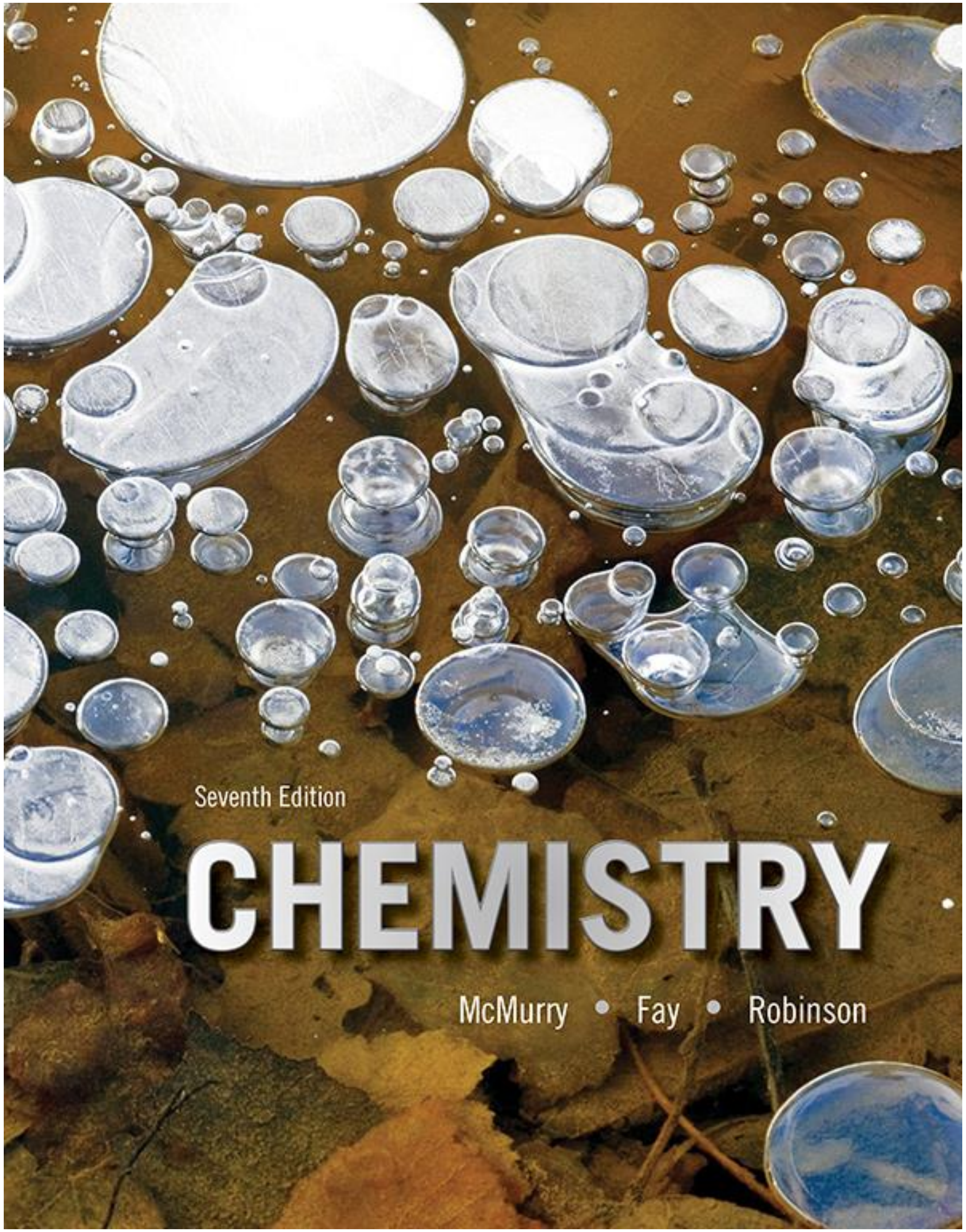

Lecture Presentation

Chapter 14

Chemical Equilibrium

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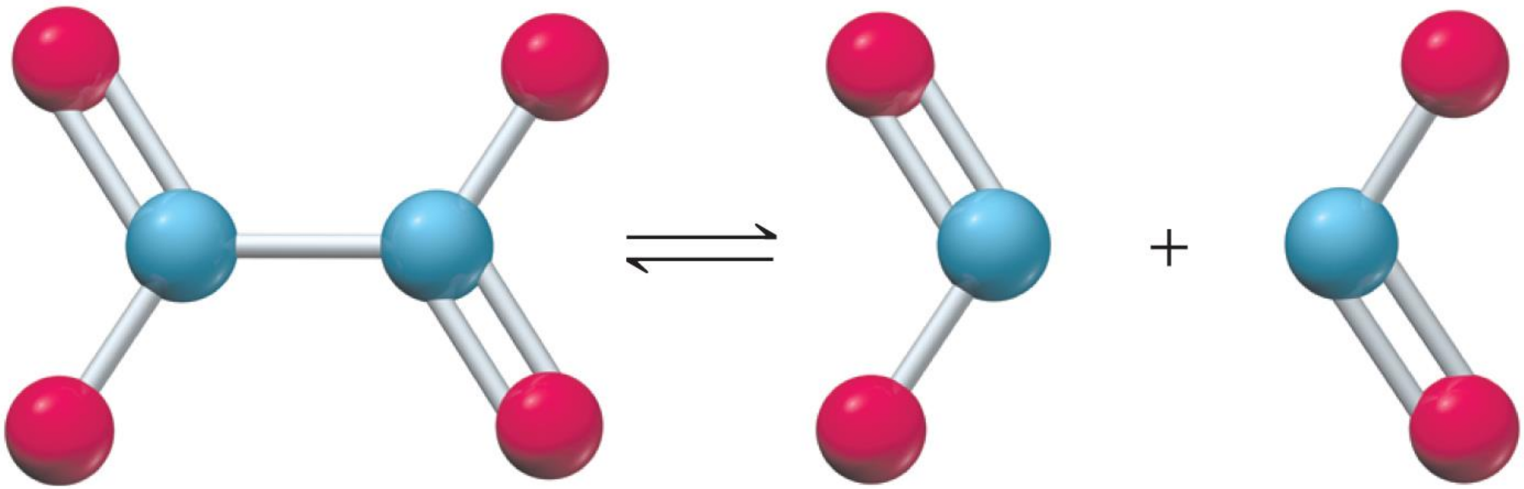
The Equilibrium State

