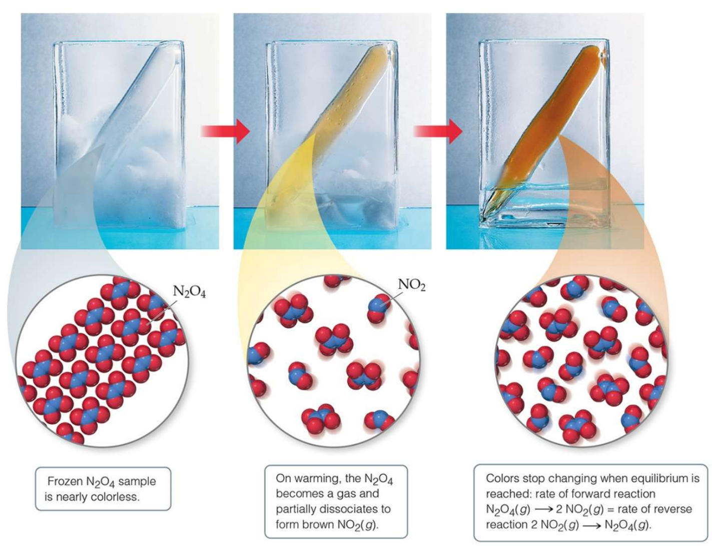
Chapter 15
Chemical Equilibrium

Learning goals and key skills:

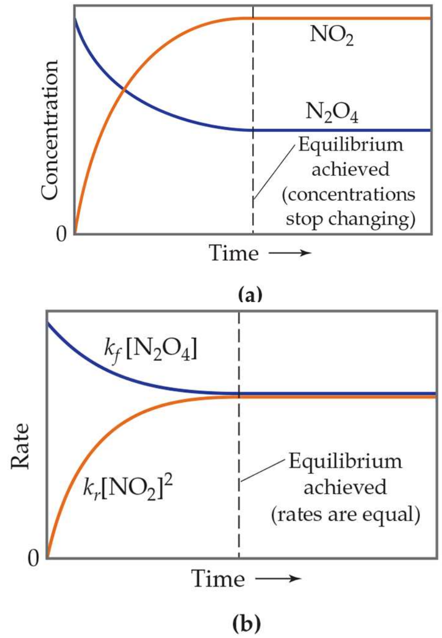
- Explain what is meant by chemical equilibrium and how it relates to reaction rates
- Write the equilibrium-constant expression for any reaction
- Convert K_c to K_p and vice versa
- Relate the magnitude of an equilibrium constant to the relative amounts of reactants and products present in an equilibrium mixture.
- Manipulate the equilibrium constant to reflect changes in the chemical equation
- Write the equilibrium-constant expression for a heterogeneous reaction
- Calculate an equilibrium constant from concentration measurements
- Predict the direction of a reaction given the equilibrium constant and the concentrations of reactants and products
- Calculate equilibrium concentrations given the equilibrium constant and all but one equilibrium concentration
- Calculate equilibrium concentrations given the equilibrium constant and the starting concentrations
- Use Le Chatelier's principle to predict how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position.

The Concept of Equilibrium

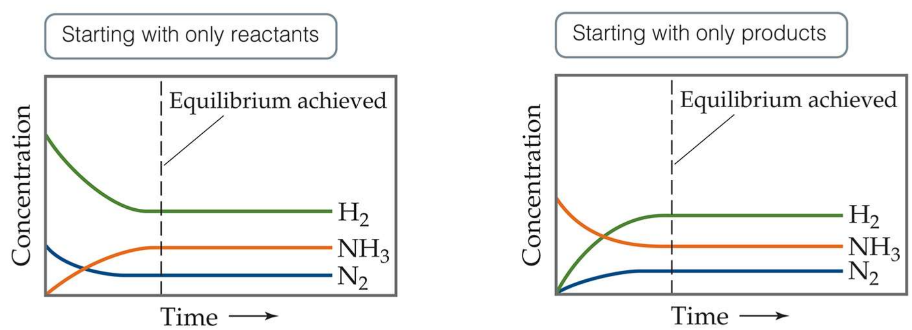


Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

Concept of Equilibrium



- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding *at the same rate*.
- Once equilibrium is achieved, the *amount* of each reactant and product remains constant.



