Topic 3.3. Chemical Equilibrium

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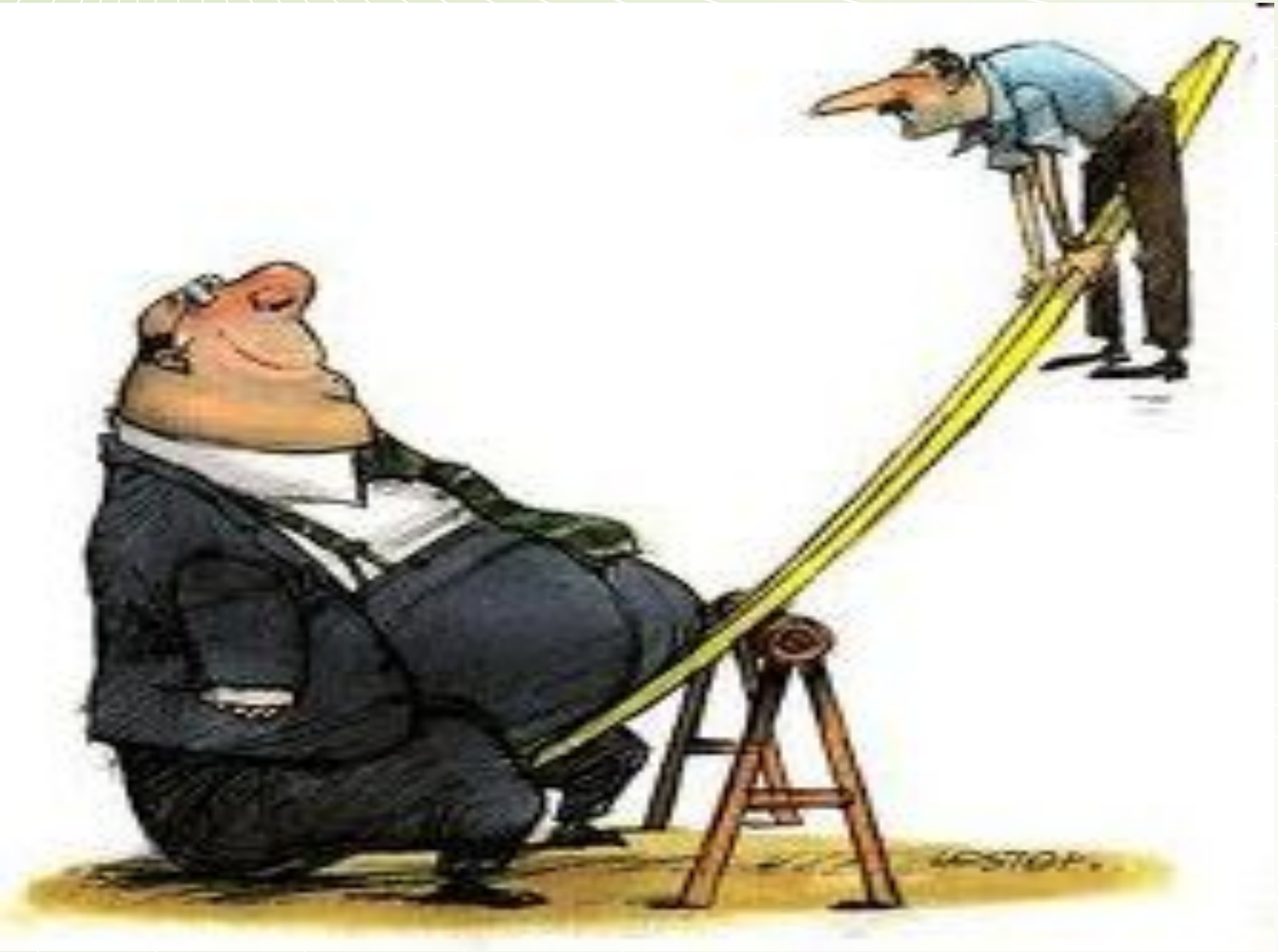
Outline

- **Introduction**
- **Main part**
- What is equilibrium?
- Expressions for equilibrium constants, K_c;
- 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**

