

CHEMICAL EQUILIBRIUM

Chapter 13

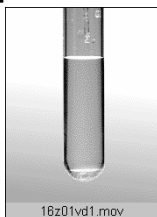
Chemical Equilibrium

- The state where the concentrations of all reactants and products remain constant with time.
- On the molecular level, there is frantic activity. Equilibrium is not static, but is a highly dynamic situation.

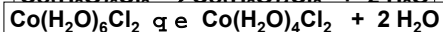
Properties of an Equilibrium

Equilibrium systems are

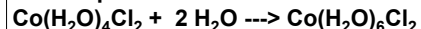
- DYNAMIC (in constant motion)
- REVERSIBLE
- can be approached from either direction



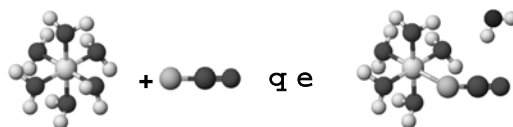
Pink to blue



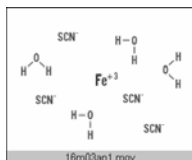
Blue to pink



Chemical Equilibrium

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


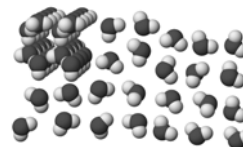
Chemical Equilibrium

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


- After a period of time, the concentrations of reactants and products are constant.
- The forward and reverse reactions continue after equilibrium is attained.

Examples of Chemical Equilibria

Phase changes such as

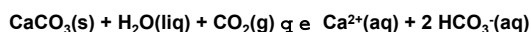
$$\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{liq})$$


Examples of Chemical Equilibria

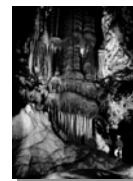


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- Formation of stalactites and stalagmites



Chemical Equilibria



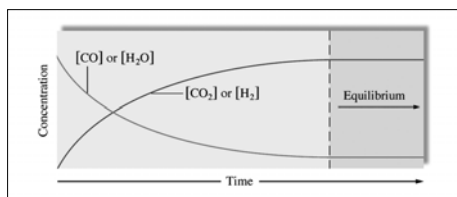
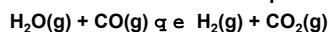
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- $\text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{liq}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{HCO}_3^{-}(\text{aq})$
- At a given T and P of CO_2 , $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^{-}]$ can be found from the **EQUILIBRIUM CONSTANT**.

Example

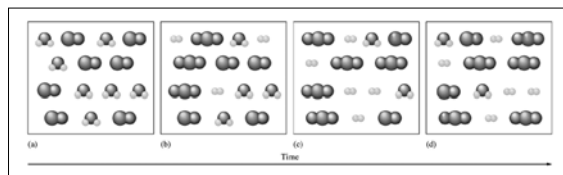
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- Remember we are looking at a net change.
- Reactions at equilibrium still react. It is just that the forward and reverse reactions are equal.



- Figure 13.2: The changes in concentrations with time for the reaction $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$ when equimolar quantities of $\text{H}_2\text{O}(\text{g})$ and $\text{CO}(\text{g})$ are mixed.

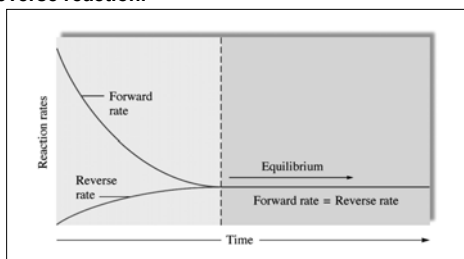
- Figure 13.3: (a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2 . After time has passed, equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time (d).



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- Figure 13.4: The changes with time in the rates of forward and reverse reactions for $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$ when equimolar quantities of $\text{H}_2\text{O}(\text{g})$ and $\text{CO}(\text{g})$ are mixed. The rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction.

