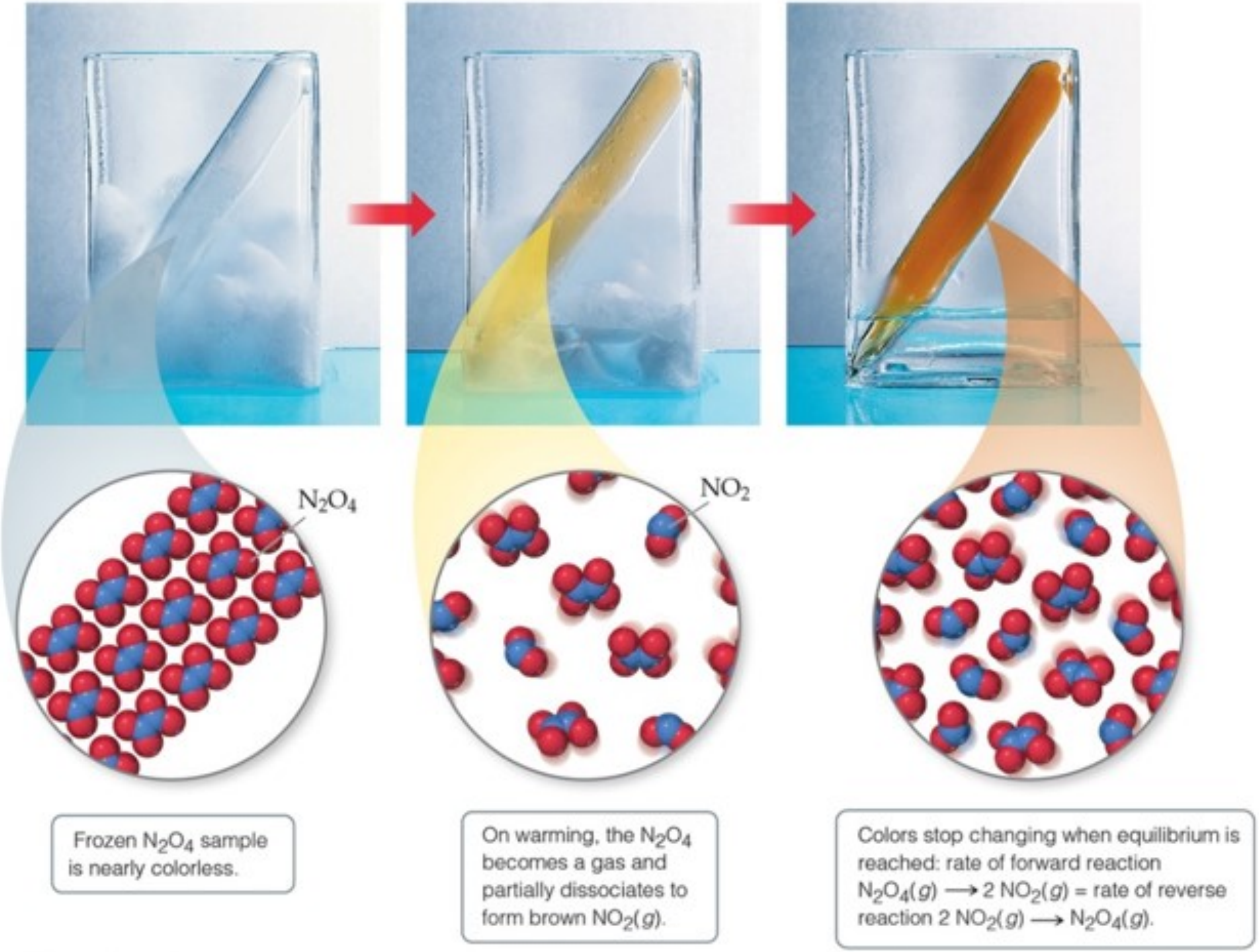
Chapter 15 Chemical Equilibrium

15.1 The Concept of Chemical Equilibrium



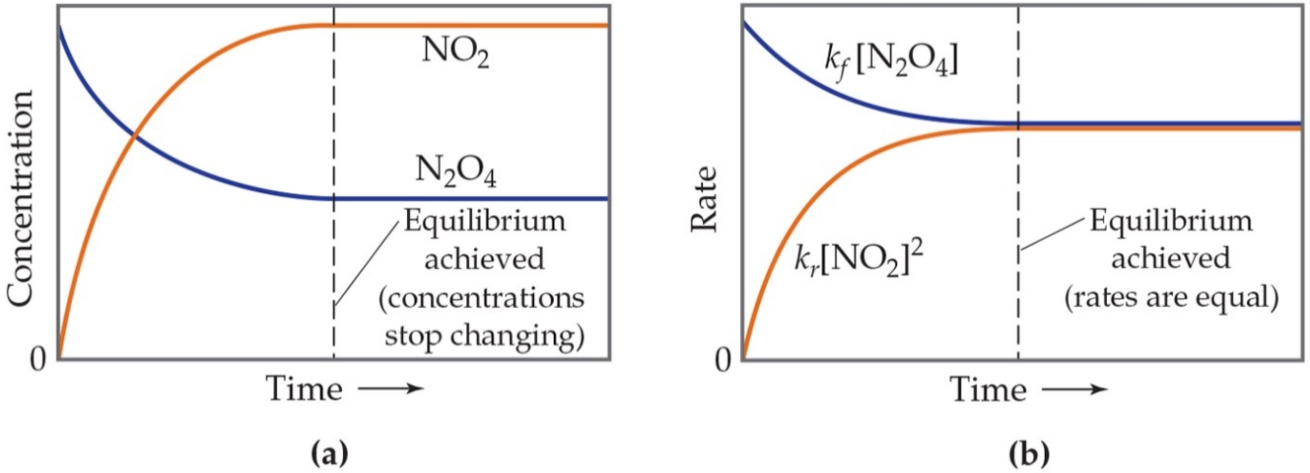
Frozen N_2O_4 sample is nearly colorless.

