

GENERAL CHEMISTRY

Chapter 5

Chemical Equilibrium

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OUTLINE

- ✓ Basic concepts
- ✓ The equilibrium constant
- ✓ LeChatelier's Principle
- ✓ Relationship between K_p & K_c
- ✓ Relationship between ΔG^0_{rxn} and K
- ✓ Evaluation of K at difference temperature.

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Basic concepts

❖ Reversible reactions:

- ✓ Reactions that do **not go to completion** and that can occur in **either direction**.
- ✓ Both the **forward and reverse reactions** occur simultaneously.



❖ In the balanced equation:

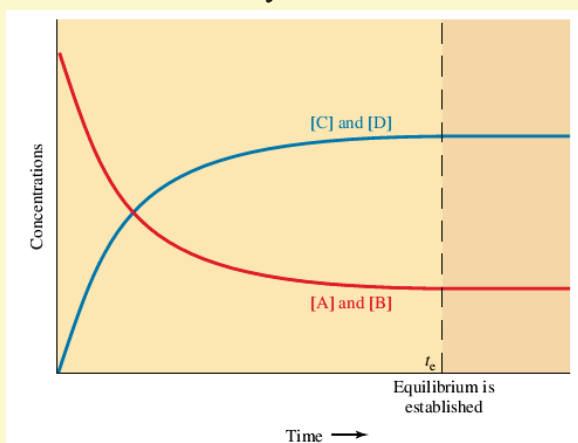
- ✓ “a, b, c, d” represent the stoichiometric coefficients
- ✓ A, B are called the “reactants”
- ✓ C, D are called the “products.”
- ✓ The double arrow (\rightleftharpoons) indicates that the reaction is reversible

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Basic concepts

- ❖ **Chemical equilibrium** exists when two opposing reactions occur simultaneously at the same rate.



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The equilibrium constant

❖ For a general reaction in the gas phase:



✓ The equilibrium constant expression is:

$$K_{eq} = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

✓ K_{eq} is the equilibrium constant.

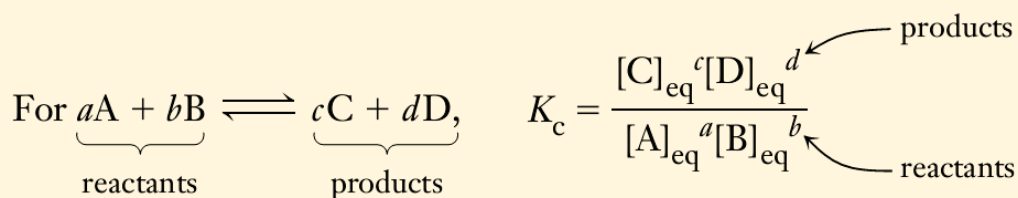
✓ The subscript “eq” to emphasize that **partial pressure** in the equilibrium constant expression are those **at equilibrium**.

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The equilibrium constant

❖ For a general reaction:



K_c values always involve **equilibrium values of concentrations**.

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The equilibrium constant

- ❖ The equilibrium constant K_{eq} has no units.
- ❖ The value of K_{eq} :
 - ✓ Is constant at a given temperature,
 - ✓ Changes if the temperature changes,
 - ✓ Does not depend on the initial concentrations.
 - ✓ $K_c > 1$: most of the reactants would be converted into products, we called a reaction “product-favored.”
 - ✓ $K_c < 1$: most of the reactants remain and only small amounts of products are formed.

