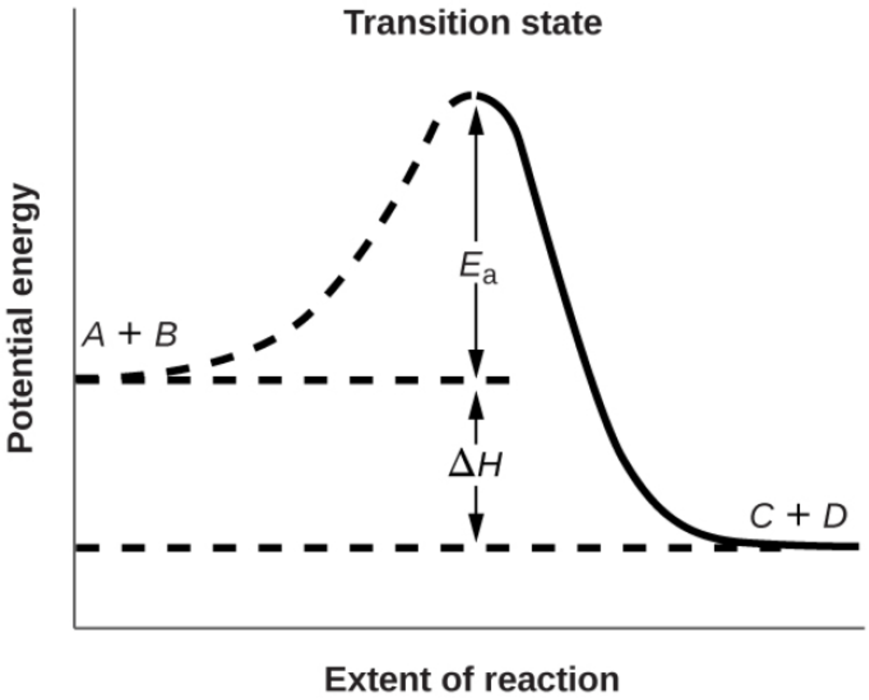
Chapter 13 Part 1

Dr. Turner

Reaction Reversibility

- Forward Reaction
- Reverse Reaction
- Reversible Reactions
- Collision Theory
- Equilibrium



Reversible Reactions

Reversible Reaction

$$N_2O_4(g) \leftrightharpoons 2\ N_2O_2(g)$$

Forward Reaction

$$N_2O_4(g) \rightarrow 2\ N_2O_2(g)$$

Reverse Reaction

$$2\ N_2O_2(g) \rightarrow N_2O_4(g)$$

Chemical Equilibrium

- Chemical equilibrium is established when
  - The forward reaction and reverse reactions occur at the same rate
  - The concentrations of products and reactants remain constant
- Reversible reactions are most likely when reactions are run in a closed system so that the products cannot escape

Chemical Equilibrium

$$Br_2(l) \leftrightharpoons Br_2(g)$$

- The liquid bromine will evaporate to gaseous bromine and condense back to liquid bromine until an equilibrium is reached between the two states
- The pressure of the gaseous state once the equilibrium has been reached is the equilibrium vapor pressure

Equilibrium

At equilibrium ____.

A. the amount of reactants and products are equal
B. the rate of the forward and reverse reactions are equal
C. no new products or reactants are formed
D. the reaction arrow (→) is written as an equals sign (=)

Reaction Quotients

- Reaction Quotients tell the ratio of the concentrations of the products and reactants at any one point between the initial mixing of the reactant until the establishment of equilibrium
- For the reaction,

$$mA + nB \leftrightharpoons xC + yD$$

- The reaction quotient (Q) is equal to

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

Products (numerator)

Reactants (denominator)

Reaction Quotients

$$mA + nB \leftrightharpoons xC + yD$$

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

For the reaction $N_2O_4(g) \leftrightharpoons 2NO_2(g)$, the reaction quotient is

