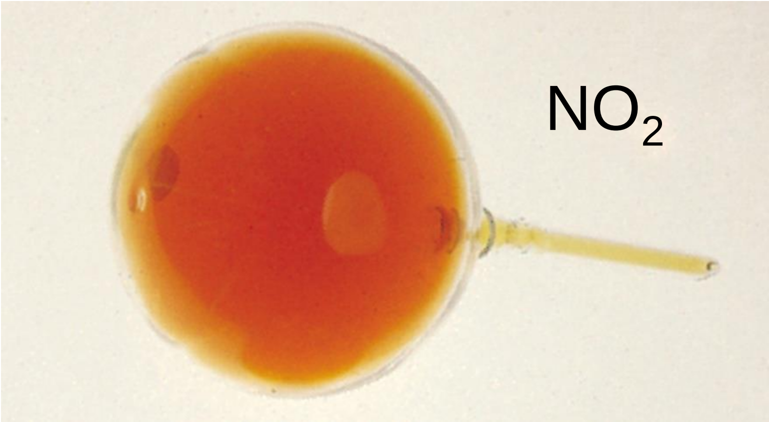
Chemical Equilibrium

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



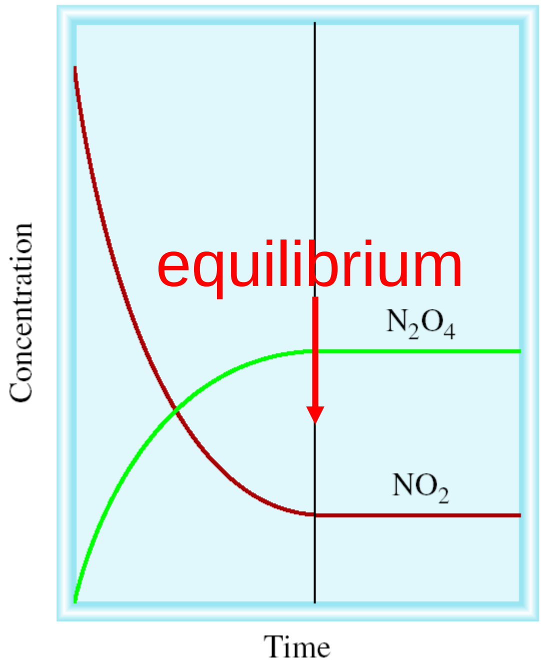
Physical equilibrium

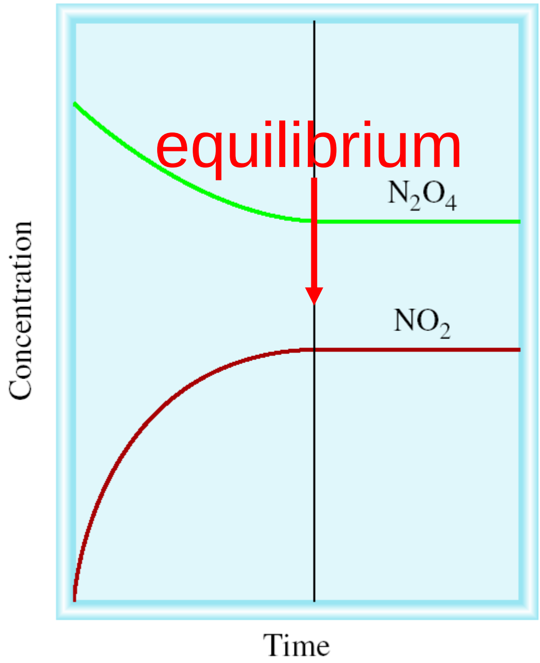
$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