Chemical Equilibrium: The state reached when the concentrations of reactants and products remain constant over time

The Equilibrium State

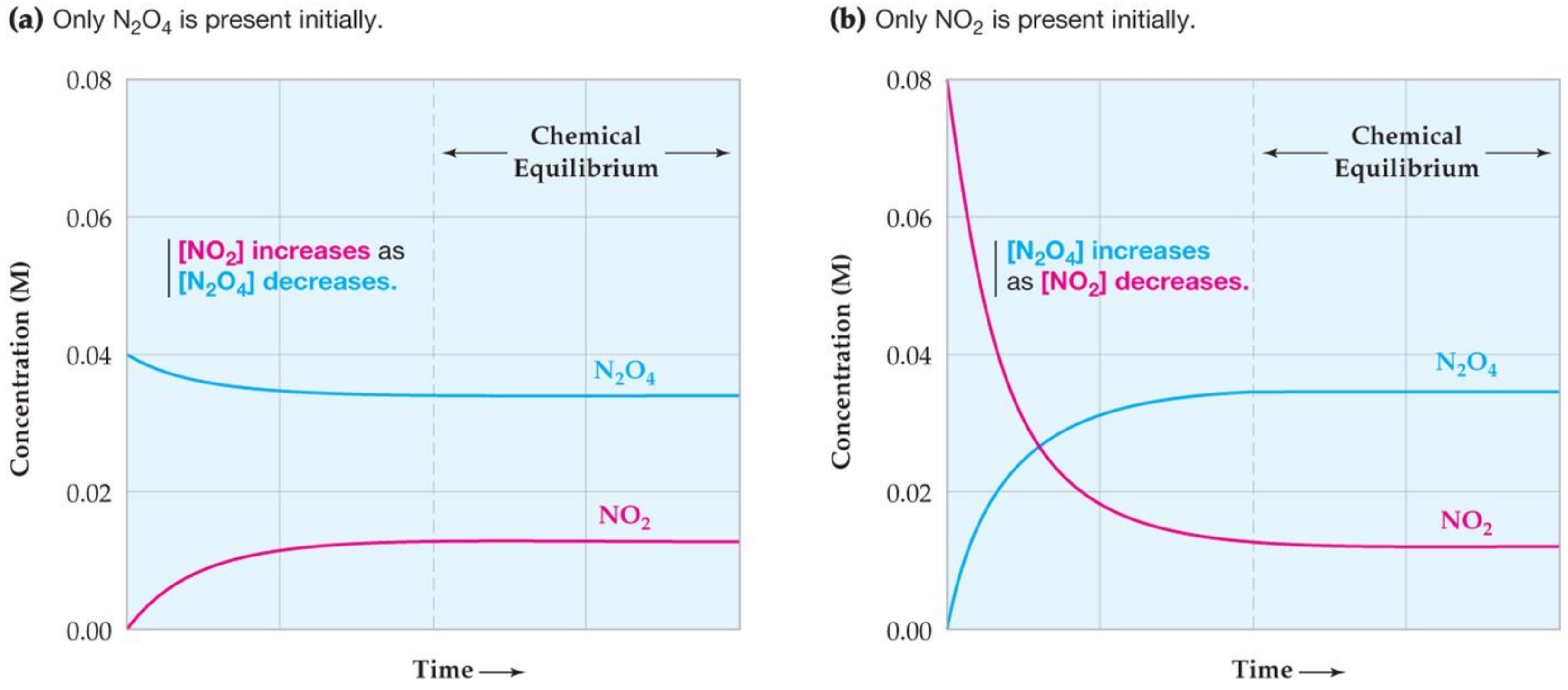
$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Colorless Brown