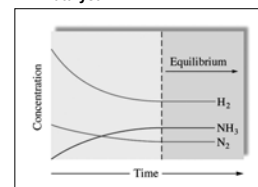
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Characteristics of Chemical Equilibrium

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- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- The second reason applies.
 - Remember
 - N_2 triple bond = 941 kJ/mol
 - H_2 single bond = 432 kJ/mol
 - How can we speed up the reaction?
 - Catalyst
 - Two possibilities exist
 - The system is at chemical equilibrium
 - The forward and reverse reactions are so slow that the system moves towards equilibrium at a rate that cannot be detected.



The Equilibrium Constant

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- NOT TO BE CONFUED WITH THE RATE CONSTANT!!!!
- Equilibrium Constant: The value obtained when equilibrium concentrations of the chemical species are substituted in the equilibrium expression.
- Equilibrium Expression: The expression (from the law of mass action) obtained by multiplying the product concentrations and dividing by the multiplied reactant concentrations, with each concentration raised to a power represented by the coefficient in the balanced equation.
- Law of Mass Action: A general description of the equilibrium condition; it defines the equilibrium constant expression.
- WHAT THE *%#@!



The Law of Mass Action

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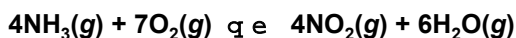
- Two Norwegian chemist
 - Cato Maximilian Guldberg (1836-1902)
 - Peter Waage (1833-1900)
- Proposed in 1864 a general description of an equilibrium condition.
 - Based upon observations of many chemical reactions.
- For some reaction

$$jA + kB \leftrightarrow lC + mD$$
- The law of mass action is represented by the equilibrium expression & K is the constant:

$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

Equilibrium Expression Example

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$$K = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$$

Example

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- $[\text{NH}_3] = 3.1 \times 10^{-2} \text{ M}$
- $[\text{N}_2] = 8.5 \times 10^{-2} \text{ M}$
- $[\text{H}_2] = 3.1 \times 10^{-3} \text{ M}$
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- What is the value of K?

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

Example

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- $[\text{NH}_3] = 3.1 \times 10^{-2} \text{ M}$
- $[\text{N}_2] = 8.5 \times 10^{-2} \text{ M}$
- $[\text{H}_2] = 3.1 \times 10^{-3} \text{ M}$
- $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
- Just the reverse of the previous example
- What is the value of K'?

$$K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K} = 2.6 \times 10^{-5}$$

Example

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- $[\text{NH}_3] = 3.1 \times 10^{-2} \text{ M}$
- $[\text{N}_2] = 8.5 \times 10^{-2} \text{ M}$
- $[\text{H}_2] = 3.1 \times 10^{-3} \text{ M}$
- $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$
- Just $\frac{1}{2}$ of the original example
- What is the value of K''?

$$K'' = (K)^{1/2} = 1.9 \times 10^2$$

Notes on Equilibrium Expressions (EE) 19

- 📖 The Equilibrium Expression for a reaction is the reciprocal of that for the reaction written in reverse.
- 📖 When the equation for a reaction is multiplied by n , $EE_{\text{new}} = (EE_{\text{original}})^n$
 - 📖 $K_{\text{new}} = (K_{\text{original}})^n$
- 📖 The units for K depend on the reaction being considered.
 - 📖 Customarily written without units.

Equilibrium with Pressure 20

- We have been talking about equilibrium of gases in terms of concentration.
- Why not pressure?
- You should know

$$PV = nRT \quad \& \quad M = \frac{\text{mols}}{\text{Vol(L)}}$$

$$P = \frac{n}{V}RT$$

$$P = CRT \quad \& \quad C = \frac{P}{RT}$$

Equilibrium with Pressure 21

But 22

- There must be some sort of relationship between K and K_p .
- So we have the following reaction.