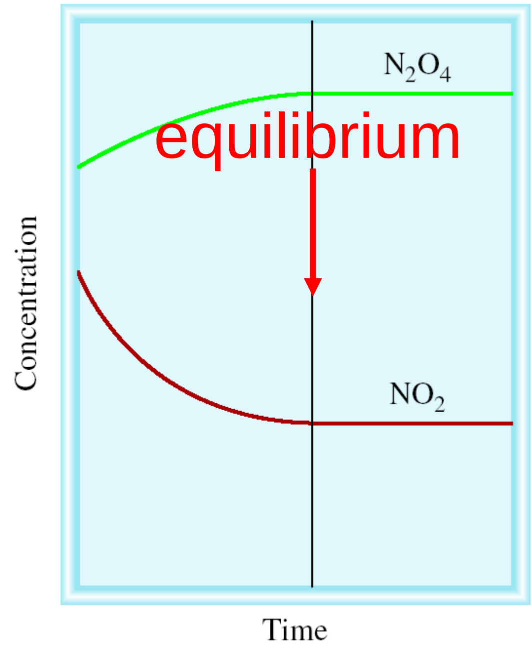
Chemical equilibrium

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

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



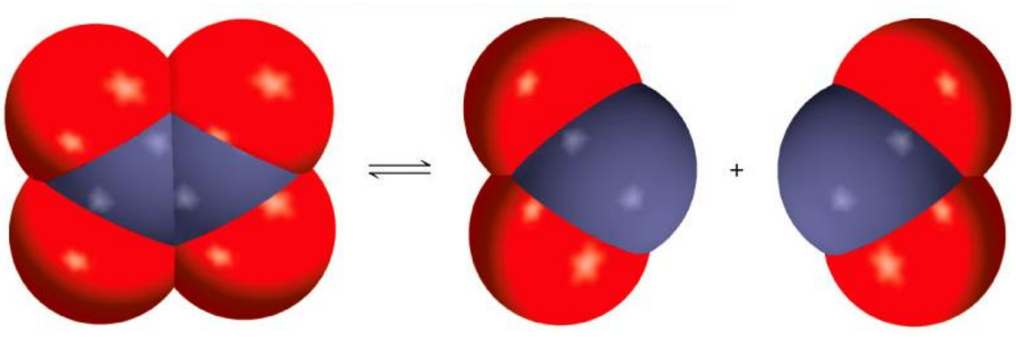


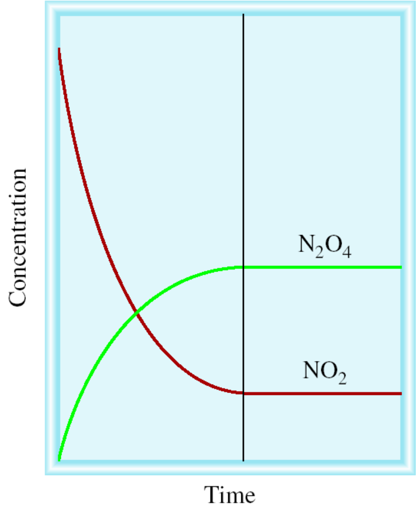


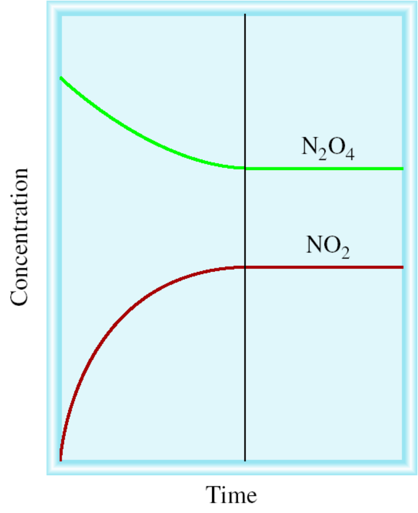
Start with NO_2

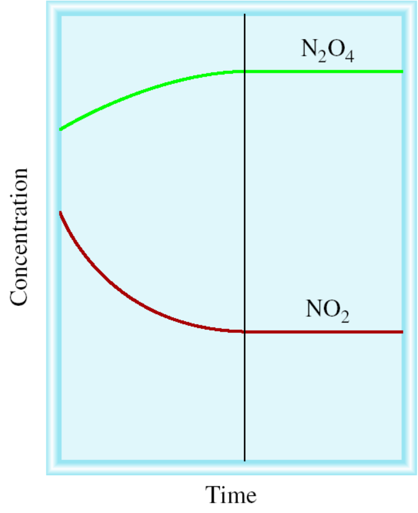
Start with N_2O_4

Start with NO_2 & N_2O_4









constant

TABLE 14.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
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}

