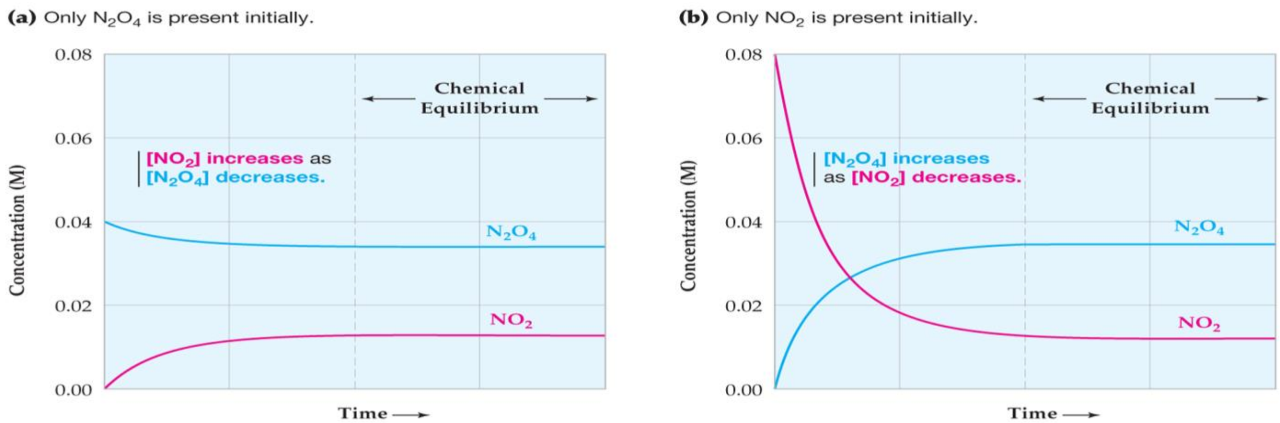
Chapter 15 - Chemical Equilibrium

Many reactions do not go to completion instead of reaching an **equilibrium state**

15.1- Chemical Equilibrium -The Concept of Dynamic Equilibrium:

- The state reached when the concentrations of reactants and products remain constant over time.
  - The rate forward and reverse have become equal
    - **Chemical equilibrium ($\rightleftharpoons$) is reversible .** Reaction occurs in both direction

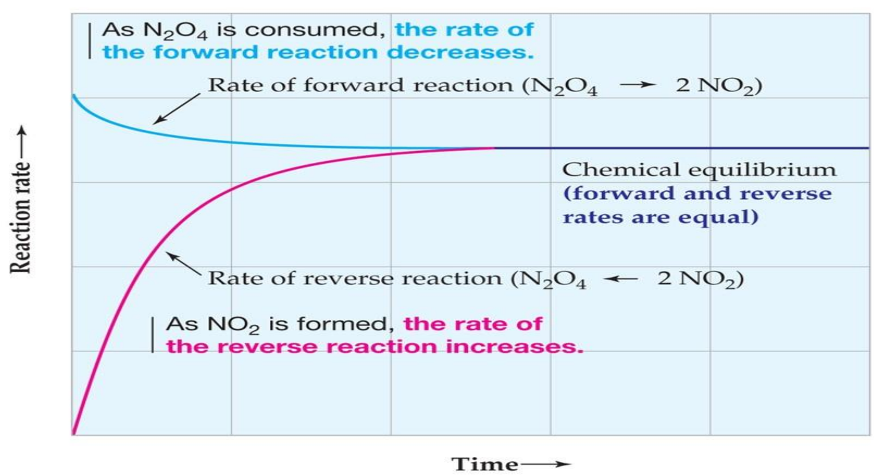
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



In both experiments, a state of chemical equilibrium is reached when the concentrations level off at constant values: $[N_2O_4]$ = 0.0337 M; $[NO_2]$ = 0.0125 M.

Equilibrium is a **dynamic process.** The conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules.

Rate forward = k_f $[N_2O_4]$ = Rate reverse = k_r $[NO_2]^2$



When the two rates become equal, an equilibrium state is attained and there are no further changes in concentrations.

