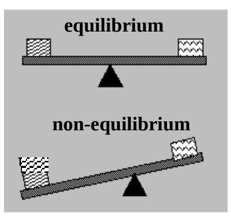
Principles of Reactivity: Chemical Equilibria

This chapter addresses the *principle of equilibrium*

What can you do to reestablish equilibrium?



Whose principle supports this?

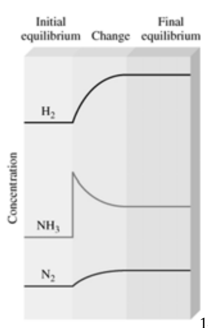
Le Châtelier's Principle

If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

• Changes in Concentration

$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

Equilibrium shifts left to offset stress ← Add NH_3



14.5

Le Châtelier's Principle

• Changes in Concentration continued

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

Change	Shifts the Equilibrium
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

Le Châtelier's Principle

• Changes in Volume and Pressure

$$A\ (g) + B\ (g) \rightleftharpoons C\ (g)$$

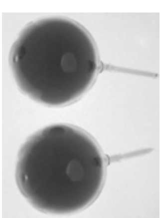
Change	Shifts the Equilibrium
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

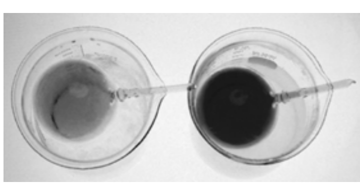
14.5

Le Châtelier's Principle

• Changes in Temperature

Change	Exothermic Rx	Endothermic Rx
Increase temperature	*K* decreases	*K* increases
Decrease temperature	*K* increases	*K* decreases



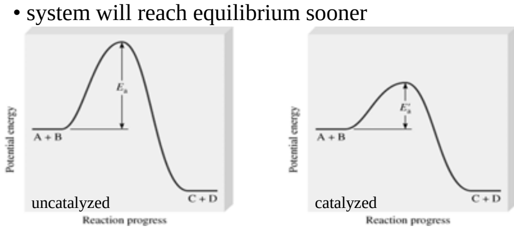


colder hotter

14.5

Le Châtelier's Principle

- Adding a Catalyst
  - does not change *K*
  - does not shift the position of an equilibrium system
  - system will reach equilibrium sooner



Catalyst lowers E_a for **both** forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium.

14.5

Le Châtelier's Principle

Change	Shift Equilibrium	Change Equilibrium Constant
Concentration	yes	no
Pressure	yes	no
Volume	yes	no
Temperature	yes	yes
Catalyst	no	no

14.5

The Nature of the Equilibrium State

$$Ca^{2+} (aq) + 2HCO_3^- (aq) \Leftrightarrow CaCO_3 (s) + CO_2 (g) + H_2O(l)$$

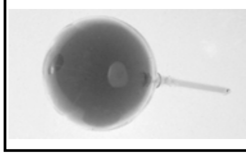
Chemical equilibria are dynamic

When the system is at equilibrium, the forward and reverse reactions continue, but at the same rate.

Equilibrium is a state in which there are no observable changes as time goes by.

Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant



Physical equilibrium

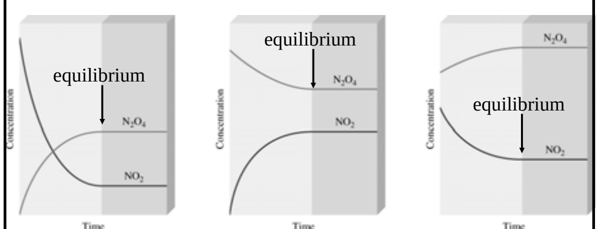
$H_2O\ (l) \rightleftharpoons H_2O\ (g)$

Chemical equilibrium

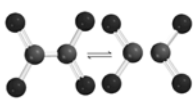
$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

14.1

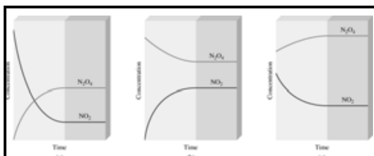
$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$



Start with NO_2 Start with N_2O_4 Start with NO_2 & N_2O_4



14.1



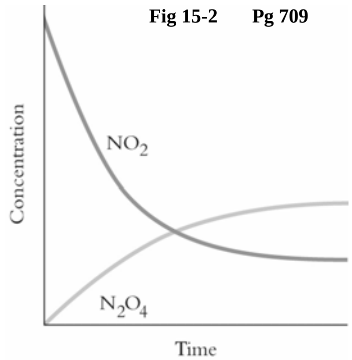
constant

TABLE 14.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*) $[NO_2]$	Initial Concentrations (*M*) $[N_2O_4]$	Equilibrium Concentrations (*M*) $[NO_2]$	Equilibrium Concentrations (*M*) $[N_2O_4]$	Ratio of Concentrations at Equilibrium $\frac{[NO_2]}{[N_2O_4]}$	Ratio of Concentrations at Equilibrium $\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

14.1

Fig 15-2 Pg 709



Changes in the concentrations of NO_2 and N_2O_4 with time. The system reaches equilibrium before either substance is fully consumed.