We KNOW

$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k} \quad \& \quad K_p = \frac{(P_C)^l (P_D)^m}{(P_A)^j (P_B)^k}$$

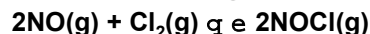
$$P = CRT$$

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

$$\begin{aligned} K_p &= \frac{(P_C)^l (P_D)^m}{(P_A)^j (P_B)^k} = \frac{(C_C \times RT)^l (C_D \times RT)^m}{(C_A \times RT)^j (C_B \times RT)^k} \\ &= \frac{(C_C)^l (C_D)^m}{(C_A)^j (C_B)^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)} \\ &= K(RT)^{\Delta n} \end{aligned}$$

Example 24

$$K_p = 1.9 \times 10^3 \text{ @ } 25^\circ \text{C}$$



Calculate K from K_p

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

$$1.9 \times 10^3 = K(RT)^{\Delta n}$$

$$\Delta n = 2 - (2+1) = -1$$

$$1.9 \times 10^3 = K(RT)^{-1}$$

$$1.9 \times 10^3 (RT) = K$$

$$1.9 \times 10^3 (0.082057)(298) = K = 4.6 \times 10^4$$

Heterogeneous Equilibria

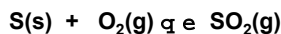
- Heterogeneous Equilibrium: an equilibrium involving reactants and/or products in more than one phase.
- Example: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- You would think that the equilibrium constant would be

$$K' = \frac{[\text{CO}_2][\text{CaO}]}{[\text{CaCO}_3]}$$

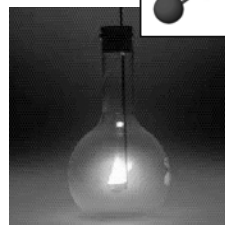
- But heterogeneous equilibrium does not depend on the amounts of pure solid or liquids present.
- Therefore
- $K = [\text{CO}_2]$

Writing and Manipulating K Expressions

Solids and liquids *NEVER* appear in equilibrium expressions.

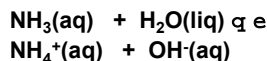


$$K = \frac{[\text{SO}_2]}{[\text{O}_2]}$$

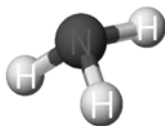


Writing and Manipulating K Expressions

Solids and liquids *NEVER* appear in equilibrium expressions.



$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$



The Reaction Quotient, Q

In general, all reacting chemical systems are characterized by their **REACTION QUOTIENT, Q**.

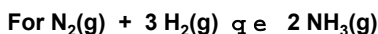
Under Any Reaction Conditions

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

- If $Q = K$, then system is at equilibrium.
- If $Q > K$, then conc. of products too large shifts towards reactants.
- If $Q < K$, then conc. of reactants too large shifts towards products.

The Meaning of K

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

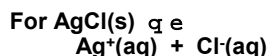


$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 3.5 \times 10^8$$

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

The reaction is strongly **product-favored**.

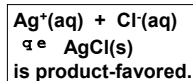
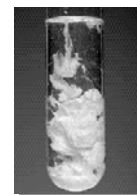
The Meaning of K



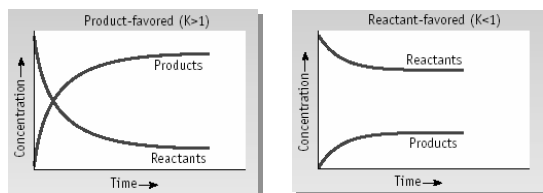
$$K_c = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-5}$$

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

The reaction is strongly **reactant-favored**.



Product- or Reactant Favored



Product-favored

Reactant-favored

The Meaning of K

K comes from thermodynamics.

See Chapter 19, page 812-813

$\Delta G^\circ < 0$: reaction is product favored

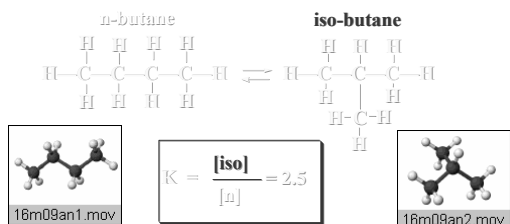
$\Delta G^\circ > 0$: reaction is reactant-favored

$$\Delta G^\circ = -RT \ln K$$

If $K > 1$, then ΔG° is negative
If $K < 1$, then ΔG° is positive

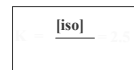
The Meaning of K

2. Can tell if a reaction is at equilibrium.
If not, which way it moves to approach equilibrium.



The Meaning of K

iso-butane



If $[\text{iso}] = 0.35 \text{ M}$ and $[\text{n}] = 0.15 \text{ M}$, are you at equilibrium?