On warming, the N_2O_4 becomes a gas and partially dissociates to form brown $NO_2(g)$.

Colors stop changing when equilibrium is reached: rate of forward reaction $N_2O_4(g) \longrightarrow 2\ NO_2(g)$ = rate of reverse reaction $2\ NO_2(g) \longrightarrow N_2O_4(g)$.

Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate. In the figure above, equilibrium is finally reached in the third picture.

15.1 The Concept of Chemical 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** (vertical dashed line**)**.
- At equilibrium, the **amount** of each reactant and product remains constant.

15.2 The Equilibrium Constant

In a system at equilibrium, both the forward and reverse reactions are being carried out. The equation is written with a double arrow:

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

- For the forward reaction: $N_2O_4(g) \rightarrow 2\,NO_2(g)$

$$\text{Rate} = k_f\left[N_2O_4\right]$$

- For the reverse reaction: $2\,NO_2(g) \rightarrow N_2O_4(g)$

$$\text{Rate} = k_r\left[NO_2\right]^2$$

Equilibrium Constant Expression

- At equilibrium

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

$$k_f\left[\text{N}_2\text{O}_4\right] = k_r\left[\text{NO}_2\right]^2$$

- Rewriting, it becomes the expression for the equilibrium constant (K):

$$\frac{\left[\text{NO}_2\right]^2}{\left[\text{N}_2\text{O}_4\right]} = \frac{k_f}{k_r} = \text{K}$$

The Equilibrium Constant

- Consider the generalized reaction

$$\mathrm{aA + bB \rightleftharpoons dD + eE}$$

- The equilibrium expression for this reaction would be

$$K_c = \frac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b} \quad \begin{array}{l} \leftarrow \text{products} \\ \leftarrow \text{reactants} \end{array}$$

- Also, since *pressure* is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

$$K_p = \frac{(P_\mathrm{D})^d(P_\mathrm{E})^e}{(P_\mathrm{A})^a(P_\mathrm{B})^b}$$

- *How does the rate law figure into all of this?*

The Equilibrium Constant

- Consider the generalized reaction

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- Also, since *pressure* is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

$$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$$

- *How does the rate law figure into all of this?*
- *It doesn't!!!!!!!!!!!!*

The Haber Process

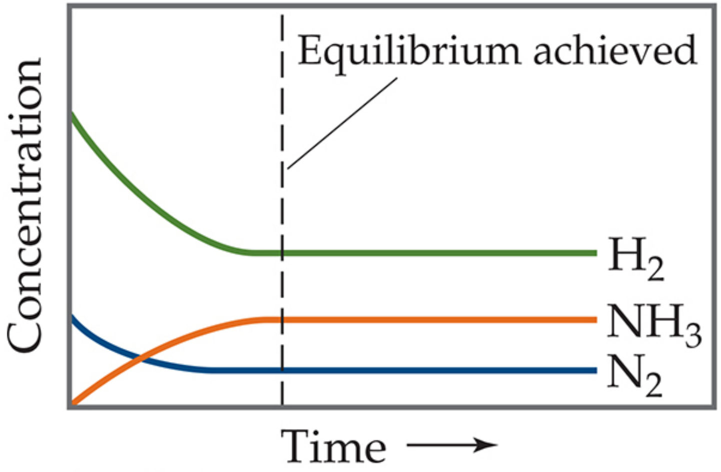
- Consider the Haber process, which is the industrial preparation of ammonia:

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

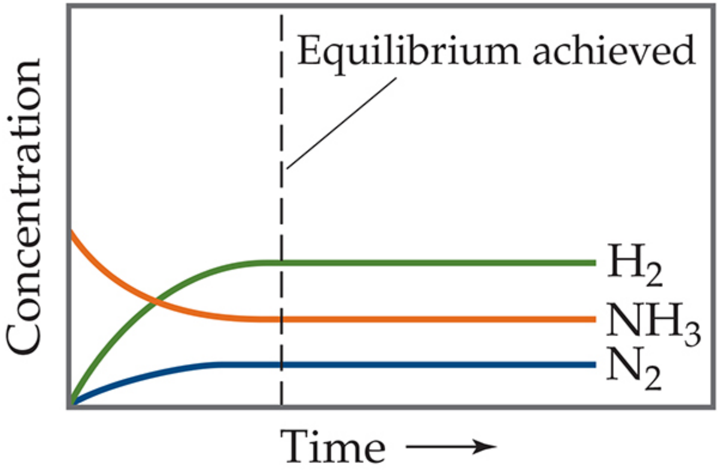
- The equilibrium constant depends on stoichiometry:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Achieving Equilibrium



Starting with only reactants



Starting with only products

it doesn't matter where you start;

The same equilibrium is reached.

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

Relative amount of *change* is based on stoichiometry.

Evaluating K_c (1 of 2)

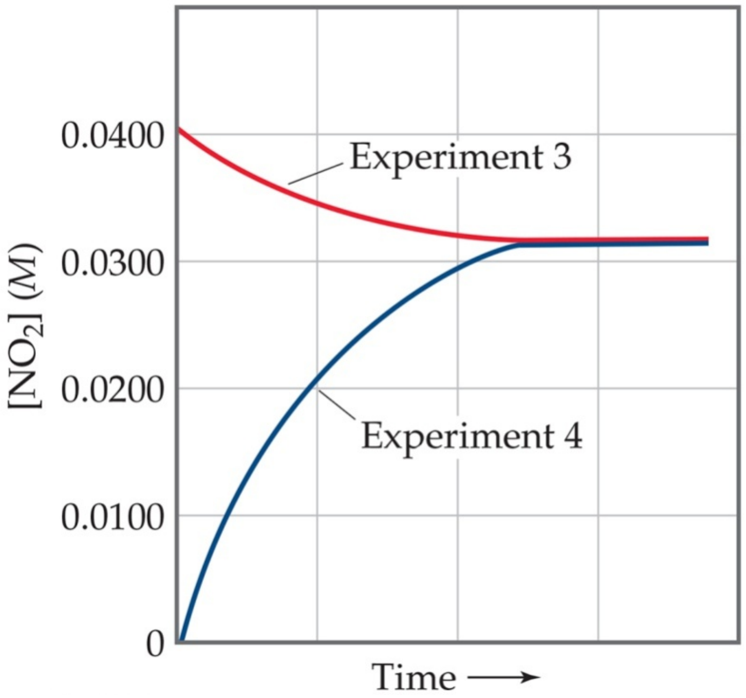
Table 15.1 Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C