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

The reaction quotient is unitless

Evaluating Reaction Quotients

Provide the reaction quotient expression for the reaction

$$CO(g) + 2\ H_2(g) \leftrightharpoons CH_3OH(g)$$

and evaluate it for the initial concentrations

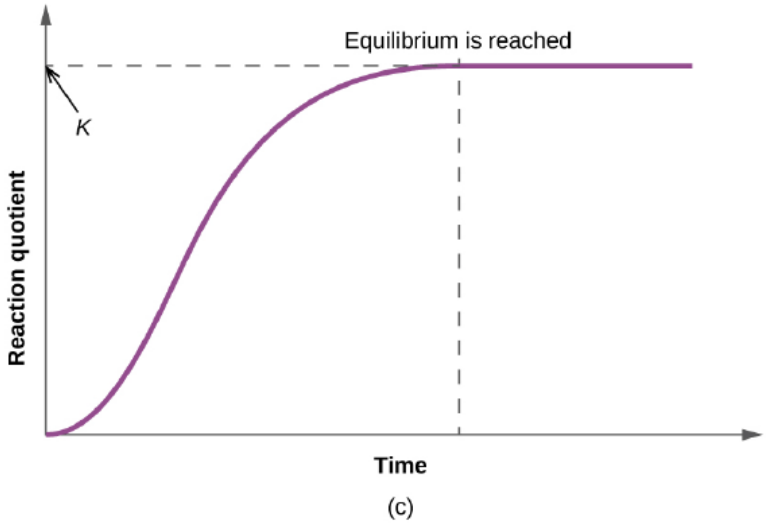
A. $[CO] = 1.000\ M, [H_2] = 1.000\ M, [CH_3OH] = 0.000\ M$
B. $[CO] = 1.000\ M, [H_2] = 1.000\ M, [CH_3OH] = 1.000\ M$
C. $[CO] = 0.500\ M, [H_2] = 0.250\ M, [CH_3OH] = 1.000\ M$

Equilibrium Constant (K)

- When a mixture of reactants and products reaches equilibrium at a given temperature, its reaction quotient always has the same value.
- This value is called the equilibrium constant (K) and is unitless

$$Q_c \text{ at equilibrium} = K_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

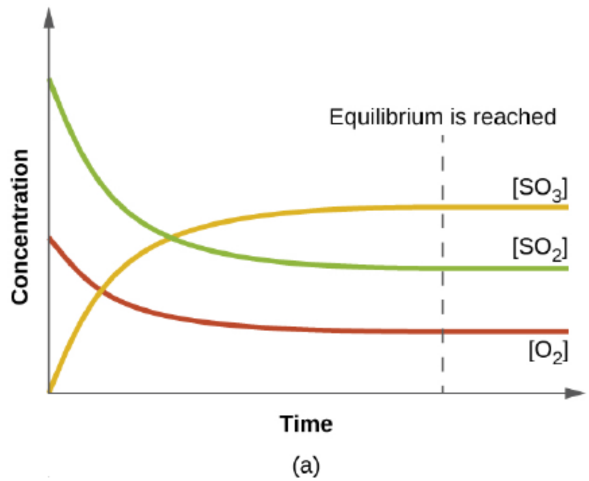
Establishing Equilibrium

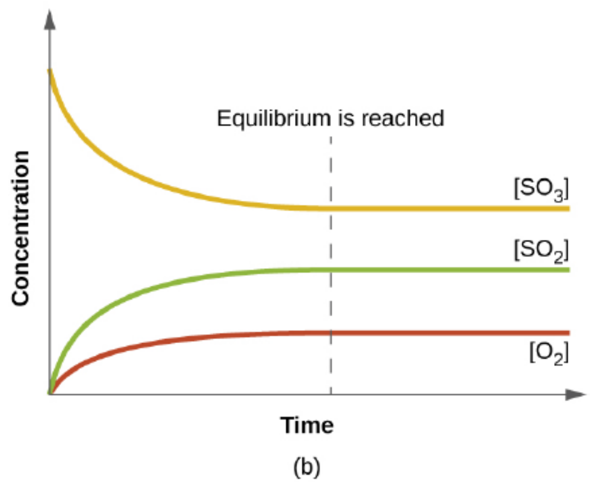


$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

Establishing Equilibrium





$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

a) The change in the concentrations of reactants and products is depicted as the $2\ SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium.

b) The change in concentrations of reactants and products is depicted as the reaction $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$ approaches equilibrium.