15.2 – 15.3:The Equilibrium Constant, K_c and K_p

Law of mass action - The value of the equilibrium constant expression, **K_c,** is constant for a given reaction at equilibrium and at a constant temperature.

- The equilibrium concentrations of reactants and products may vary, but the value for **K_c** remains the same.

Other Characteristics of K_c

1) Equilibrium can be approached from either direction.
2) K_c does not depend on the initial concentrations of reactants and products.
3) K_c does depend on temperature.
4) K_c value is written without units

Because the molarity of each substance is divided by its molarity (1M) in thermodynamic sate

For a reaction $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant, **K_c**, is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients

Equilibrium constant

Coefficients

$$K_c = \frac{[C]^c[D]^d}{\underbrace{[A]^a[B]^b}_{\text{Equilibrium constant expression when concentrations are used}}}$$

Coefficients

Table 15.1 Concentration Data at 25 °Celsius for the Reaction

	Initial Concentrations (M)	Initial Concentrations (M)	Equilibrium Concentrations (M)	Equilibrium Concentrations (M)	Equilibrium Constant Expression
Experiment	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2 / [N_2O_4]$
1	0.0400	0.0000	0.0337	0.0125	4.64×10^{-3}
2	0.0000	0.0800	0.0337	0.0125	4.64×10^{-3}
3	0.0600	0.0000	0.0522	0.0156	4.66×10^{-3}
4	0.0000	0.0600	0.0246	0.0107	4.65×10^{-3}
5	0.0200	0.0600	0.0429	0.0141	4.63×10^{-3}

Experiment 1

Experiment 5

Writing Equilibrium Expression

- Simply write the chemical formula products over the chemical formula of the reactants
- For **homogenous** equilibrium
  - Reactants and products are in the same phases
  - E.g $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)$

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

The equilibrium constant and the equilibrium constant expression are for the chemical equation **as written**.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\qquad K_c = \dfrac{[NH_3]^2}{[N_2]\,[H_2]^3}$

$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ $\qquad K'_c = \dfrac{[N_2]\,[H_2]^3}{[NH_3]^2} = \dfrac{1}{K_c}$

$2N_2(g) + 6H_2(g) \rightarrow 4NH_3(g)$ $\qquad K''_c = \dfrac{[NH_3]^4}{[N_2]^2\,[H_2]^6} = Kc^2$

When you add equations to get a new equation, the equilibrium constant of the new equation is the product of the equilibrium constants of the old equations.

$$\begin{array}{lcl} A & \rightleftharpoons & \cancel{2B} \\ \cancel{2B} & \rightleftharpoons & 3C \\ \hline A & \rightleftharpoons & 3C \end{array}$$

$K_1 = \dfrac{[B]^2}{[A]}$

$K_2 = \dfrac{[C]^3}{[B]^2}$

Determine $K_{overall}$

$K_{overall} = K_1 \times K_2$

The Equilibrium Constant K_p

- When writing an equilibrium expression for a gaseous reaction in terms of partially pressure, we call it equilibrium constant, K_p

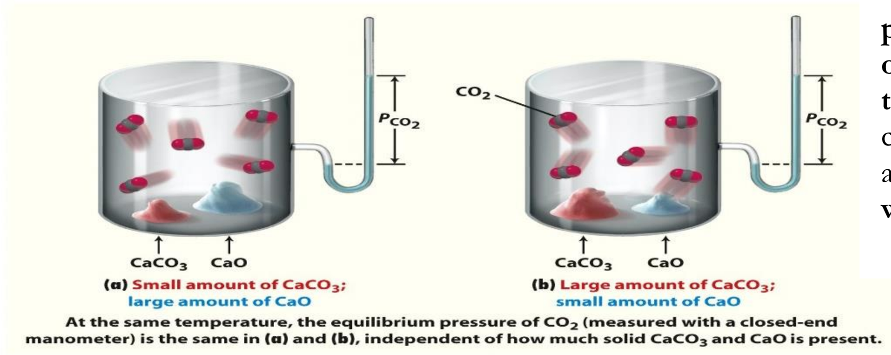
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\mathbf{K_p} = \frac{(P_{NO2})^2}{P_{N2O4}}$$