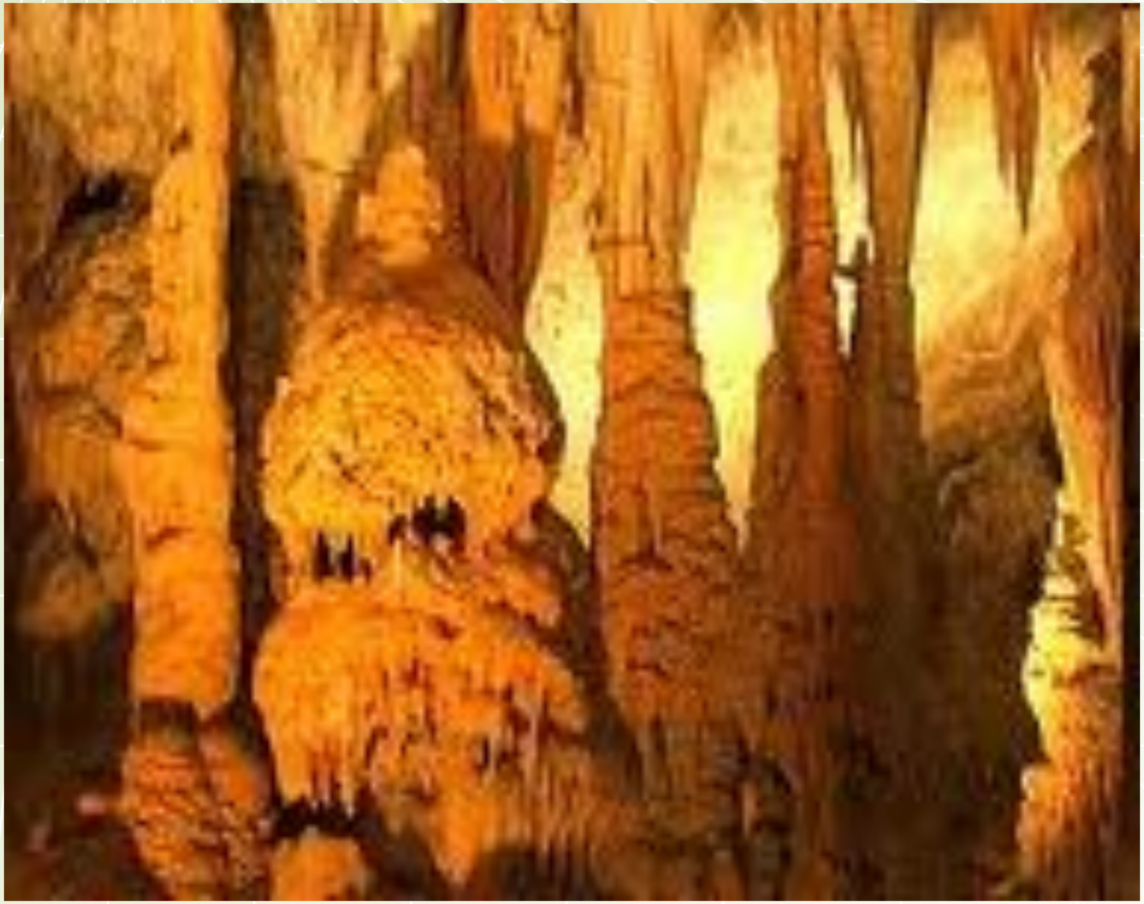
- **Literature**

What is Equilibrium?

This is not Equilibrium?



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



Chemical Equilibrium

- Consider the following reactions:

  $CaCO_3(s) + CO_2(aq) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$ ..(1)

  and

  $Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3(s) + CO_2(aq) + H_2O(l)$ ..(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:

$$wA + xB \rightleftarrows yC + zD$$

$$K_c = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

- The numerical value of K_c is calculated using the concentrations of reactants and products that exist at equilibrium.

Expressions for Equilibrium Constants

- Examples:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}; \quad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$PCl_{5}(g) \rightleftarrows PCl_{3}(g) + Cl_{2}(g); \quad K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$CH_{4}(g) + H_{2}(g) \rightleftarrows CO(g) + 3H_{2}(g);$$

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

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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.

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

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.

Calculating Equilibrium Constant for reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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	$H_2(g)$	+ $I_2(g)$ $\rightleftharpoons$	$2\ HI(g)$
Initial [ ], M:	0.200	0.200	0.000
Change in [ ], M:	-0.158	-0.158	+ 0.316
Equilibrium [ ], M	0.042	0.042	0.316

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.316)^2}{(0.042)^2} = 57$$

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 H_2 and I_2 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 H_2, I_2 and HI, and the equilibrium constant K_c for the following reaction:

$$H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)},$$

Calculating Equilibrium Constant

- The reaction: $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$, proceeds from right to left.
- ———————————————————————————————
- $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$
- ———————————————————————————————