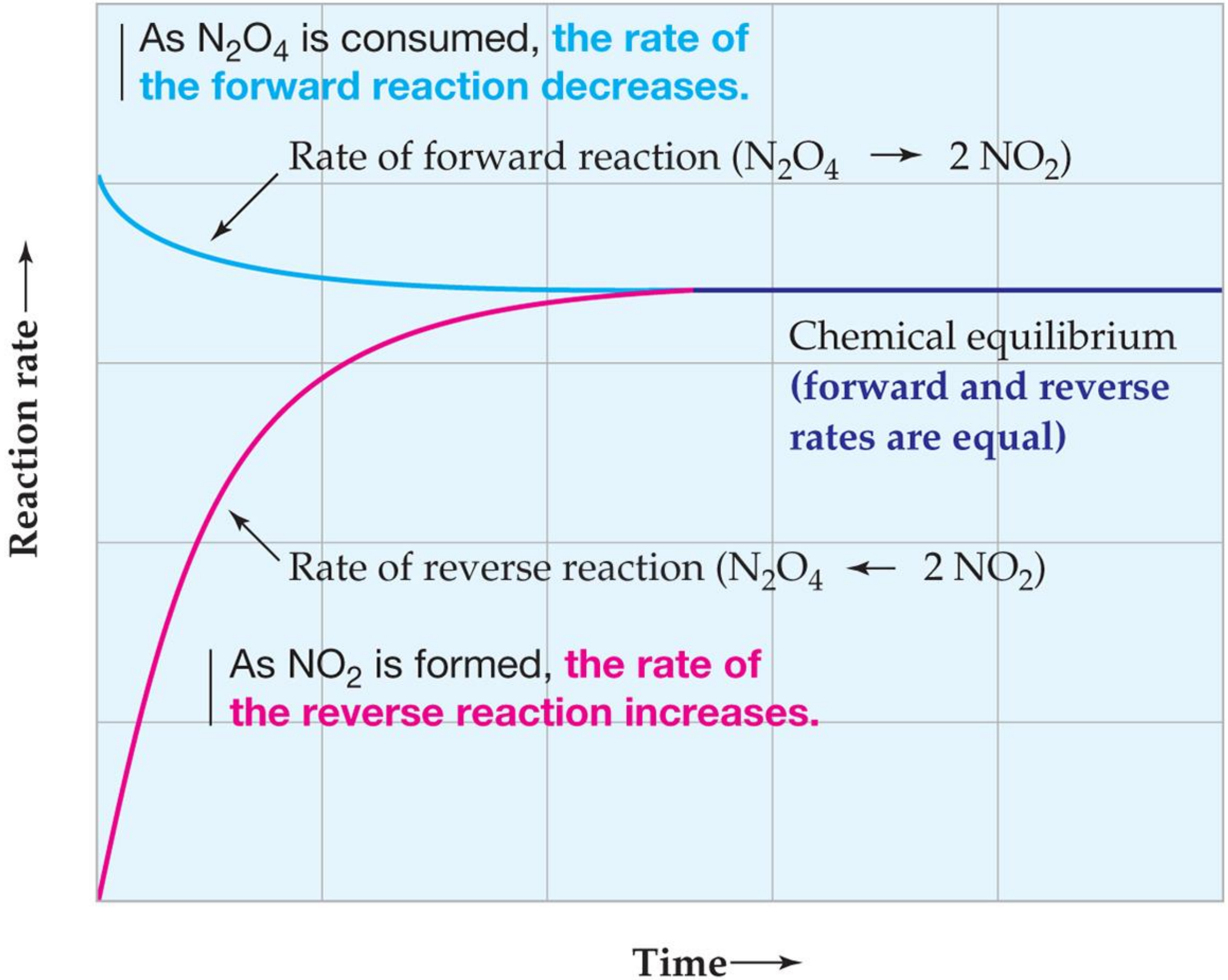
The Equilibrium State

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



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.

The Equilibrium State



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

The Equilibrium Constant K_c

TABLE 14.1 Concentration Data at 25°C for the Reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

Experiment	Initial Concentrations (M) $[N_2O_4]$	Initial Concentrations (M) $[NO_2]$	Equilibrium Concentrations (M) $[N_2O_4]$	Equilibrium Concentrations (M) $[NO_2]$	Equilibrium Constant Expression $[NO_2]^2/[N_2O_4]$
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}

Why?

The Equilibrium Constant K_c

For a general reversible reaction:

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

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

Equilibrium constant

Products

Reactants

For the following reaction: $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.64 \times 10^{-3} \text{ (at 25 °C)}$$

The Equilibrium Constant K_c

TABLE 14.1 Concentration Data at 25°C for the Reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

	Initial 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}
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5	0.0200	0.0600	0.0429	0.0141	4.63×10^{-3}

Experiment 1 — Experiment 5

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad \frac{(0.0125)^2}{0.0337} = 4.64 \times 10^{-3} \qquad \frac{(0.0141)^2}{0.0429} = 4.63 \times 10^{-3}$$

The Equilibrium Constant K_c

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

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) \qquad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$2\ NH_3(g) \rightleftharpoons N_2(g) + 3\ H_2(g) \qquad K_c' = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K_c}$$

$$2\ N_2(g) + 6\ H_2(g) \rightleftharpoons 4\ NH_3(g) \qquad K_c'' = \frac{[NH_3]^4}{[N_2]^2[H_2]^6} = K_c^{\ 2}$$

The Equilibrium Constant K_c

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

$$K_p = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O_4}}$$

P is the partial pressure of that component.

The Equilibrium Constant K_c

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

R is the gas constant, $0.08206 \dfrac{\text{L atm}}{\text{K mol}}$.

T is the absolute temperature (kelvin).

Δ*n* is the number of moles of gaseous products minus the number of moles of gaseous reactants.