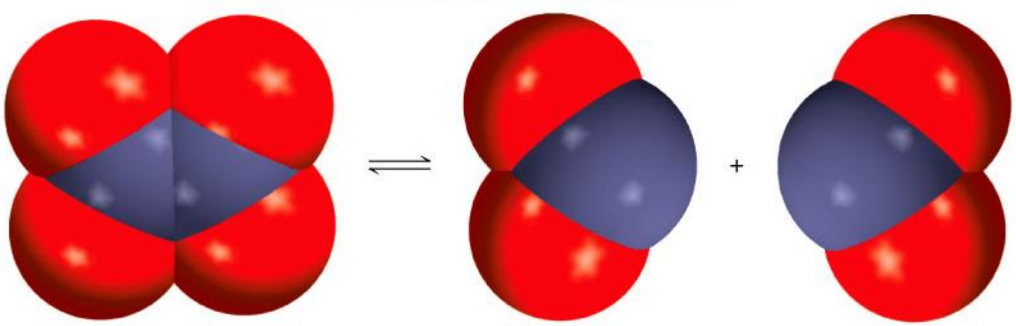
$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

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

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

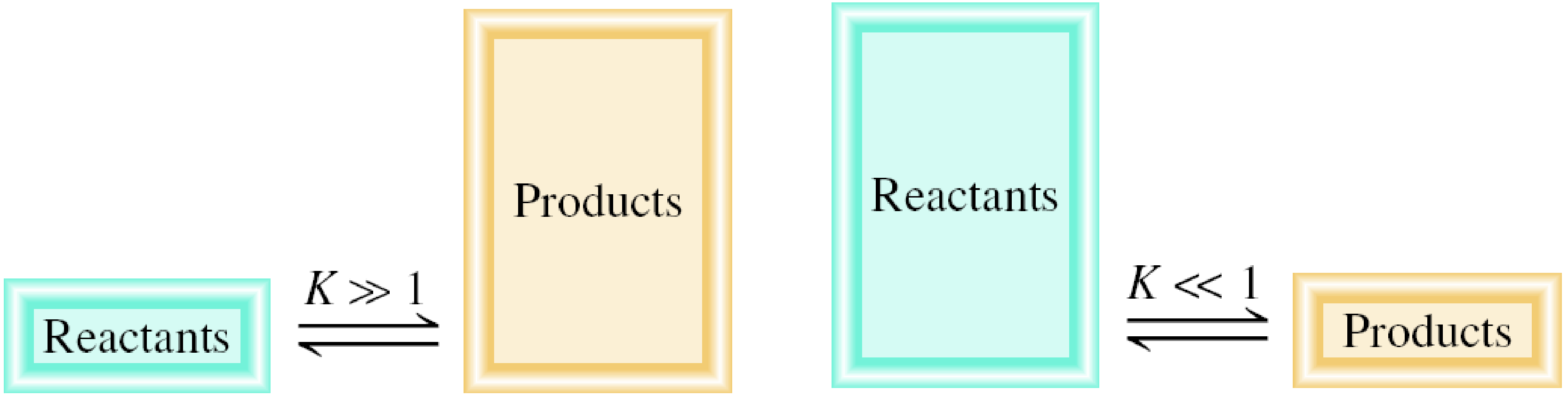
Law of Mass Action



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

<u>Equilibrium Will</u>

$K >> 1$	Lie to the right	Favor products
$K << 1$	Lie to the left	Favor reactants



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

= $(c + d) - (a + b)$

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.

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (*g*) at 74 ^{0}C are [CO] = 0.012 *M*, [Cl_2] = 0.054 *M*, and [$COCl_2$] = 0.14 *M*. Calculate the equilibrium constants K_c and K_p.