If not, which way does the reaction “shift” to approach equilibrium?

The Meaning of K

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

$$Q = \frac{\text{product concentrations}}{\text{reactant concentrations}}$$

If $Q = K$, then system is at equilibrium.

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

$$Q (2.33) < K (2.5)$$

Reaction is NOT at equilibrium, so [iso] must become _____ and [n] must _____.

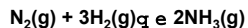
The Extent of a Reaction

- The inherent tendency for a reaction to occur is indicated by the magnitude of the equilibrium constant.
- A value of K much larger than 1 mean?
 - At equilibrium the reaction system will consist of mostly products.
 - Lies to the right.
- A very small value of K
 - At equilibrium the reaction system will consist of mostly reactants.
 - Lies to the left.
- Remember the size of K and the time required to reach equilibrium are NOT directly related.
- The time is dependent on the Activation Energy.

MANY MANY EXAMPLES

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- For the reaction



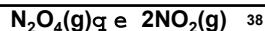
- $K = 6.0 \times 10^{-2}$ @ 500 °C
- Predict the direction in which the system will shift to reach equilibrium if
- $[\text{NH}_3] = 1.0 \times 10^{-5} \text{ M}$
- $[\text{N}_2] = 1.0 \times 10^{-5} \text{ M}$
- $[\text{H}_2] = 2.0 \times 10^{-3} \text{ M}$

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(1.0 \times 10^{-5})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3} = 1.3 \times 10^7$$

Therefore, since $Q > K$ the direction goes towards the reactants



Apollo II lunar landing module at Tranquility Base, 1969.



- N_2O_4 used as one of the fuels on the lunar lander.
- Closed container of $\text{N}_2\text{O}_4(\text{g})$ allowed to reach equilibrium.
- $K_p = 0.133$
- $P_{\text{N}_2\text{O}_4}$ at eq = 2.71 atm
- $P_{\text{NO}_2} = ?$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 0.133$$

$$\therefore 0.133 = \frac{X^2}{2.71 \text{ atm}}$$

$$X = \sqrt{0.360} = 0.600$$



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Determining K

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

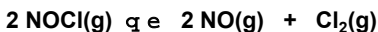
Solution

Set of an "ICE" table of concentrations

	[NOCl]	[NO]	[Cl ₂]
Initial	2.00	0	0
Change			
Equilibrium		0.66	

Determining K

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

Solution

Set of a table of concentrations

	[NOCl]	[NO]	[Cl ₂]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

Determining K

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	[NOCl]	[NO]	[Cl ₂]
Initial	2.00	0	0
Change	-0.66	+0.66	+0.33
Equilibrium	1.34	0.66	0.33

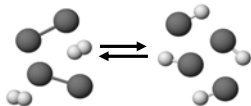
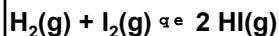
$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2}$$

$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.66)^2(0.33)}{(1.34)^2} = 0.080$$

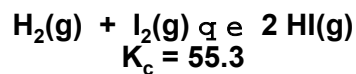
Typical Calculations

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



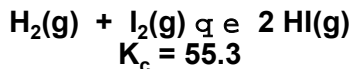
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 55.3$$



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

	$[\text{H}_2]$	$[\text{I}_2]$	$[\text{HI}]$
Initial	1.00	1.00	0
Change			
Equilib			

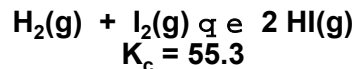


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Step 1. Set up ICE table to define EQUILIBRIUM concentrations.