Heterogeneous Equilibria

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

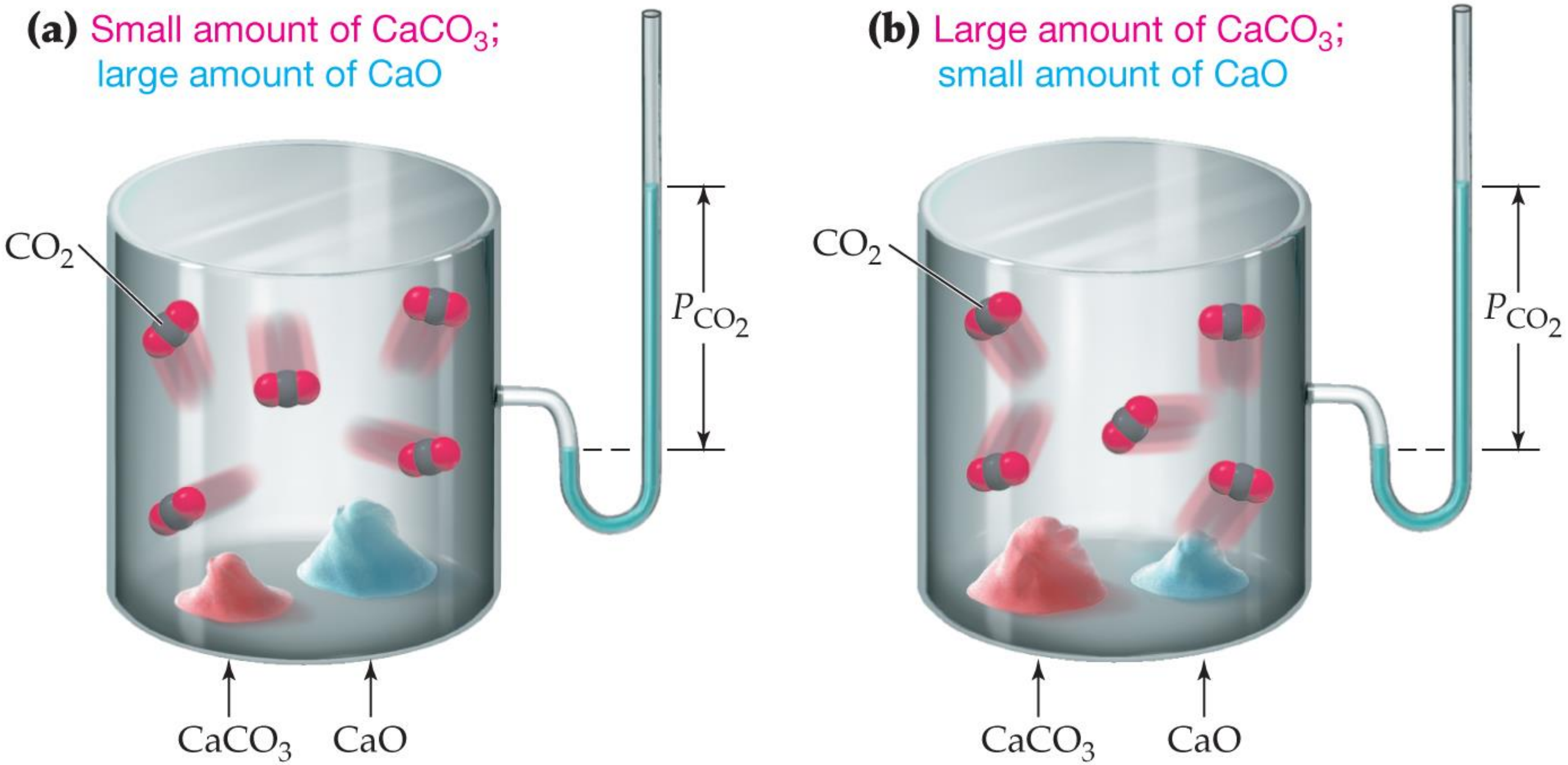
Limestone Lime

$$K_c = \frac{[\mathrm{CaO}][\mathrm{CO_2}]}{[\mathrm{CaCO_3}]} = \frac{(1)[\mathrm{CO_2}]}{(1)} = [\mathrm{CO_2}]$$

Pure solids and pure liquids are not included.

$$K_c = [\mathrm{CO_2}] \qquad K_p = P_{\mathrm{CO_2}}$$

Heterogeneous Equilibria

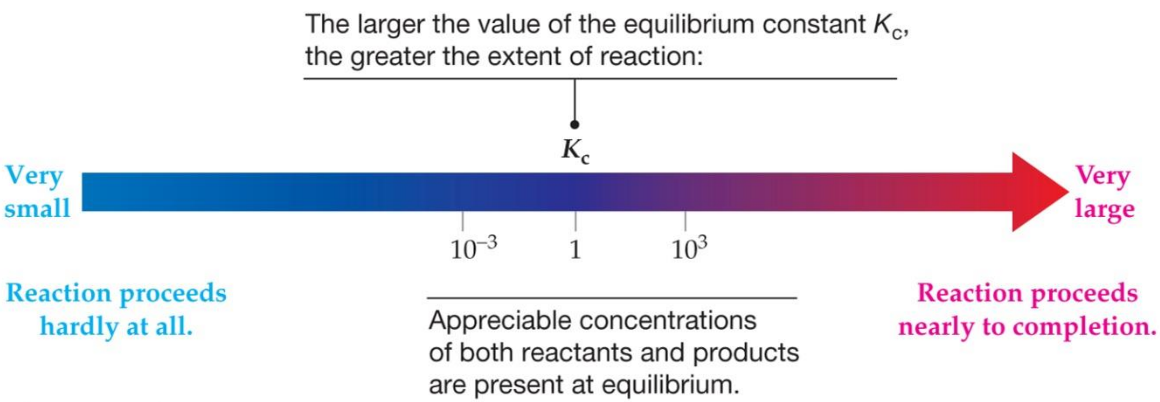


At the same temperature, the equilibrium pressure of CO_2 is the same in (**a**) and (**b**), independent of how much solid $CaCO_3$ and CaO is present.

