

Topic 3.3. Chemical Equilibrium

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Outline

- Introduction
- Main part
- ♦ What is equilibrium?
- **Expressions for equilibrium constants,** K_c ;
- **\diamond** Calculating K_c using equilibrium concentrations;
- Calculating equilibrium concentrations using initial concentration and K_c value;
- **Relationship between** K_{c} and K_{p} ;
- Factors that affect equilibrium;
- Le Chatelier's Principle
- Conclusion

Literature



What is Equilibrium?





This is not Equilibrium?



Chemical Equilibrium in Nature (The formation of stalagmites and Stalactites)



Chemical Equilibrium

2225

Consider the following reactions:

 $CaCO_{3}(s) + CO_{2}(aq) + H_{2}O(l) \rightarrow Ca^{2+}(aq) + 2HCO_{3}(aq)$..(1)

and

 $Ca^{2+}(aq) + 2HCO_{3}(aq) \rightarrow CaCO_{3}(s) + CO_{2}(aq) + H_{2}O(l)$..(2)

Reaction (2) is the reverse of reaction (1).

At equilibrium the two opposing reactions occur at the same rate.

Concentrations of chemical species do not change once equilibrium is established.



Expression for Equilibrium Constant

Consider the following equilibrium system:

- $wA + xB \nleftrightarrow yC + zD$
 - $K_{c} = \frac{[C]^{y}[D]^{z}}{[A]^{w}[B]^{x}}$
- The numerical value of K_c is calculated using the concentrations of reactants and products that exist at equilibrium.

Expressions for Equilibrium Constants



✤ Examples:

 $N_{2}(g) + 3H_{2}(g) \neq 2NH_{3}(g); K_{c} = \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}}$

 $PCl_{5}(g) \neq PCl_{3}(g) + Cl_{2}(g); \quad K_{c} = \frac{[PCl_{3}][Cl_{2}]}{[PCl_{5}]}$

 $CH_4(g) + H_2(g) \not\cong CO(g) + 3H_2(g);$

 $K_{c} = \frac{[CO][H_{2}]^{3}}{[CH_{4}][H_{2}O]}$

Calculating Equilibrium Constant



Example-1:

1 mole of H_2 gas and 1 mole of I_2 vapor are introduced into a 5.00-liter sealed flask. The mixture is heated to a certain temperature and the following reaction occurs until equilibrium is established.

 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

At equilibrium, the mixture is found to contain 0,316 mole of HI. (a) What are the concentrations of H_2 , I_2 and HI at equilibrium? (b) Calculate the equilibrium constant K_c .





H ₂ (g)	+ $I_2(g)$	₹ 2 HI(g)	
Initial [], M:	0.200	0.200 0.000	
Change in [], M: Equilibrium [], M	-0.158 0.042	-0.158 + 0.316 0.042 0.316	

$$K_{c} = \frac{[HI]^{2}}{[H_{2}][I_{2}]^{2}} - \frac{(0.316)^{2}}{(0.0\overline{4}2)^{2}}$$

Calculating Equilibrium Constant

Example-2:

0.500 mole of HI is introduced into a 1.00 liter sealed flask and heated to a certain temperature. Under this condition HI decomposes to produce H₂ and I₂ until an equilibrium is established. An analysis of the equilibrium mixture shows that 0.105 mole of HI has decomposed. Calculate the equilibrium concentrations of H₂, I₂ and HI, and the equilibrium constant K_c for the following reaction:

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

Calculating Equilibrium Constant



★ The reaction: $H_2(g) + I_2(g) \neq 2HI(g)$, proceeds from right to left.

 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

♦ Initial [], M: 0.000
♦ Change in [], M: +0.0525
♦ Equil'm [], M 0.0525
0.0525
0.395

$$K_{\rm c} = \frac{(0.395)^2}{(0.0525)^2} = 56.6$$

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Expression and Value of Equilibrium Constant for a Reaction

- \clubsuit The expression for *K* depends on the equation;
- The value of K applies to that equation; it does not depend on how the reaction occurs;
- Concentrations used to calculate the value of K are those measured at equilibrium.

