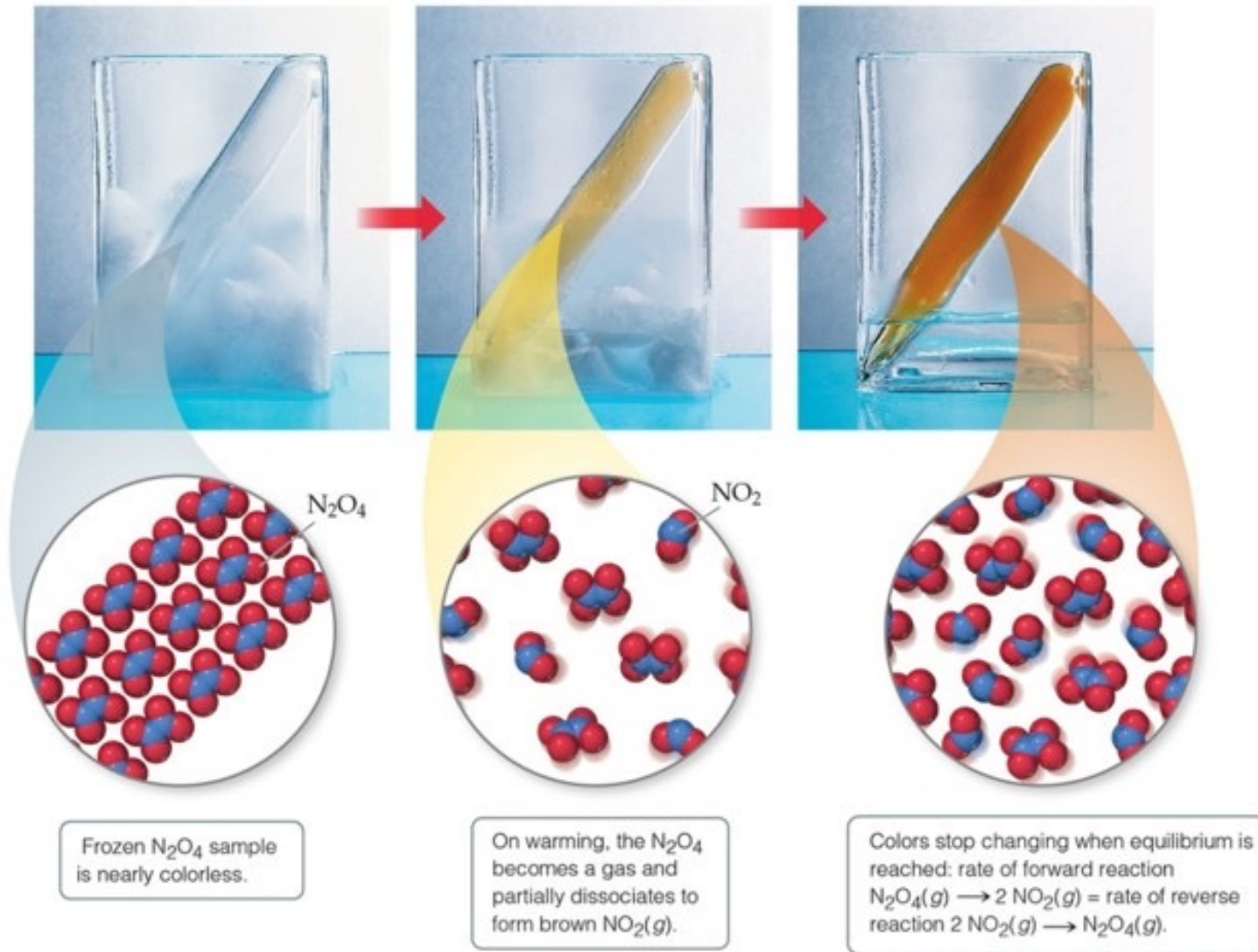


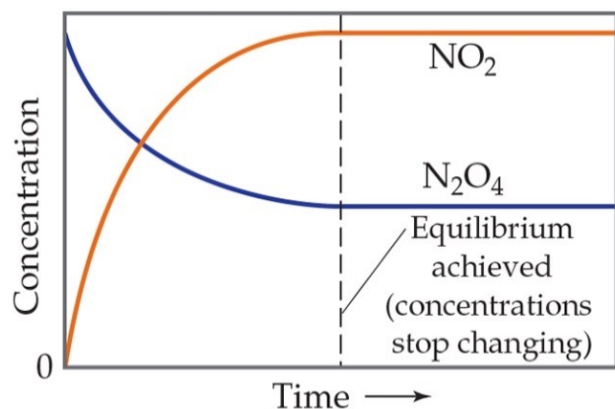
# Chapter 15 Chemical Equilibrium

# 15.1 The Concept of Chemical Equilibrium

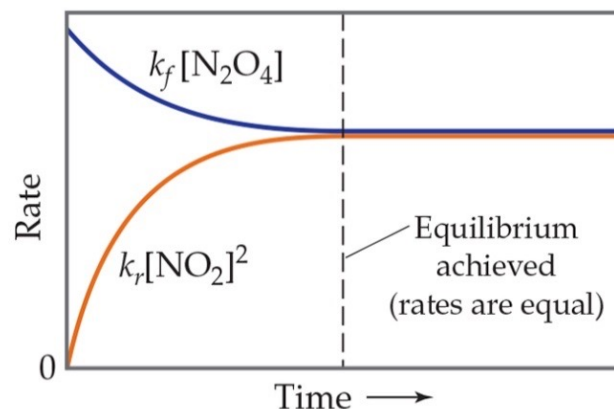


**Chemical equilibrium** occurs when a reaction and its reverse reaction proceed at the same rate. In the figure above, equilibrium is finally reached in the third picture.

# 15.1 The Concept of Chemical Equilibrium



(a)

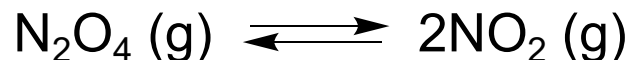


(b)

- 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:



- For the forward reaction:  $\text{N}_2\text{O}_4 (\text{g}) \rightarrow 2\text{NO}_2 (\text{g})$

$$\text{Rate} = k_f [\text{N}_2\text{O}_4]$$

- For the reverse reaction:  $2\text{NO}_2 (\text{g}) \rightarrow \text{N}_2\text{O}_4 (\text{g})$

$$\text{Rate} = k_r [\text{NO}_2]^2$$

# Equilibrium Constant Expression

- At equilibrium

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

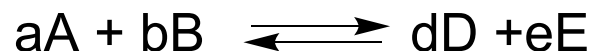
$$k_f [\text{N}_2\text{O}_4] = k_r [\text{NO}_2]^2$$

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