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The equilibrium constant

Example:

	Initial Concentrations			Equilibrium Concentrations		
	[SO ₂]	[O ₂]	[SO ₃]	[SO ₂]	[O ₂]	[SO ₃]
Experiment 1	0.400 M	0.200 M	0 M	0.344 M	0.172 M	0.056 M
Experiment 2	0 M	0 M	0.500 M	0.424 M	0.212 M	0.076 M

From experiment 1:

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.056)^2}{(0.344)^2(0.172)} = 0.15$$

From experiment 2:

$$K_c = \frac{(0.076)^2}{(0.424)^2(0.212)} = 0.15$$

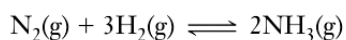
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The equilibrium constant

EXAMPLE 17-13 Calculation of K_p

In an equilibrium mixture at 500°C, we find $P_{\text{NH}_3} = 0.147$ atm, $P_{\text{N}_2} = 6.00$ atm, and $P_{\text{H}_2} = 3.70$ atm. Evaluate K_p at 500°C for the following reaction.



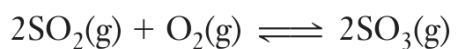
$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(0.147)^2}{(6.00)(3.70)^3} = 7.11 \times 10^{-5}$$

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Variation of K_c

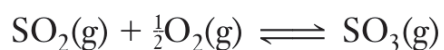
- ❖ The value of K_c depends on the form of the balanced equation for the reaction.



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$



$$K'_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{1}{K_c}$$



$$K''_c = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = K_c^{1/2}$$

- ❖ If an equation for a reaction is multiplied by any factor, n , then the original value of K_c is raised to the n^{th} power.

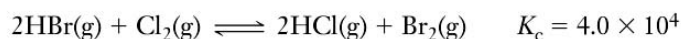
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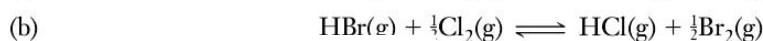
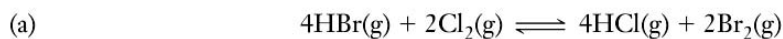
Variation of K_c

EXAMPLE 17-3 Variation of the Form of K_c

You are given the following reaction and its equilibrium constant at a given temperature.



Write the expression for, and calculate the numerical value of, the equilibrium constant for each of the following at the same temperature.



$$K_c = \frac{[\text{HCl}]^2[\text{Br}_2]}{[\text{HBr}]^2[\text{Cl}_2]} = 4.0 \times 10^4$$

$$K'_c = \frac{[\text{HCl}]^4[\text{Br}_2]^2}{[\text{HBr}]^4[\text{Cl}_2]^2} \quad K'_c = (K_c)^2 = (4.0 \times 10^4)^2 = 1.6 \times 10^9$$

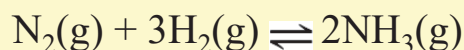
$$K''_c = \frac{[\text{HCl}][\text{Br}_2]^{1/2}}{[\text{HBr}][\text{Cl}_2]^{1/2}} = \sqrt{K_c} = \sqrt{4.0 \times 10^4} = 2.0 \times 10^2$$

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Calculating K_{eq}

- ❖ In one of their experiments, Harber and co-workers introduced a mixture of hydrogen and nitrogen into a reaction vessel and allowed the system to attain chemical equilibrium at 472°C. The equilibrium mixture of gases was analyzed and found to contain 0.1207 M H_2 , 0.0402 M N_2 , and 0.00272 M NH_3 . From these data, calculate the equilibrium constant, K_{eq} , for

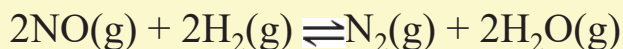


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Calculating K_{eq}

- ❖ Gaseous Hydrogen iodide is placed in a closed container at 425 °C, where it partially decomposes to hydrogen and iodine: $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$. At equilibrium, it is found that $[\text{HI}] = 3.35 \times 10^{-3} \text{M}$; $[\text{H}_2] = 4.79 \times 10^{-4} \text{M}$; $[\text{I}_2] = 4.79 \times 10^{-4} \text{M}$. What is the value of K_{eq} at this temperature.
- ❖ A mixture of 0.100 mole of NO, 0.050 mole of H_2 , and 0.050 mole of H_2O is placed in a 1.00-L vessel. The following equilibrium is established:



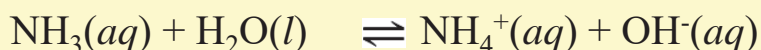
Calculate the K_{eq} for the reaction.