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$$

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

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

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

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

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 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 x $(0.400)^2/(0.270)^2$ = 347 atm

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

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

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

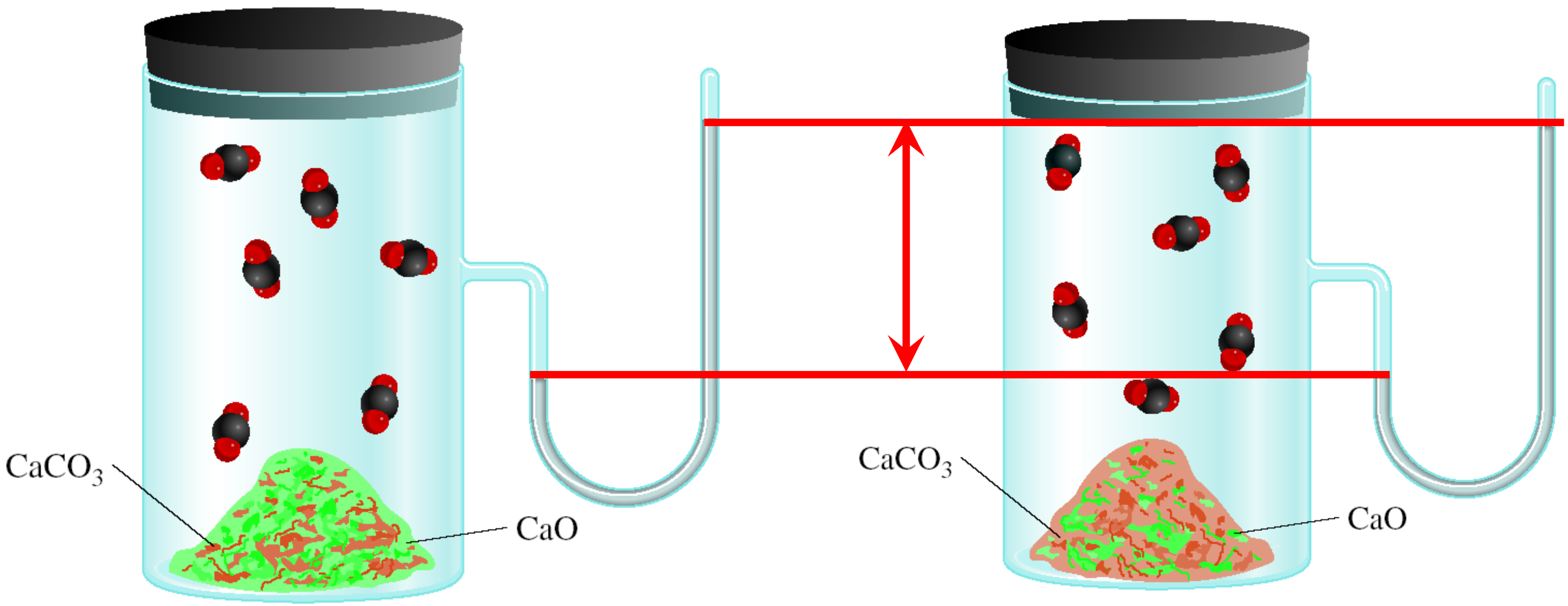
$[CaCO_3]$ = constant
$[CaO]$ = constant

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

$$K_p = P_{CO_2}$$

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

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



$$P_{CO_2} = K_p$$

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

Consider the following equilibrium at 295 K:

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

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

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

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

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

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

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

$$A + B \rightleftharpoons \cancel{C} + \cancel{D} \qquad K_c'$$

$$\cancel{C} + \cancel{D} \rightleftharpoons E + F \qquad K_c''$$

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

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

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

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

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.

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

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3} \qquad\qquad K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