$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{k_f}{k_r} = \text{a constant}$$

# The Equilibrium Constant

- Consider the generalized reaction



- The equilibrium expression for this reaction would be

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

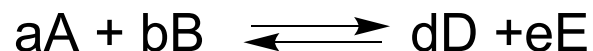
- Also, since *pressure* is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

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

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

# The Equilibrium Constant

- Consider the generalized reaction



- The equilibrium expression for this reaction would be

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

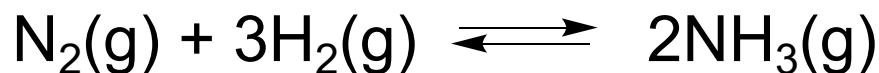
- Also, since *pressure* is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

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

- *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:



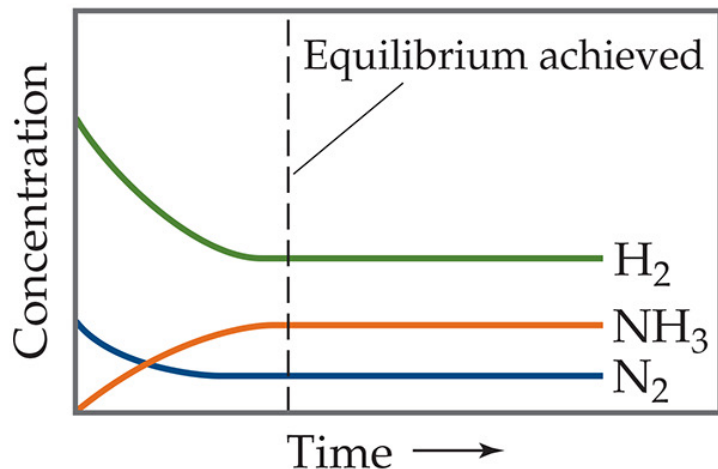
- The equilibrium constant depends on stoichiometry:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

