Each equilibrium has different concentrations, but the same value for $K_c$.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial Concentrations</th>
<th>Equilibrium Concentrations</th>
<th>$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$[\text{N}_2] = 1.000 \text{ M}$</td>
<td>$[\text{N}_2] = 0.921 \text{ M}$</td>
<td>$K = 6.02 \times 10^{-2}$ L/mol²</td>
</tr>
<tr>
<td></td>
<td>$[\text{H}_2] = 1.000 \text{ M}$</td>
<td>$[\text{H}_2] = 0.763 \text{ M}$</td>
<td>$K = 6.02 \times 10^{-2}$ L/mol²</td>
</tr>
<tr>
<td></td>
<td>$[\text{NH}_3] = 0$</td>
<td>$[\text{NH}_3] = 0.157 \text{ M}$</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>$[\text{N}_2] = 0$</td>
<td>$[\text{N}_2] = 0.399 \text{ M}$</td>
<td>$K = 6.02 \times 10^{-2}$ L/mol²</td>
</tr>
<tr>
<td></td>
<td>$[\text{H}_2] = 0$</td>
<td>$[\text{H}_2] = 1.197 \text{ M}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$[\text{NH}_3] = 1.000 \text{ M}$</td>
<td>$[\text{NH}_3] = 0.203 \text{ M}$</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>$[\text{N}_2] = 2.00 \text{ M}$</td>
<td>$[\text{N}_2] = 2.59 \text{ M}$</td>
<td>$K = 6.02 \times 10^{-2}$ L/mol²</td>
</tr>
<tr>
<td></td>
<td>$[\text{H}_2] = 1.00 \text{ M}$</td>
<td>$[\text{H}_2] = 2.77 \text{ M}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$[\text{NH}_3] = 3.00 \text{ M}$</td>
<td>$[\text{NH}_3] = 1.82 \text{ M}$</td>
<td></td>
</tr>
</tbody>
</table>

Relating $\Delta_R G^°$ to $K$

$$\Delta_R G^° = -RT \ln K$$

$$K = \exp(-\Delta_R G^°/RT)$$

$\Delta_R G^° < 0$ then $K > 1$ favors products

$\Delta_R G^° > 0$ then $K < 1$ favors reactants

$K$ can be very large or very small

For the following reaction $\Delta_R G^° = -474 \text{ kJ mol}^{-1}$

2H₂(g) + O₂(g) $\rightarrow$ 2H₂O(l)

at 300K the equilibrium constant is

A. $K = 1$
B. $K = 0.25$
C. $K = 1.55 \times 10^{83}$
D. $K = 6.83 \times 10^{82}$

This is the only one $> 1$ -474 kJ mol⁻¹ is “big”

For the following reaction $\Delta_R G^° = +194 \text{ kJ mol}^{-1}$

2HgO(s) $\rightarrow$ O₂(g) + 2Hg(l)

at 300K the equilibrium constant is

A. $K = 1$
B. $K = 85,432$
C. $K = 1.66 \times 10^{34}$
D. $K = 7.23 \times 10^{33}$

This is the only one $< 1$ 194 kJ mol⁻¹ is “big”
\[
\text{CH}_3\text{COOH}(aq) \rightarrow \text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq)
\]

for the following reaction at 300K, \( K = 1.78 \times 10^{-5} \)

\( \Delta R G^\circ \) for this reaction is

- A. \( \Delta R G^\circ = 0 \)
- B. \( \Delta R G^\circ = -10.4 \text{ kJ mol}^{-1} \) this is the only one >0 equilibrium constant not hugely small or hugely large
- C. \( \Delta R G^\circ = -312 \text{ kJ mol}^{-1} \)
- D. \( \Delta R G^\circ = +3.28 \text{ kJ mol}^{-1} \)

Equilibria and Perturbations (Stress)

What happens to a system at equilibrium if I change something like

- The concentration of one of the chemicals
- The Pressure
- The Temperature

Qualitatively Understanding "stress"

Le Chatlier's Principle

If a chemical system at equilibrium experiences a change, then the equilibrium shifts to partially counter-act the imposed change.

N\(_2\)(g) + 3H\(_2\)(g) \rightarrow 2\text{NH}_3(g)

You find the system at equilibrium, then you decide to add more H\(_2\) to the mixture

What happens as the reaction goes to a new equilibrium?

- A. the concentration of N\(_2\) decreases
  The system will compensate by moving to "reduce" the stress.
  You added H\(_2\)
  The reaction will try to reduce the amount of H\(_2\)
Stressing the concentrations

Add Reactants  →  Reaction Shifts towards Product

Add Products  →  Reaction Shifts towards Reactants

What if I increase the pressure?

