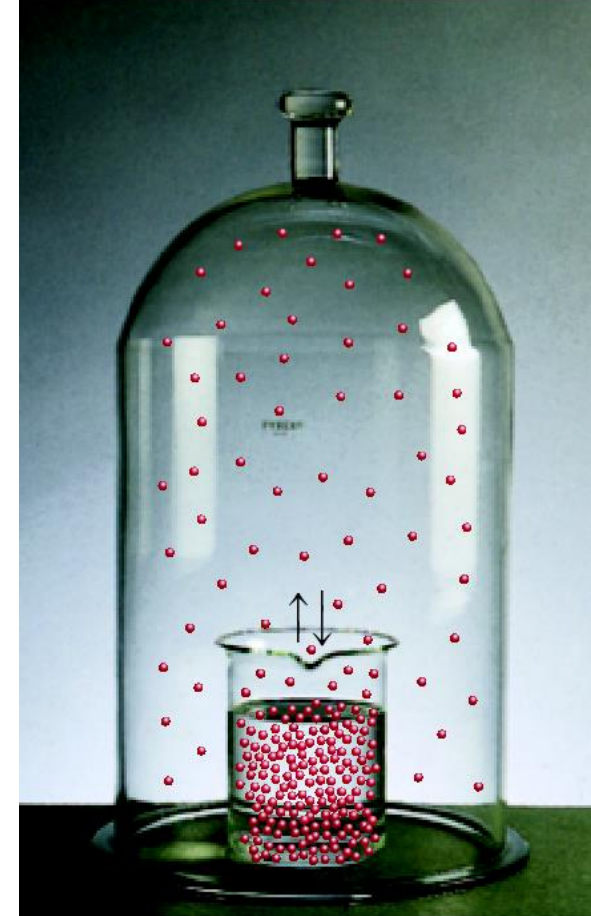




Chemical Equilibrium

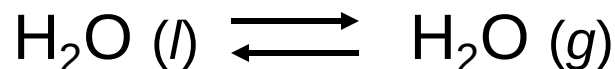
Chapter 14

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

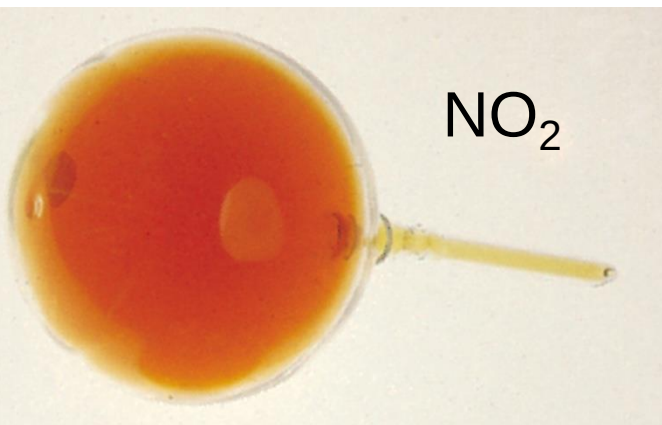
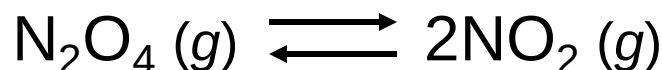
Chemical equilibrium is achieved when:

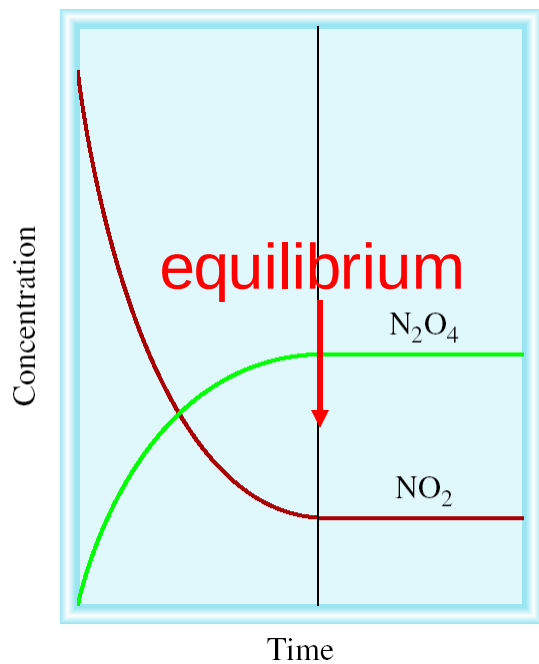
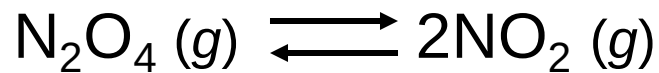
- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant

Physical equilibrium

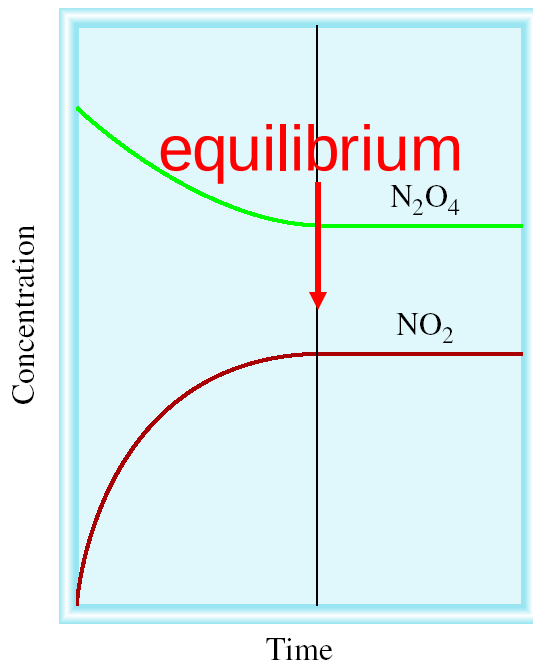


Chemical equilibrium

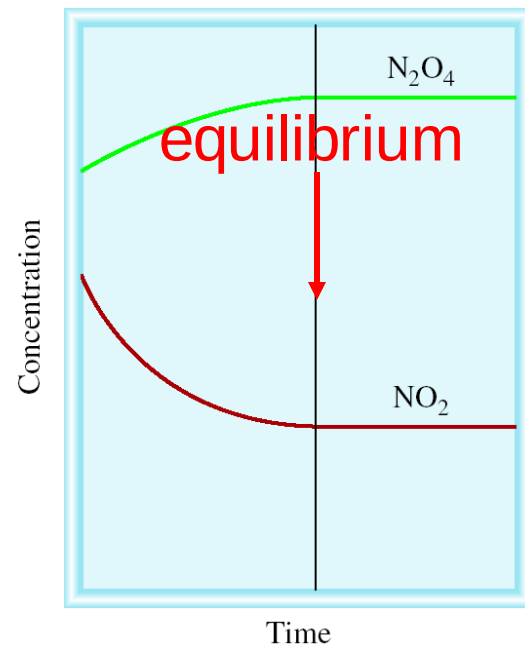




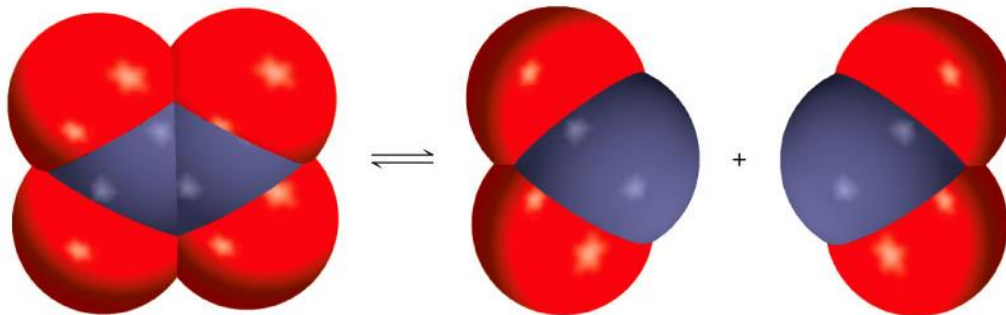
Start with NO_2

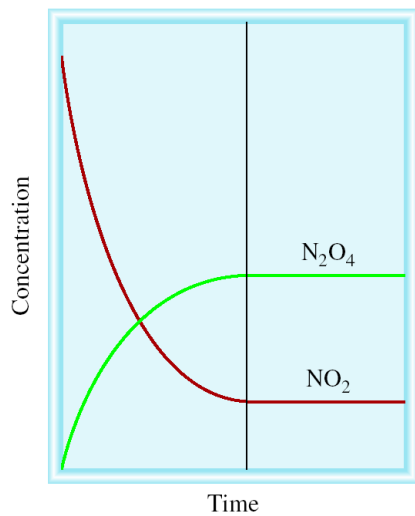


Start with N_2O_4

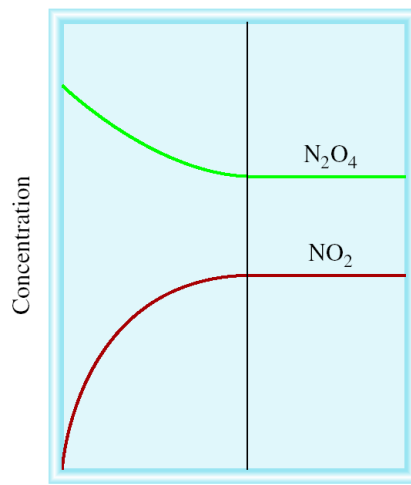


Start with NO_2 & N_2O_4

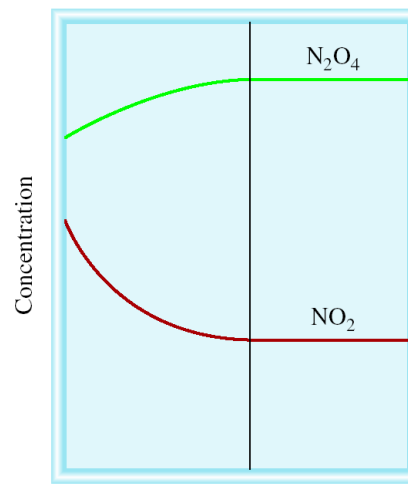




Time



Time

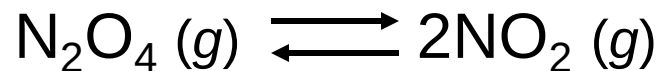


Time

constant

TABLE 14.1 The $\text{NO}_2\text{--N}_2\text{O}_4$ System at 25°C

Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium	
$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$\frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]}$	$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
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}