	$H_2(g)$	$I_2(g)$	$2HI(g)$
Initial [ ], *M*:	0.000	0.000	0.500
Change in [ ], *M*:	+0.0525	+0.0525	-0.105
Equil'm [ ], *M*	0.0525	0.0525	0.395

- ———————————————————————————————

$$K_c = \frac{(0.395)^2}{(0.0525)^2} = 56.6$$

Expression and Value of Equilibrium Constant for a Reaction

- 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 and the expressions of equilibrium constants

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- The expression of equilibrium constant depends on how the equilibrium equation is written. For example, for the following equilibrium:
- $H_2(g) + I_2(g) \rightleftarrows 2\ HI(g)$; $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$
- For the reverse reaction:
- $2HI(g) \rightleftarrows H_2(g) + I_2(g)$; $K_c' = \dfrac{[H_2][I_2]}{[HI]^2} = 1/K_c$
- And for the reaction: $HI(g) \rightleftarrows \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$;

$$K_c'' = \sqrt{\frac{[H_2][I_2]}{[HI]^2}} = \sqrt{K_c'} = 1 / \sqrt{K_c}$$

Expression and Values of Equilibrium Constant Using Partial Pressures

- Consider the following reaction involving gases:

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

$$K_p = \frac{(P_{SO3})^2}{(P_{SO2})^2 (P_{O2})}$$

The Relationship between K_c and K_p

- Consider the reaction: $2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)}$
- $K_c = \dfrac{[SO]^2}{[SO_2]^2[O_2]}$ and $K_p = \dfrac{(P_{SO3})^2}{(P_{SO2})^2(P_{O2})}$
- Assuming ideal behavior,
- where $PV = nRT$ and $P = (n/V)RT = [M]RT$
- and $P_{SO3} = [SO_3]RT$; $P_{SO2} = [SO_2]RT$; $P_{O2} = [O_2]RT$

$$K_p = \frac{[SO_3]^2(RT)^2}{[SO_2]^2(RT)^2[O_2](RT)} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}(RT)^{-1} = K_c(RT)^{-1}$$

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Relationship between K_c and K_p

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

$$K_p = \frac{(P_{PCl3})(P_{Cl2})}{(P_{PCl5})} = \frac{[PCl_3](RT) \text{ x } [Cl_2](RT)}{[PCl_5](RT)}$$

$$= \frac{[PCl_3][Cl_2]}{[PCl_5]}(RT)^1 = K_C(RT)^1$$

Relationship between K_c and K_p

- In general, for reactions involving gases such that,

  - $a\mathrm{A} + b\mathrm{B} \rightleftarrows c\mathrm{C} + d\mathrm{D}$

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

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

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

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

Relationship between K_c and K_p

- For other reactions:
- 1. $2NO_2(g) \rightleftarrows N_2O_4(g)$; $K_p = K_c(RT)^{-1}$
- 2. $H_2(g) + I_2(g) \rightleftarrows 2\ HI(g)$; $K_p = K_c$
- 3. $N_2(g) + 3H_2(g) \rightleftarrows 2\ NH_3(g)$; $K_p = K_c(RT)^{-2}$

Homogeneous & Heterogeneous Equilibria

Homogeneous equilibria:

$CH_4(g) + H_2O(g) \rightleftarrows CO(g) + 3H_2(g)$;

$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$;

Heterogeneous equilibria:

$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$;

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

$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2\,Cl^-(aq)$;

Equilibrium Constant Expressions for Heterogeneous System

- Examples:

$$CaCO_{3}(s) \rightleftarrows CaO(s) + CO_{2}(g);$$

$$K_c = [CO_2] \qquad K_p = P_{CO2}; \quad K_p = K_c(RT)$$

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

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

Solubility Eqilibrium

$$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^{-}(aq);$$

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2$$

(K_{sp} is called *solubility product*)

Combining Equations and Equilibrium Constants

- when two or more equations are added to yield a net equation, the equilibrium constant for the net equation, K_{net}, is equal to the product of equilibrium constants of individual equations.
- For example,

Eqn(1): A + B ⇄ C + D; $K_1 = \dfrac{[C][D]}{[A][D]}$

Eqn(2): C + E ⇄ B + F; $K_2 = \dfrac{[B][F]}{[C][E]}$

Combining Equations and Equilibrium Constants

❖ *Net* equation: A + E ⇄ D + F;

$$K_{net} = K_1 \text{ x } K_2 = \frac{[D][F]}{[A][E]}$$

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

Equilibrium Exercise #1

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A flask is charged with 2.00 atm of nitrogen dioxide and 1.00 atm of dinitrogen tetroxide at 25 ºC and allowed to reach equilibrium. When equilibrium is established, the partial pressure of NO_2 has decreased by 1.24 atm. (a) What are the partial pressures of NO_2 and N_2O_4 at equilibrium? (b) Calculate K_p and K_c for following reaction at 25 ºC.