The Magnitude of K and Its Meaning

Would a large value of K_c mean that there are relatively more reactants or products at equilibrium?

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The Magnitude of K and Its Meaning

- The value of K for a reaction gives quantitative information about the extent of the reaction. reactants ⇌ products
- If the forward and reverse reactions are equally favored, then [reactants] ≈ [products] at equilibrium, and K ≈1.
- If the forward reaction is favored, then [reactants] ≪ [products] at equilibrium, and K ≫ 1.
- If the reverse reaction is favored, then [reactants] ≫ [products] at equilibrium, and K ≪ 1.

The Magnitude of K and Its Meaning

Which equilibrium constant value indicates that the reverse reaction is favored?

A. $K = 1.0 \times 10^{6}$

B. $K = -1.0 \times 10^{6}$

C. $K = 1.0 \times 10^{-6}$

D. $K = -1.0 \times 10^{-6}$

Equilibrium Constant

Evaluate the equilibrium constant for the reaction

$$CO(g) + 2\ H_2(g) \leftrightharpoons CH_3OH(g)$$

if the equilibrium concentration of the reactants are $[CO] = 0.0911\ M, [H_2] = 0.0822\ M, [CH_3OH] = 0.00892\ M.$

Calculating Equilibrium Constants

Calculate K_c for this reaction at 735 K when the reactants each have a concentration of 1 M and the product concentration is 7 M.

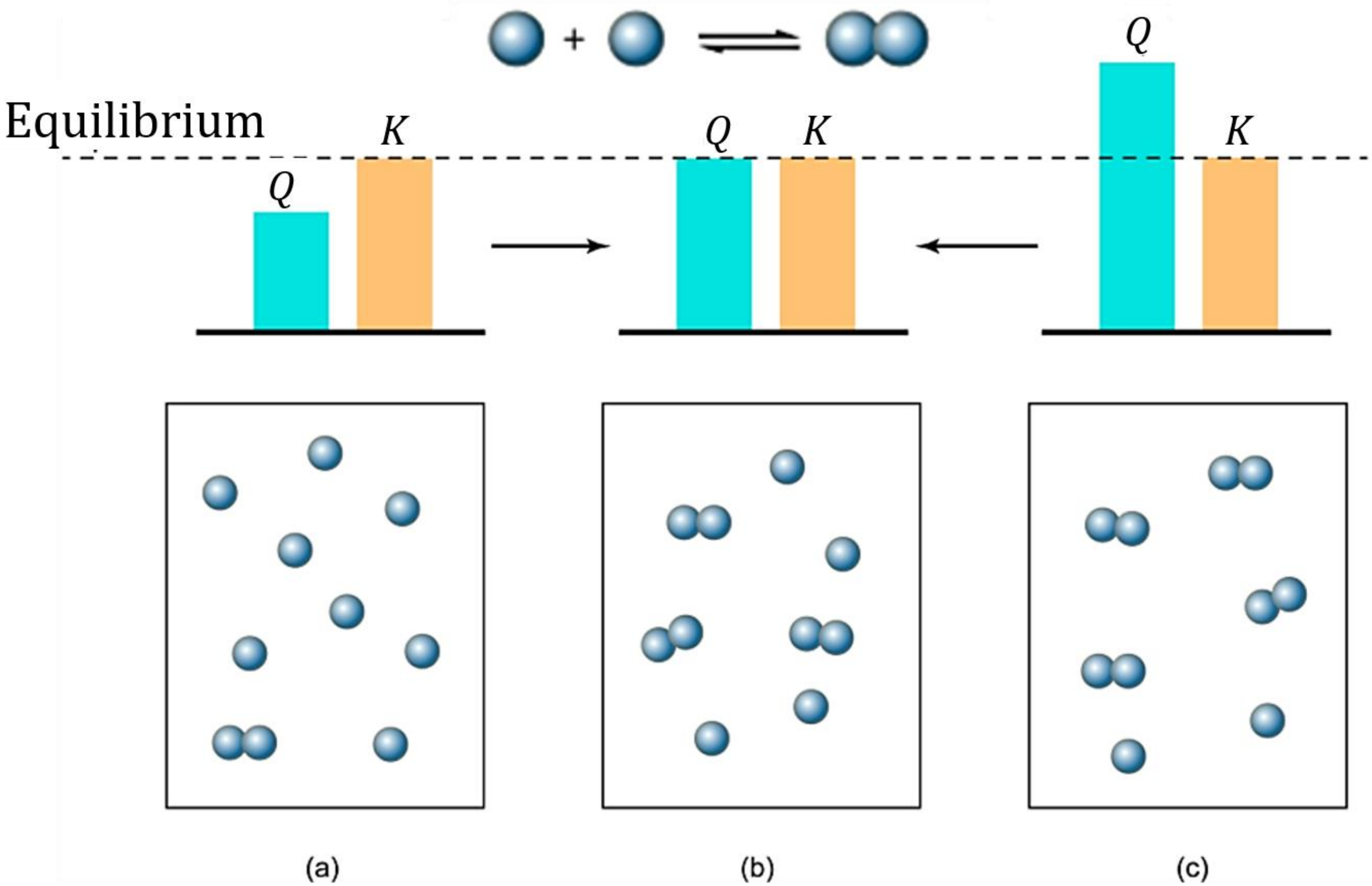
$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