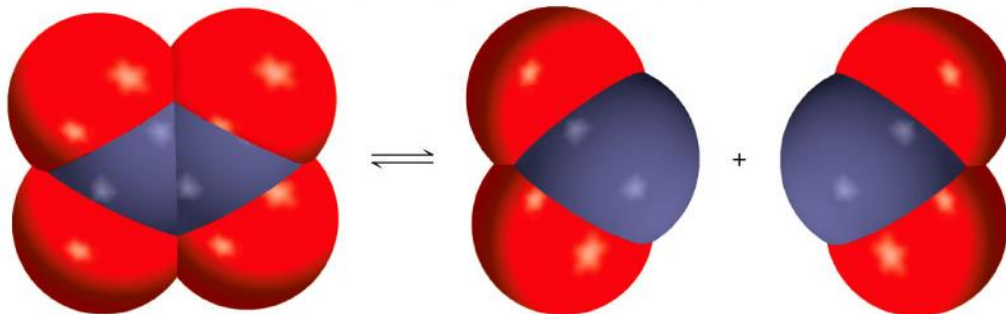


$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3}$$

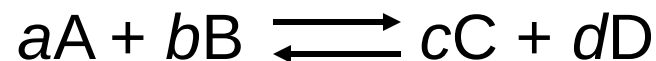


$$K = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

Law of Mass Action



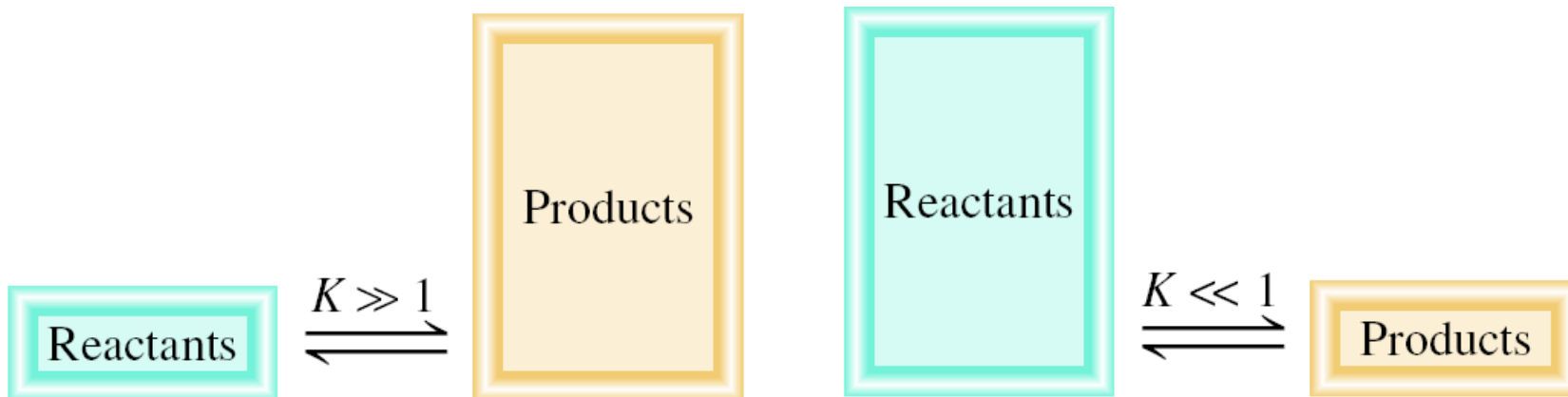
$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$



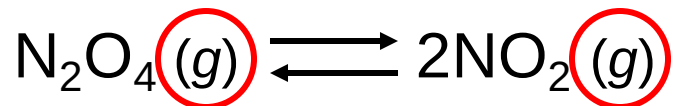
Equilibrium Will

$K \gg 1$ Lie to the right Favor products

$K \ll 1$ Lie to the left Favor reactants



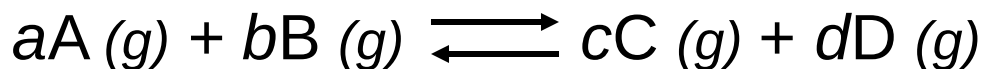
Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase**.



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \qquad K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

In most cases

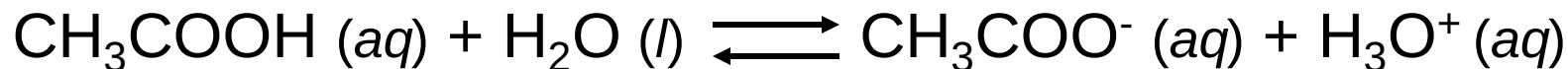
$$K_c \neq K_p$$



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

$$\begin{aligned} \Delta n &= \text{moles of gaseous products} - \text{moles of gaseous reactants} \\ &= (c + d) - (a + b) \end{aligned}$$

Homogeneous Equilibrium

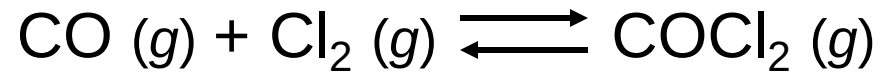


$$K'_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]} \quad [\text{H}_2\text{O}] = \text{constant}$$

$$K_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = K'_c [\text{H}_2\text{O}]$$