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

$$A + 2B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} AB_2$$

$$\text{rate}_\text{f} = k_\text{f}\,[A][B]^2$$

$$\text{rate}_\text{r} = k_\text{r}\,[AB_2]$$

Equilibrium

$$\text{rate}_\text{f} = \text{rate}_\text{r}$$

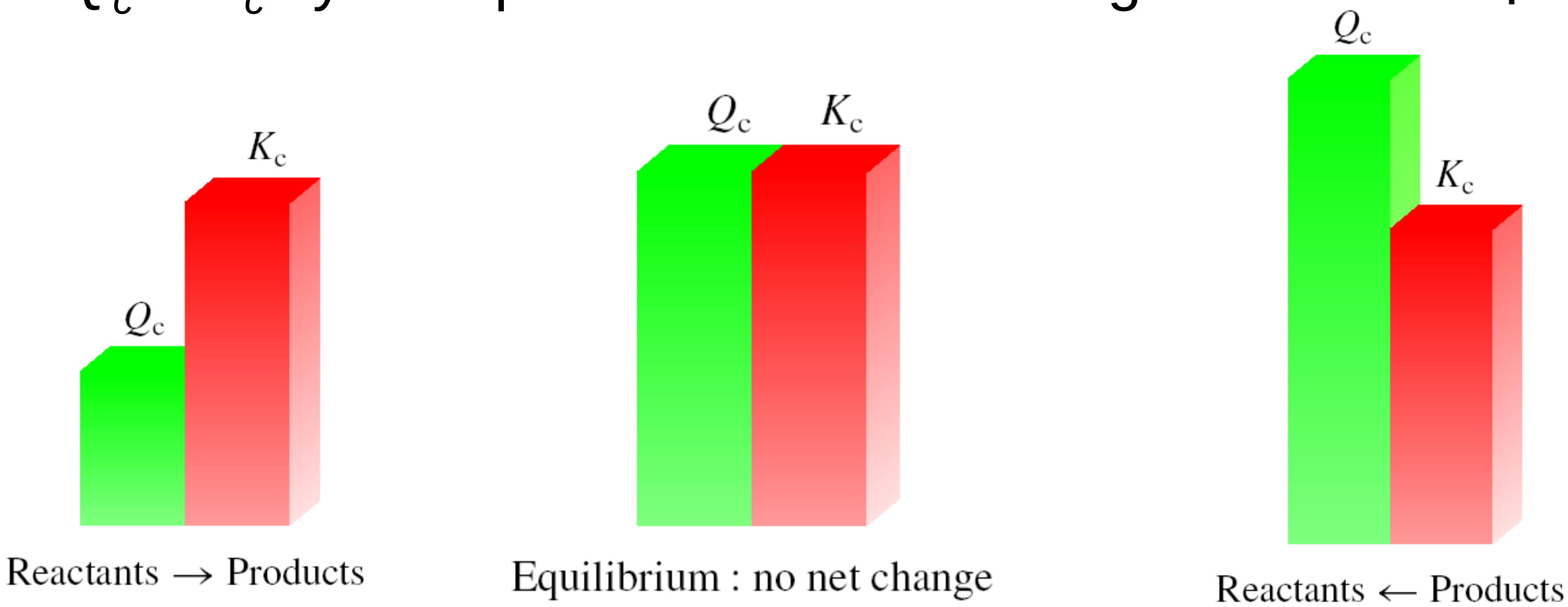
$$k_\text{f}\,[A][B]^2 = k_\text{r}\,[AB_2]$$

$$\frac{k_f}{k_r} = K_c = \frac{[AB_2]}{[A][B]^2}$$

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



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 ^{o}C the equilibrium constant (K_c) for the reaction

$$Br_2\,(g) \rightleftharpoons 2Br\,(g)$$

Is 1.1×10^{-3}. If the initial concentrations are $[Br_2] = 0.063\ M$ and $[Br] = 0.012\ M$, calculate the concentrations of these species at equilibrium.

Let x be the change in concentration of Br_2

ICE

	$Br_2\,(g)$	$\rightleftharpoons$ $2Br\,(g)$
Initial (M)	0.063	0.012
Change (M)	$-x$	$+2x$
Equilibrium (M)	$0.063 - x$	$0.012 + 2x$

$$K_c = \frac{[Br]^2}{[Br_2]} \qquad K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

Solve for x

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

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

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

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = -0.0105 \qquad x = -0.00178$$

$$Br_2\,(g) \rightleftharpoons 2Br\,(g)$$

	$Br_2\,(g)$	$2Br\,(g)$
Initial (*M*)	0.063	0.012
Change (*M*)	$-x$	$+2x$
Equilibrium (*M*)	$0.063 - x$	$0.012 + 2x$