A. 730
B. 49
C. 7
D. 0.14
E. 0.02

Predicting the Direction of a Reaction

- You can predict the direction in which the reaction will shift by comparing the values of Q and K:
  - When $Q = K$, the reaction is at equilibrium (no shift occurs).
  - When $Q > K$, more reactants must be formed to achieve equilibrium and the reaction shifts left.
  - When $Q < K$, more products must be formed to achieve equilibrium and the reaction shifts right.

Q, K and the Direction of a Reaction



Q, K and the Direction of a Reaction

$K_c = 377$ at 22°C for the decomposition of BrCl gas to give gaseous bromine and chlorine. $2\ BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

A. Calculate Q_c for this reaction when the reaction mixture contains 0.32 M Br_2, 0.37 M Cl_2, and 0.15 M BrCl.

B. Is the reaction at equilibrium? If not, will it proceed to form more reactants or more products?

Establishing equilibrium

When $Q > K$, which statement is true?

A. More reactants will be formed to achieve equilibrium.
B. More reactants will be consumed to achieve equilibrium.
C. More products will be formed to achieve equilibrium.
D. The reaction is at equilibrium.

K and Q Summary

- If $Q < K$, the reaction will shift towards the products
- If $Q = K$, the reaction is at equilibrium
- If $Q > K$, the reaction will shift towards the reactants

Homogeneous Equilibrium

- A homogeneous equilibrium is one in which all of the reactants or products are present in the same phase
- We will primarily focus on equilibria occurring in liquid phase solutions and gas phase solutions
- When writing equilibrium expressions, solids and liquids to do not appear in the equilibrium expression

Writing Equilibrium Expressions

Write an equilibrium expression for each of the following reactions

A. $I_2(aq) + I^-(aq) \leftrightharpoons I_3^-(aq)$

B. $HF(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + F^-(aq)$

C. $Hg_2{}^{2+}(aq) + NO_3{}^-(aq) + 3\ H_3O^+(aq) \leftrightharpoons 2\ Hg^{2+}(aq) + HNO_2(aq) + 4H_2O(l)$

Writing Equilibrium Expressions

Write an equilibrium expression for each of the following reactions

A. $3\ O_2(g) \leftrightharpoons 2\ O_3(g)$

B. $N_2(g) + 3\ H_2(g) \leftrightharpoons 2\ NH_3(g)$

C. $C_3H_8(g) + 5\ O_2(g) \leftrightharpoons 3\ CO_2(g) + 4H_2O(g)$

Equilibrium and Ideal Gases

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

$$P = MRT$$

Equilibrium and Ideal Gases

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = MRT$$

Thus the pressure of an ideal gas is directly proportional to it's concentration!