	$[\text{H}_2]$	$[\text{I}_2]$	$[\text{HI}]$
Initial	1.00	1.00	0
Change	-x	-x	+2x
Equilib	1.00-x	1.00-x	2x

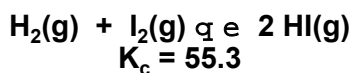
where x is defined as am't of H_2 and I_2 consumed on approaching equilibrium.



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Step 2. Put equilibrium concentrations into K_c expression.

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



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

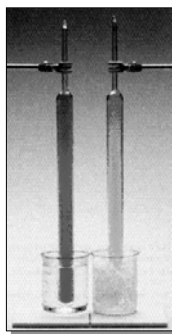
$$K_c = \frac{[2x]^2}{[1.00-x][1.00-x]} = 55.3 \implies 7.44 = \frac{2x}{1.00-x}$$

$$x = 0.79$$

Therefore, at equilibrium

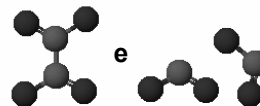
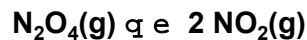
$$[\text{H}_2] = [\text{I}_2] = 1.00 - x = 0.21 \text{ M}$$

$$[\text{HI}] = 2x = 1.58 \text{ M}$$



Nitrogen Dioxide Equilibrium

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Nitrogen Dioxide Equilibrium

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.0059 \text{ at } 298 \text{ K}$$

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

Step 1. Set up an ICE table

	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$
Initial	0.50	0
Change		
Equilib		

Nitrogen Dioxide Equilibrium

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.0059 \text{ at } 298 \text{ K}$$

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

Step 1. Set up an ICE table

	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$
Initial	0.50	0
Change	-x	+2x
Equilib	0.50 - x	2x

Nitrogen Dioxide Equilibrium

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

Step 2. Substitute into K_c expression and solve.

$$K_c = 0.0059 = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{(0.50 - x)}$$

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**

$$ax^2 + bx + c = 0$$

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

Nitrogen Dioxide Equilibrium

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

Solve the quadratic equation for x.

$$ax^2 + bx + c = 0$$

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

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

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

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

Nitrogen Dioxide Equilibrium

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

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

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

$$x = 0.026 \text{ or } -0.028$$

But a negative value is not reasonable.

Conclusion: $x = 0.026 \text{ M}$

$$[\text{N}_2\text{O}_4] = 0.50 - x = 0.47 \text{ M}$$

$$[\text{NO}_2] = 2x = 0.052 \text{ M}$$

Solving Quadratic Equations

- Recommend you solve the equation exactly on a calculator or use the "method of successive approximations"



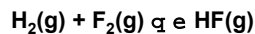
Solving Equilibrium Problems

55

1. Balance the equation.
2. Write the equilibrium expression.
3. List the initial concentrations.
4. Calculate Q and determine the shift to equilibrium.
5. Define equilibrium concentrations.
6. Substitute equilibrium concentrations into equilibrium expression and solve.
7. Check calculated concentrations by calculating K .

Example

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- $K = 1.15 \times 10^2$ @ some temperature.
- 3.00 mols of each component is added to a 1.50 L flask.
- Calculate the equilibrium concentrations of all species.

	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	\rightleftharpoons	$2\text{HF}(\text{g})$
I	2.00 M		2.00 M		2.00 M
C					
E					

But which direction does the reaction go?

57

	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	\rightleftharpoons	$2\text{HF}(\text{g})$
I	2.00 M		2.00 M		2.00 M
C					
E					

$$Q = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$

$Q < K$, so the reaction goes towards the products

Keep Going...