Experiment	**Initial** $[N_2O_4]$ (M)	**Initial** $[NO_2]$ (M)	**Equilibrium** $[N_2O_4]$ (M)	**Equilibrium** $[NO_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

Each experiment can begin and end with different concentrations. But all end with the ***same*** equilibrium.

Evaluating K_c (2 of 2)

The ratio of $[NO_2]^2$ to $[N_2O_4]$ remains constant at 100°C no matter the initial concentrations of NO_2 and N_2O_4



Equilibrium Constants in Terms of Pressure, K_p

- For gases, $PV = nRT$ (the ideal-gas law).
- Rearranging, $P = (n/V)RT; (n/V)$ is [ ].

$$\mathrm{P} = \mathrm{MRT}$$

$$K_c = \frac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b} \quad \begin{matrix}\leftarrow \text{products} \\ \leftarrow \text{reactants}\end{matrix} \qquad K_p = \frac{(P_{\mathrm{D}})^d(P_{\mathrm{E}})^e}{(P_{\mathrm{A}})^a(P_{\mathrm{B}})^b}$$

- Substituting into $\mathrm{K_p}$: $K_p = K_c(RT)^{\Delta n}$

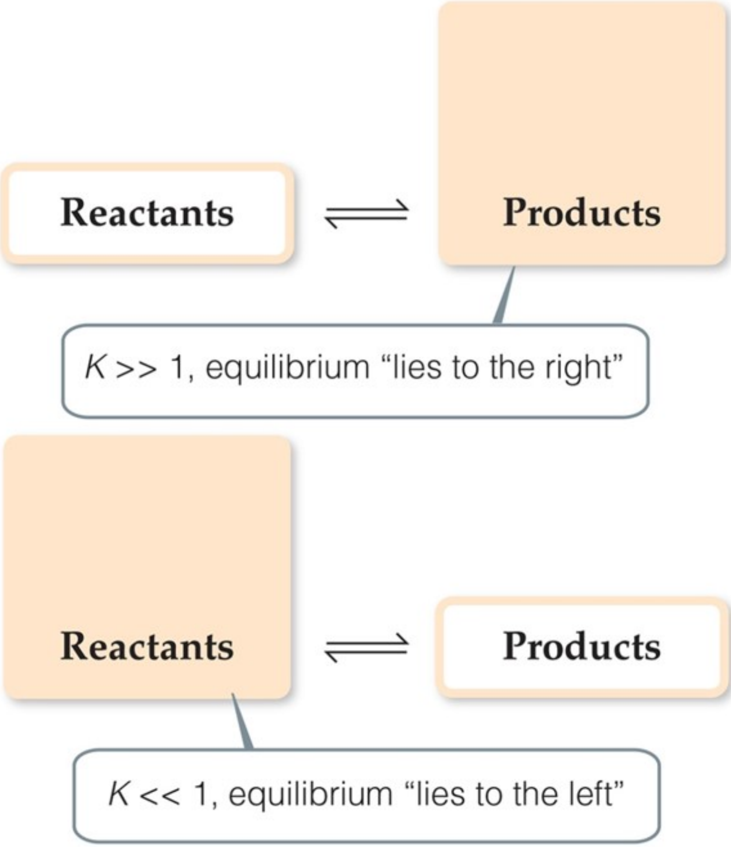
where

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$$

15.2 Using Equilibrium Constants

Magnitude of K

- If $K >> 1$, the reaction favors products; products predominate at equilibrium.
- If $K << 1$, the reaction favors reactants; reactants predominate at equilibrium.



The Direction of the Chemical Equation and *K*

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

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\ ^\circ C$$

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

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 \text{ at } 100\ ^\circ C$$

$$1/0.212 = 4.72$$

Relating Stoichiometry and Equilibrium Constants

- To find the new equilibrium constant of a reaction when the equation has been
  - multiplied by a number, simply raise the original equilibrium constant to that power. Here, the stoichiometry is doubled; the constant is the squared

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

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

  - divided by a number, take the appropriate root. If divided by two, take the square root.

Exam1, The review

- Topics:
  - The Ideal gas law.

    PV=nRT. Can you rearrange it?

    Can you use it in terms of density?

    Any other permutation you saw in homework or recitation.
  - Partial pressures

    Gases act like they're all alone when mixed.

Exam1, The review

- Topics:
  - Partial pressures

    Gases act like they're all alone when mixed.

    $P_{tot} = P_A + P_B + \ldots P_n$
  - Effusion/diffusion:

$$\frac{rate_2}{rate_1} = \sqrt{\frac{M_1}{M_2}}$$

Exam1, The review

- Topics:
  - Nonideal gases
    - What makes a gas non ideal?
      - Attraction
      - Size.
  - Intermolecular forces
    - Dipole/dipole
      - Hydrogen bonding
    - Induced dipole(London dispersion)
    - Trends? Who’s more sticky
      - Higher boiling point/viscosity etc.