$K_c = ???$

- For **heterogeneous** equilibrium
  - Reactants and products are in different phases

E.g $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ **$K_c = [CO_2]$**

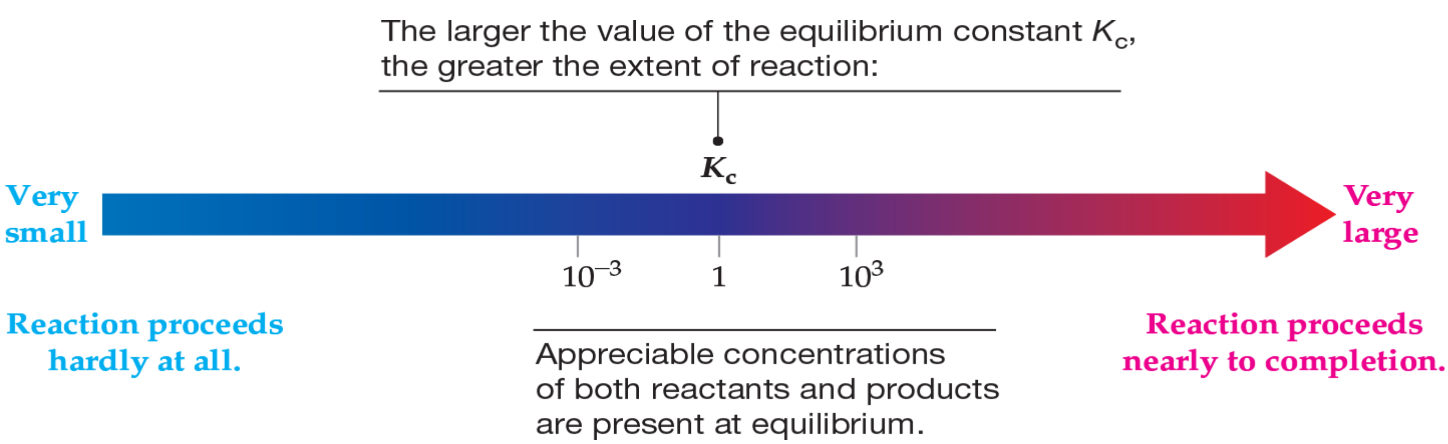


pure solids and liquids: concentrations of pure solids and liquids are fixed by their density and molar mass (both constants) and do not vary with the amount. **They are not included when writing an equilibrium equation.**

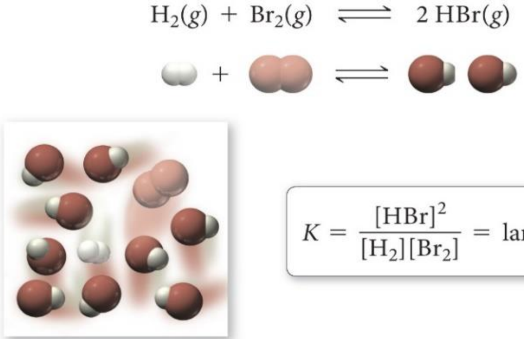
$$\text{Concentration} = \mathbf{M} = \frac{\textbf{Density}}{\textbf{Molar Mass}}$$

15.5 Using the Equilibrium Constant

Knowing the value of the equilibrium constant for a chemical reaction lets us judge the extent of the reaction, predict the direction of the reaction, and calculate equilibrium concentrations from initial concentrations.