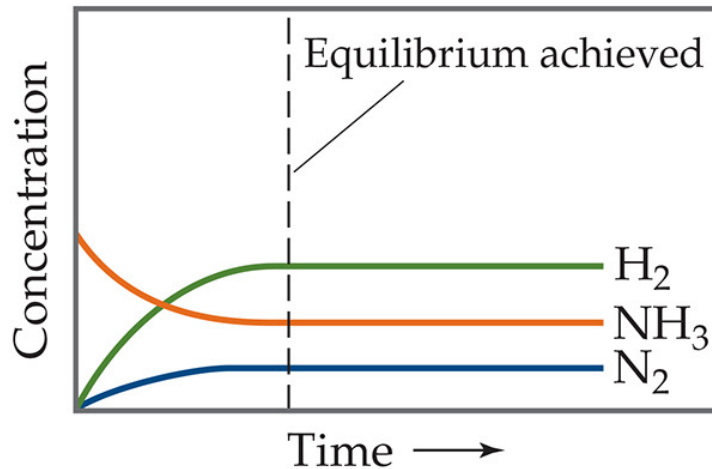


# Achieving Equilibrium

Starting with only reactants

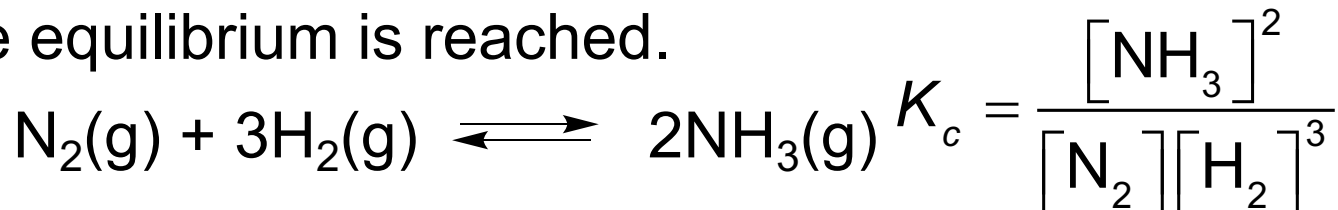


Starting with only products



it doesn't matter where you start;

The same equilibrium is reached.



Relative amount of *change* is based on stoichiometry.

# Evaluating $K_c$ (1 of 2)

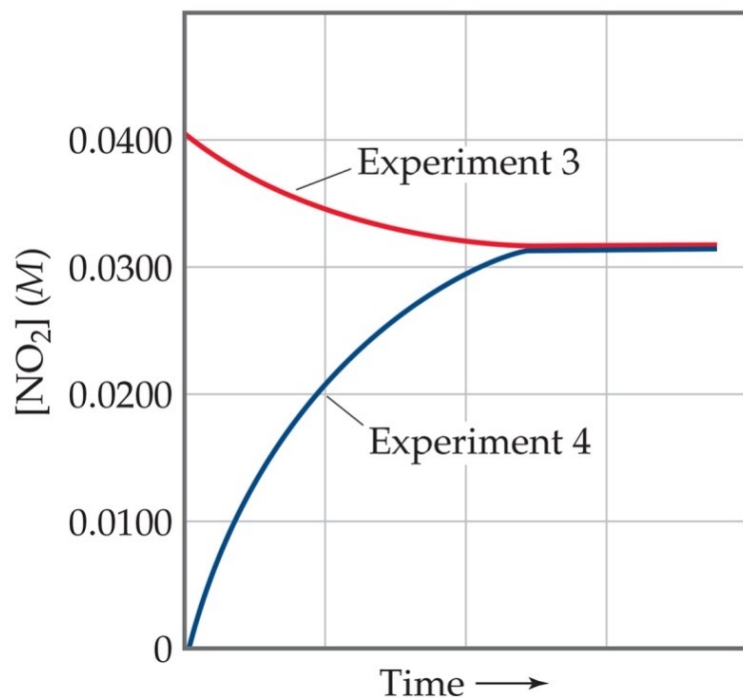
**Table 15.1** Initial and Equilibrium Concentrations of  $\text{N}_2\text{O}_4(g)$  and  $\text{NO}_2(g)$  at  $100\text{ }^\circ\text{C}$

Experiment	Initial $[\text{N}_2\text{O}_4](M)$	Initial $[\text{NO}_2](M)$	Equilibrium $[\text{N}_2\text{O}_4](M)$	Equilibrium $[\text{NO}_2](M)$	$K_c$
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  $[\text{NO}_2]^2$  to  $[\text{N}_2\text{O}_4]$  remains constant at  $100^\circ\text{C}$  no matter the initial concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$



# Equilibrium Constants in Terms of Pressure, $K_p$

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

$$P = MRT$$

$$K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b} \quad \begin{array}{l} \leftarrow \text{products} \\ \leftarrow \text{reactants} \end{array} \quad K_p = \frac{(P_D)^d (P_E)^e}{(P_A)^a (P_B)^b}$$