Exam1, The review

- Topics:
  - Kinetics

    Rate laws from experimental data

    - 1st/2nd/3rd order.
    - Overall order

    Elementary steps/molecularity

    Integrated rate laws

    - Amount of stuff versus time.

    Mechanisms

    - Mechanisms from rate laws.

    Predicting a rate law from mechanism.

Combining Equilibrium Expressions

- When two consecutive equilibria occur, the equations can be added to give a single equilibrium.
- The equilibrium constant of the new reaction is the **product** of the two constants:

$$K_3 = K_1 \times K_2$$

- Example:

$$\begin{array}{llll}
 & 2NOBr\ (g) \rightleftharpoons 2NO\ (g) + \cancel{Br_2} & & K_1 = 0.014 \\
 & \cancel{Br_2} + Cl_2\ (g) \rightleftharpoons 2BrCl & & K_2 = 7.2 \\
\hline
 & 2NOBr + Cl_2 \rightleftharpoons 2NO\ (g) + 2BrCl & & K_3 = K_1 \text{ x } K_2
\end{array}$$

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

15.4 Heterogeneous Equilibria

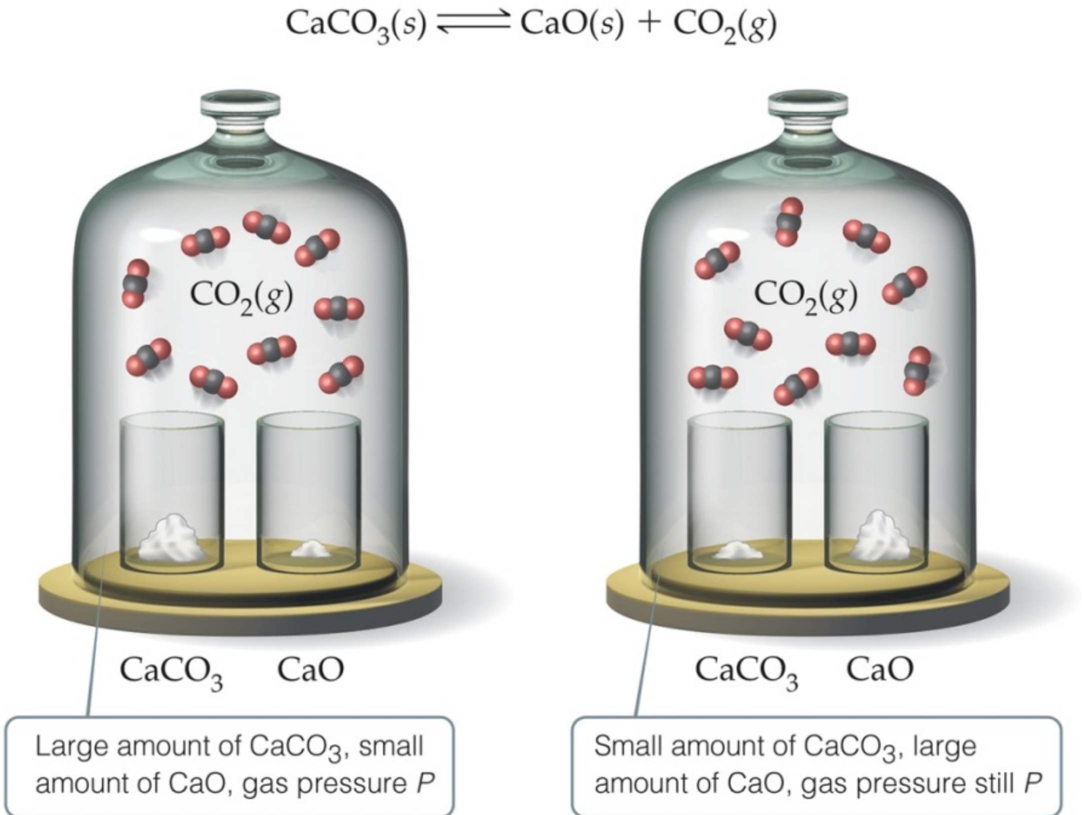
- **Homogeneous equilibria** all reactants and products are in the **same phase.**
- **Heterogeneous equilibria** occur when a component in the equilibrium is in a different phase.
- Whenever a pure solid (s) or pure liquid (l) is involved in a heterogeneous equilibrium, its concentration **is not included** in the equilibrium-constant expression.

Decomposition of $CaCO_3$ — Heterogeneous Equilibrium

- The equation for the reaction is

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

- This results in $K_c = [CO_2]$ and $K_p = P_{CO_2}$



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

Large amount of $CaCO_3$, small amount of CaO, gas pressure *P*

Small amount of $CaCO_3$, large amount of CaO, gas pressure still *P*

15.5 Equilibrium Constant problems

1) **Tabulate** all known initial and equilibrium **concentrations**.
2) **calculate the change in concentrations**.
    1) If initial and final are known
    2) Or, use the reaction stoichiometry
3) Use **initial concentrations** and **changes** to find **equilibrium concentration** of all species.
4) **Calculate** equilibrium constant using the **equilibrium concentrations**.

A K_c Calculation Example

A closed system initially containing $1.000 \times 10^{-3}\ M$ H_2 and $2.000 \times 10^{-3}\ M$ I_2 at 448 °C is allowed to reach equilibrium. At equilibrium the mixture shows concentration of HI is $1.87 \times 10^{-3}\ M$. Calculate K_c at 448 °C.

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

Ice Tables!

A closed system initially containing $1.000 \times 10^{-3}\ M\ \mathrm{H_2}$ and $2.000 \times 10^{-3}\ M\ \mathrm{I_2}$ at 448 °C is allowed to reach equilibrium. At equilibrium the mixture shows concentration of HI is 1.87×10^{-3} *M*. Calculate K_c at 448 °C.

$$\mathrm{H_2}\,(g) \quad + \quad \mathrm{I_2}\,(g) \rightleftharpoons \mathrm{2HI}\,(g)$$

	$[\mathrm{H_2}], M$	$[\mathrm{I_2}], M$	$[\mathrm{HI}], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

A K_c Calculation Example (3 of 6)

2. **Calculate changes.**

change in [HI] is easy.