Relationships between chemical equations the expressions of equilibrium constants

The expression of equilibrium constant depends on how the equilibrium equation is written. For example, for the following equilibrium: $K_{\rm c} = \frac{[\rm HI]^2}{[\rm H_2][\rm I_2]}$

♦
$$H_2(g) + I_2(g) \neq 2$$
 HI(g);

For the reverse reaction:

★ 2HI(g) ₹ H₂(g) + I₂(g);
K_c' =
$$\frac{[H_2][I_2]}{[HI]^2} = 1/K_c$$
★ And for the reaction: HI(g) ₹ ½H₂(g) + ½I₂(g);

$$K_{\rm c}'' = \sqrt{\frac{[{\rm H}_2][{\rm I}_2]}{[{\rm HI}]^2}} = \sqrt{K_{\rm c}'} = \frac{1}{\sqrt{K_{\rm c}}}$$

Expression and Values of Equilibrium Constant Using Partial Pressures



Consider the following reaction involving gases:

$$2SO_{2^{(g)}} + O_{2^{(g)}} \rightleftharpoons 2SO_{3^{(g)}}$$

$$K_{\rm p} = \frac{({\rm P}_{\rm SO3})^2}{({\rm P}_{\rm SO2})^2 ({\rm P}_{\rm O2})}$$



♦ Consider the reaction: $2SO_2(g) + O_2(g) \neq 2SO_3(g)$

The Relationship between K_c and K_r

$$K_{c} = \frac{[SO]^{2}_{and}}{[SO_{2}]^{2}[O_{2}]} K_{p} = \frac{(P_{SO3})^{2}}{(P_{SO2})^{2}(P_{O2})}$$

Assuming ideal behavior,

• where PV = nRT and P = (n/V)RT = [M]RT

 \diamond and $P_{SO3} = [SO_3]RT; P_{SO2} = [SO_2]RT; P_{O2} = [O_2]RT$

 $K_{\rm p} = \frac{[{\rm SO}_3]^2 ({\rm RT})^2}{[{\rm SO}_2]^2 ({\rm RT})^2 [{\rm O}_2] ({\rm RT})} = \frac{[{\rm SO}_3]^2}{[{\rm SO}_2]^2 [{\rm O}_2]} ({\rm RT})^{-1} = K_{\rm c} ({\rm RT})^{-1}$



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♦ For reaction: $PCl_{5}(g) \rightarrow PCl_{3}(g) + Cl_{2}(g);$

$$K_{p} = \frac{(P_{PCl3})(P_{Cl2})}{(P_{PCl5})} = \frac{[PCl_{3}](RT) \times [Cl_{2}](RT)}{[PCl_{5}](RT)}$$
$$= \frac{[PCl_{3}][Cl_{2}]}{[PCl_{5}]}(RT)^{1} = K_{C}(RT)^{1}$$

In general, for reactions involving gases such that,

• $aA + bB \neq cC + dD$

where A, B, C, and D are all gases, and *a*, *b*, *c*, and *d* are their respective coefficients,

Relationship between K and

•
$$K_{\rm p} = K_{\rm c} ({\rm RT})^{\Delta n}$$

and $\Delta n = (c + d) - (a + b)$

(In heterogeneous systems, only the coefficients of the gaseous species are counted.)

For other reactions:

★ 1. 2NO₂(g) ₹ N₂O₄(g); K_p = K_c(RT)⁻¹
★ 2. H₂(g) + I₂(g) ₹ 2 HI(g); K_p = K_c
★ 3. N₂(g) + 3H₂(g) ₹ 2 NH₃(g); K_p = K_c(RT)⁻²

Relationship between K and **R**

Homogeneous & Heterogeneous Equilibria

Homogeneous equilibria: $CH_4(g) + H_2O(g) \neq CO(g) + 3H_2(g);$ $CO(g) + H_2O(g) \neq CO_2(g) + H_2(g);$