You find the system at equilibrium at 1 atm, then you decide to increase the pressure to 2 atm. What happens as the reaction goes to a new equilibrium?

A. moves towards the products as they have fewer molecules

You increased the pressure. The reaction will try to reduce the pressure. The only way to do this is to reduce the number of molecules (move toward products)

Dealing with Stress from a Quantitative Perspective

\[
N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)
\]

Equilibrium

\[
[N_2] = 0.921 \text{ M} \\
[H_2] = 0.763 \text{ M} \\
[NH_3] = 0.157 \text{ M}
\]

\[
K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.06
\]

If I increase \([N_2]\) to 3 M the system will no longer be at equilibrium. Which way will it shift to get back to equilibrium?

\[
Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.0185
\]

\[
K = 0.06 \\
Q < K
\]

therefore reaction needs to increase products to get to equilibrium
K is constant

\[ K = \frac{\text{Products}}{\text{Reactants}} \]

Constant!

So if products goes up
the reaction will shift to get
back to the same constant ratio

This can happen if
Product goes down slightly
and Reactant goes up slightly

Two equilibrium constants

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

Concentrations

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

Partial Pressures

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

solutions

gas

Increasing Pressure

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

\[ K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = \frac{X_{\text{N}_2\text{O}_4} P}{X_{\text{NO}_2}^2 P^2} = \frac{X_{\text{N}_2\text{O}_4}}{X_{\text{NO}_2}^2} \]

If you increase P
Then the mole fraction of NO2
must go down since K is constant

Relating \( K_p \) and \( K_c \)

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

\[ K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \]

\[ K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} \]

\[ P_{\text{N}_2\text{O}_4} = \frac{[\text{N}_2\text{O}_4]RT}{V} = [\text{N}_2\text{O}_4]RT \]

concentration
Relating $K_p$ and $K_c$

$2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$

$$K_p = \frac{P_{\text{NO}_2}}{P_{\text{N}_2\text{O}_4}} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \frac{RT}{RT} = K_c \frac{1}{RT}$$

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

In general $K_p = K_c(\text{RT})^{\Delta n}$

$\Delta n$ is the change in the number of moles of gas

**Temperature Change**

$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) + \text{heat}$

this reaction is exothermic

If you increase $T$ then to "partially compensate" the reactions shifts to the reactants (consuming heat)

**How to change the pressure (constant $T$)**

- Increase $P$ (decrease $V$) Shifts to side with fewer gas molecules
- Decrease $P$ (increase $V$) Shifts to side with more gas molecules
- Add an inert gas (one that doesn’t react. Like He)

<table>
<thead>
<tr>
<th>Constant $P$</th>
<th>Constant $V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This is like diluting the system increase in $V$ like lowering $P$ shift to side with more gas molecules</td>
<td>This is like essentially doing nothing The partial pressures of all the molecules that matter are unchanged (the number of collisions is unchanged) the reaction is unchanged</td>
</tr>
</tbody>
</table>

$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) + \text{heat}$

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

$K$ is a function of $T$!
\[ \Delta R G^\circ(T) = -RT \ln K \]

\[ \Delta R G^\circ(T) = \Delta R H^\circ - T \Delta R S^\circ \]

\[ -RT \ln K = \Delta R G^\circ(T) = \Delta R H^\circ - T \Delta R S^\circ \]

\[ \ln K = -\Delta R H^\circ/RT + \Delta R S^\circ/R \]

Temperature dependence of \( K \) depends on \( \Delta R H^\circ \)

\[ y = mx + b \]

\( y \) is \( \ln K \)

\( x \) is \( 1/T \)

\( m \) is \( -\Delta R H^\circ/R \)

\( b \) is \( \Delta R S^\circ/R \)

A different way to do calorimetry measure \( K \) to find \( \Delta R H^\circ \)

Drug Binding Question

Enzyme/Drug Complex \[\rightarrow\] Drug + Enzyme

inhibited \hspace{2cm} functioning

The equilibrium for this constant is \(10^{-6}\) (I made this up) at what concentration of drug is half the enzyme inhibited? (note: at this point [enzyme]=[complex])

A. \( K = 1 \)
B. \( K = 10^2 \text{ M} \)
C. \( K = 10^{-3} \text{ M} \)
D. \( K = 10^{-4} \text{ M} \)

\[ K = \frac{[\text{drug}][\text{enzyme}]}{[\text{complex}]} \]

\[ [\text{drug}] = K \frac{[\text{complex}]}{[\text{enzyme}]} \]

\[ [\text{drug}] = K \]