Equilibrium and Ideal Gases

For the following reaction where A, B, C, and D are all gases

$$m\ \mathrm{A(g)} + n\ \mathrm{B(g)} \leftrightharpoons x\ \mathrm{C(g)} + y\ \mathrm{D(g)}$$

The reaction quotient (Q) and equilibrium expressions may be written using the partial pressures, in atmospheres, in place of the concentrations

$$\mathrm{Q_p} = \mathrm{K_p} = \frac{(\mathrm{P_C})^x(\mathrm{P_D})^y}{(\mathrm{P_A})^m(\mathrm{P_B})^n}$$

Where $\mathrm{P_A}$, $\mathrm{P_B}$, $\mathrm{P_C}$, and $\mathrm{P_D}$ are the partial pressures of A, B, C, and D, respectively.

Writing K_p Expressions

Write K_p expression for each of the following reactions using the partial pressures of the gases

A. $3\ O_2(g) \leftrightharpoons 2\ O_3(g)$

B. $N_2(g) + 3\ H_2(g) \leftrightharpoons 2\ NH_3(g)$

C. $C_3H_8(g) + 5\ O_2(g) \leftrightharpoons 3\ CO_2(g) + 4H_2O(g)$

Using the K_p Expression

The equilibrium between N_2O_4 and NO_2 has a K_p value of 47.9 at 400 K. Calculate the partial pressure of NO_2 in a sealed vessel at 400 K if the partial pressure of N_2O_4 is 0.335 atm.

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

Relating K_c to K_p

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

$$\Delta n = (\text{sum of coeficients of gaseous products}) - (\text{sum of coeficients of gaseous reactants})$$

- R is the ideal gas constant $\left(0.0821 \frac{\text{L atm}}{\text{mol K}}\right)$
- T is the temperature in Kelvin

Finding Δn

Determine Δn for the following reactions

A. $3\ O_2(g) \leftrightharpoons 2\ O_3(g)$
B. $N_2(g) + 3\ H_2(g) \leftrightharpoons 2\ NH_3(g)$
C. $C_3H_8(g) + 5\ O_2(g) \leftrightharpoons 3\ CO_2(g) + 4H_2O(g)$

Relating K_c to K_p

Write the equations for the conversion of K_p to K_c for each of the following reactions

A. $3\ O_2(g) \leftrightharpoons 2\ O_3(g)$

B. $N_2(g) + 3\ H_2(g) \leftrightharpoons 2\ NH_3(g)$

C. $C_3H_8(g) + 5\ O_2(g) \leftrightharpoons 3\ CO_2(g) + 4H_2O(g)$

Relating K_c to K_p

The reaction below has $K_c = 1.2 \times 10^{-4}$ at 1000.0°C. Calculate K_p for this reaction.

$$F_2(g) \rightleftharpoons 2\ F(g)$$

Heterogeneous Equilibrium

- Heterogeneous Equilibrium is a system in which reactants and products are found in two or more phases
- When writing equilibrium expressions, remember that solids and liquids to do not appear in the equilibrium expression

Writing Equilibrium Expressions

Write an equilibrium expression for each of the following reactions

A. $AgCl(s) \leftrightharpoons Ag^{+}(aq) + Cl^{-}(aq)$

B. $CaO(s) + CO_2(g) \leftrightharpoons CaCO_3(s)$

C. $H_2O(l) \leftrightharpoons H_2O(g)$ (include states)