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Calculating K_{eq}

- ❖ Enough ammonia is dissolved in 5.00 liters of water at 25°C to produce a solution that is 0.0124 M in ammonia. The solution is then allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of OH^- is $4.64 \times 10^{-4} \text{M}$. Calculate K_{eq} at 25 °C for the reaction.

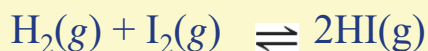


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Calculating K_{eq}

- ❖ A mixture of 5.00×10^{-3} mol of H_2 and 1.00×10^{-2} mol of I_2 is placed in a 5.00 L container at 448 °C and allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate the K_c at 448 °C for the reaction.



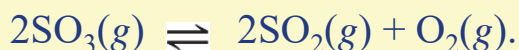
$$K_{eq} = 50.51$$

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Calculating K_{eq}

- ❖ Sulfur trioxide decomposes at high temperature in a sealed container:



Initially the vessel is charged at 1000K with $SO_3(g)$ at a concentration of 6.09×10^{-3} M. At equilibrium, the SO_3 concentration is 2.44×10^{-3} M. Calculate the value for K_{eq} at 1000 K.

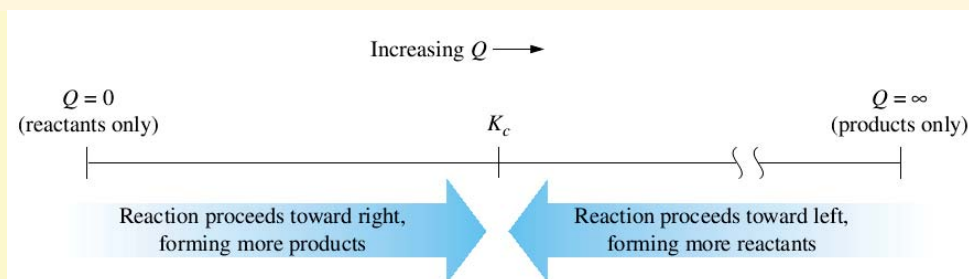
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The reaction quotient

- ❖ The reaction quotient, Q , for the general reaction is given as follows:

For $aA + bB \rightleftharpoons cC + dD$, $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
 \leftarrow
 \leftarrow
 not necessarily equilibrium concentrations



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The reaction quotient

- ✓ $Q < K_c$: Forward reaction predominates until equilibrium is established.
- ✓ $Q = K_c$: System is at equilibrium.
- ✓ $Q > K_c$: Reverse reaction predominates until equilibrium is established.

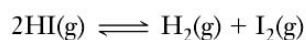
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The reaction quotient

EXAMPLE 17-4 The Reaction Quotient

At a very high temperature, $K_c = 65.0$ for the following reaction.



The following concentrations were detected in a mixture. Is the system at equilibrium? If not, in which direction must the reaction proceed for equilibrium to be established?

$$[\text{HI}] = 0.500 \text{ M}, \quad [\text{H}_2] = 2.80 \text{ M}, \quad \text{and} \quad [\text{I}_2] = 3.40 \text{ M}$$

$$Q = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(2.80)(3.40)}{(0.500)^2} = 38.1 \quad \mathbf{Q < K_c}$$

- ✓ The system is not at equilibrium the forward reaction must occur to a greater extent than the reverse reaction;
- ✓ Some HI must react to form more H_2 and I_2 to reach equilibrium **19**

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The reaction quotient

- ❖ At 448 °C the equilibrium constant, K_{eq} , for the reaction: $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$ is 50.5. Predict how the reaction will proceed to reach equilibrium at 448 °C if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2 , and 3.0×10^{-2} mol of I_2 in a 2.0L container.

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LeChatelier's Principle

❖ LeChatelier's Principle:

If a change of conditions (stress) is applied to a system at equilibrium, the system shifts in the direction that reduces the stress to move toward a new state of equilibrium.