Using the Equilibrium Constant

$$2\ H_2O(g) \rightleftharpoons 2\ H_2(g) + O_2(g)$$

(at 500 K) $K_c = 4.2 \times 10^{-48}$



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

(at 700 K) $K_c = 57.0$

$$2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(g)$$

(at 500 K) $K_c = 2.4 \times 10^{47}$

Using the Equilibrium Constant

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

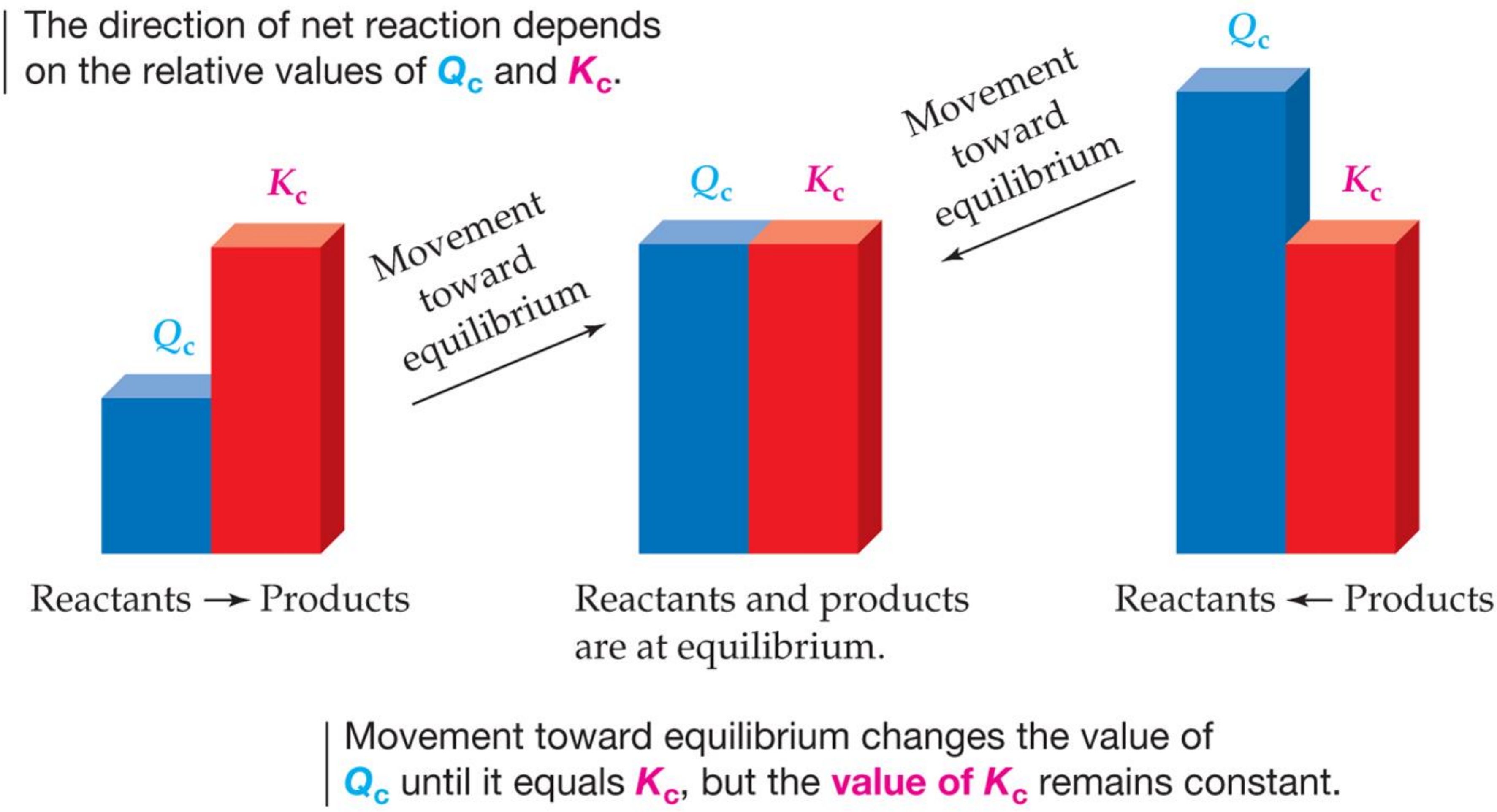
Reaction quotient: $$Q_c = \frac{[\text{C}]_t^c[\text{D}]_t^d}{[\text{A}]_t^a[\text{B}]_t^b}$$

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.

Using the Equilibrium Constant

- If $Q_c < K_c$ net reaction goes from left to right (*reactants to products*).
- If $Q_c > K_c$ net reaction goes from right to left (*products to reactants*).
- If $Q_c = K_c$ no net reaction occurs.

Using the Equilibrium Constant



Using the Equilibrium Constant

At 700 K, 0.500 mol of HI 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 . $K_\mathbf{c}$ is 57.0 at 700 K.

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

Using the Equilibrium Constant

Step 1. Compute Q_c and compare to K_c to determine the direction of reaction.