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

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

A K_c Calculation Example

2. **Calculate changes.**

Use equation **stoichiometry** to complete **changes**

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

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

A K_c Calculation Example (5 of 6)

3. Calculate the **equilibrium** concentrations

$$H_2\,(g) \quad + \quad I_2\,(g) \rightleftarrows 2HI\,(g)$$

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

A K_c Calculation Example (6 of 6)

4. Substitute values into the K_c expression.

Note: Equilibrium constants are unitless.

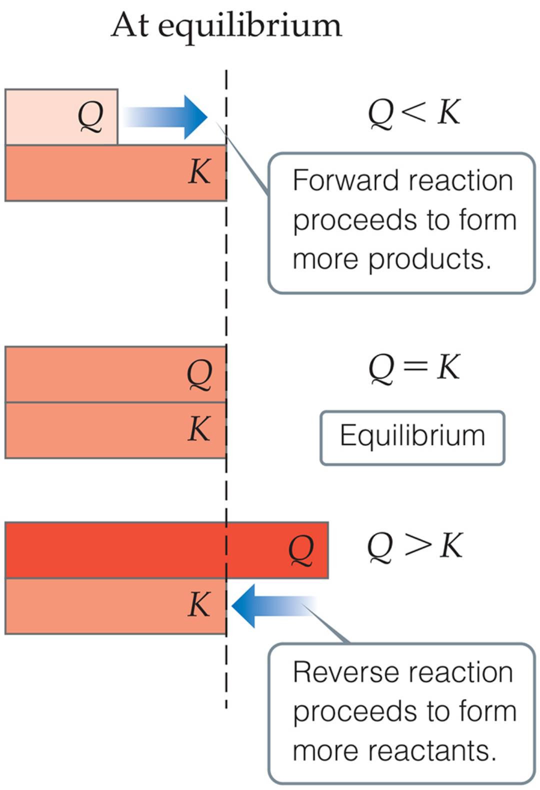
$$
\begin{aligned}
K_c &= \frac{[HI]^2}{[H_2][I_2]} \\
&= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} \\
&= 51
\end{aligned}
$$

15.6 The reaction quotient, Q
When you’re not at equilibrium.

- Is a mixture at equilibrium? *Which way does the reaction go?*
- To answer these questions, we calculate the **reaction quotient**, *Q*.
- The expression for *Q* is **identical** to the equilibrium constant ***expression***, but the values used to calculate it are the **current conditions**, *not necessarily equilibrium conditions.*

Comparing *Q* and *K*

- Nature wants $Q = K$.
- If $Q < K$, nature will make the reaction proceed to products.
- If $Q = K$, the reaction is in equilibrium.
- If $Q > K$, nature will make the reaction proceed to reactants.



Calculating Equilibrium Concentrations

- If you know the equilibrium constant, you can find equilibrium concentrations from initial concentrations and changes (based on stoichiometry).
- You will set up a table similar to the ones used to find the equilibrium concentration, but the “change in concentration” row will be a factor of “*x*” based on the stoichiometry.

An Equilibrium Concentration Calculation Example

A 1.000 L flask is filled with 1.000 mol of H_2 (*g*) 2.000 mol of I_2 (g) at 448 °C. Given K_c= 50.5 at 448 °C, what are the equilibrium concentrations of H_2 (*g*), I_2 (*g*) and HI (*g*)?

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

Initial concentration (*M*)	1.000	2.000	0
Change in concentration (*M*)	$-x$	$-x$	$+2x$
Equilibrium concentration (*M*)	$1.000 - x$	$2.000 - x$	$2x$

An Equilibrium Concentration Calculation Example

- Set up the equilibrium constant expression, filling in equilibrium concentration expressions from the table.

$$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

$$50.5(2 – 3x + x^2) = 4x^2$$

$$(2 – 3x + x^2) = 4/50.5x^2$$

$$0.9207x^2 – 3x + 2 = 0$$

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

- Solving for x is done using the quadratic formula, resulting in x = 2.323 **or** 0.935.

An Equilibrium Concentration Calculation Example (3 of 3)

- Since *x* must be subtracted from 1.000 *M*, 2.323 makes no physical sense. (It results in a negative concentration!) The value **must** be 0.935.
- So
- $\left[\mathrm{H}_2\right]_{\mathrm{eq}} = 1.000 - 0.935 = 0.065\ M$
- $\left[\mathrm{I}_2\right]_{\mathrm{eq}} = 2.000 - 0.935 = 1.065\ M$
- $[\mathrm{HI}]_{\mathrm{eq}} = 2(0.935) = 1.87\ M$

Another example

Consider the formation reaction of NH_3,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \quad \text{for which } K_c = 0.105 \text{ at } 472\ ^{o}C.$$

Suppose we place 2.00 mol of H2, 1.00 mol of N2, and 2.00 mol of NH3 in a 1.00-L container at 473°C. How will the mixture react to reach equilibrium? Will N2 and H2 react to form more NH3, or will NH3 decompose to N2, and H2?

Another example

Consider the formation reaction of NH_3,

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- Calculate Q = $\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2.00)^2}{(1.00)(2.00)^3} = 0.500$
- $Q=0.500 > K_c$
- Reaction will proceed from right to left

Another example

Consider the formation reaction of NH_3,

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Suppose we place 2.00 mol of H2, 1.00 mol of N2, and 2.00 mol of NH3 in a 1.00-L container at 473°C. How will the mixture react to reach equilibrium? Will N2 and H2 react to form more NH3, or will NH3 decompose to N2, and H2?