The same equilibrium is reached whether we start with only reactants (N_2 and H_2) or with only product (NH_3).

Equilibrium is reached from either direction.

The Equilibrium Constant

- Consider the generalized reaction

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

The equilibrium expression for this reaction would be

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

Since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

$$K_p = \frac{(P_C)^c\,(P_D)^d}{(P_A)^a\,(P_B)^b}$$

Chemical equilibrium occurs when opposing reactions are proceeding at equal rates.

$$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow.

Forward reaction:

$$N_2O_{4\,(g)} \longrightarrow 2\,NO_{2\,(g)}$$

Rate Law:

Rate = $k_f\,[N_2O_4]$

Reverse reaction:

$$2\,NO_{2\,(g)} \longrightarrow N_2O_{4\,(g)}$$

Rate Law:

Rate = $k_r\,[NO_2]^2$

Equilibrium Constant

- Therefore, at equilibrium

$$Rate_f = Rate_r$$

$$k_f\,[N_2O_4] = k_r\,[NO_2]^2$$

- Rewriting this, it becomes

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} = \text{a constant}$$

Example

Write the equilibrium constant expression of the following reaction:

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

Relationship Between K_c and K_p

From the Ideal Gas Law we know that:

$PV = nRT$ *and* $P = (n/V)RT = [A]RT$

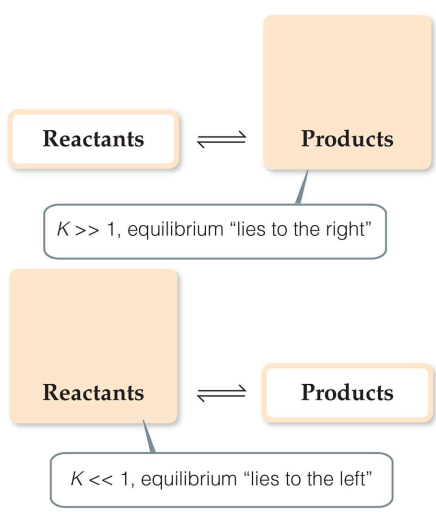
Plugging this into the expression for K_p for each substance, the relationship between K_c and K_p becomes

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

where

Δn = (moles of gaseous product) - (moles of gaseous reactant)

What Does the Value of K Mean?



- If $K>>1$, the reaction is *product-favored*; product predominates at equilibrium.
- If $K<<1$, the reaction is *reactant-favored*; reactant predominates at equilibrium.

*When $10^{-3} < K < 10^{3}$, the reaction is considered to contain a significant amount of both reactants and products at equilibrium.

Direction of Chemical Equation and K

$N_2O_4\ (g) \rightleftharpoons\ 2\ NO_2\ (g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\ °C$

$2\ NO_2\ (g) \rightleftharpoons\ N_2O_4\ (g) \quad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 \text{ at } 100\ °C$

The equilibrium constant of a reaction in the reverse direction is the reciprocal of the equilibrium constant of the forward reaction.

Stoichiometry and K

$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\ °C$

$2\ N_2O_4(g) \rightleftharpoons\ 4\ NO_2(g) \quad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2 \text{ at } 100\ °C$

The equilibrium constant of a reaction that has been multiplied by a number, is the equilibrium constant raised to a power that is equal to that number.

Multiple equilibria and K

$$2\ NOBr \rightleftharpoons 2\ NO + Br_2 \qquad K_1 = 0.014$$

$$Br_2 + Cl_2 \rightleftharpoons 2\ BrCl \qquad K_2 = 7.2$$

$$2\ NOBr + Cl_2 \rightleftharpoons 2\ NO + 2\ BrCl$$

$$K_3 = K_1 \times K_2 = 0.014 \times 7.2 = 0.10$$

The equilibrium constant for a net reaction made up of two or more steps is the *product* of the equilibrium constants for the individual steps.

Example

Consider the following reactions at 1200 K.

$$CO(g) + 3\ H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad K_{c,1} = 3.92$$

$$CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + 4\ H_2(g) \qquad K_{c,2} = 3.3x10^4$$

Use the above reactions to determine the equilibrium constant (K_c) for the following reaction at 1200 K.

$$CO(g) + 2\ H_2S(g) \rightleftharpoons H_2O(g) + CS_2(g) + H_2(g)$$

Homogeneous vs Heterogeneous

Homogeneous equilibria occur when all reactants and products are in the same phase.