Step 2. Write the balanced equation for the reaction. Under the balanced equation, make a table that lists for each substance involved in the reaction:

- **(a)** The initial concentration
- **(b)** The change in concentration on going to equilibrium
- **(c)** The equilibrium concentration

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium and then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you must solve a quadratic equation, choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

Using the Equilibrium Constant

Set up a table:

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

0	0	0.250
$+x$	$+x$	$-2x$
x	x	$0.250 - 2x$

Substitute values into the equilibrium expression:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad 57.0 = \frac{(0.250 - 2x)^2}{x^2}$$

Using the Equilibrium Constant

Solve for "*x*":

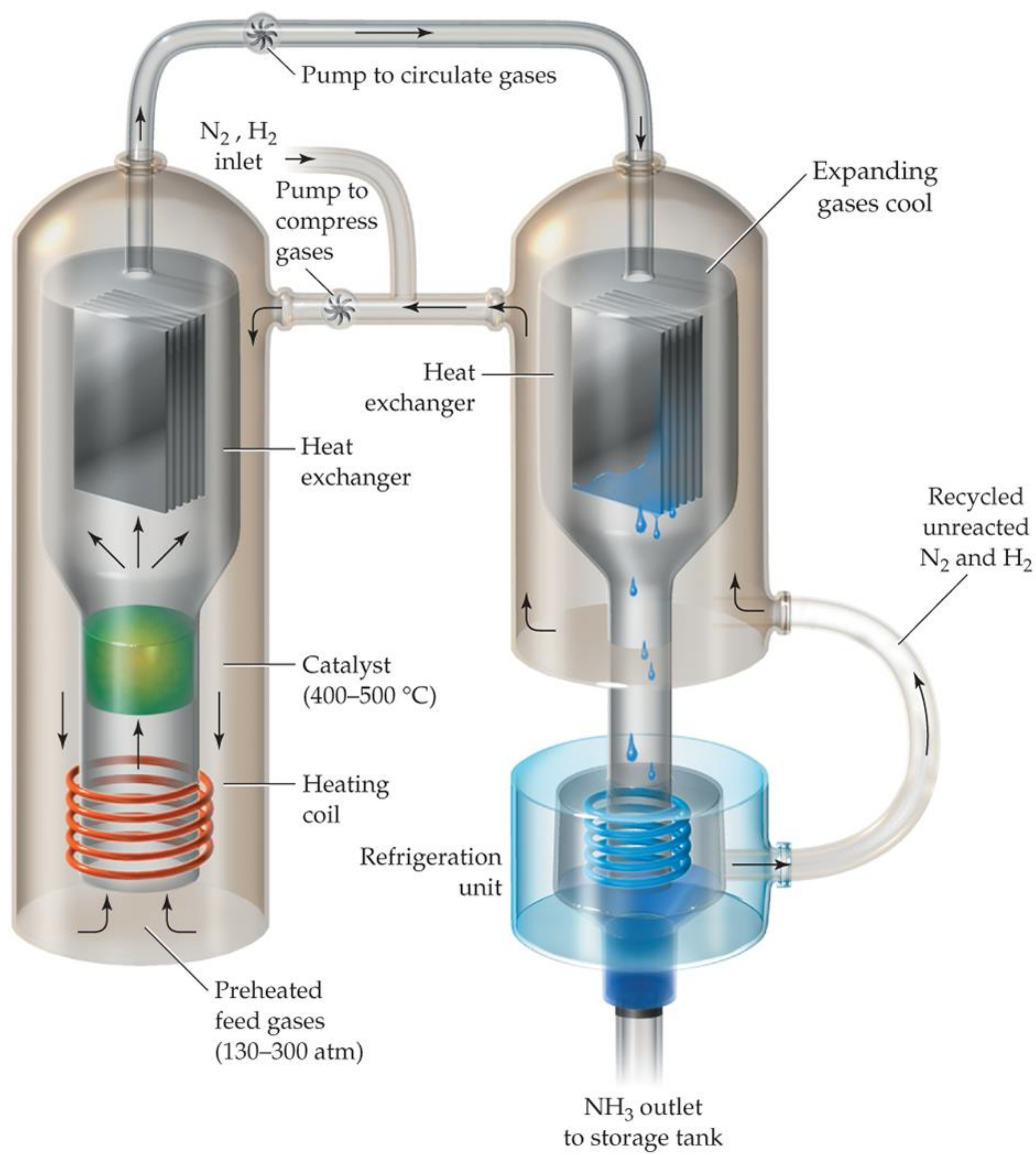
$$\sqrt{57.0} = \sqrt{\frac{(0.250 - 2x)^2}{x^2}} \qquad x = 0.0262$$

Determine the equilibrium concentrations:

H_2: 0.0262 M

I_2: 0.0262 M

HI: 0.250 – 2(0.0262) = 0.198 M


Pump to circulate gases
N_2, H_2 inlet
Pump to compress gases
Expanding gases cool
Heat exchanger
Heat exchanger
Recycled unreacted N_2 and H_2
Catalyst (400–500 °C)
Heating coil
Refrigeration unit
Preheated feed gases (130–300 atm)
NH_3 outlet to storage tank