- Once the reaction reaches equilibrium, what will be the final concentrations of N2, H2, and NH3?
- ICE table!

Another example

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Suppose we place 2.00 mol of H2, 1.00 mol of N2, and 2.00 mol of NH3 in a 1.00-L container at 473°C. How will the mixture react to reach equilibrium? Will N2 and H2 react to form more NH3, or will NH3 decompose to N2, and H2?

	N_2 +	$3H_2$ $\rightleftharpoons$	$2NH_3$
Initial concentration (*M*)	1.00	2.00	2.00
Change in concentration (*M*)	$+x$	$+3x$	$-2x$
Equilibrium concentration (*M*)	$1.00 + x$	$2.00 + 3x$	$2.00 - 2x$

- $K = \dfrac{(2.00 - 2x)^2}{(1.00 + x)(2.00 + 3x)^3} = 0.105$: Too complicated to solve by hand
- If we can get x, we can calculate the final concentrations

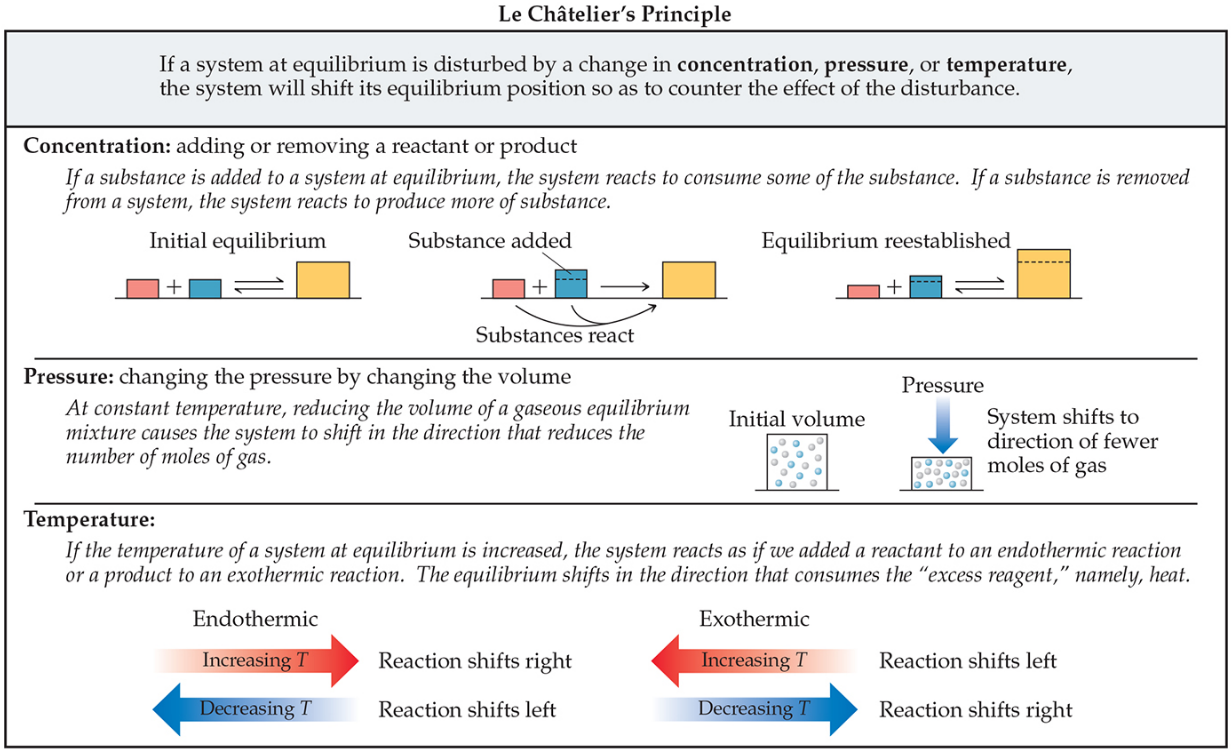
15.7 Le Châtelier’s Principle

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

- After the shift, the system will return to equilibrium.
- Concentration and pressure will change but the value of the equilibrium constant remains the same.

How Conditions Change Equilibrium

We use Le Châtelier’s Principle qualitatively to predict shifts in equilibrium based on changes in conditions.



Le Châtelier’s Principle

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

Concentration: adding or removing a reactant or product

If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.

Pressure: changing the pressure by changing the volume

At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.

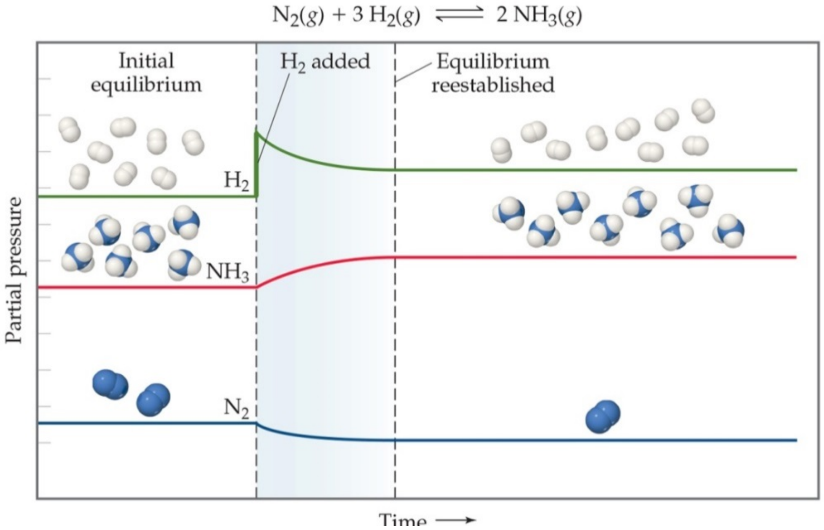
Temperature:

If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the “excess reagent,” namely, heat.