The Equilibrium Constant (K)

The equilibrium constant relates concentrations of reactants and products at equilibrium at a given temperature to a numerical constant

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

$$K = \frac{[\text{products}]^{\text{raised to the stoich. coefficient}}}{[\text{reactants}]^{\text{raised to the stoich. coefficient}}}$$

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

$$\therefore \quad K = \frac{[HI]^2}{[H_2]\;[I_2]}$$

The equilibrium expression will tell you the value of the equilibrium constant as well as the concentrations of the reactants and products at equilibrium

You may write you equilibrium expression solving for either Kc or Kp.

What do you think is the difference?

Kc is used in expressions for solution concentrations. Include only gases and aqueous solutions.

Kp is used in expression for pressure…so the units are in pressure instead of concentration
*****Remember to only include gases in your expression for Kp*****

Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$aA\ (g) + bB\ (g) \rightleftharpoons cC\ (g) + dD\ (g)$$

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

Δn = moles of gaseous products – moles of gaseous reactants
= $(c + d) - (a + b)$

14.2

Homogeneous Equilibrium

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

$$K_c' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = K_c'\,[H_2O]$$

General practice **not** to include units for the equilibrium constant.

14.2

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

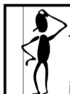
$$K'_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2] = K'_c \times \frac{[CaCO_3]}{[CaO]} \qquad K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

14.2



The equilibrium constant K_p for the reaction

$$2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$$

is 158 at 1000K. What is the equilibrium pressure of O_2 if the equilibrium pressures of P_{NO_2} = 0.400 atm and P_{NO} = 0.270 atm?

$$K_p = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2}$$

$$P_{O_2} = K_p \frac{P_{NO_2}^2}{P_{NO}^2}$$

$$P_{O_2} = 158 \times (0.400)^2/(0.270)^2 = 347 \text{ atm}$$

14.2

How do you solve the expression for either K or the equilibrium concentrations?

ICE Table

Initial concentration → I
change → C
Equilibrium concentration → E

How to set up an ice table

There are two ways to solve this: either for the equilibrium constant (K) or the equilibrium concentrations

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

I — **Initial concentration**

C — **Change**

E — **Equilibrium concentration**

$$H_2 (g) + I_2 (g) \Leftrightarrow 2 HI (g) \quad K = \frac{[HI]^2}{[H_2]\ [I_2]}$$

	H_2	I_2	HI
I	0.0175	0.0175	0
C	-x	-x	+2x
E	0.0175 - x	0.0175 - x	2x

K = 56

$$K = \frac{[2x]^2}{[.0175 - x]\ [.0175 - x]}$$

quad

How do you solve this?

Reaction $H_2O(l)$ +	$C_6H_5CO_2H(aq)$ $\rightleftharpoons$	$C_6H_5CO_2^-(aq)$ +	$H_3O^+(aq)$
Initial concentration (M)	0.125	0	0
Change in concentration (M)			
Equilibrium concentration (M)	*Need to find*	*Need to find*	0.0028

Reaction $H_2O(l)$ +	$C_6H_5CO_2H(aq)$ ⇌	$C_6H_5CO_2^-(aq)$ +	$H_3O^+(aq)$
Initial concentration (M)	0.125	0	0
Change in concentration (M)	−0.0028	+0.0028	+0.0028
Equilibrium concentration (M)	*Need to find*	*Need to find*	0.0028

Reaction $H_2O(l)$ +	$C_6H_5CO_2H(aq)$ ⇌	$C_6H_5CO_2^-(aq)$ +	$H_3O^+(aq)$
Initial concentration (M)	0.125	0	0
Change in concentration (M)	−0.0028	+0.0028	+0.0028
Equilibrium concentration (M)	0.122	0.0028	0.0028

Reaction (substance)	2 AB ⇌	AB_2 +	A
Initial pressure (atm)	8.0	0	0
Change in pressure (atm)			
Equilibrium pressure (atm)			

Reaction (substance)	$2\ AB \rightleftharpoons$	AB_2 +	A
Initial pressure (atm)	8.0	0	0
Change in pressure (atm)	$-2x$	$+x$	$+x$
Equilibrium pressure (atm)	$8.0 - 2x$	x	x