Heterogeneous equilibria: $CaCO_3(s) \neq CaO(s) + CO_2(g);$ $HF(aq) + H_2O(l) \neq H_3O^+(aq) + F^-(aq);$ $PbCl_2(s) \neq Pb^{2+}(aq) + 2 Cl^-(aq);$

Expressions for Heterogeneous System



Examples: $CaCO_{3}(s) \rightleftharpoons CaO(s) + CO_{2}(g);$ $K_{c} = [CO_{2}] \qquad K_{p} = P_{CO2}; \qquad K_{p} = K_{c}(RT)$

♦ $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq);$

$$K_{\rm a} = \frac{[{\rm H}_{3}{\rm O}^{+}][{\rm F}^{-}]}{[{\rm HF}]}$$



Solubility Eqilibrium



$$PbCl_{2}(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq);$$
$$K_{sp} = [Pb^{2+}][Cl^{-}]^{2}$$

$(K_{sp} \text{ is called solubility product})$

Constants



✤ For example,

Eqn(1): $A + B \rightleftharpoons C + D$; $K_1 = \frac{[C][D]}{[A][D]}$ Eqn(2): $C + E \rightleftharpoons B + F$; $K_2 = \frac{[B][F]}{[C][E]}$



♦ *Net* equation: $A + E \neq D + F$;

$K_{\text{net}} = K_{\overline{1}} \times \frac{[D_{R}][F]}{[A][E]}$

If Eqn(1) + Eqn(2) = Net equation,
then $K_1 \ge K_2 = K_{net}$

Equilibrium Exercise #1



A flask is charged with 2.00 atm of nitrogen dioxide and 1.00 atm of dinitrogen tetroxide at 25 °C and allowed to reach equilibrium. When equilibrium is established, the partial pressure of NO₂ has decreased by 1.24 atm. (a) What are the partial pressures of NO₂ and N₂O₄ at equilibrium? (b) Calculate K_p and K_c for following reaction at 25 °C. $2 \text{ NO}_2(g) \neq N_2O_4(g)$

(Answer: $K_{\rm p} = 2.80; K_{\rm c} = 68.6$)

Equilibrium Exercise #2a



Methanol is produced according to the following equation: $CO(g) + 2H_2(g) \neq CH_3OH(g)$

★ In an experiment, 1.000 mol each of CO and H₂ were allowed to react in a sealed 10.0-L reaction vessel at 500 K. When the equilibrium was established, the mixture was found to contain 0.0892 mole of CH₃OH. What are the equilibrium concentrations of CO, H₂ and CH₃OH? Calculate the equilibrium constants K_c and K_p for this reaction at 500 K? (R = 0.0821 L.atm/Mol.K)

(Answer: [CO] = 0.0911 *M*; [H₂] = 0.0822 *M*; [CH₃OH] = 0.00892 M; (b) $K_c = 14.5$; $K_p = 8.60 \times 10^{-3}$)

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Applications of Equilibrium Constant

For any system or reaction:

- 1. Knowing the equilibrium constant, we can predict whether or not a reaction mixture is at equilibrium, and we can predict the direction of net reaction.
 - $Q_c = K_c \square$ equilibrium (no net reaction)
 - $Q_{c} < K_{c} \square$ a net forward reaction;
 - $Q_c > K_c \square$ a net reverse reaction
- 2. The value of *K* tells us whether a reaction favors the products or the reactants.

Equilibrium constant is used to predict



The direction of net reaction

- For a reaction of known K_c value, the direction of net reaction can be predicted by calculating the reaction quotient, Q_c .
 - Q_{c} is called the *reaction quotient*, where for a reaction such as:

$$aA + bB \neq cC + dD;$$
 $Q_c = \frac{[C]^c[D]^a}{[A]^a[B]^b}$

Q_c has the same expression as K_c, but
 Q_c is calculated using concentrations that are not necessarily at equilibrium.

What does the reaction quotient tell us?