Endothermic		Exothermic	
Increasing *T*	Reaction shifts right	Increasing *T*	Reaction shifts left
Decreasing *T*	Reaction shifts left	Decreasing *T*	Reaction shifts right

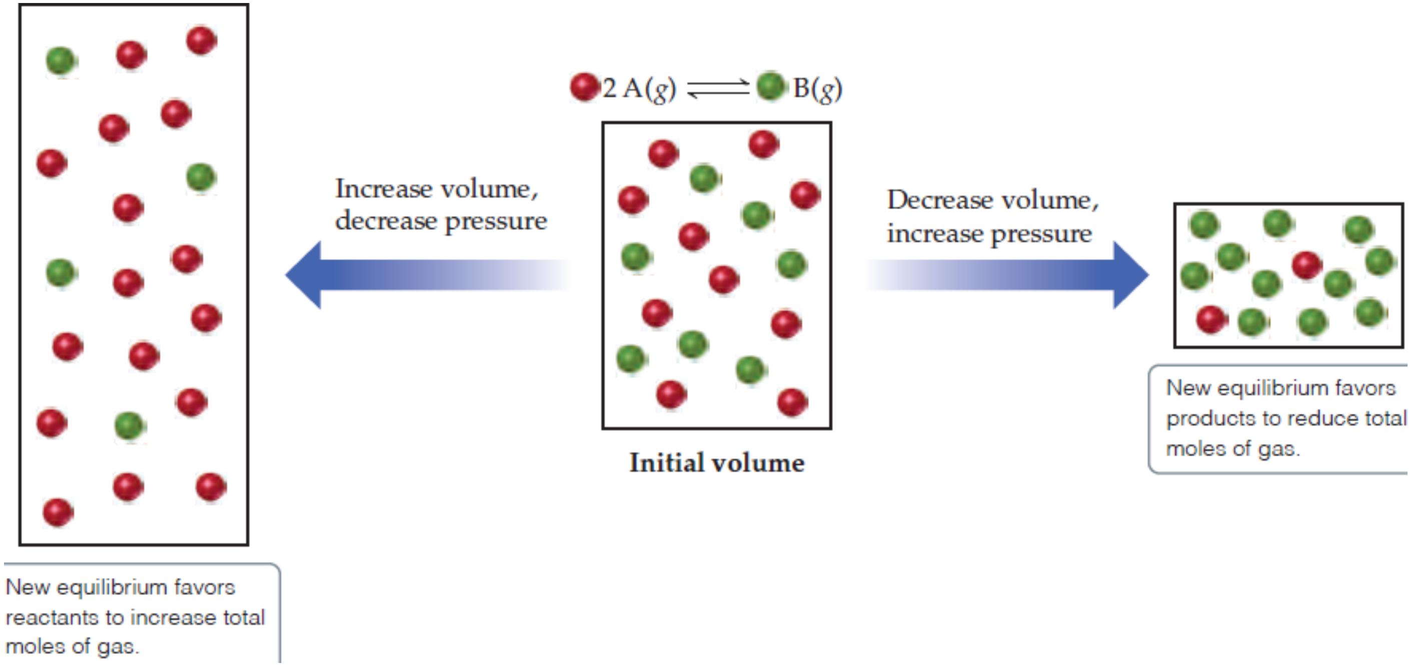
Change in Reactant or Product Concentration

- If the system is in equilibrium
  - adding a reaction component will result in some of it being used up.
  - removing a reaction component will result in some of it being produced.
  - magnitude of equilibrium constant remains the same.



Change in Volume or Pressure

When gases are involved in an equilibrium, a change in pressure or volume will affect equilibrium: Higher volume or lower pressure favors the side of the equation with more moles (and vice versa). K remains the same.



$2\,A(g) \rightleftharpoons B(g)$

Increase volume, decrease pressure

Decrease volume, increase pressure

Initial volume

New equilibrium favors reactants to increase total moles of gas.

New equilibrium favors products to reduce total moles of gas.

Change in Temperature

- Is the reaction endothermic or exothermic as written?
- Decide, then assess as you would for a concentration change.
  - Unlike concentration or pressure changes, K changes in value.
- Endothermic: Heat acts **like** a reactant; adding heat drives a reaction toward products. K increases.
  - Reactants plus heat forms products
- Exothermic: Heat acts **like** a product; adding heat drives a reaction toward reactants. K decreases.
  - Reactants form products plus heat