Le Châtelier's Principle

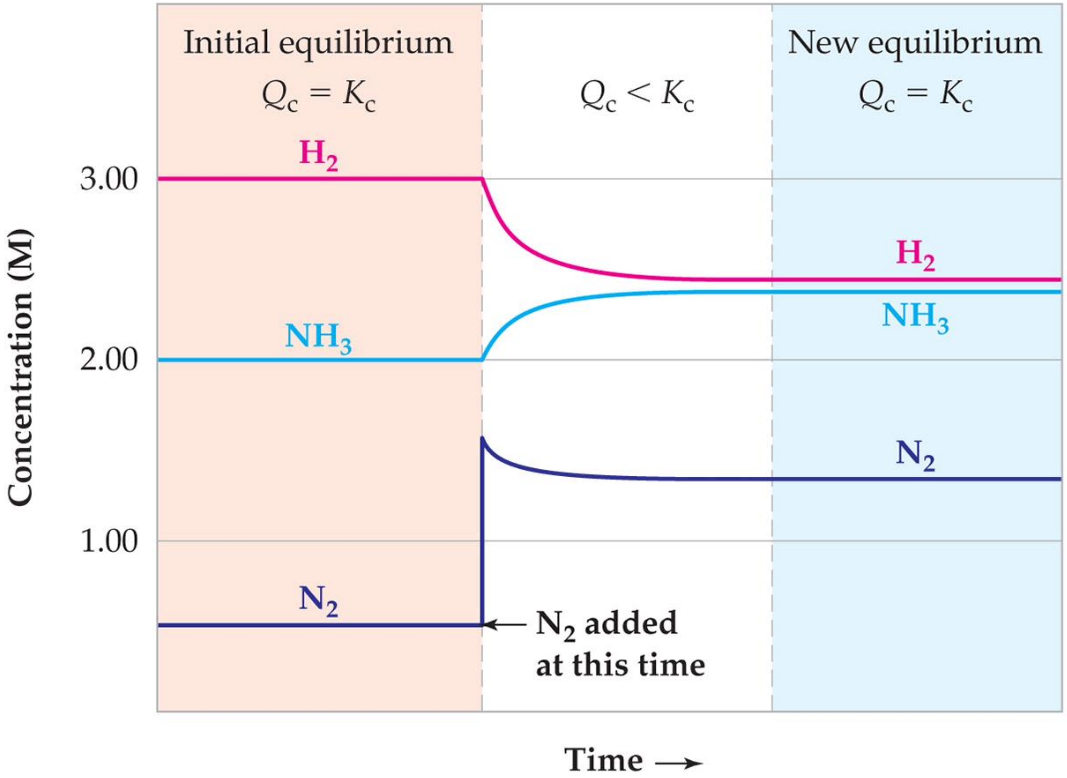
Le Châtelier's Principle: If a stress is applied to a reaction mixture *at equilibrium*, net reaction occurs in the direction that relieves the stress.

- The concentration of reactants or products can be changed.
- The pressure and volume can be changed.
- The temperature can be changed.

Altering an Equilibrium Mixture: Changes in Concentration

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

Net conversion of N_2 and H_2 to NH_3 occurs until a new equilibrium is established. That is, the N_2 and H_2 concentrations decrease, while the NH_3 concentration increases.



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Altering an Equilibrium Mixture: Changes in Concentration

In general, when an equilibrium is disturbed by the addition or removal of any reactant or product,
Le Châtelier's principle predicts that

- the concentration stress of an *added* reactant or product is relieved by net reaction in the direction that *consumes* the added substance.

- the concentration stress of a *removed* reactant or product is relieved by net reaction in the direction that *replenishes* the removed substance.

Altering an Equilibrium Mixture: Changes in Concentration

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) \text{ at 700 K, } K_c = 0.291$$

An equilibrium mixture of 0.50 M N_2, 3.00 M H_2, and 1.98 M NH_3 is disturbed by increasing the N_2 concentration to 1.50 M.

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.98)^2}{(1.50)(3.00)^3} = 0.0968 < K_c$$

Since $Q_c < K_c$, more reactants will be *consumed* and the net reaction will be from *left* to *right*.

Altering an Equilibrium Mixture: Changes in Concentration

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeNCS^{2+}(aq)$$

Pale yellow Colorless Red

(a) Original solution: Fe^{3+}(pale yellow), SCN^{-}(colorless), and $FeNCS^{2+}$(red).

(b) After adding $FeCl_3$ to **(a)**: $[FeNCS^{2+}]$ increases.

(c) After adding KSCN to **(a)**: $[FeNCS^{2+}]$ increases.

(d) After adding $H_2C_2O_4$ to **(a)**: $[FeNCS^{2+}]$ decreases as $[Fe(C_2O_4)_3{}^{3-}]$ increases.

(e) After adding $HgCl_2$ to **(a)**: $[FeNCS^{2+}]$ decreases as $[Hg(SCN)_4{}^{2-}]$ increases.

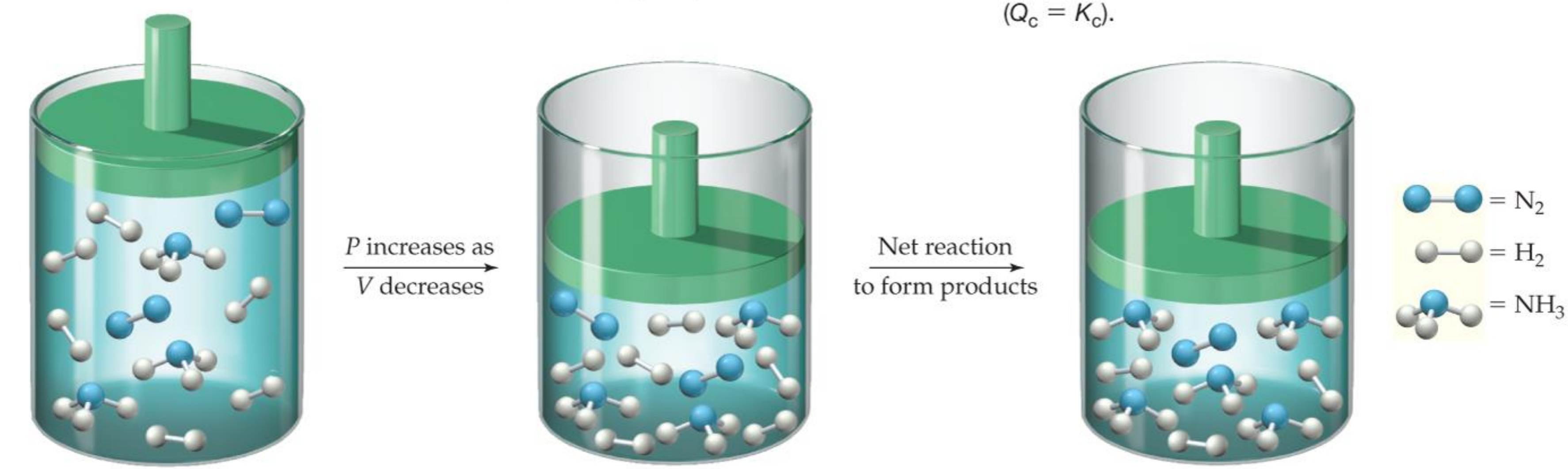
Altering an Equilibrium Mixture: Changes in Pressure and Volume