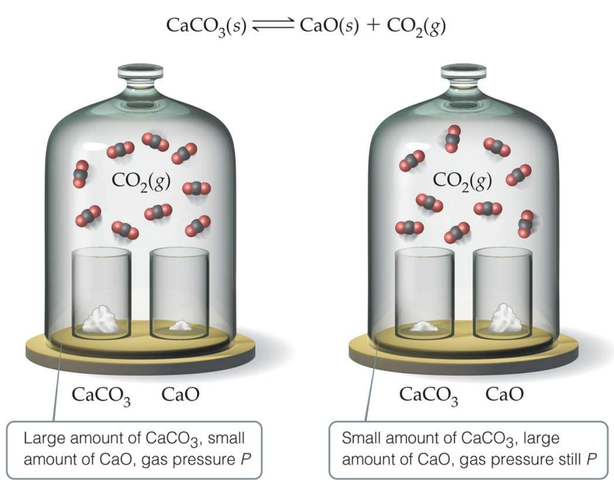
Heterogeneous equilibria occur when reactant or product in the equilibrium is in a different phase.

- The value used for the concentration of a pure substance is always 1.

Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^{-}(aq)$$

$$K_c = [Pb^{2+}][Cl^{-}]^2$$



As long as *some* $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.

$$K_c = [CO_2] \text{ and } K_p = P_{CO_2}$$

Equilibrium constant, K_c (K_{eq} or K)

- Always products divided by reactants. (Although sometimes products are equal to 1 and reactants are equal to 1.)
- All concentrations are equilibrium values.
- Each concentration is raised to its stoichiometric coefficient.
- K_c depends on the rate constants which in turn depend on the reaction (E_a) and temperature.
- No units on K_c.
- Pure solids and pure liquids are excluded from K_c.
- A catalyst does not change the equilibrium concentrations, so it does not change K_c.

Calculating Equilibrium Constants

A closed system initially containing 1.000 x 10^{-3} *M* H_2 and 2.000 x 10^{-3} *M* I_2 at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87 x 10^{-3} *M*. Calculate K_c at 448 °C for the reaction taking place, which is

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2\,HI_{\,(g)}$$

What Do We Know?

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
Equilibrium			1.87×10^{-3}

[HI] Increases by 1.87×10^{-3} *M*

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
Equilibrium			1.87×10^{-3}

Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much.

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
Equilibrium			1.87×10^{-3}

Calculate the equilibrium concentrations of all three compounds…

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
Equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} = 51$$

Example

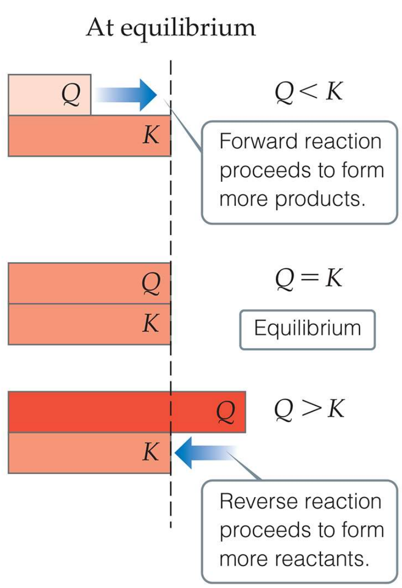
Phosphorus pentachloride gas partially decomposes to phosphorus trichloride gas and chlorine gas. 1.20 mol PCl_5 is placed in a 1.00 L container at 200 °C. At equilibrium 1.00 mol PCl_5 remains. Calculate K_c and K_p at 200 °C.

The Reaction Quotient (Q)

- Q gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
- To calculate Q, substitute the (*initial*) concentrations of reactants and products into the equilibrium expression.

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

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



Comparing K and Q

If Q < K

- There's too much reactant
- Need to increase the amount of products and decrease the amount of reactants

If Q > K

- There's too much product
- Need to decrease the amount of products and increase the amount of reactants

Example

A 50.0 L reaction vessel contains 1.00 mol N_2, 3.00 mol H_2, and 0.500 mol NH_3. Will more ammonia (NH_3) be formed or will NH_3 dissociate when the reaction mixture approaches equilibrium at 400 °C?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad K_c = 0.500 \text{ at } 400\ °C.$$

Example

In the *steam-reforming reaction*, methane reacts with water vapor to form carbon monoxide and hydrogen gas. At 900 K, $K_c = 2.4 \times 10^{-4}$.