If $Q_c = K_c$, \Box the reaction is at equilibrium;

If $Q_c < K_c$, \Box the reaction is not at equilibrium and there's a net forward reaction;

If $Q_c > K_c$, \Box the reaction is not at equilibrium and there's a net reaction in the opposite direction.

sing the ICE table to calculate equilibrium



★ Equation: $H_2(g) + I_2(g) \neq 2 HI(g)$,
★ Initial [], M 0.1000 0.1000 0.0000
★ Change [], M -x -x +2x
★ Equilibrium [], M (0.1000 - x) (0.1000 - x) 2x

$$K_{\rm c} = \frac{[{\rm HI}]^2}{[{\rm H}_2][{\rm I}_2]} = \frac{(2x)^2}{(0.100 - x)^2} = 55.6$$

Calculation of equilibrium concentrations

$$\frac{2x}{(0.100 - x)} = \sqrt{55.6} = 7.46$$

$$2x = 0.746 - 7.46x; => 9.46x = 0.746$$

$$x = 0.0789;$$

$$[H_2] = [I_2] = 0.0211 \text{ M}; [HI] = 0.158 \text{ M}$$

Equilibrium Exercise #6



For the reaction:

 $2 \operatorname{NO}_2(g) \rightleftharpoons \operatorname{N}_2\operatorname{O}_4(g); \quad K_p = 1.27 \text{ at } 353 \text{ K.}$ If the initial pressure of NO_2 was 3.92 atm, and initially there was no $\operatorname{N}_2\operatorname{O}_4$, what are the partial pressures of the gases at equilibrium at 353 K? What is the total gas pressure at equilibrium?

(Answer: $P_{NO2} = 1.06 \text{ atm}; P_{N2O4} = 1.43 \text{ atm}; P_{total} = 2.49 \text{ atm}$)

Le Châtelier's Principle



✤ The Le Châtelier's principle states that:

when factors that influence an equilibrium are altered, the equilibrium will shift to a new position that tends to minimize those changes.

Factors that influence equilibrium:
 Concentration, temperature, and partial pressure (for gaseous)

The Effect of Changes in Concentration



♦ Consider the reaction: $N_2(g) + 3H_2(g) \neq 2 NH_3(g);$ $K_{\rm c} = \frac{[\rm NH]^2}{[\rm N_2][\rm H_2]^3}$

- If $[N_2]$ and/or $[H_2]$ is increased, $Q_c < K_c$
- | a net forward reaction will occur to reach new equilibrium position.
- ♦ If [NH₃] is increased, $Q_c > K_c$, and a net reverse reaction will occur to come to new equilibrium position.

and shift left when pressure increases



Consider the reaction:

 $2\mathrm{SO}_2(g) + \mathrm{O}_2(g) \not\rightleftharpoons 2\mathrm{SO}_3(g),$

- 1. The total moles of gas decreases as reaction proceeds in the forward direction.
- 2. If pressure is increased by decreasing the volume (compression), a forward reaction occurs to reduce the stress.
- 3. Reactions that result in fewer moles of gas favor high pressure conditions.

nation that shifts left when pressure increases, but shifts right when pressure decreases



Consider the reaction: $PCl_5(g) \neq PCl_3(g) + Cl_2(g);$

- 1. Forward reaction results in more gas molecules.
- 2. Pressure increases as reaction proceeds towards equilibrium.
- 3. If mixture is compressed, pressure increases, and reverse reaction occurs to reduce pressure;
- 4. If volume expands and pressure drops, forward reaction occurs to compensate.
- 5. This type of reactions favors low pressure condition

Reactions not affected by pressure changes



Consider the following reactions:

- 1. $CO(g) + H_2O(g) ≠ CO_2(g) + H_2(g);$ 2. $H_2(g) + Cl_2(g) ≠ 2HCl(g);$
- 2. Reactions have same number of gas molecules in reactants and products.
- 3. Reducing or increasing the volume will cause equal effect on both sides no net reaction will occur.
- 4. Equilibrium is not affected by change in pressure.