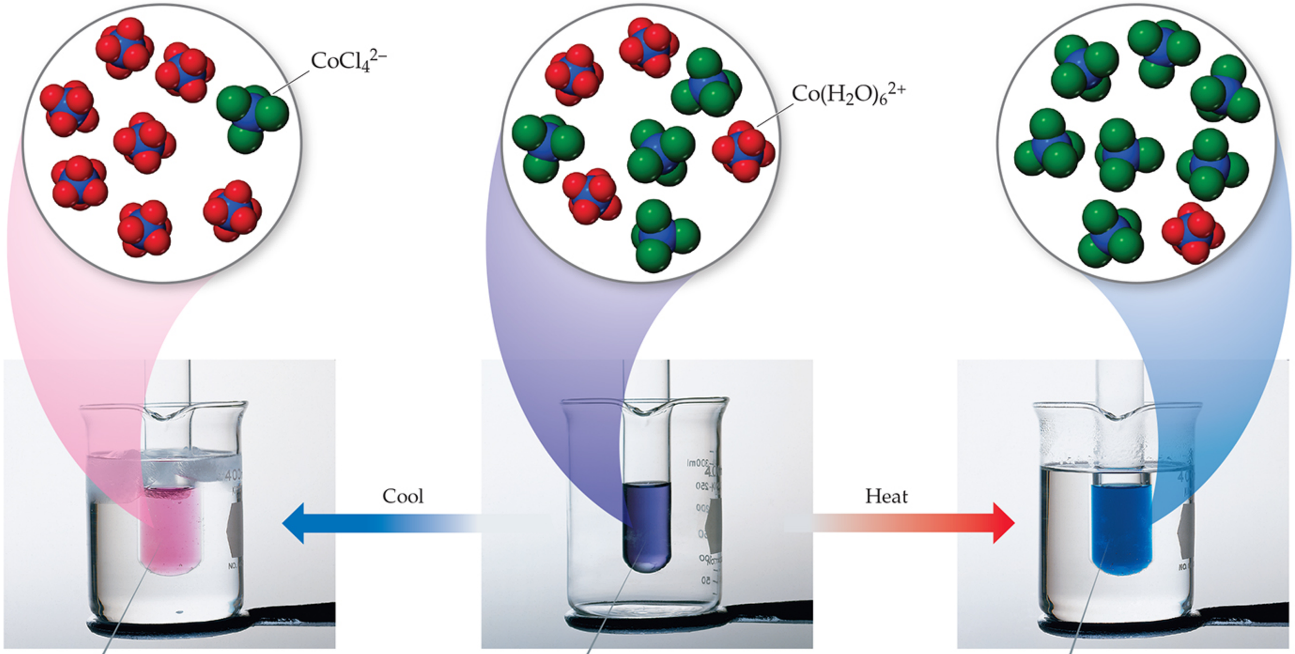
Equilibrium Affected by Temperature

$\Delta H > 0$, endothermic reaction

$$\text{Heat} + Co(H_2O)_6^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6\,H_2O(l)$$

Pink

Blue



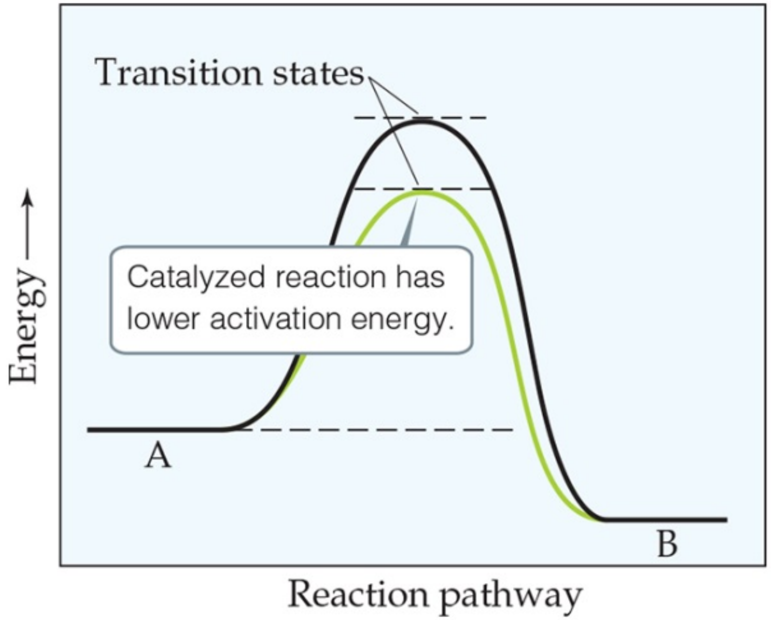
Solution appears pink because lowering the temperature shifts the equilibrium to favor formation of the pink $Co(H_2O)_6^{2+}$ ion.

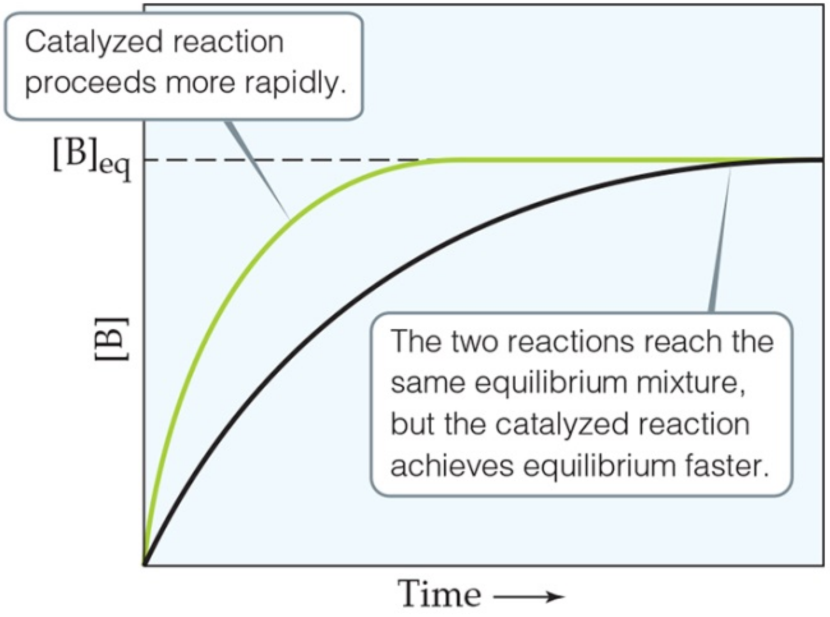
Solution appears violet because appreciable amounts of both pink $Co(H_2O)_6^{2+}$ and blue $CoCl_4^{2-}$ are present.

Solution appears blue because raising the temperature shifts the equilibrium to favor formation of the blue $CoCl_4^{2-}$ ion.

The Effect of Catalysts

- **Catalysts** increase the rate of both the forward **and** reverse reactions.
- Equilibrium is achieved faster, but the equilibrium composition remains unaltered.
- Activation energy is lowered, allowing equilibrium to be established at lower temperatures.


Catalyzed reaction has lower activation energy.


Catalyzed reaction proceeds more rapidly.

The two reactions reach the same equilibrium mixture, but the catalyzed reaction achieves equilibrium faster.