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

At equilibrium, [Br_2] = $0.062 - x$ = 0.0648 *M*

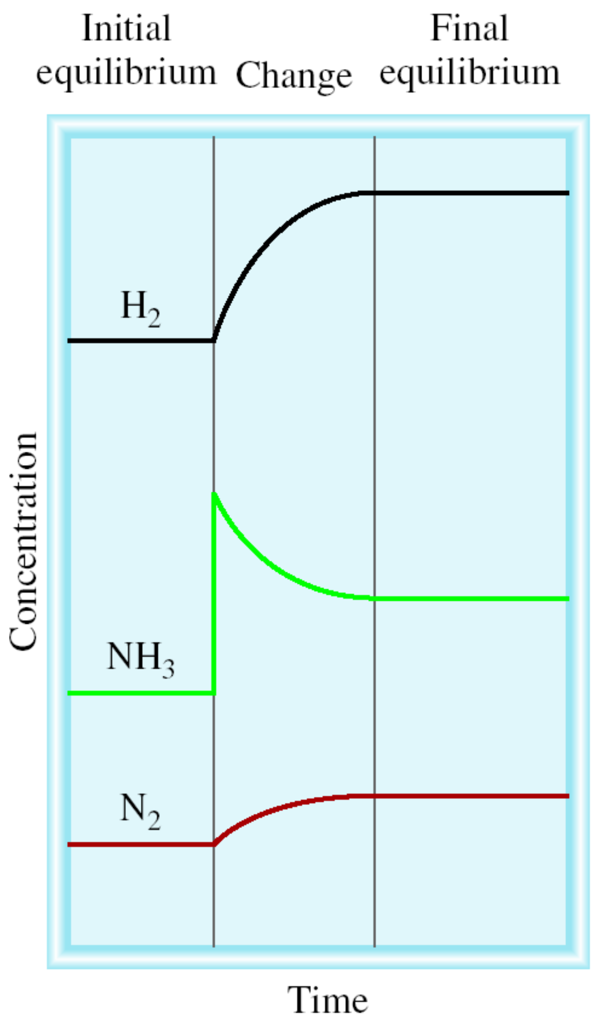
Le Châtelier's Principle

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

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

Equilibrium shifts left to offset stress ← Add NH_3



Le Châtelier's Principle

- Changes in Concentration continued

Remove Add　　　　　　Remove Add

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

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

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

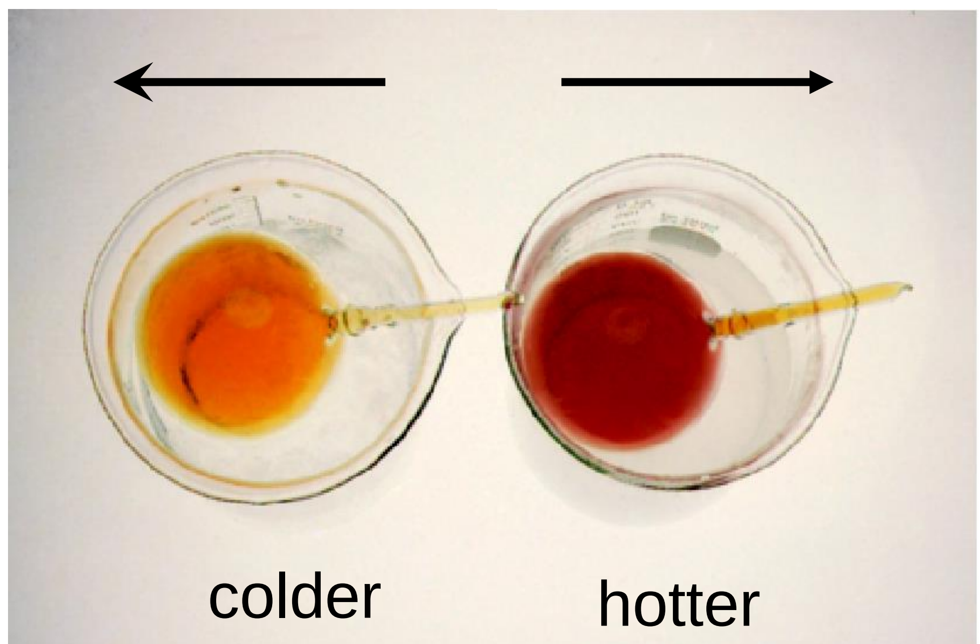
Change	**Shifts the Equilibrium**
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