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	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	\rightleftharpoons	$2\text{HF}(\text{g})$
I	2.00 M		2.00 M		2.00 M
C	-x		-x		+2x
E	2.00 - x		2.00 - x		2.00 + 2x

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2.00 + 2x)^2}{(2.00 - x)(2.00 - x)}$$

$$\sqrt{1.15 \times 10^2} = \frac{2.00 + 2x}{2.00 - x}$$

$$x = 1.528$$

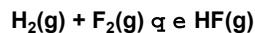
Finally

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- $x = 1.528$
- So,
- $[\text{H}_2] = 2.00 - 1.528 = 0.472 \text{ M}$
- $[\text{F}_2] = 2.00 - 1.528 = 0.472 \text{ M}$
- $[\text{HF}] = 2.00 + 2(1.528) = 5.056 \text{ M}$

Example

60



- $K = 1.15 \times 10^2$ @ some temperature.
- 3.00 mols of H_2 in a 3.000 L flask
- 6.00 mols F_2 in a 3.000 L flask
- Calculate the equilibrium concentrations of all species.

	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	\rightleftharpoons	$2\text{HF}(\text{g})$
I	1.00 M		2.00 M		0.00 M
C	-x		-x		+2x
E	1.00 - x		2.00 - x		2x

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2x)^2}{(1.00-x)(2.00-x)} \quad 61$$

$$1.11 \times 10^2 (x^2) - 3.45 \times 10^2 (x) + 2.30 \times 10^2 = 0$$

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

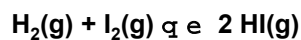
$$x = 2.14 \text{ M or } 0.968 \text{ M}$$

Cannot be 2.14 M

Why? (Look at $[\text{H}_2]$)

$$x = 0.968$$

Another #\$\$% Example!



- $K_p = 1.00 \times 10^2$
- The following gasses are mixed in a 5.000 L Flask
 - $P_{\text{HI}} = 5.000 \times 10^{-1} \text{ atm}$
 - $P_{\text{H}_2} = 1.000 \times 10^{-2} \text{ atm}$
 - $P_{\text{I}_2} = 5.000 \times 10^{-3} \text{ atm}$
- Check Q

$$Q = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(5.00 \times 10^{-1} \text{ atm})^2}{(1.000 \times 10^{-2} \text{ atm})(5.000 \times 10^{-3} \text{ atm})}$$

$$Q = 5.000 \times 10^3$$

$Q > K$, therefore the system will shift toward the reactants

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
I	1.00×10^{-2}		5.00×10^{-3}		5.00×10^{-1}
C	+x		+x		-2x
E	$1.00 \times 10^{-2} + x$		$5.00 \times 10^{-3} + x$		$5.00 \times 10^{-1} - 2x$

$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(5.00 \times 10^{-1} - 2x)^2}{(1.000 \times 10^{-2} + x)(5.000 \times 10^{-3} + x)} \quad 64$$

Reduces to

$$(9.60 \times 10^1)x^2 + 3.5x - (2.45 \times 10^{-1}) = 0$$

$$x = 3.55 \times 10^{-2}$$

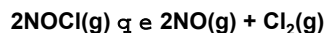
	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
I	$1.00 \times 10^{-2} \text{ M}$		$5.00 \times 10^{-3} \text{ M}$		$5.00 \times 10^{-1} \text{ M}$
C	+x		+x		-2x
E	$1.00 \times 10^{-2} + x$		$5.00 \times 10^{-3} + x$		$5.00 \times 10^{-1} - 2x$

$$x = 3.55 \times 10^{-2} \text{ atm}$$

• Therefore at eq.

- $P_{\text{HI}} = 4.29 \times 10^{-1} \text{ atm}$
- $P_{\text{H}_2} = 4.55 \times 10^{-2} \text{ atm}$
- $P_{\text{I}_2} = 4.05 \times 10^{-3} \text{ atm}$

ONE MORE



- In an experiment in which 1.0 mol NOCl is placed in a 2.0 L flask, what are the equilibrium concentrations?

$$K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5}$$

	$2\text{NOCl}(\text{g})$	\rightleftharpoons	$2\text{NO}(\text{g})$	+	$\text{Cl}_2(\text{g})$
I	0.50		0		0
C	-2x		+2x		+x
E	$0.5 - 2x$		$2x$		x

$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}$$

- The problem is you end up with an x^3 component, which are not fun to solve for
- But, since K is so small the reaction will not proceed that far to the right.
- Which means that x is a relatively small number.
- So $2x$ does nothing to 0.50