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

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $\text{COCl}_2 (g)$ at 74°C are $[\text{CO}] = 0.012 \text{ M}$, $[\text{Cl}_2] = 0.054 \text{ M}$, and $[\text{COCl}_2] = 0.14 \text{ M}$. Calculate the equilibrium constants K_c and K_p .



$$K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

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

$$\Delta n = 1 - 2 = -1 \quad R = 0.0821 \quad T = 273 + 74 = 347 \text{ K}$$

$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.7$$

The equilibrium constant K_p for the reaction



is 158 at 1000K. What is the equilibrium pressure of O_2 if the $P_{\text{NO}_2} = 0.400 \text{ atm}$ and $P_{\text{NO}} = 0.270 \text{ atm}$?

$$K_p = \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2}$$

$$P_{\text{O}_2} = K_p \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2}$$

$$P_{\text{O}_2} = 158 \times (0.400)^2 / (0.270)^2 = 347 \text{ atm}$$

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



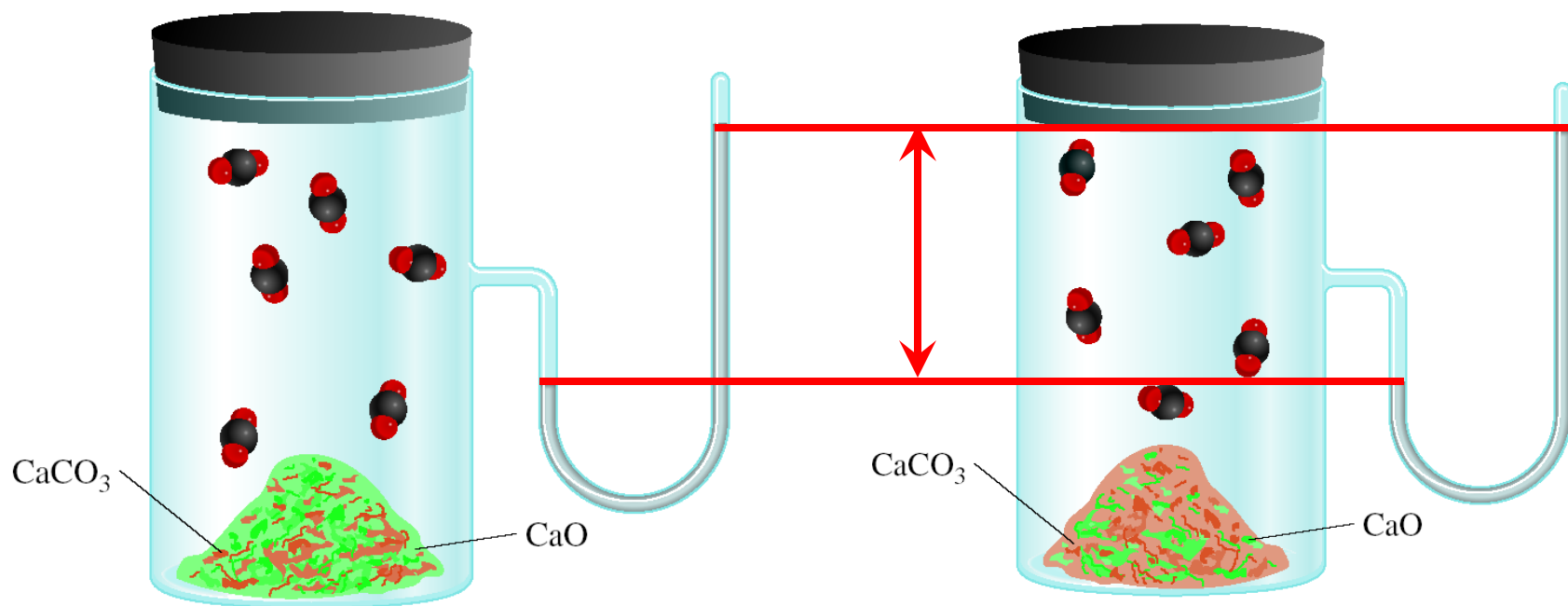
$$K'_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

$$\begin{aligned} [\text{CaCO}_3] &= \text{constant} \\ [\text{CaO}] &= \text{constant} \end{aligned}$$

$$K_c = [\text{CO}_2] = K'_c \times \frac{[\text{CaCO}_3]}{[\text{CaO}]}$$

$$K_p = P_{\text{CO}_2}$$

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



$$P_{\text{CO}_2} = K_p$$

P_{CO_2} does not depend on the amount of CaCO_3 or CaO

Consider the following equilibrium at 295 K:



