Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.
The 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.
A System at Equilibrium

Once equilibrium is achieved, the *amount* of each reactant and product remains constant.
Depicting Equilibrium

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

$$N_2O_4 (g) \rightleftharpoons 2 NO_2 (g)$$
The Equilibrium Constant
The Equilibrium Constant

• Forward reaction:
  \[ \ce{N2O4 (g) \rightarrow 2 NO2 (g)} \]

• Rate Law:
  \[ \text{Rate} = k_f [\ce{N2O4}] \]
The Equilibrium Constant

• Reverse reaction:
  \[ 2 \text{NO}_2 (g) \rightarrow \text{N}_2\text{O}_4 (g) \]

• Rate Law:
  \[ \text{Rate} = k_r [\text{NO}_2]^2 \]
The Equilibrium Constant

• Therefore, at equilibrium

\[ \text{Rate}_f = \text{Rate}_r \]

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

• Rewriting this, it becomes

\[ \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \]
The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes

\[ K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \]
The Equilibrium Constant

• Consider the generalized reaction

\[ aA + bB \rightleftharpoons cC + dD \]

• The equilibrium expression for this reaction would be

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

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

\[ K_p = \frac{(P_C^c)(P_D^d)}{(P_A^a)(P_B^b)} \]
Relationship Between $K_c$ and $K_p$

• From the Ideal Gas Law we know that

$$PV = nRT$$

• Rearranging it, we get

$$P = \frac{n}{V} RT$$
Relationship Between $K_c$ and $K_p$

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

$$\Delta n = \text{(moles of gaseous product)} - \text{(moles of gaseous reactant)}$$
Equilibrium Can Be Reached from Either Direction

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial $[N_2O_4]$ (M)</th>
<th>Initial $[NO_2]$ (M)</th>
<th>Equilibrium $[N_2O_4]$ (M)</th>
<th>Equilibrium $[NO_2]$ (M)</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.0200</td>
<td>0.00140</td>
<td>0.0172</td>
<td>0.211</td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>0.0300</td>
<td>0.00280</td>
<td>0.0243</td>
<td>0.211</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.0400</td>
<td>0.00452</td>
<td>0.0310</td>
<td>0.213</td>
</tr>
<tr>
<td>4</td>
<td>0.0200</td>
<td>0.0</td>
<td>0.00452</td>
<td>0.0310</td>
<td>0.213</td>
</tr>
</tbody>
</table>

As you can see, the ratio of $[NO_2]^2$ to $[N_2O_4]$ remains constant at this temperature no matter what the initial concentrations of $NO_2$ and $N_2O_4$ are.
Equilibrium Can Be Reached from Either Direction

This is the data from the last two trials from the table on the previous slide.
Equilibrium Can Be Reached from Either Direction

It doesn’t matter whether we start with \( \text{N}_2 \) and \( \text{H}_2 \) or whether we start with \( \text{NH}_3 \): we will have the same proportions of all three substances at equilibrium.
What Does the Value of $K$ Mean?

- If $K >> 1$, the reaction is product-favored; product predominates at equilibrium.
What Does the Value of $K$ Mean?

- If $K \gg 1$, the reaction is *product-favored*; product predominates at equilibrium.

- If $K \ll 1$, the reaction is *reactant-favored*; reactant predominates at equilibrium.
Manipulating Equilibrium Constants

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

\[ \text{N}_2\text{O}_4 (g) \quad \text{2 NO}_2 (g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \text{ at } 100 \, ^\circ\text{C} \]

\[ \text{2 NO}_2 (g) \quad \text{N}_2\text{O}_4 (g) \quad K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = 4.72 \text{ at } 100 \, ^\circ\text{C} \]
Manipulating Equilibrium Constants

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.

\[ K_c = (0.212)^2 \text{ at } 100 \, ^\circ \text{C} \]

\[ 2 \, \text{NO}_2(g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \text{ at } 100 \, ^\circ \text{C} \]

\[ 4 \, \text{NO}_2(g) \quad K_c = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}_4]^2} = (0.212)^2 \text{ at } 100 \, ^\circ \text{C} \]
Manipulating Equilibrium Constants

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.
Heterogeneous Equilibrium
The Concentrations of Solids and Liquids Are Essentially Constant