Reaction $H_2O(l)$ +	$C_6H_5CO_2H(aq) \rightleftharpoons$	$C_6H_5CO_2^-(aq)$ +	$H_3O^+(aq)$
Initial concentration (M)	0.050	0	0
Change in concentration (M)			
Equilibrium concentration (M)	*Need to find*	*Need to find*	*Need to find*

Reaction $H_2O(l)$ +	$C_6H_5CO_2H(aq) \rightleftharpoons$	$C_6H_5CO_2^-(aq)$ +	$H_3O^+(aq)$
Initial concentration (M)	0.050	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	*Need to find*	*Need to find*	*Need to find*

Reaction $H_2O(l)$ +	$C_6H_5CO_2H(aq)$ $\rightleftharpoons$	$C_6H_5CO_2^-(aq)$ +	$H_3O^+(aq)$
Initial concentration (M)	0.050	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.50 - x$	x	x

Consider the following equilibrium at 295 K:

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_p and K_c for the reaction?

$$K_p = P_{NH_3} P_{H_2S} = 0.265 \times 0.265 = 0.0702$$

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

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

$\Delta n = 2 - 0 = 2$ $\quad T = 295$ K

$$K_c = 0.0702 \times (0.0821 \times 295)^{-2} = 1.20 \times 10^{-4}$$

14.2

$A + B \rightleftharpoons \not{C} + \not{D}$ $\quad K_c'$

$\not{C} + \not{D} \rightleftharpoons E + F$ $\quad K_c''$

$A + B \rightleftharpoons E + F$ $\quad K_c$

$$K_c' = \frac{[C][D]}{[A][B]} \qquad K_c'' = \frac{[E][F]}{[C][D]}$$

$$K_c = \frac{[E][F]}{[A][B]}$$

$$K_c = K_c' \times K_c''$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

14.2

What About Solving for Kp?

$$Br_2(l) \rightleftharpoons Br_2(g) \qquad K_{eq} = (p_{Br_2})_{eq} = \text{Vapor pressure}$$

$$H_2O(l) \rightleftharpoons H_2O(g) \qquad K_{eq} = (p_{H_2O})_{eq} = \text{Vapor pressure}$$

$$O_2(g) \rightleftharpoons O_2(aq) \qquad K_{eq} = \frac{[O_2(aq)]_{eq}}{(p_{O_2})_{eq}} = K_H$$

Remember:

$$K_{forward} = 1/K_{reverse}$$

In addition:

If you add two equations together, the Knet is the product of the two Ks.

$$K_{net} = K_1 \bullet K_2$$

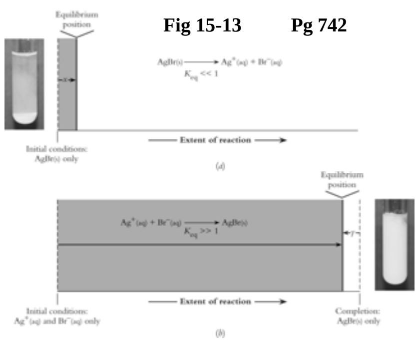
Helpful Hints

Do not include concentrations of solids in your equilibrium expression. It is a fixed amount.

Do not include water in your expression unless you are solving for Kp which has H_2O (g) in the equation. Water is present in such a large amounts that it essentially state unchanged throughout the reaction.

If the value of K is very large, what does that tell you about the reaction?

Fig 15-13 Pg 742



Schematic representation of the relationship between K_{eq} and the extent of reaction. (a) When K_{eq}<<1, the difference from initial conditions, *x*, is small. (b) When K_{eq}>>1, the difference from completion, y, is small.

What happens if you are not at equilibrium?

Instead of solving for K, you solve for Q, the reaction quotient

$$A + B \Leftrightarrow C + D$$

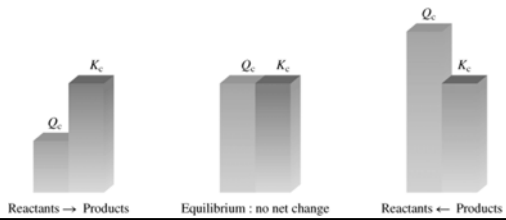
$$Q = \frac{[C]\,[D]}{[A]\,[B]}$$

Looks like K, but the concentrations in the expression are not the concentrations at equilibrium

The ***reaction quotient (Q_c)*** is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.

IF

- $Q_c > K_c$ system proceeds from right to left to reach equilibrium
- $Q_c = K_c$ the system is at equilibrium
- $Q_c < K_c$ system proceeds from left to right to reach equilibrium



14.4

What would be the purpose of knowing the value of Q?

If Q< K, the reaction will move to the right
To re-establish equilibrium

If Q> K, the reaction will move to the left
To re-establish equilibrium