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

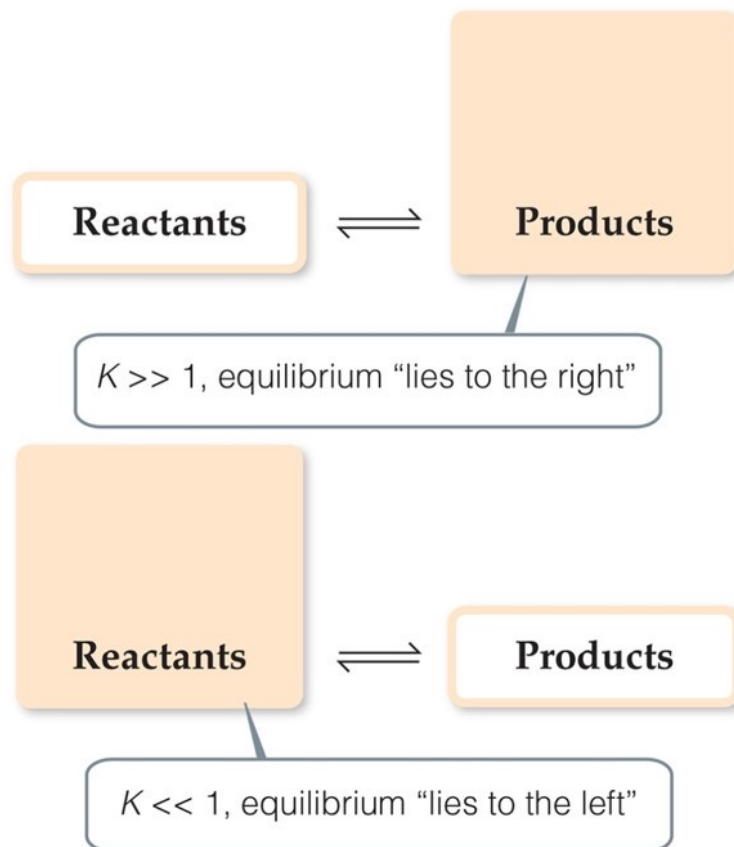
where

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

# 15.2 Using Equilibrium Constants

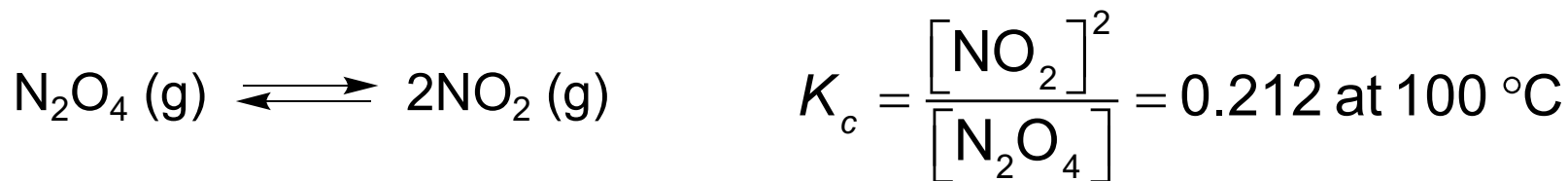
## Magnitude of $K$

- If  $K \gg 1$ , the reaction favors products; products predominate at equilibrium.
- If  $K \ll 1$ , the reaction favors reactants; reactants predominate at equilibrium.



# The Direction of the Chemical Equation and $K$

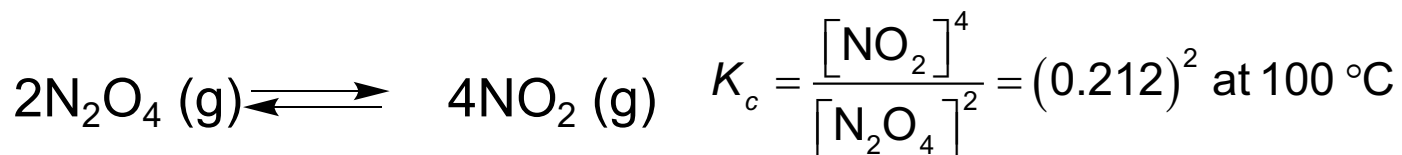
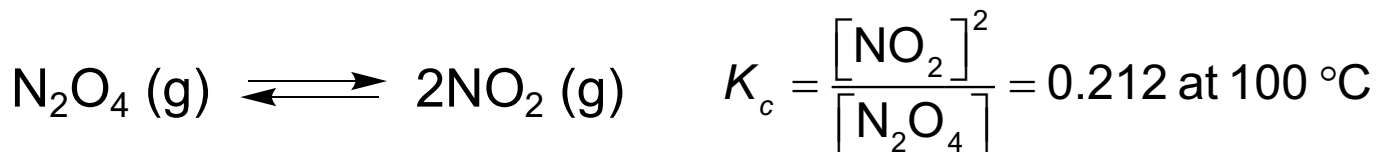
The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction:



$$1/0.212 = 4.72$$

# 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



- 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.

$$P_{\text{tot}} = P_A + P_B + \dots P_n$$

- Effusion/diffusion:

$$\frac{\text{rate}_2}{\text{rate}_1} = \sqrt{\frac{M_1}{M_2}}$$

# 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

- 1<sup>st</sup>/2<sup>nd</sup>/3<sup>rd</sup> 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.