The Effect Temperature on Equilibrium



- ♦ Consider the following exothermic reaction: $N_2(g) + 3H_2(g) ≠ 2NH_3(g); \Delta H^0 = -92 kJ,$
- \clubsuit The forward reaction produces heat => heat is a product.
- When heat is added to increase temperature, reverse reaction will take place to absorb the heat;
- If heat is removed to reduce temperature, a net forward reaction will occur to produce heat.
- Exothermic reactions favor low temperature conditions.

Equilibrium Exercise #8



Determine whether the following reactions favor high or low pressures?

- 1. $2SO_2(g) + O_2(g) \neq 2SO_3(g);$
- 2. $PCl_5(g) \neq PCl_3(g) + Cl_2(g);$
- 3. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g);$
- 4. $N_2O_4(g) \neq 2 NO_2(g);$
- 5. $H_2(g) + F_2(g) \neq 2 HF(g);$

Equilibrium Exercise #9



Determine whether the following reactions favors high or low temperature?

1. $2SO_{2}(g) + O_{2}(g) \neq 2SO_{3}(g); \quad \Delta H^{0} = -180 \text{ kJ}$ 2. $CO(g) + H_{2}O(g) \neq CO_{2}(g) + H_{2}(g); \quad \Delta H^{0} = -46 \text{ kJ}$ 3. $CO(g) + Cl_{2}(g) \neq COCl_{2}(g); \quad \Delta H^{0} = -108 \text{ kJ}$ 4. $N_{2}O_{4}(g) \neq 2NO_{2}(g); \quad \Delta H^{0} = +57 \text{ kJ}$ 5. $CO(g) + 2H_{2}(g) \neq CH_{3}OH(g); \quad \Delta H^{0} = -270 \text{ kJ}$



Production of Sulfuric Acid, H₂SO₄;

1. $S_8(s) + 8 O_2(g) \rightarrow 8SO_2(g)$

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- 2. $2\text{SO}_2(g) + O_2(g) \rightleftharpoons 2\text{SO}_3(g); \quad \Delta H = -198 \text{ kJ}$
- 3. $SO_3(g) + H_2 \overline{SO}_4(l) \rightarrow H_2 S_2 O_7(l)$
- 4. $H_2 \tilde{S}_2 O_7(l) + H_2 O(l) \rightarrow 2 H_2 SO_4(l)$
- The second reaction is exothermic and has high *activation energy*;
- though thermodynamically favored the reaction is very slow at low temperature,.
 - At high temperature reaction goes faster, but the yield would be very low.
- An optimum condition is achieved at moderate temperatures and using catalysts to speed up the reaction. Reaction also favors high pressure.



The production of ammonia by the *Haber-Bosch* process:

- This reaction is exothermic and very slow at low temperature.
 Increasing the temperature will increase reaction rate, but will lower the yield.
- An optimum condition is achieved at moderate temperature of 250 to 300°C with catalyst added to increase the reaction rate.
- Increasing the pressure will favor product formation.
- Reaction favors low temperature and high pressure conditions.



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Questions for self control

1.The expression of the equilibrium constant for following reaction :





2)1.000 mole of H_2 gas and 1.000 mole of I_2 vapor are introduced into a 5.00-liter sealed flask. The mixture is heated to a certain temperature and the following reaction occurs until equilibrium is established.

 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ At equilibrium, the mixture is found to contain 0,316 mole of HI. What are the concentration of H_2 , at equilibrium? A)0mol/1 B) 0,042mol/1 C) 1mol/1 D)5mol/1

Questions for self control



 $2SO_2(g) + O_2(g) \neq 2 SO_3(g); \qquad \Delta H^o = -180 \text{ kJ}$

- A) When pressure is increased
- B) When pressure is decreased
- C) When temperature is increased
- D) When temperature is decreased
- E) When concentration of SO3 is increased
- F) When concentration of SO3 is decreased
- J) When concentration of O2 is increased.
- H) When concentration of O2 is decreased



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Do you have any questions?