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

(a) A mixture of gaseous N_2, H_2, and NH_3 at equilibrium ($Q_c = K_c$).

(b) When the pressure is increased by decreasing the volume, the mixture is no longer at equilibrium ($Q_c < K_c$).

(c) Net reaction occurs from reactants to products, decreasing the total number of gaseous molecules until equilibrium is re-established ($Q_c = K_c$).



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Altering an Equilibrium Mixture: Changes in Pressure and Volume

In general, when an equilibrium is disturbed by a change in volume that results in a corresponding change in pressure, Le Châtelier’s principle predicts that

- an *increase* in pressure by reducing the volume will bring about net reaction in the direction that *decreases* the number of moles of gas.
- a *decrease* in pressure by expanding the volume will bring about net reaction in the direction that *increases* the number of moles of gas.

Altering an Equilibrium Mixture: Changes in Pressure and Volume

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) \text{ at 700 K, } K_c = 0.291$$

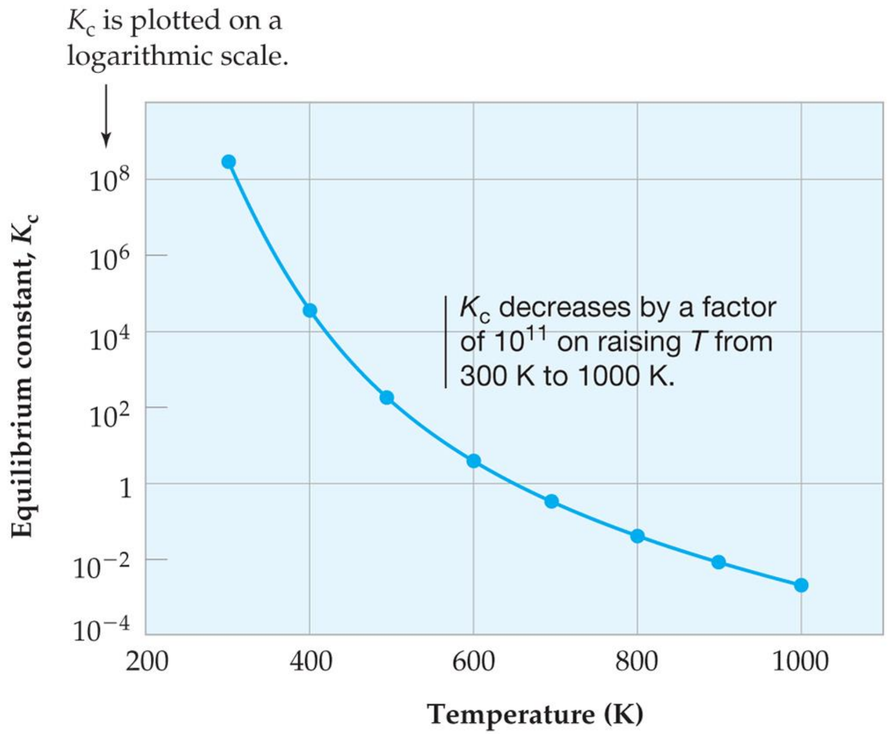
An equilibrium mixture of 0.50 M N_2, 3.00 M H_2, and 1.98 M NH_3 is disturbed by reducing the volume by a factor of 2.

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.96)^2}{(1.00)(6.00)^3} = 0.0726 < K_c$$

Since $Q_c < K_c$, more reactants will be *consumed* and the net reaction will be from *left* to *right*.

Altering an Equilibrium Mixture: Changes in Temperature

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)\ \Delta H° = –2043\ \text{kJ}$$



Temp (K)	K_c
300	2.6×10^8
400	3.9×10^4
500	1.7×10^2
600	4.2
700	2.9×10^{-1}
800	3.9×10^{-2}
900	8.1×10^{-3}
1000	2.3×10^{-3}

As the temperature increases, the equilibrium shifts from products to reactants.

Altering an Equilibrium Mixture: Changes in Temperature

In general, when an equilibrium is disturbed by a change in temperature, Le Châtelier's principle predicts that

- the equilibrium constant for an *exothermic* reaction (negative $\Delta H°$) *decreases* as the temperature *increases*.

- the equilibrium constant for an *endothermic* reaction (positive $\Delta H°$) *increases* as the temperature *increases.*

Altering an Equilibrium Mixture: Changes in Temperature

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g);\ \Delta H^\circ > 0$$

K_c increases as

T increases

The darker **brown** color of the sample at the highest temperature indicates that the equilibrium $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ shifts from reactants to products with increasing temperature, as expected for an endothermic reaction.

The Effect of a Catalyst on Equilibrium