = 2.50

Solution

Calculate Q immediately after adding more butane and compare with K.

$$Q = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25}{0.50 + 1.50} = 0.625$$

Q is *LESS THAN* K. Therefore, the reaction will shift to the _____.

MAR

Butane ⇌ Isobutane

You are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane.

Solution

Q is less than K, so equilibrium shifts right - away from butane and toward isobutane.

Set up concentration (ICE) table

	[butane]	[isobutane]
Initial		
Change		
Equilibrium		

MAR

Butane ⇌ Isobutane

You are at equilibrium with [iso] = 1.25 M and [butane] = 0.50 M. Now add 1.50 M butane.

Solution

$$K = 2.50 = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25 + x}{2.00 - x}$$

x = 1.07 M

At the new equilibrium position,

[butane] = 0.93 M and [isobutane] = 2.32 M

Equilibrium has shifted toward isobutane.

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Le Chatelier's Principle - Overview

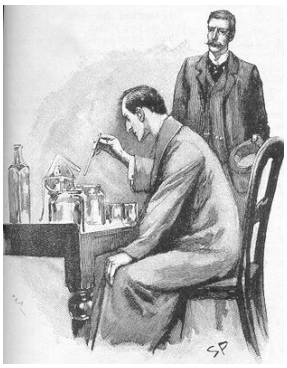
- **Change T**
  - change in K
  - therefore change in P, V or concentrations at equilibrium
- **Use a catalyst:**
  - reaction comes more quickly to equilibrium. K not changed.
- **Add or take away reactant or product:**
  - K does not change
  - Reaction adjusts to new equilibrium "position"

MAR

End of Chapter 13

See:

- *Chapter Thirteen Study Guide*
- *Chapter Thirteen Concept Guide*
- *Types of Equilibrium Constants*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*



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Important Equations, Constants, and Handouts from this Chapter:

for: a A + b B ⇌ c C + d D

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

conc. of products; conc. of reactants; equilibrium constant

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

R = 0.082057 L atm mol^{-1} K^{-1}

Under Any Reaction Conditions

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

(Product concentrations / Reactant concentrations)

Handouts:

- *Manipulating Equilibrium Constant Expressions*
- *Types of Equilibrium Constants*

Le Chatelier's Principle

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End of Chapter Problems: *Test Yourself*

1. Write an equilibrium constant expression for the following reaction: C(s) + CO_2(g) ⇄ 2 CO(g)
2. K = 5.6 x 10^{-12} at 500 K for the dissociation of iodine molecules to iodine atoms: **I_2(g) ⇄ 2 I(g)** A mixture has [I_2] = 0.020 mol/L and [I] = 2.0 x 10^{-8} mol/L. Is the reaction at equilibrium (at 500 K)? If not, which way must the reaction proceed to reach equilibrium?
3. The reaction: PCl_5(g) ⇄ PCl_3(g) + Cl_2(g) was examined at 250 °C. At equilibrium, [PCl_5] = 4.2 x 10^{-5} mol/L, [PCl_3] = 1.3 x 10^{-2} mol/L, and [Cl_2] = 3.9 x 10^{-3} mol/L. Calculate K for the reaction.
4. The equilibrium constant for the dissociation of iodine molecules to iodine atoms: **I_2(g) ⇄ 2 I(g)** is 3.76 x 10^{-3} at 1000 K. Suppose 0.105 mol of I_2 is placed in a 12.3 L flask at 1000 K. What are the concentrations of I_2 and I when the system comes to equilibrium?
5. Dinitrogen trioxide decomposes to NO and NO_2 in an endothermic process (ΔH = 40.5 kJ/mol): **N_2O_3(g) ⇄ NO(g) + NO_2(g)** Predict the effect of the following changes on the position of the equilibrium (left, right, or no change):
   a. adding more N_2O_3(g)
   b. adding more NO_2(g)
   c. increasing the volume of the reaction flask
   d. lowering the temperature

MAR

End of Chapter Problems: *Answers*

1. $K_c = [CO]^2 / [CO_2]$ or $K_p = P_{CO}^2 / P_{CO2}$
2. No, Q < K, reaction will proceed to the right (more products)
3. K = 1.2
4. [I_2] = 0.00614 M, [I] = 0.00480 M
5. a. right b. left c. right d. left

MAR