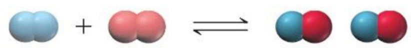
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$

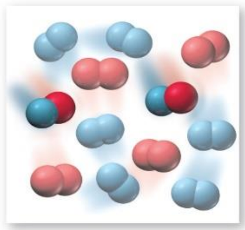


$$K = \frac{[HBr]^2}{[H_2][Br_2]} = \text{large number}$$

When the value of $K_{eq} >> 10^3$, when the reaction reaches equilibrium there will be many more product molecules present than reactant molecules.
The position of equilibrium favors products

$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$





$$K = \frac{[NO]^2}{[N_2][O_2]} = \text{small number}$$

When the value of $K_{eq} << 10^{-3}$, when the reaction reaches equilibrium there will be many more reactant molecules present than product molecules.
The position of equilibrium favors reactants.

Example: When wine spoils, ethanol is oxidized to acetic acid as O_2 from the air reacts with the wine:

$CH_3CH_2OH(aq) + O_2(aq) \rightleftharpoons CH_3CO_2H(aq) + H_2O(l)$

Ethanol Acetic acid

The value of K_c for this reaction at 25 °C is 1.2×10^{82}. What are the relative amounts of ethanol and acetic acid once the reaction has reached equilibrium?

A. The concentration of ethanol will be significantly greater than the concentration of acetic acid.
B. The concentration of ethanol will be nearly the same as the concentration of acetic acid.
C. The concentration of ethanol will be slightly less than the concentration of acetic acid.
D. The concentration of ethanol will be extremely small and much less than the concentration of acetic acid.

Relating the Equilibrium Constant K_p and K_c

The constant K_c an K_p are related because the pressure of each component in a mixture of ideal gases directly proportional to its molar concentration.

$$aA + bB \rightleftharpoons cC + dD$$

For component A $P_AV = n_ART$ (Ideal Gas Law)

$$P_A = \frac{n_A}{V} RT = [A]\,RT$$

Similarly, $P_B = [B]RT$, $P_C = [C]RT$, and $P_D = [D]RT$. The equilibrium equation for K_p is therefore given by

$$K_p = \frac{(P_C)^c\,(P_D)^d}{(P_A)a\,(P_B)^b} = \frac{([C]RT)^c\,([D]RT)^d}{([A]RT)^a\,([B]RT)^b} = \frac{[C]^c\,[D]^d}{[A]^c\,[B]^d} x\,(RT)^{(c+d)-(a+b)}$$

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

R = gas constant (0.08206 L•atm/K•mol)

T = Temperature (in K)

Δn = is the number of moles of **gaseous** products **minus** the number of moles of gaseous reactants.

Example: For the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(a) write the equilibrium constant expression, K_p and K'_p?

(b) What is the value for K_p if $K_c = 2.8 \times 10^2$ at 1000 K?

(c) What is the value of K'_c?

Predicting the Direction of Reaction from initial concentrations

- For a chemical system whether in equilibrium or not, we can calculate the value given by the law of mass action. We called it **reaction quotient, Q_c**
- The reaction quotient, Q_c, is defined in the same way as the equilibrium constant, K_c, except that the concentrations in Q_c are not necessarily equilibrium values

$$aA + bB \rightleftharpoons cC + dD \qquad Q_c = \frac{[C]_i^c [D]_i^d}{[A]_i^a [B]_i}$$

If **Q > K**, the reaction will go to the left.

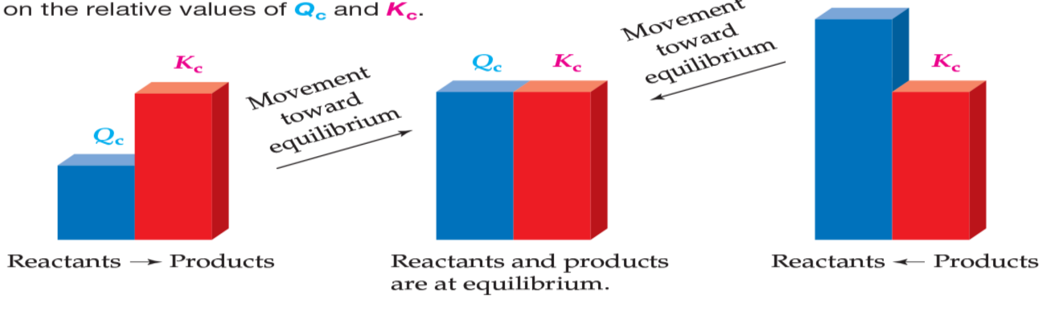
• The ratio of products over reactants is too large & the reaction will move toward equilibrium by forming more reactants.