# Exam 1, the Breakdown.

Breakdown:

Gas Laws.	III
Effusion/diffusion	I
Kinetic/molecular theory	I
Nonideal gases	I
Partial Pressures	I
Intermolecular forces	III
Rate Law	I
Integrated rate law	I
Mechanisms	I
General kinetics	I
Rate law from a mechanism	I

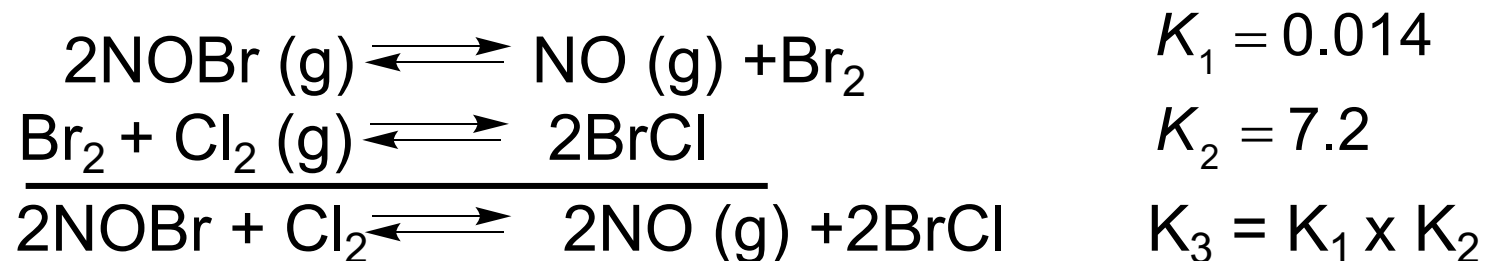


# Combining Equilibrium Expressions

- 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:



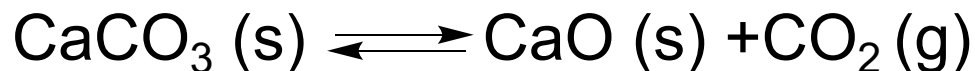
$$K_3 = K_1 \times K_2 = 0.014 \times 7.2 = 0.10$$

# 15.4 Heterogeneous Equilibria

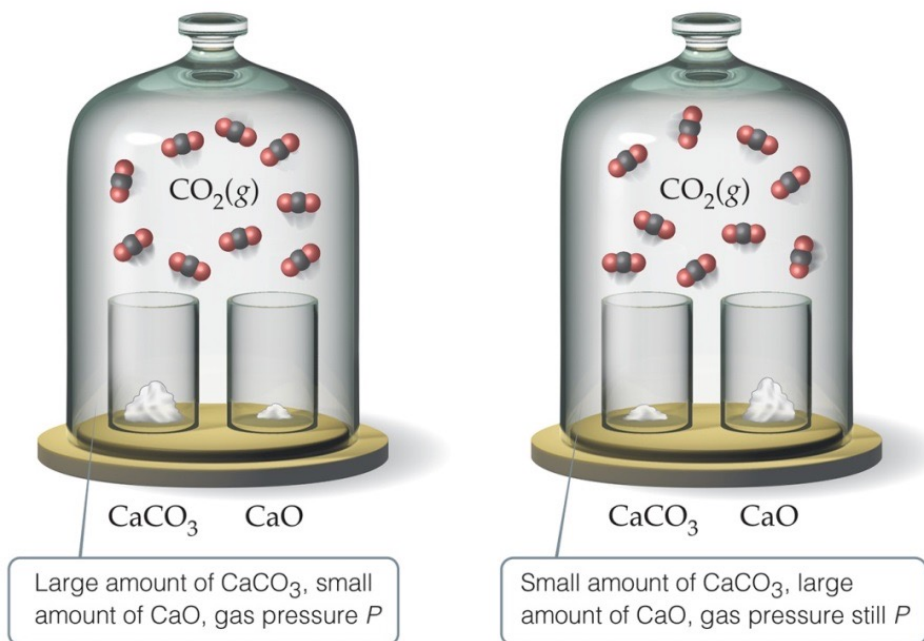
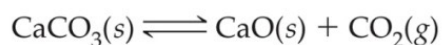
- **Homogeneous equilibria** all reactants and products are in the **same phase**.
- **Heterogeneous equilibria** occur when a component in the equilibrium is in a **different phase**.
- Whenever a **pure solid (s)** or **pure liquid (l)** is involved in a heterogeneous equilibrium, its concentration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