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

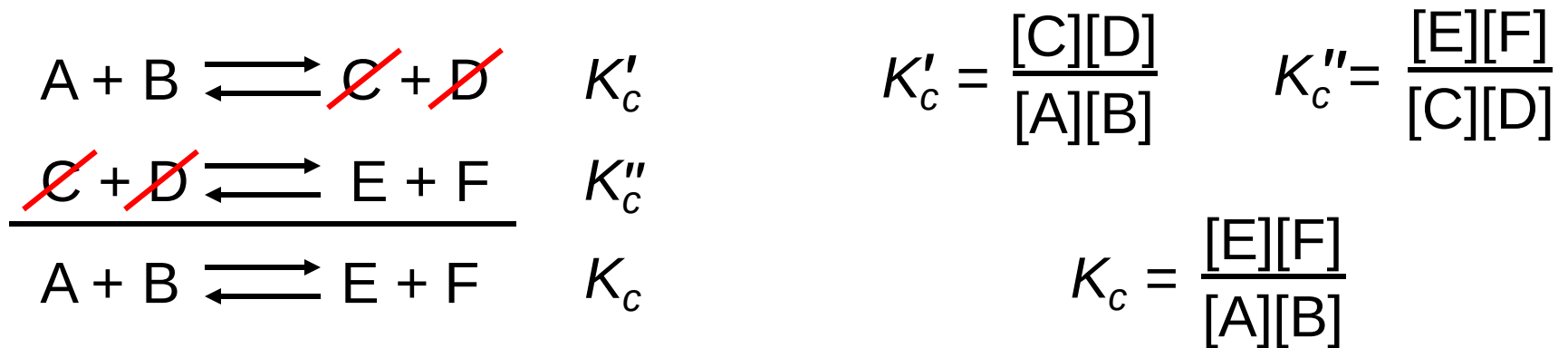
$$K_p = P_{\text{NH}_3} P_{\text{H}_2\text{S}} = 0.265 \times 0.265 = 0.0702$$

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

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

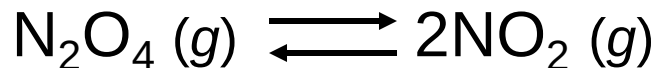
$$\Delta n = 2 - 0 = 2 \quad T = 295 \text{ K}$$

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

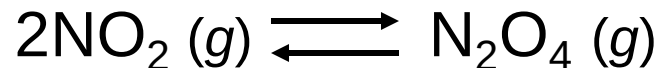


$$K_c = K'_c \times K''_c$$

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.



$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3}$$



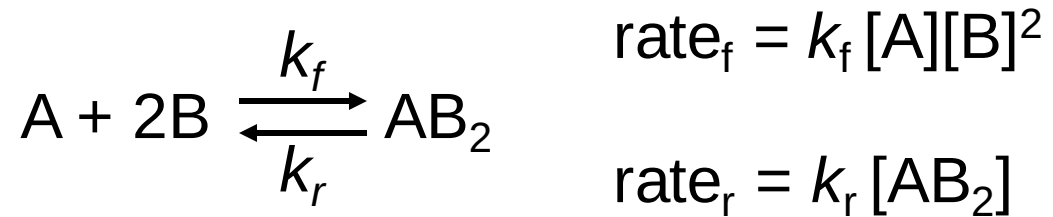
$$K' = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{K} = 216$$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in M . In the gaseous phase, the concentrations can be expressed in M or in atm.
2. The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
5. If a reaction can be expressed as a 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.

Chemical Kinetics and Chemical Equilibrium



Equilibrium

$$\text{rate}_f = \text{rate}_r$$

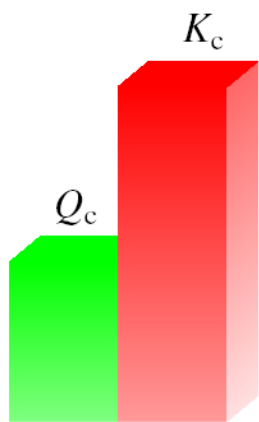
$$k_f [\text{A}][\text{B}]^2 = k_r [\text{AB}_2]$$

$$\frac{k_f}{k_r} = K_c = \frac{[\text{AB}_2]}{[\text{A}][\text{B}]^2}$$

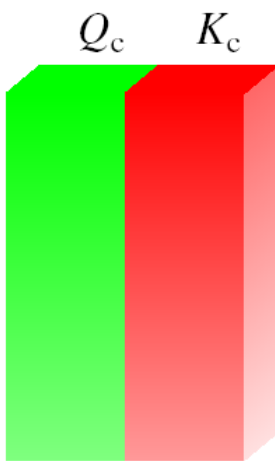
The **reaction quotient (Q_c)** is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.

IF

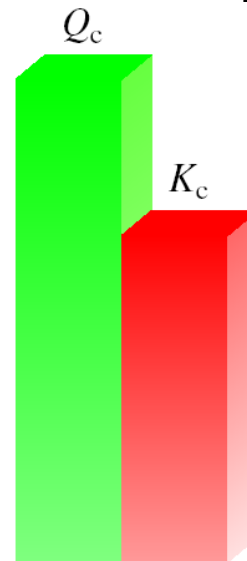
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium
- $Q_c = K_c$ the system is at equilibrium
- $Q_c < K_c$ system proceeds from left to right to reach equilibrium



Reactants $\rightarrow$ Products



Equilibrium : no net change



Reactants $\leftarrow$ Products

Calculating Equilibrium Concentrations

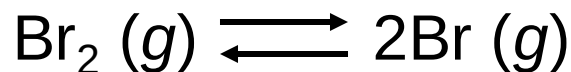
1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown x , which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x .
3. Having solved for x , calculate the equilibrium concentrations of all species.

At 1280°C the equilibrium constant (K_c) for the reaction



Is 1.1×10^{-3} . If the initial concentrations are $[\text{Br}_2] = 0.063 \text{ M}$ and $[\text{Br}] = 0.012 \text{ M}$, calculate the concentrations of these species at equilibrium.