If 0.012 mol of methane, 0.0080 mol of water vapor, 0.016 mol of carbon monoxide and 0.0060 mol of hydrogen gas are placed in a 2.0-L steel reactor and heated to 900 K, which way will the reaction proceed: to the right (products) or left (reactants)?

Example

Problem: Finding equilibrium concentrations from initial concentrations and the equilibrium constant.

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.10$ at 2000 °C

A reaction mixture at 2000 °C initially contains $[N_2] = 0.200$ M and $[O_2] = 0.200$ M.

Find the *equilibrium* concentrations of the reactants and products at this temperature.

- Represent the change in concentration of one of the reactants (or products) with the variable '*x*'.
- Define the changes in concentration of the other reactants and/or products in terms of *x*.
- Tip: Usually convenient to let *x* represent the change in concentration of the reactant (or product) with the smallest stoichiometric coefficient.

Example

Problem: Finding equilibrium concentrations from initial concentrations and the equilibrium constant.

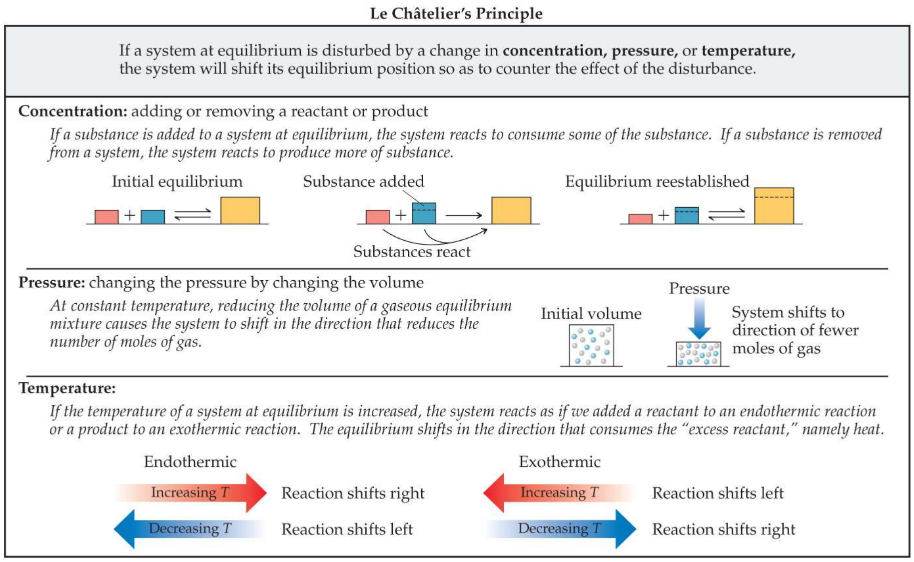
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_c = 0.36$ at 100 °C

A reaction mixture at 100 °C initially contains $[NO_2] = 0.100$ M. Find the *equilibrium* concentrations of the reactants and products at this temperature.

Le Châtelier's Principle

If a system at equilibrium is disturbed by a change in temperature, pressure or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

Changing concentration
Temperature
Changing volume/pressure

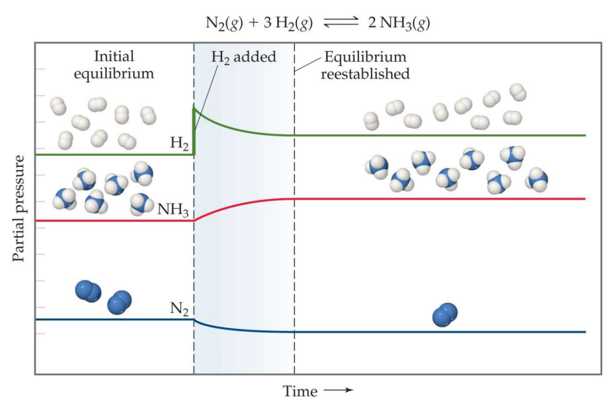


Example: Le Châtelier's Principle

$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$ $K_p = 0.0214$ at 540 K

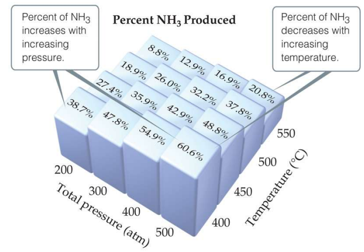
At equilibrium
$P_{H2} = 2.319$ atm
$P_{NH3} = 0.454$ atm
$P_{N2} = 0.773$ atm