# The Decomposition of $\text{CaCO}_3$ —A Heterogeneous Equilibrium

- The equation for the reaction is



- This results in  $K_c = [\text{CO}_2]$  and  $K_p = P_{\text{CO}_2}$



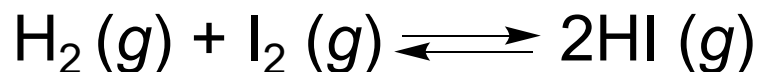


## 15.5 Calculating Equilibrium Constants

- 1) Tabulate all known initial and equilibrium concentrations.
- 2) Where the initial **and** equilibrium concentrations are known, calculate the change.
- 3) Use the balanced equation to find change for all other reactants and products.
- 4) Use initial concentrations and changes to find equilibrium concentration of all species.
- 5) Calculate the equilibrium constant using the equilibrium concentrations.

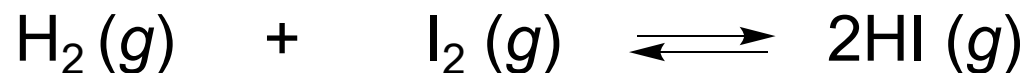
# A $K_c$ Calculation Example (1 of 6)

A closed system initially containing  $1.000 \times 10^{-3} \text{ M H}_2$  and  $2.000 \times 10^{-3} \text{ M I}_2$  at  $448 \text{ }^\circ\text{C}$  is allowed to reach equilibrium. At equilibrium mixture shows concentration of HI is  $1.87 \times 10^{-3} \text{ M}$ . Calculate  $K_c$  at  $448 \text{ }^\circ\text{C}$ .



# A $K_c$ Calculation Example (2 of 6)

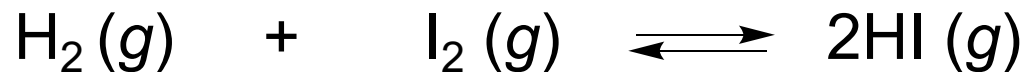
Make a table using the known information.



	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change			
At equilibrium			$1.87 \times 10^{-3}$

# A $K_c$ Calculation Example (3 of 6)

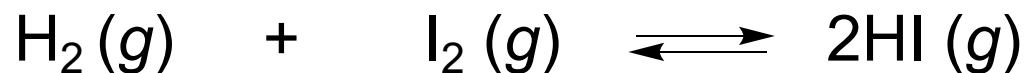
Change line of [HI] is known.



	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change			<b><math>+1.87 \times 10^{-3}</math></b>
At equilibrium			$1.87 \times 10^{-3}$

# A $K_c$ Calculation Example (4 of 6)

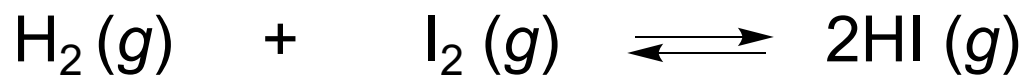
Use equation stoichiometry to complete change line.



	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change	<b><math>-9.35 \times 10^{-4}</math></b>	<b><math>-9.35 \times 10^{-4}</math></b>	<b><math>+1.87 \times 10^{-3}</math></b>
At equilibrium			$1.87 \times 10^{-3}$

# A $K_c$ Calculation Example (5 of 6)

Calculate the equilibrium  $\text{H}_2$  and  $\text{I}_2$  concentrations



	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change	$-9.35 \times 10^{-4}$	$-9.35 \times 10^{-4}$	$+1.87 \times 10^{-3}$
At equilibrium	$6.5 \times 10^{-5}$	$1.065 \times 10^{-3}$	$1.87 \times 10^{-3}$

# A $K_c$ Calculation Example (6 of 6)

Substitute values into the  $K_c$  expression.