Le Châtelier's Principle

- Changes in Temperature

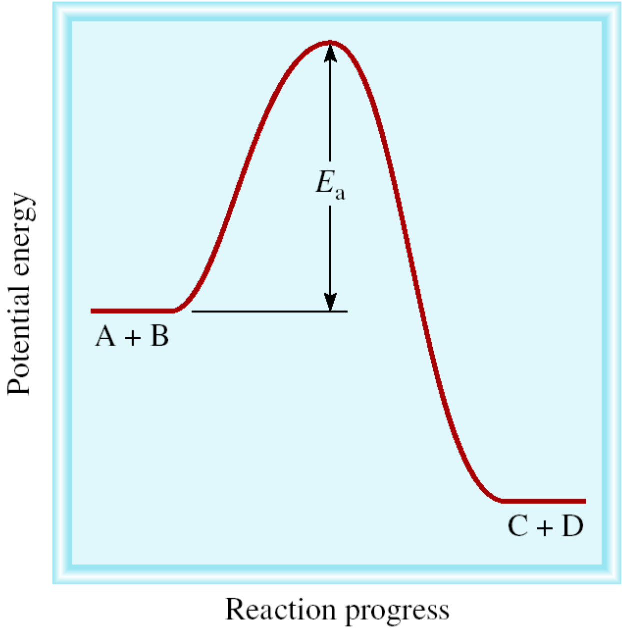
Change	**Exothermic Rx**	**Endothermic Rx**
Increase temperature	*K* decreases	*K* increases
Decrease temperature	*K* increases	*K* decreases

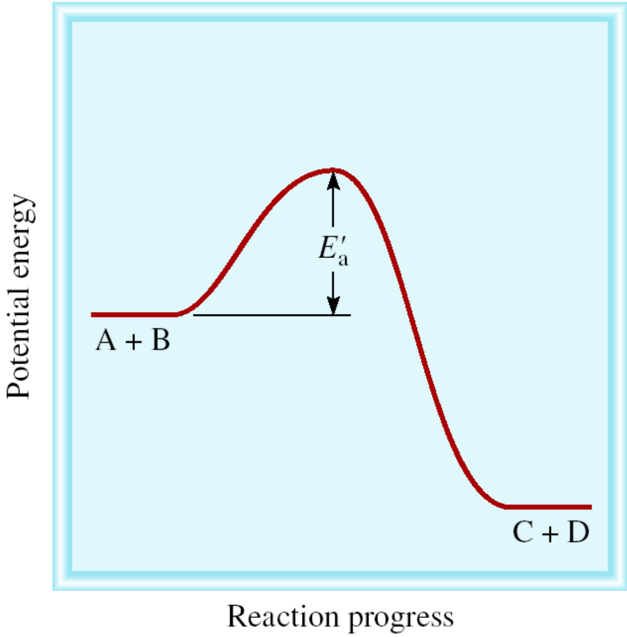
$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g) \qquad \Delta H^\circ = 58.0\ \text{kJ/mol}$$



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





Catalyst provides a alternative pathway with a lower E_a for **both** forward and reverse reactions.

Chemistry In Action

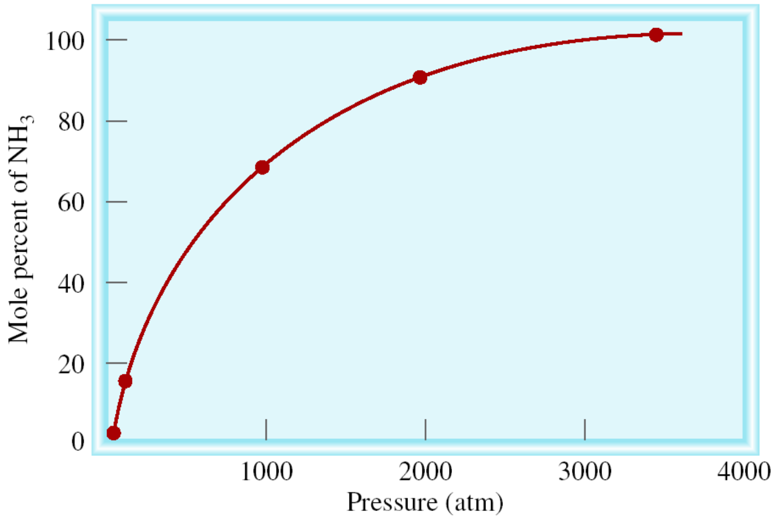
Life at High Altitudes and Hemoglobin Production