Let x be the change in concentration of Br_2



ICE	Initial (M)	0.063	0.012
	Change (M)	-x	+2x
	Equilibrium (M)	0.063 - x	0.012 + 2x

$$K_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} \quad K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3} \quad \text{Solve for } x$$

$$K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

$$4x^2 + 0.048x + 0.000144 = 0.0000693 - 0.0011x$$

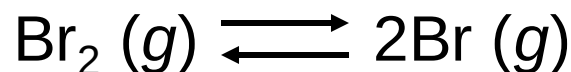
$$4x^2 + 0.0491x + 0.0000747 = 0$$

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

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

$$x = -0.0105$$

$$x = -0.00178$$



Initial (M) 0.063 0.012

Change (M) -x +2x

Equilibrium (M) 0.063 - x 0.012 + 2x

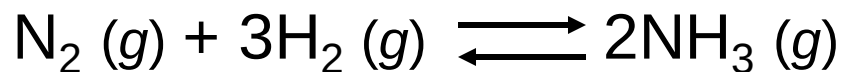
At equilibrium, $[\text{Br}] = 0.012 + 2x = -0.009 \text{ M}$ or 0.00844 M

At equilibrium, $[\text{Br}_2] = 0.062 - x = 0.0648 \text{ M}$

Le Châtelier's Principle

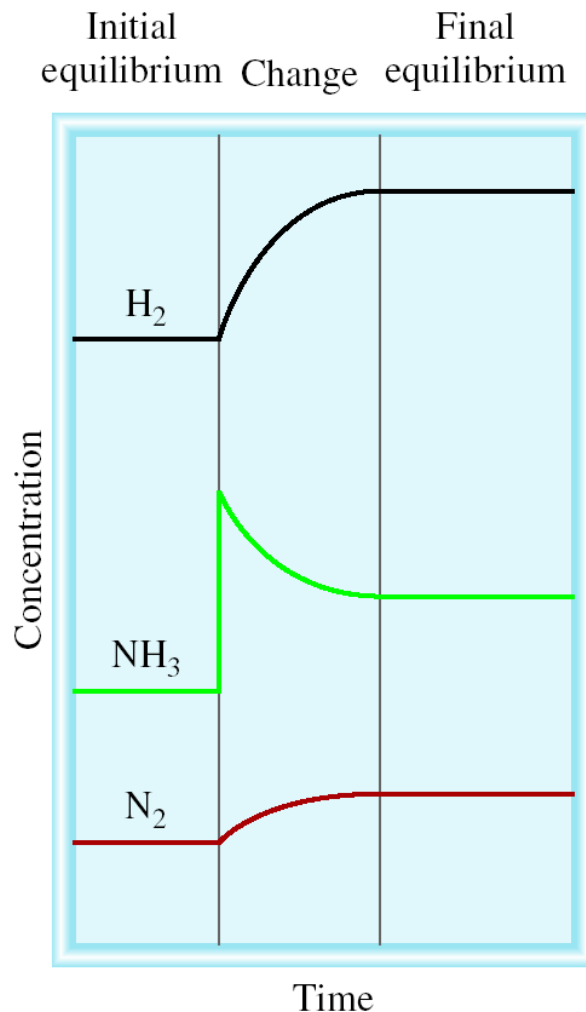
If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

- **Changes in Concentration**



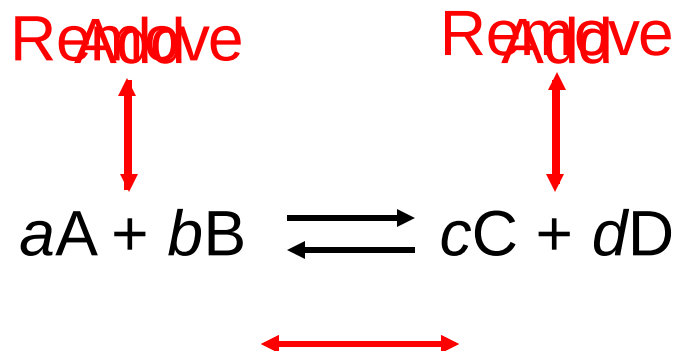
Equilibrium
shifts left to
offset stress

↑
Add
 NH_3



Le Châtelier's Principle

- Changes in Concentration continued



Change

Shifts the Equilibrium

Increase concentration of product(s)

left

Decrease concentration of product(s)

right

Increase concentration of reactant(s)

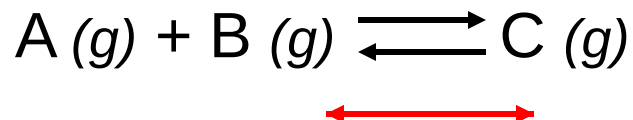
right

Decrease concentration of reactant(s)

left

Le Châtelier's Principle

- Changes in Volume and Pressure

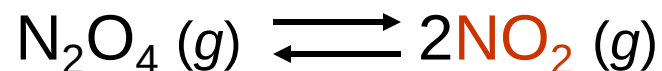


<u>Change</u>	<u>Shifts the Equilibrium</u>
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