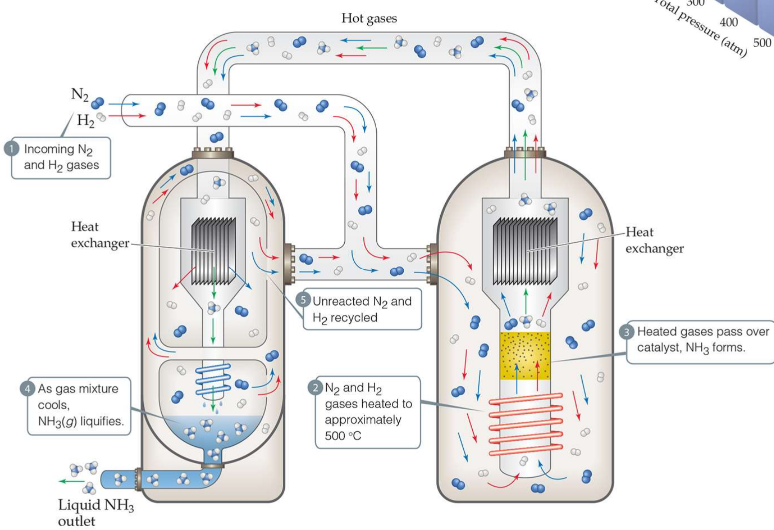
What happens upon addition of 1 atm of H_2?



The Haber Process

This apparatus helps push the equilibrium to the right by removing the ammonia (NH_3) from the system as a liquid.

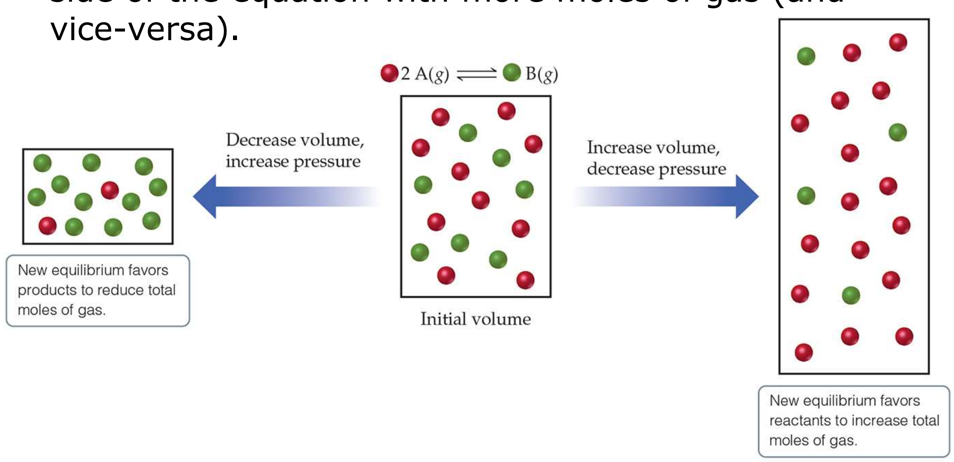




Change in Volume or Pressure

If gases are involved in an equilibrium, a change in pressure or volume will affect K:

- Higher volume or lower pressure favors the side of the equation with more moles of gas (and vice-versa).



Le Châtelier's Principle: pressure

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Boyle's law: at a fixed temperature, PV = k

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

Double the pressure (concentration)

$$Q_c = \frac{(2[CH_4])(2[H_2O])}{(2[CO])(2[H_2])^3} = \frac{K_c}{4}$$

$Q_c < K_c$, reaction forms products

In summary, if the pressure is increased by decreasing the volume of a reaction mixture, the reaction shifts in the direction of fewer moles of gas.