❖ **Three types of changes** can disturb the equilibrium of a reaction:

1. Changes in concentration
2. Changes in pressure or volume (for reactions that involve gases)
3. Changes in temperature.

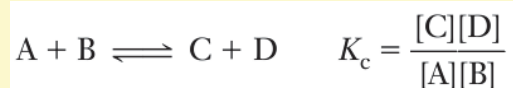
LeChatelier's Principle (is pronounced "le-SHOT-lee-ay.")

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FACTORS THAT AFFECT EQUILIBRIA

❖ Changes in Concentration:



Stress	Q	Direction of Shift of $A + B \rightleftharpoons C + D$
Increase concentration of A or B	$Q < K$	→ right
Increase concentration of C or D	$Q > K$	left ←
Decrease concentration of A or B	$Q > K$	left ←
Decrease concentration of C or D	$Q < K$	→ right

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FACTORS THAT AFFECT EQUILIBRIA

❖ Changes in Concentration:

- ✓ Adding a reactant or product shifts the equilibrium away from the increase.
- ✓ Removing a reactant or product shifts the equilibrium towards the decrease.
- ✓ To optimize the amount of product at equilibrium, we need to flood the reaction vessel with reactant and continuously remove product (*LeChatelier's Principle*).

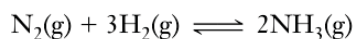
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FACTORS THAT AFFECT EQUILIBRIA

EXAMPLE 17-8 *Applying a Stress to a System at Equilibrium*

Given the following reaction at equilibrium in a closed container at 500°C, predict the effect of each of the following changes on the amount of NH₃ present at equilibrium: (a) forcing more H₂ into the system; (b) removing some NH₃ from the system.



(a) forcing more H₂ into the system;

More NH₃ is formed.

(b) removing some NH₃ from the system.

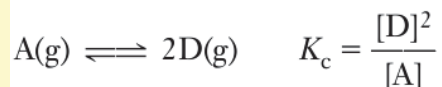
More NH₃ is formed.

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FACTORS THAT AFFECT EQUILIBRIA

❖ Changes in Volume and Pressure:



Stress	Direction of Shift of $\text{A(g)} \rightleftharpoons 2\text{D(g)}$
Volume decrease, pressure increase	Toward smaller number of moles of gas (left for <i>this</i> reaction)
Volume increase, pressure decrease	Toward larger number of moles of gas (right for <i>this</i> reaction)

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FACTORS THAT AFFECT EQUILIBRIA

❖ Changes in Volume and Pressure:

✓ If there is **no change** in the total number of **moles of gases**, a **volume (pressure)** change **does not affect** the position of equilibrium.

✓ If changing in the total number of moles of gases:

- A decrease in volume (increase in pressure) shifts a reaction in the direction that produces the smaller total number of moles of gas.
- An increase in volume (decrease in pressure) shifts a reaction in the direction that produces the larger total number of moles of gas.

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FACTORS THAT AFFECT EQUILIBRIA

❖ Changes in Temperature:

- ✓ Adding heat (i.e. heating the vessel) favors away from the increase:
 - if $\Delta H > 0$, adding heat favors the forward reaction.
 - if $\Delta H < 0$, adding heat favors the reverse reaction.
- ✓ Removing heat (i.e. cooling the vessel), favors towards the decrease:
 - if $\Delta H > 0$, cooling favors the reverse reaction.
 - if $\Delta H < 0$, cooling favors the forward reaction.

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FACTORS THAT AFFECT EQUILIBRIA

❖ Addition of a Catalyst:

- ✓ A catalyst lowers the activation energy barrier for the reaction.
- ✓ Therefore, a catalyst will decrease the time taken to reach equilibrium.
- ✓ A catalyst does not effect the composition of the equilibrium mixture.