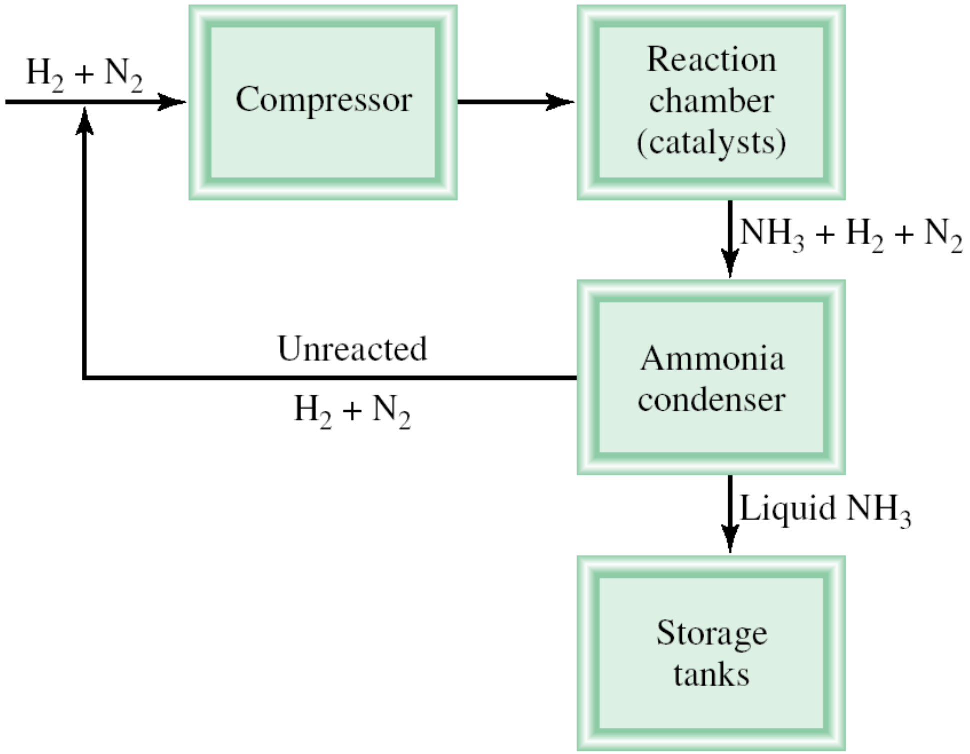
$$Hb\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq)$$

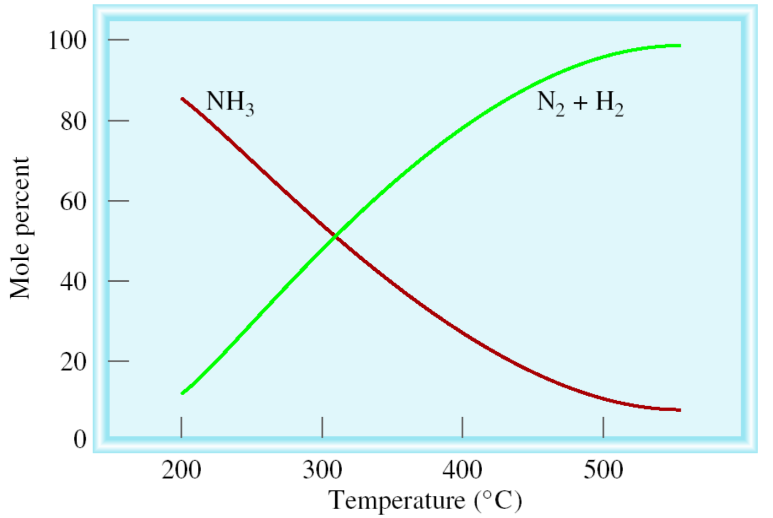
$$K_c = \frac{[HbO_2]}{[Hb][O_2]}$$

Chemistry In Action: The Haber Process

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \quad \Delta H^0 = -92.6\ \mathrm{kJ/mol}$$







Le Châtelier's Principle - Summary

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

*Dependent on relative moles of gaseous reactants and products