Le Châtelier's Principle: temperature

endothermic $\Delta H > 0$

heat can be thought of as a reactant

increasing T results in an increase in *K*

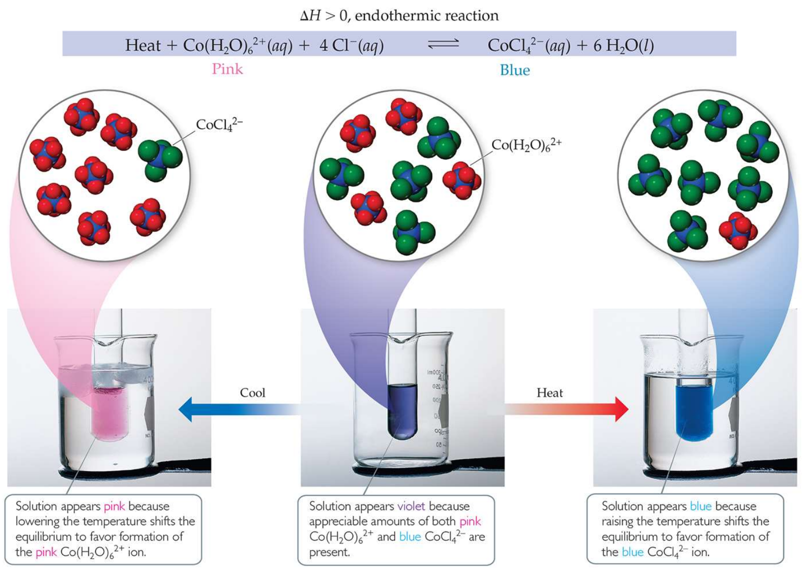
exothermic $\Delta H < 0$

heat can be thought of as a product

increasing T results in an decrease in *K*

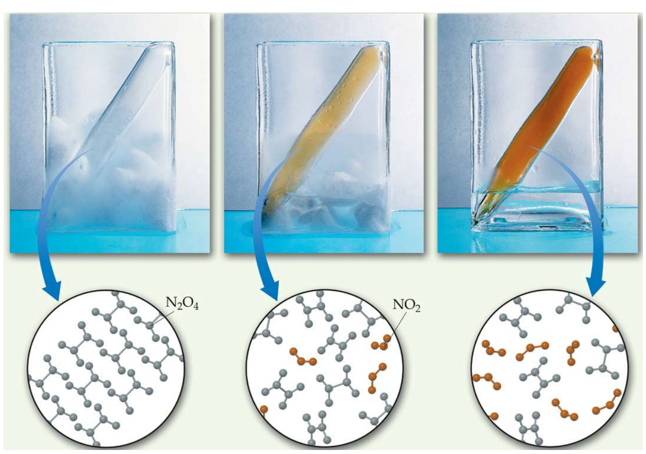
The Effect of Changes in Temperature

$Co(H_2O)_6^{2+}$ (*aq*) + 4 Cl^- (*aq*) ⇌ $CoCl_4^{2-}$ (*aq*) + 6 H_2O (*l*)

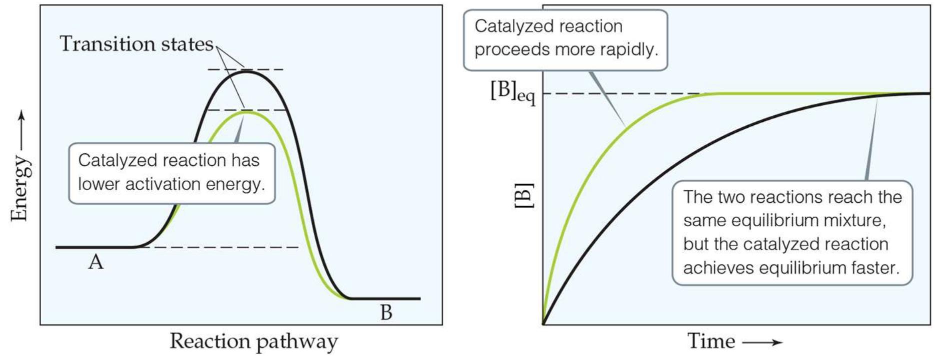


Example: Le Châtelier's Principle

N_2O_4 (g) ⇌ 2 NO_2 (g) is endothermic.
What occurs with increasing temperature?



Catalysts



Catalysts increase the rate of both the forward *and* reverse reactions.

When one uses a catalyst, equilibrium is achieved *faster*, but the equilibrium composition remains *unaltered*.