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RELATIONSHIP BETWEEN K_p & K_c

In general, the relationship between K_c and K_p is:

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

$$\Delta n = (n_{\text{gas prod}}) - (n_{\text{gas react}})$$

Be Careful About the Value of R

$$R = 0.082 \frac{\text{L.atm}}{\text{mol.K}}$$

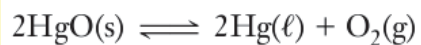
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HETEROGENEOUS EQUILIBRIA

✓ Heterogeneous equilibria involve species in more than one phase.

✓ Example:



$$K_c = [\text{O}_2] \quad \text{and} \quad K_p = P_{\text{O}_2}$$

✓ Pure liquids and pure solids do not appear in the K expressions for heterogeneous equilibria.

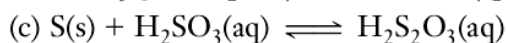
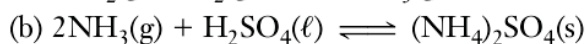
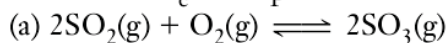
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HETEROGENEOUS EQUILIBRIA

EXAMPLE 17-15 K_c and K_p for Heterogeneous Equilibrium

Write both K_c and K_p for the following reversible reactions.



(a)	$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$	$K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})}$
(b)	$K_c = \frac{1}{[\text{NH}_3]^2} = [\text{NH}_3]^{-2}$	$K_p = \frac{1}{(P_{\text{NH}_3})^2} = (P_{\text{NH}_3})^{-2}$
(c)	$K_c = \frac{[\text{H}_2\text{S}_2\text{O}_3]}{[\text{H}_2\text{SO}_3]}$	K_p undefined; no gases involved

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RELATIONSHIP BETWEEN $\Delta G^\circ_{\text{rxn}}$ & K



$$\Delta G_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + RT \ln Q$$

$$0 = \Delta G^\circ_{\text{rxn}} + RT \ln K \quad (\text{at equilibrium})$$

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K$$

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RELATIONSHIP BETWEEN ΔG^0_{rxn} & K

When the relationship $\Delta G^0_{\text{rxn}} = -RT \ln K$ is used with

1. all gaseous reactants and products, K represents K_p ;
2. all solution reactants and products, K represents K_c ;
3. a mixture of solution and gaseous reactants, K represents the thermodynamic equilibrium constant, and we do not make the distinction between K_p and K_c .

ΔG^0_{rxn}	K	Product Formation
$\Delta G^0_{\text{rxn}} < 0$	$K > 1$	Products favored over reactants at equilibrium
$\Delta G^0_{\text{rxn}} = 0$	$K = 1$	At equilibrium when $[C]^c[D]^d \dots = [A]^a[B]^b \dots$
$\Delta G^0_{\text{rxn}} > 0$	$K < 1$	Reactants favored over products at equilibrium

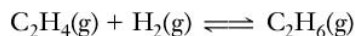
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RELATIONSHIP BETWEEN ΔG^0_{rxn} & K

EXAMPLE 17-19 K versus ΔG^0_{rxn}

The equilibrium constant, K_p , for the following reaction is 5.04×10^{17} at 25°C . Calculate ΔG^0_{298} for the hydrogenation of ethylene to form ethane.



Solution

$$\begin{aligned}
 \Delta G^0_{298} &= -RT \ln K_p \\
 &= -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln (5.04 \times 10^{17}) \\
 &= -1.01 \times 10^5 \text{ J/mol} \\
 &= -101 \text{ kJ/mol}
 \end{aligned}$$

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Evaluation of K at difference temperature

❖ The van't Hoff equation

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

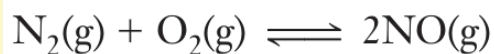
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Evaluation of K at difference temperature

Example:

We found that $K_p = 4.4 \times 10^{-31}$ at 25°C (298 K) for the following reaction, $\Delta H^0 = 180.5 \text{ kJ/mol}$ for this reaction. Evaluate K_p at 2400K.



$$K_{T_2} = 2.2 \times 10^{-3} \text{ at } 2400. \text{ K}$$

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