If Q < K, the reaction will go to the right.

• The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.

If **Q = K**, the reaction mixture is already at equilibrium, so no shift occurs.

The direction of net reaction depends on the relative values of Q_c and K_c.



Movement toward equilibrium changes the value of Q_c until it equals K_c, but the **value of K_c** remains constant.

Example: For the reaction, B $\rightleftharpoons$ 2A, $K_c = 2.0$. Suppose 3.0 moles of A and 3.0 moles of B are introduced into a 2.00 L flask. (a) In which direction will the reaction proceed to attain equilibrium?

(b) Will the concentration of B increase, decrease or remain the same as the system moves towards equilibrium?

Calculating the Equilibrium Constant from Measured Equilibrium Concentrations

a. Using the balanced equation as a guide

b. Prepare an ICE table (what is an ICE table?)

- **(I)** - The initial concentrations
- **(C)** - The change in concentration on going to equilibrium, defined as x
- **(E)** - The equilibrium concentration

c. For the reactant or product whose concentration is known both initially and at equilibrium

d. Calculate the change in concentration that occurs

e. Complete the table by sum each column for each reactant and product then determine the concentrations for all at equilibrium

f. Write the equilibrium constant expression then substitute all the values from the table to calculate $\mathbf{K_c}$ **or** $\mathbf{K_p}$

Example: Consider the following reaction:

A reaction mixture at 780°C initially contains [CO] = 0.500M and [H_2] = 1.00M. At equilibrium, [CO] is found to be 0.150M. What is the value of K_c?

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

Finding Equilibrium concentrations from Initial Concentrations

- Steps to follow in calculating equilibrium concentrations from initial concentration
  - Write a balance equation for the reaction
  - Make an ICE (**Initial, Change, Equilibrium**) table
  - Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x
  - Calculate the equilibrium concentrations form the calculated value of x
  - Check your answers

Calculating Equilibrium Concentrations

- Sometimes you must use quadratic equation to solve for x, choose the mathematical solution that makes chemical sense

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

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

For homogeneous equilibrium

	$aA(g)$ $\rightleftharpoons$	$bB(g)$ +	$cC(g)$
Initial concentration (M)	$[A]_{initial}$	$[B]_{initial}$	$[C]_{initial}$
Change in concentration(unknown M)	**- ax**	**+ bx**	**+ cx**
Equilibrium	$[A]_{initial}$ **- ax**	$[B]_{initial}$ **+ bx**	$[C]_{initial}$ **+ cx**

For heterogeneous equilibrium

	$aA(g)$ $\rightleftharpoons$	$bB(g)$ +	$cC(s)$
Initial concentration (M)	$[A]_{initial}$	$[B]_{initial}$	N/A
Change in concentration(unknown M)	**- ax**	**+ bx**	**N/A**
Equilibrium	$[A]_{initial}$ **- ax**	$[B]_{initial}$ **+ bx**	N/A

Example: At 700 K, 0.500 mol of H_2 and I_2 is added to a 2.00 L container and allowed to come to equilibrium. Calculate the equilibrium concentrations of H_2, I_2, and HI . K_c is 57.0 at 700 K.

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

Example: Under certain conditions, the equilibrium constant K_c for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 in a mixture that initially contained only PCl_5 at a concentration of 1.00 M?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Approximate Solution (The 5% error rule)

Example: What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ $\quad\quad$ $Kc = 4.9\times10^{-10}$

Example: The equilibrium constant for the reaction is 2.44 at 1000 K. What are the equilibrium partial pressures of , CO, and if the initial partial pressures are $P_{H2O} = 1.20$ atm, $P_{CO} = 1.00$ atm , and $P_{H2} = 1.40$?

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$