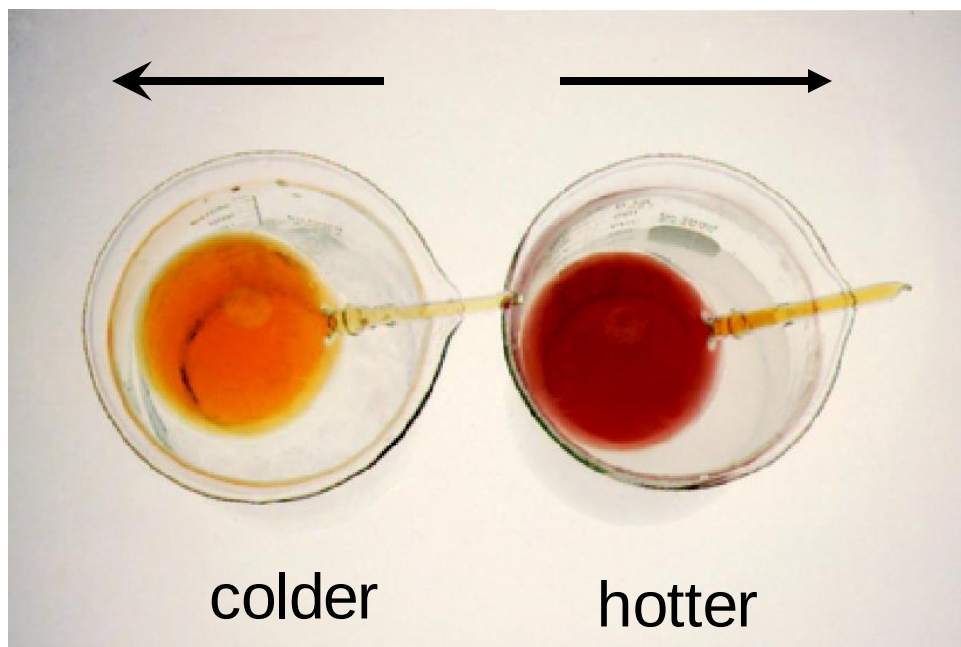
Le Châtelier's Principle

- Changes in Temperature

<u>Change</u>	<u>Exothermic Rx</u>	<u>Endothermic Rx</u>
Increase temperature	K decreases	K increases
Decrease temperature	K increases	K decreases

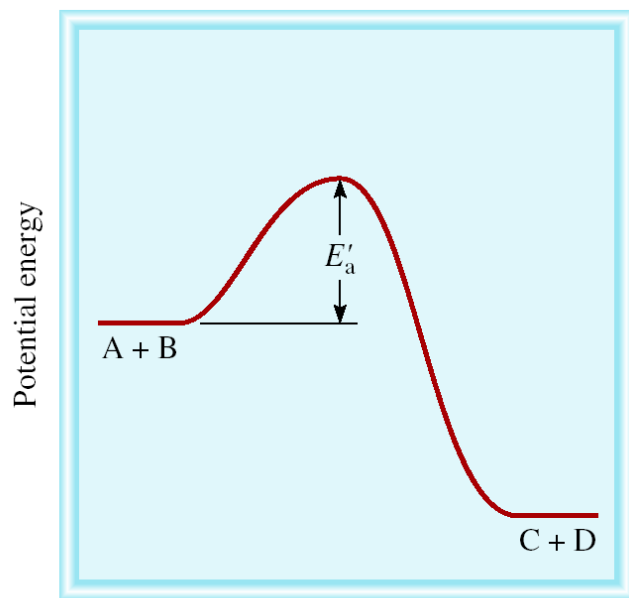


$$\Delta H^\circ = 58.0 \text{ kJ/mol}$$

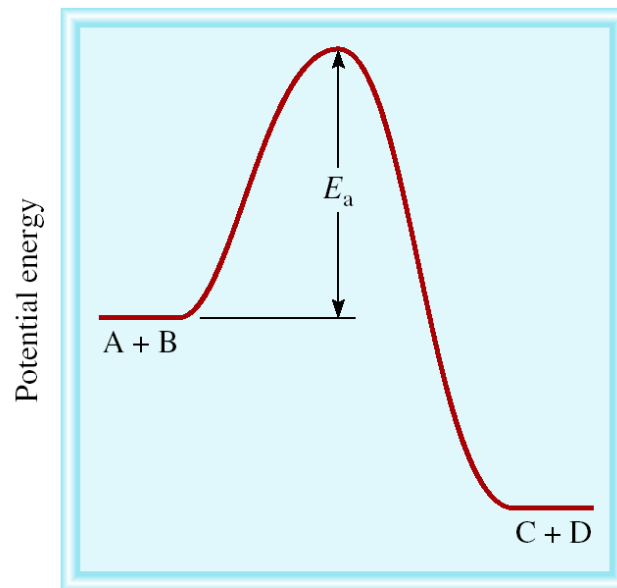


Le Châtelier's Principle

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



Reaction progress



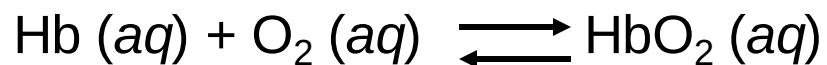
Reaction progress

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

Catalyst does not change equilibrium constant or shift equilibrium.