Do not include molarity labels. Equilibrium constants are unitless.

$$\begin{aligned}k_c &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \\&= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} \\&= 51\end{aligned}$$

## 15.6 The reaction quotient, $Q$

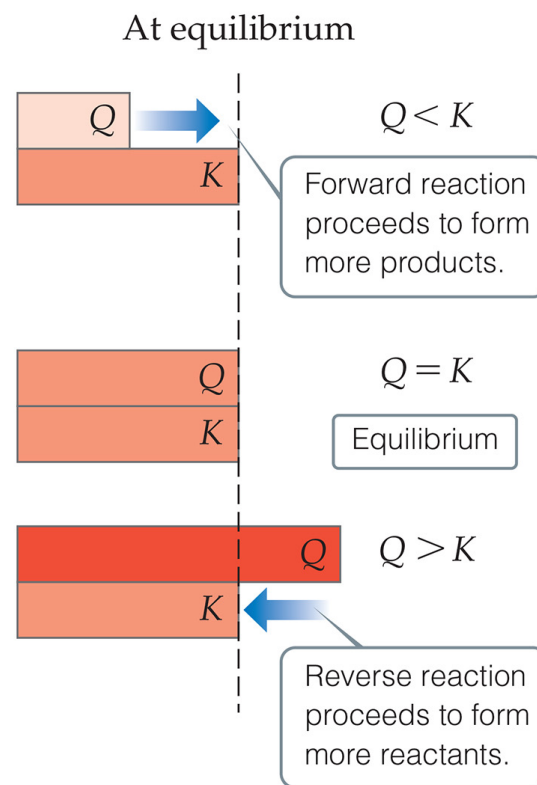
### When your not at equilibrium.

- Is a mixture in 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 those for equilibrium.
- To calculate  $Q$ , substitute the concentrations or pressures of reactants and products at any given time during a reaction into the equilibrium expression.



# 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.

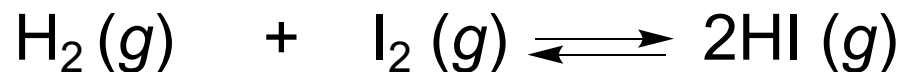


# Calculating Equilibrium Concentrations

- 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  $\text{H}_2 (g)$  2.000 mol of  $\text{I}_2 (g)$  at 448 °C. Given  $K_c = 50.5$  at 448 °C, what are the equilibrium concentrations of  $\text{H}_2 (g)$ ,  $\text{I}_2 (g)$  and  $\text{HI} (g)$ ?



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

# An Equilibrium Concentration Calculation

## Example (2 of 3)

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

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

$$50.5(2 - 3x + x^2) = 4x^2$$

$$(2 - 3x + x^2) = 4/50.5x^2$$

$$0.9207x^2 - 3x + 2 = 0$$

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

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

## 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.

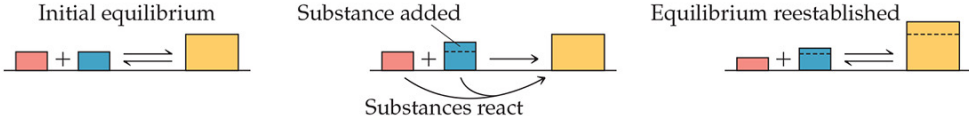
**Le Châtelier's Principle**

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.*

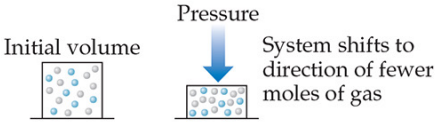
Initial equilibrium      Substance added      Equilibrium reestablished



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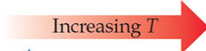

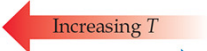

**Pressure:** changing the pressure by changing the volume  
*At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.*

Initial volume      Pressure      System shifts to direction of fewer moles of gas



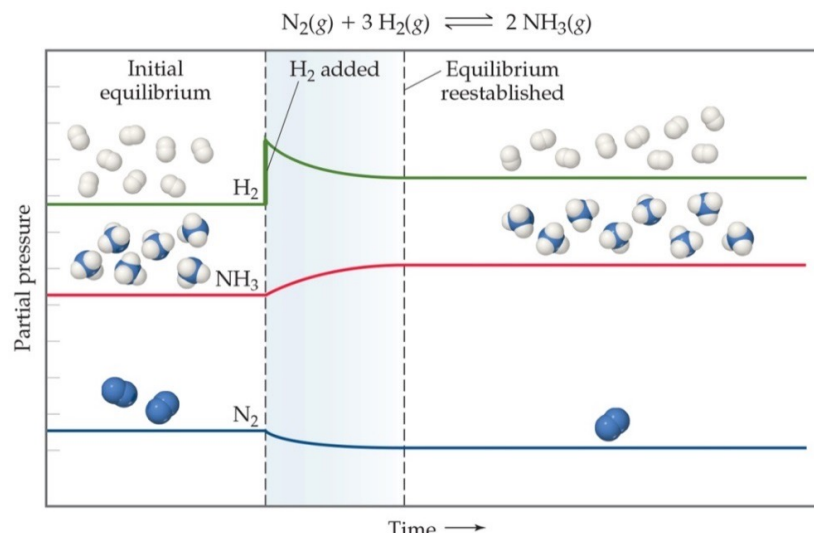
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**Temperature:**  
*If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the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