$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}$$



$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

Therefore, $x = 1.0 \times 10^{-2}$

	2NOCl(g) ⇌	2NO(g) +	Cl ₂ (g)
I	0.50	0	0
C	-2x	+2x	+x
E	0.5 - 2x	2x	x

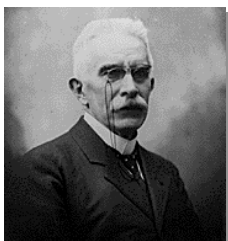
$$x = 1.0 \times 10^{-2}$$

- Therefore at eq.
 - $[\text{NOCl}]_i = 0.50 \text{ M}$
 - $[\text{NO}] = 2.0 \times 10^{-2} \text{ M}$
 - $[\text{Cl}] = 1.0 \times 10^{-2} \text{ M}$

EQUILIBRIUM AND EXTERNAL EFFECTS

- Temperature, catalysts, 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."

EQUILIBRIUM AND EXTERNAL EFFECTS



Henri Le Chatelier
1850-1936
Studied mining engineering.
Interested in glass and ceramics.

EQUILIBRIUM AND EXTERNAL EFFECTS

- Temperature change ---> **change in K**
- Consider the fizz in a soft drink
 $\text{CO}_2(\text{aq}) + \text{HEAT} \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{liq})$
- $K = P(\text{CO}_2) / [\text{CO}_2]$
- Increase T. What happens to equilibrium position? To value of K?
- K increases as T goes up because $P(\text{CO}_2)$ increases and $[\text{CO}_2]$ decreases.
- Decrease T. Now what?
- Equilibrium shifts left and K decreases.

Temperature Effects on Equilibrium

N_2O_4 (colorless) + heat

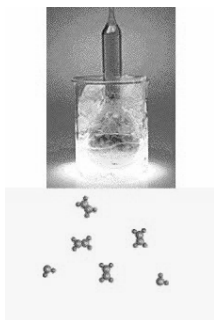
$\rightleftharpoons 2 \text{NO}_2$ (brown)

$\Delta H^\circ = +57.2 \text{ kJ}$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

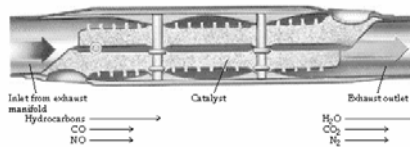
$K_c (273 \text{ K}) = 0.00077$

$K_c (298 \text{ K}) = 0.0059$

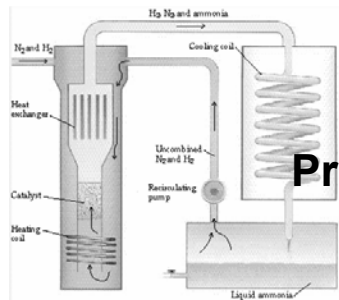


EQUILIBRIUM AND EXTERNAL EFFECTS

- Add catalyst \rightarrow no change in K
- A catalyst only affects the RATE of approach to equilibrium.



Catalytic exhaust system



NH_3 Production

$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{heat}$

$K = 3.5 \times 10^8$ at 298 K

Haber-Bosch Ammonia Synthesis



Fritz Haber
1868-1934
Nobel Prize, 1918

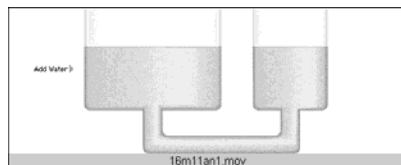


Carl Bosch
1874-1940
Nobel Prize, 1931

EQUILIBRIUM AND EXTERNAL EFFECTS

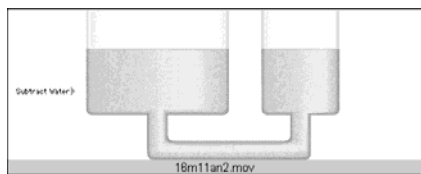
- Concentration changes
 - no change in K
 - only the position of equilibrium changes.

