Reversible Elementary Reaction

\[ 2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \]

- At equilibrium, forward and backward rates equal:
  \[ \dot{k}_f \text{[NO]}^2 = \dot{k}_r \text{[N}_2\text{O}_2] \]

- From this:
  \[
  \frac{\dot{k}_f}{\dot{k}_r} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} = \text{constant} = K_{eq}
  \]
Equilibrium Constants

- In general, for ANY reversible chemical reaction:

\[ \alpha A + \beta B \rightleftharpoons \gamma C + \delta D \]

- We define an equilibrium constant:

\[ K_{eq} = \frac{[C]_{eq}^{\gamma}[D]_{eq}^{\delta}}{[A]_{eq}^{\alpha}[B]_{eq}^{\beta}} = \frac{"products"}{"reactants"} \]

- Value of \( K_{eq} \) depends on specific reaction and temperature.

\[ K_{eq} \ - \ important \ features \]

- Although we have introduced the concept of an equilibrium constant in discussing reaction rates, the value of the equilibrium constant depends only on thermodynamics! The quantitative relationship is \( \Delta G^\circ = -RT \ln K_{eq} \) (more on this later).

- If a catalyst decreases \( E_a \), it will increase both \( k_f \) and \( k_r \) and does not affect \( K_{eq} \).
Equilibrium: Connection to Thermodynamics

Magnitude of $K_{eq}$

- What does it mean if $K_{eq}$ is very large?
  
  \[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

- At 25°C, $K_{eq}$ is about $10^{140}$

- Recall form of $K_{eq}$:
  
  "products/reactants"

- With huge $K_{eq}$, lots of products, no reactants. Reaction goes to completion. ($\Delta G^\circ \ll 0$)
Magnitude of $K_{eq}$

- What does it mean if $K_{eq}$ is very small?
  
  \[ \text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \]

- At 25°C, $K_{eq}$ is $4.6 \times 10^{-31}$

- Recall form of $K_{eq}$:
  
  \[ \frac{\text{products}}{\text{reactants}} \]

- With tiny $K_{eq}$, lots of reactants, no products. No detectable reaction. ($\Delta G^\circ \gg 0$)

Equilibrium Calculations

- If $K_{eq}$ is neither huge nor tiny, both products and reactants will be present at equilibrium. ($\Delta G$ is neither very positive nor very negative.)

- We can use value of $K_{eq}$ to find equilibrium amounts from initial amounts.

- Use stoichiometry to relate changes in concentration of various substances.
Equilibrium Calculation

- Consider the reaction
  \[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]
  — called the “water-gas shift reaction”
- Place 1.00 mol each of CO, H\textsubscript{2}O in a 50.0 L vessel at 1000 °C.
- If \( K_{eq} = 0.58 \), what will the equilibrium concentrations of all 4 substances be?
- Some hints on next slide.

Equilibrium Calculation: Strategy

- Start by writing expression for \( K_{eq} \)
- Think about what will happen. Which concentrations will increase? Decrease?
- Use stoichiometry to write changes in concentrations in terms of one variable.
- Set up equilibrium constant expression and solve for the variable introduced above, then calculate final concentrations.
\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]

Write equilibrium constant expression in terms of equilibrium concentrations:

\[
K_{eq} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}
\]

Think about the chemistry. Starting with only \(\text{CO} \) & \(\text{H}_2\text{O}\), reaction must go to the right to form some \(\text{CO}_2\) & \(\text{H}_2\).

Use stoichiometry to write equilibrium concentrations in terms of one variable.

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]

initial: 0.02 M 0.02 M 0 0
change: \(-x\) \(-x\) \(+x\) \(+x\)
final: 0.02 \(-x\) 0.02 \(-x\) \(x\) \(x\)
CO + H₂O ⇌ CO₂ + H₂

- Find x by plugging into expression for $K_{eq}$ and solving for x.

$K_{eq} = \frac{[CO₂][H₂]}{[CO][H₂O]} = \frac{(x)(x)}{(0.02 - x)(0.02 - x)}$

$0.58 = \frac{x^2}{(0.02 - x)^2}$

- Solve and find x = 0.0086
- Finally, use x to find concentrations.

Direction of Reaction

- In that example, we knew which way reaction had to go because only reactants were present at start.
- Suppose both reactants & products are present. How can we tell which way reaction would go to reach equilibrium?
Reaction Quotient ($Q$)

- Define a “reaction quotient,” $Q$. Looks just like $K_{eq}$, except that concentrations need not be equilibrium ones.

\[
\alpha A + \beta B \rightleftharpoons \gamma C + \delta D
\]

\[
K_{eq} = \frac{[C]_\text{eq}^\gamma [D]_\text{eq}^\delta}{[A]_\text{eq}^\alpha [B]_\text{eq}^\beta}
\]

\[
Q = \frac{[C]_\text{eq}^\gamma [D]_\text{eq}^\delta}{[A]_\text{eq}^\alpha [B]_\text{eq}^\beta}
\]

Reaction Quotient

- Compare $Q$ and $K$ to see which way reaction should go.
- $Q < K$: need more products, so reaction goes from left to right
- $Q > K$: need more reactants, so reaction goes from right to left
- $Q = K$: reaction is already at equilibrium
Example Problem (Haber Process)

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \]

- 1.00 mol N\(_2\), 3.00 mol H\(_2\), and 0.500 mol NH\(_3\) are placed in a 50.0 L vessel at 400 °C. At this T, \(K_{eq} = 0.500\).
- Will more NH\(_3\) form, or will NH\(_3\) dissociate to form more N\(_2\) and H\(_2\)?
- Set up an equation to find the equilibrium concentrations.