Both can be obtained by multiplying the density of the substance by its molar mass — and both of these are constants at constant temperature.
The Concentrations of Solids and Liquids Are Essentially Constant

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

\[ \text{PbCl}_2 (s) \rightarrow \text{Pb}^{2+} (aq) + 2 \text{Cl}^- (aq) \]

\[ K_c = [\text{Pb}^{2+}] [\text{Cl}^-]^2 \]
As long as some CaCO$_3$ or CaO remain in the system, the amount of CO$_2$ above the solid will remain the same.
Equilibrium
Calculations
An Equilibrium Problem

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. Analysis of the equilibrium mixture shows that the concentration of HI is $1.87 \times 10^{-3} \ M$. Calculate $K_c$ at 448 °C for the reaction taking place, which is

$$H_2 (g) + I_2 (s) \rightarrow 2 \ HI (g)$$
## What Do We Know?

<table>
<thead>
<tr>
<th></th>
<th>[H₂], M</th>
<th>[I₂], M</th>
<th>[HI], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially</td>
<td>1.000 x 10⁻³</td>
<td>2.000 x 10⁻³</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At equilibrium</td>
<td></td>
<td>1.87 x 10⁻³</td>
<td></td>
</tr>
</tbody>
</table>
[HI] Increases by $1.87 \times 10^{-3} \ M$

<table>
<thead>
<tr>
<th></th>
<th>[H$_2$], $M$</th>
<th>[I$_2$], $M$</th>
<th>[HI], $M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially</td>
<td>$1.000 \times 10^{-3}$</td>
<td>$2.000 \times 10^{-3}$</td>
<td>$0$</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td>$+1.87 \times 10^{-3}$</td>
</tr>
<tr>
<td>At equilibrium</td>
<td></td>
<td></td>
<td>$1.87 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much.

<table>
<thead>
<tr>
<th></th>
<th>$[H_2]$, $M$</th>
<th>$[I_2]$, $M$</th>
<th>$[HI]$, $M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially</td>
<td>$1.000 \times 10^{-3}$</td>
<td>$2.000 \times 10^{-3}$</td>
<td>$0$</td>
</tr>
<tr>
<td>Change</td>
<td>$-9.35 \times 10^{-4}$</td>
<td>$-9.35 \times 10^{-4}$</td>
<td>$+1.87 \times 10^{-3}$</td>
</tr>
<tr>
<td>At equilibrium</td>
<td></td>
<td></td>
<td>$1.87 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
We can now calculate the equilibrium concentrations of all three compounds...

<table>
<thead>
<tr>
<th></th>
<th>([H_2], M)</th>
<th>([I_2], M)</th>
<th>([HI], M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially</td>
<td>1.000 x 10^{-3}</td>
<td>2.000 x 10^{-3}</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-9.35 x 10^{-4}</td>
<td>-9.35 x 10^{-4}</td>
<td>+1.87 x 10^{-3}</td>
</tr>
<tr>
<td>At equilibrium</td>
<td>6.5 x 10^{-5}</td>
<td>1.065 x 10^{-3}</td>
<td>1.87 x 10^{-3}</td>
</tr>
</tbody>
</table>
...and, therefore, the equilibrium constant.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$
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, one substitutes the initial concentrations on reactants and products into the equilibrium expression.
If $Q = K$, the system is at equilibrium.
If $Q > K$, there is too much product, and the equilibrium shifts to the left.
If $Q < K$, there is too much reactant, and the equilibrium shifts to the right.
Le Châtelier’s Principle
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.”
The Haber Process

The transformation of nitrogen and hydrogen into ammonia (NH₃) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.
The Haber Process

If H₂ is added to the system, N₂ will be consumed and the two reagents will form more NH₃.
The Haber Process

This apparatus helps push the equilibrium to the right by removing the ammonia (NH₃) from the system as a liquid.
The Effect of Changes in Temperature

$$\text{Co(H}_2\text{O)}_6^{2+} (aq) + 4 \text{Cl} (aq) \rightarrow \text{CoCl}_4 (aq) + 6 \text{H}_2\text{O} (l)$$
Catalysts
Catalysts increase the rate of both the forward and reverse reactions.
Catalysts

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