1 Chemical equilibrium

Chemical equilibrium is a dynamic equilibrium when the rate of the forward reaction equals the rate of the reverse reaction for a reversible reaction in a closed system. Isolated from the surroundings, no reagents can escape, and reverse reaction can take place.

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

\( \text{N}_2 \) and \( \text{H}_2 \) is sealed in a container:

<table>
<thead>
<tr>
<th>Initially:</th>
<th>Over time:</th>
<th>Eventually:</th>
</tr>
</thead>
<tbody>
<tr>
<td>High ([\text{N}_2]) and ([\text{H}_2]) → Forward reaction fast</td>
<td>([\text{N}_2]) &amp; ([\text{H}_2]) decrease (used) → Forward reaction slower</td>
<td>Chemical equilibrium reached ([\text{N}_2]), ([\text{H}_2]) &amp; ([\text{NH}_3]) constant.</td>
</tr>
<tr>
<td>([\text{NH}_3]) = 0 → No reverse reaction</td>
<td>([\text{NH}_3]) increases (produced) → Reverse reaction faster</td>
<td>([\text{N}_2]), ([\text{H}_2]) &amp; ([\text{NH}_3]) constant.</td>
</tr>
<tr>
<td>([\text{N}_2]) &amp; ([\text{H}_2]) decrease (used) → Forward reaction slower</td>
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</tbody>
</table>

Draw reaction rate vs time graphs for both reactions:

**Equilibrium constant (K\(_c\))**

The equilibrium constant is the ratio of concentration of the products to the concentration of the reactants in the equilibrium mixture and the value holds only for a specific temperature.

\[ \text{aA} + \text{bB} \rightleftharpoons \text{cC} + \text{dD} \quad K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \]

Square brackets \([\quad]\) represent concentrations and \(K_c\) has no unit. Pure solids and liquids/solvents are left out.

\( K_c > 1\): More products than reactants in the equilibrium mixture.

\( K_c < 1\): More reactants than products in the equilibrium mixture.
QUESTION 1

1.1 Write equations for the equilibrium constant for each of the following reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H₂O₂(aq) ⇌ 2H₂O(l) + O₂(g)</td>
<td></td>
</tr>
<tr>
<td>AgCl(s) ⇌ Ag⁺(aq) + Cl⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>6CO₂(g) + 6H₂O(l) ⇌ C₆H₁₂O₆(s) + 6O₂(g)</td>
<td></td>
</tr>
</tbody>
</table>

1.2 Ammonia is prepared according to the following reaction:

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

At a high temperature an equilibrium mixture for the above endothermic reaction has the following concentrations:

- \([\text{NH}_3] = 2 \text{ mol/dm}^3\)
- \([\text{H}_2] = 1.5 \text{ mol/dm}^3\)
- \([\text{N}_2] = 0.5 \text{ mol/dm}^3\)

Calculate the equilibrium constant \(K_c\) for the reaction at this temperature.

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

\[ K_c = \frac{(2 \text{ mol/dm}^3)^2}{(1.5 \text{ mol/dm}^3)^3(0.5 \text{ mol/dm}^3)} \]

\[ K_c = \frac{4}{(1.5)^3(0.5)} \]

\[ K_c = \frac{4}{3.375} \]

\[ K_c = 1.18 \text{ mol/dm}^3 \]
1.3 Hydrogen iodide can be produced by the following reversible reaction:

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \quad K_c = 56.00 \text{ at } 425^\circ\text{C} \]

At a certain time during the reaction the concentrations in the container are:

\[ [\text{H}_2] = 1.5 \text{ mol/dm}^3 \]
\[ [\text{I}_2] = 1.0 \text{ mol/dm}^3 \]
\[ [\text{HI}] = 2.5 \text{ mol/dm}^3 \]

Do a calculation to determine if the reaction has reached chemical equilibrium.

1.4 Consider the following reaction: \( 2\text{A}(g) + \text{B}(g) \rightleftharpoons \text{C}(g) \).

12 mol A and 10 mol B are sealed in a 2 dm\(^3\) container. At equilibrium there are 4 mole of A in the container. Calculate the \( K_c \) value.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Mole initially</th>
<th>Mole react</th>
<th>Mole at equilibrium</th>
<th>Concentration at equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( c = \frac{n}{V} )</td>
</tr>
</tbody>
</table>
Le Chatelier's Principle:
When the equilibrium in a closed system is disturbed, the system will re-instate a new equilibrium by favouring the reaction that will oppose the disturbance.

The following dynamic equilibrium is reached in a closed container:

\[
2A(g) + B(s) \rightleftharpoons 2C(g) + D(g) \quad \Delta H \text{ is negative}
\]

\[
K_c = \frac{[C]^2[D]}{[A]^2}
\]

If A is added to the mixture in the container:
Disturbance: [A] increases.
According to Le Chatelier's principle the system reacts to decrease the [A].
The forward reaction is favoured. (Use A)
More C and D is produced.
\( K_c \) remains the same.

If C is added to the mixture in the container:
Disturbance: [C] increases.
According to Le Chatelier's principle the system reacts to decrease the [C].
The reverse reaction is favoured. (Use C)
D decreases.
\( K_c \) remains the same.

If A is removed from the mixture in the container:
Disturbance: [A] decreases.
According to Le Chatelier's principle the system reacts to increase [A].
The reverse reaction is favoured (make A).
C and D decreases.
\( K_c \) remains the same.