$$2\ NO_{2(g)} \rightleftarrows N_2O_{4(g)}$$

(Answer: $K_p = 2.80$; $K_c = 68.6$)

Equilibrium Exercise #2a

- Methanol is produced according to the following equation:
- $CO_{(g)} + 2H_{2(g)} \rightleftarrows CH_3OH_{(g)}$
- In an experiment, 1.000 mol each of CO and H_2 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 CH_3OH. What are the equilibrium concentrations of CO, H_2 and CH_3OH? 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*; [H_2] = 0.0822 *M*; [CH_3OH] = 0.00892 M;
(b) $K_c = 14.5$; $K_p = 8.60 \times 10^{-3}$)

Equilibrium Exercise #2a

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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.
   - $Q_c = K_c$ □ equilibrium (no net reaction)
   - $Q_c < K_c$ □ a net forward reaction;
   - $Q_c > K_c$ □ 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:
- $a\text{A} + b\text{B} \rightleftarrows c\text{C} + d\text{D}$; $\quad Q_c = \dfrac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$
- 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 $Q_c = K_c$, the reaction is at equilibrium;

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

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

Using the ICE table to calculate equilibrium concentrations

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

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(0.100 - x)^2} = 55.6$$

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:

$$2\ NO_2(g) \rightleftarrows N_2O_4(g); \quad K_p = 1.27 \text{ at } 353\text{ K.}$$

If the initial pressure of NO_2 was 3.92 atm, and initially there was no N_2O_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 atm; P_{N2O4} = 1.43 atm; P_{total} = 2.49 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: $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2\ NH_{3(g)}$;

$$K_c = \frac{[NH]^2}{[N_2][H_2]^3}$$

- 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 $[NH_3]$ is increased, $Q_c > K_c$, and a net reverse reaction will occur to come to new equilibrium position.

Reactions that shift right when pressure increases and shift left when pressure decreases

Consider the reaction:

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g),$$

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.

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

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

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. $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$;
2. $H_2(g) + Cl_2(g) \rightleftarrows 2HCl(g)$;

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

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- Consider the following exothermic reaction:

  $N_{2}(g) + 3H_{2}(g) \rightleftarrows 2NH_{3}(g)$; $\Delta H^{o} = -92$ kJ,

- 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

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Determine whether the following reactions favor high or low pressures?

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

Equilibrium Exercise #9

- Determine whether the following reactions favors high or low temperature?

1. $2SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$; $\Delta H^o = -180$ kJ
2. $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$; $\Delta H^o = -46$ kJ
3. $CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$; $\Delta H^o = -108$ kJ
4. $N_2O_4(g) \rightleftarrows 2\ NO_2(g)$; $\Delta H^o = +57$ kJ
5. $CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$; $\Delta H^o = -270$ kJ

Chemical Equilibria in Industrial Processes

Production of Sulfuric Acid, H_2SO_4;

1. $S_{8(s)} + 8\,O_{2(g)} \rightarrow 8SO_{2(g)}$
2. $2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)}$; $\Delta H = -198$ kJ
3. $SO_{3(g)} + H_2SO_{4(l)} \rightarrow H_2S_2O_{7(l)}$
4. $H_2S_2O_{7(l)} + H_2O_{(l)} \rightarrow 2H_2SO_{4(l)}$

- 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.

Chemical Equilibria in Industrial Processes

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

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g); \quad \Delta H = -92 \text{ kJ}$$

- 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 :

$$wA + xB \rightleftarrows yC + zD$$

A) K= $\dfrac{[C]^y[D]^z}{[A]^w[B]^x}$

B) K= $\dfrac{[A]^w[B]^x}{[C]^y[D]^z}$

C) K= $\dfrac{[yC]\ [zD]}{[wA]\ [xB]}$

Questions for self control

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.

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

At equilibrium, the mixture is found to contain 0,316 mole of HI. What are the concentration of H_2, at equilibrium?

A)0mol/l

B) 0,042mol/l

C) 1mol/l

D)5mol/l

Questions for self control

3.On the base Le-Shatelie principle predict the reaction direction of following reaction :

$2SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$; $\Delta H^o = -180\ kJ$

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?