<p>Endothermic</p> <p>Increasing <math>T</math>  Reaction shifts right</p> <p>Decreasing <math>T</math>  Reaction shifts left</p>	<p>Exothermic</p> <p>Increasing <math>T</math>  Reaction shifts left</p> <p>Decreasing <math>T</math>  Reaction shifts right</p>
---	--

# Change in Reactant or Product Concentration

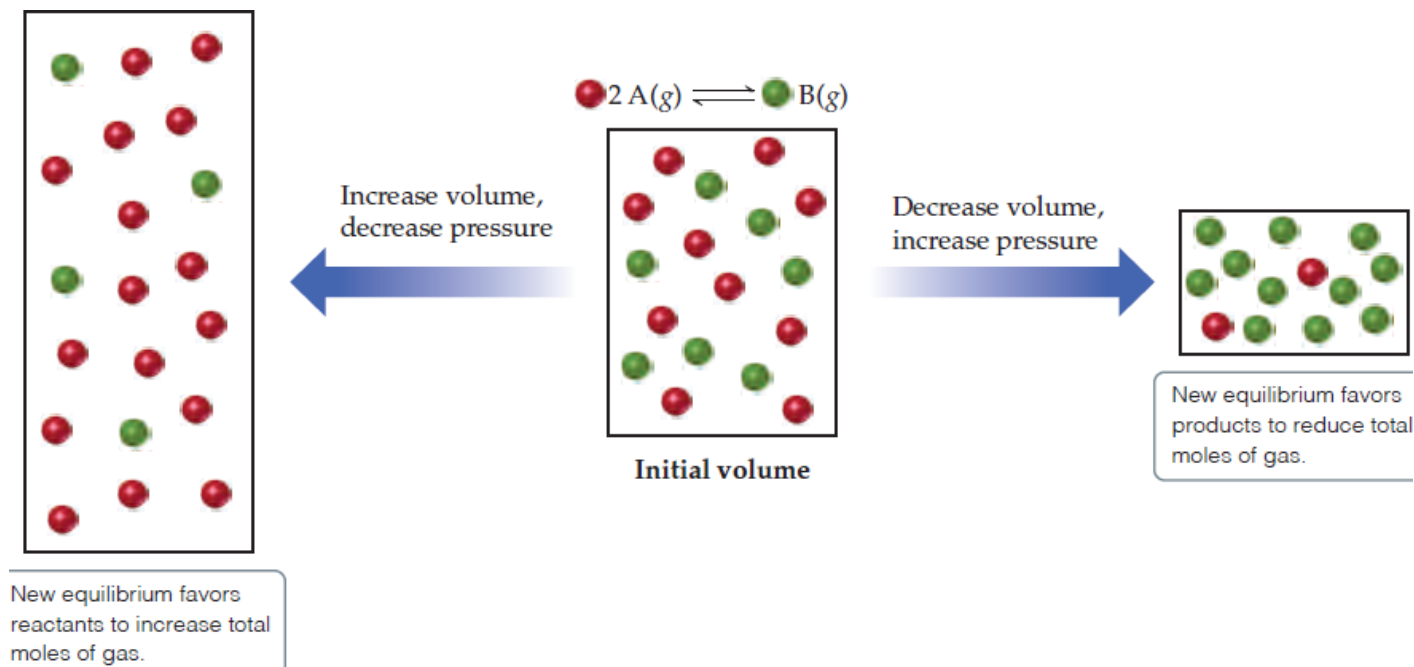
- If the system is in equilibrium
  - adding a reaction component will result in some of it being used up.
  - removing a reaction component will result in some of it being produced.
  - magnitude of equilibrium constant remains the same.





# 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.

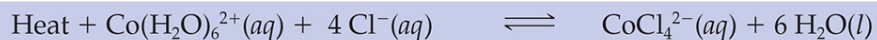


# Change in Temperature

- 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



Pink

Blue

The diagram illustrates the effect of temperature on the equilibrium between pink and blue cobalt complexes. It shows three beakers: a pink one on the left, a violet one in the middle, and a blue one on the right. Arrows labeled "Cool" and "Heat" indicate the direction of temperature change. Molecular models of  $\text{CoCl}_4^{2-}$  and  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  are shown above the beakers.

Solution appears pink because lowering the temperature shifts the equilibrium to favor formation of the pink  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ion.

Solution appears violet because appreciable amounts of both pink  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and blue  $\text{CoCl}_4^{2-}$  are present.

Solution appears blue because raising the temperature shifts the equilibrium to favor formation of the blue  $\text{CoCl}_4^{2-}$  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.