Chemistry In Action

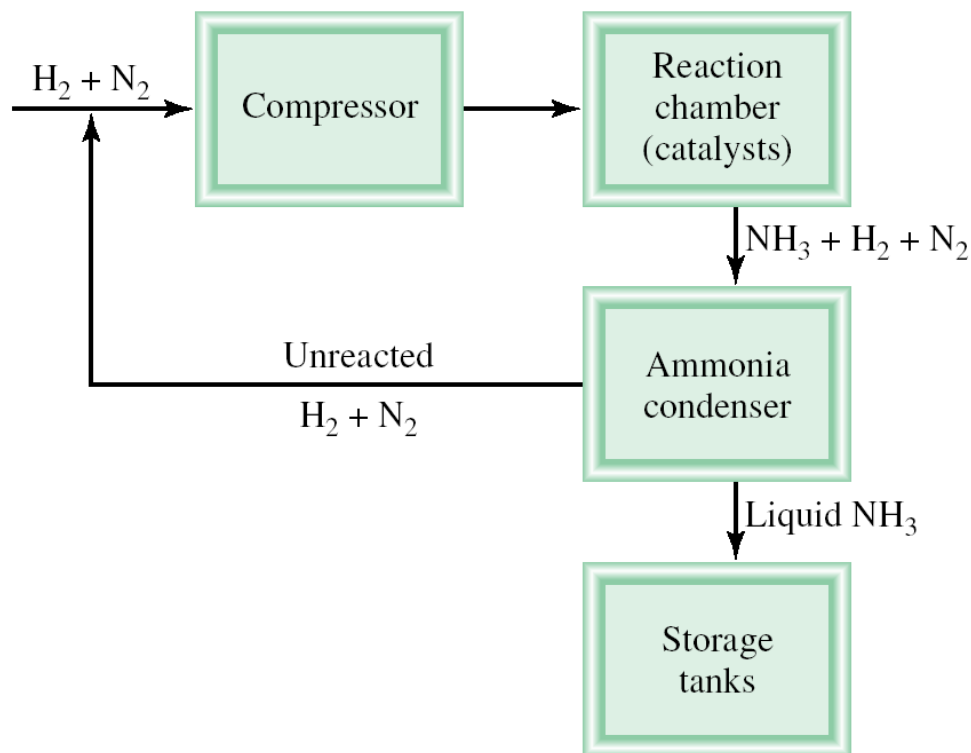
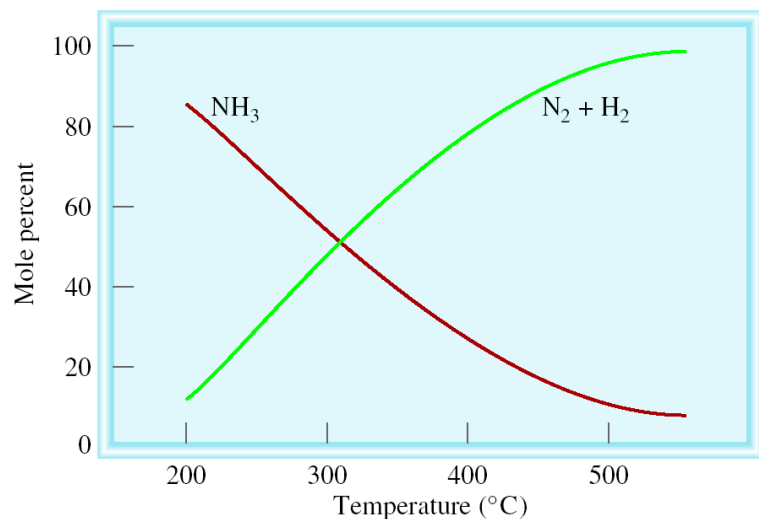
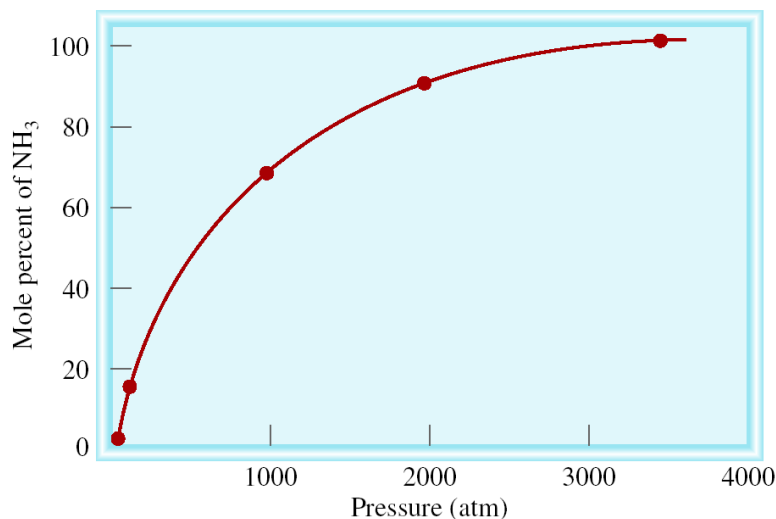
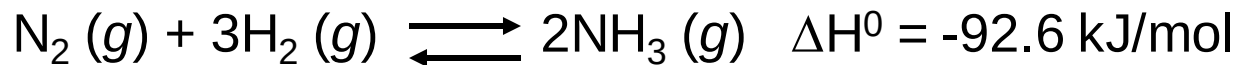
Life at High Altitudes and Hemoglobin Production



$$K_c = \frac{[\text{HbO}_2]}{[\text{Hb}][\text{O}_2]}$$



Chemistry In Action: The Haber Process



Le Châtelier's Principle - Summary

<u>Change</u>	<u>Shift Equilibrium</u>	<u>Change Equilibrium Constant</u>
Concentration	yes	no
Pressure	yes*	no
Volume	yes*	no
Temperature	yes	yes
Catalyst	no	no

*Dependent on relative moles of gaseous reactants and products