Le Chatelier's Principle



Adding a "reactant" to a chemical system.

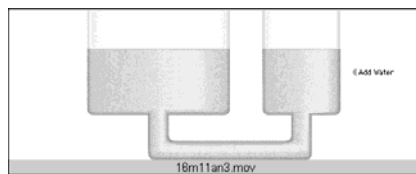
Le Chatelier's Principle



Removing a "reactant" from a chemical system.



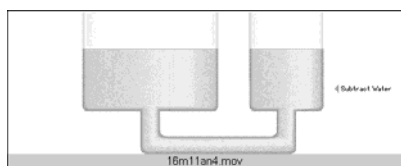
Le Chatelier's Principle



Adding a "product" to a chemical system.



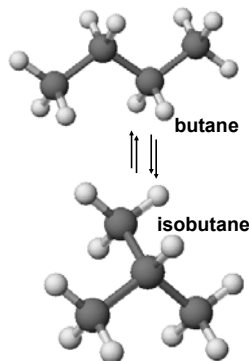
Le Chatelier's Principle



Removing a "product" from a chemical system.

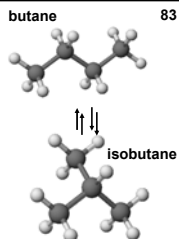
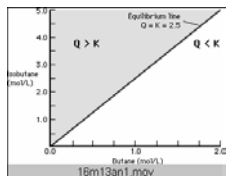


Butane- Isobutane Equilibrium



$$K = \frac{[\text{isobutane}]}{[\text{butane}]} = 2.5$$

Butane \rightleftharpoons Isobutane



- At equilibrium with $[\text{iso}] = 1.25 \text{ M}$ and $[\text{butane}] = 0.50 \text{ M}$. $K = 2.5$.
- Add 1.50 M butane.
- When the system comes to equilibrium again, what are $[\text{iso}]$ and $[\text{butane}]$?



Butane \rightleftharpoons Isobutane

Assume you are at equilibrium with $[\text{iso}] = 1.25 \text{ M}$ and $[\text{butane}] = 0.50 \text{ M}$. Now add 1.50 M butane. When the system comes to equilibrium again, what are $[\text{iso}]$ and $[\text{butane}]$? $K = 2.5$

Solution

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

$$Q = \frac{[\text{isobutane}]}{[\text{butane}]} = \frac{1.25}{0.50 + 1.50} = 0.63$$

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

Butane \rightleftharpoons 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 ICE table

	[butane]	[isobutane]
Initial	0.50 + 1.50	1.25
Change	- x	+ x
Equilibrium	2.00 - x	1.25 + x

Butane \rightleftharpoons Isobutane

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

Solution

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

$$x = 1.07 \text{ M}$$

At the new equilibrium position, [butane] = 0.93 M and [isobutane] = 2.32 M. Equilibrium has shifted toward isobutane.

EQUILIBRIUM AND EXTERNAL EFFECTS

- Temperature, catalysts, and changes in concentration affect equilibria.
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- "...if a system at equilibrium is disturbed, the system tends to shift its equilibrium position to counter the effect of the disturbance."

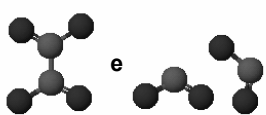


Le Chatelier's Principle

- **Change T**
 - change in K
 - therefore change in P 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"

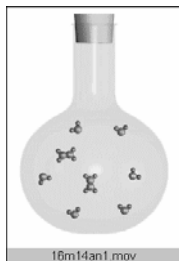
Nitrogen Dioxide Equilibrium

$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.0059 \text{ at } 298 \text{ K}$$

Increase P in the system by reducing the volume (at constant T).



Nitrogen Dioxide Equilibrium

$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.0059 \text{ at } 298 \text{ K}$$

Increase P in the system by reducing the volume.

In gaseous system the equilibrium will shift to the side with fewer molecules (in order to reduce the P).

Therefore, reaction shifts **LEFT** and P of NO_2 decreases and P of N_2O_4 increases.