B(s) is added:
Solid has no effect on equilibrium.

If the volume of the container is decreased:
Disturbance: pressure increases (Boyle’s Law).
According to Le Chatelier’s principle the system reacts to lower the pressure.
Reacts to produce less moles of gas.
Reverse reaction is favoured.
C and D decreases.
\( K_c \) remains the same.

If the temperature is increased:
Disturbance: Temperature increases.
According to Le Chatelier’s principle the system reacts to decrease the temperature.
Endothermic reaction is favoured (uses energy).
\( \Delta H \) is negative \( \therefore \) forward reaction exothermic.
The reverse reaction is favoured.
C and D decreases.
\( K_c \) decreases.
**Catalyst is added:**
No effect on equilibrium. The rate of both reactions increase **equally**.

Favoured does not indicate that the reaction happens faster than before, but that it happens faster than the reaction in the opposite direction.

<table>
<thead>
<tr>
<th>Action</th>
<th>Disturbance</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adding acid</td>
<td>[H(^+)] increases</td>
<td>Acid donates H(^+)</td>
</tr>
<tr>
<td>Adding base</td>
<td>[H(^+)] decreases</td>
<td>Base reacts with H(^+)</td>
</tr>
<tr>
<td>Adding AgNO(_3)</td>
<td>[Cl(^-)] decreases</td>
<td>Ag(^+) + Cl(^-) → AgCl(s) precipitate</td>
</tr>
<tr>
<td>Adding BaCl(_2) or Ba(NO(_3))(_2)</td>
<td>[SO(_4^{2-})] decreases</td>
<td>Ba(^{+2}) + SO(_4^{2-}) → BaSO(_4)(s) precipitate</td>
</tr>
</tbody>
</table>

The colours of compounds with transition elements are well-known. For example, consider the following equation of a reversible reaction:

\[
\begin{array}{c}
\text{yellow} \\
2\text{CrO}_4^{2-}(aq) + 2\text{H}^+(aq) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l)
\end{array}
\]

1. Write down an expression for the equilibrium constant.

2. How will the equilibrium constant (K\(_c\)) be influenced in the following situations:
   a) sodium chromate (Na\(_2\)CrO\(_4\)) is added. ______________________
   b) Hydrochloric acid is added. ______________________
   c) Sodium hydoxide is added ______________________

3. Explain in detail how the colour of the solution will be influenced when sodium hydroxide is added.

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Junior Tukkie Winter School 5 Dr. S. Swanepoel (2020)
\[2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)\]

<table>
<thead>
<tr>
<th></th>
<th>A and B into container</th>
<th>A added</th>
<th>B removed</th>
<th>D added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disturbance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Le Chatelier: System reacts to . . .</td>
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<tr>
<td>The . . . reaction is favoured</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>[C] . . .</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(K_c)</td>
<td></td>
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</table>

Reaction rate

Concentrations
\[ \Delta H < 0 \]

<table>
<thead>
<tr>
<th>Volume doubled</th>
<th>Temperatuur increased</th>
<th>Temperaturate decreased</th>
<th>Catalyst added</th>
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<tbody>
<tr>
<td></td>
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</tbody>
</table>
QUESTION 2

Choose the correct word in the brackets:

2.1 The following reaction is at equilibrium at 400K:
\[ \text{A}_2(g) + 3\text{B}_2(g) \rightleftharpoons 2\text{AB}_3(g) \quad \Delta H < 0 \]

If the temperature is increased to 600 K the K_c-value will (increase/decrease/stay the same).

2.2 A mixture of NO and Br₂ is placed in a container. The following traction occurs:
\[ 2\text{NO}(g) + \text{Br}_2(g) \rightleftharpoons 2\text{NOBr}(g) \]

After 5 minutes chemical equilibrium is reached. The following graph shows how the rate of the forward reaction changes with time:

After 15 s the temperature was (increased/decreased) and the K_c-value (increased/decreased/remained constant).

2.3 P and Q are sealed in a container and the following chemical equilibrium is reached after 5 minutes at 500 K:
\[ \text{P}(g) + 2\text{Q}(g) \rightleftharpoons \text{R}(g) \]

After 10 minutes the temperature is increased to 600 K and after 5 minutes a new chemical equilibrium is established. The following graph shows the change in concentration with time.

The K_c-value (increased/decreased/remained constant). \( \Delta H \) for the reaction is (positive/negative).
2.4 The following reaction mixture turns more red when the temperature is increased:
\[ 3H(g) \rightleftharpoons 2F(g) + 2D(g) \]

When the temperature is increased, the equilibrium constant (increases/decreases). \( \Delta H \) is (positive/negative).

2.5 The following reaction reached chemical equilibrium in a closed container:
\[ 2H(g) + I(g) \rightleftharpoons 2K(g) \quad \Delta H < 0 \]

At time X the temperature was (increased/decreased) and the \( K_c \)-value (increases/decreases/remains constant).

2.6 The following reaction is in chemical equilibrium:
\[ 3M(g) \rightleftharpoons 2N(g) + 2P(g) \]

When the temperature increases, the mixture turns more blue. \( \Delta H \) is (positive/negative).

2.7 The following reaction reached chemical equilibrium in a closed container:
\[ 2X(g) + Y(g) \rightleftharpoons Z(g) + 2A(g) \]

After time X the \( K_c \) value is (larger/smaller) than before. The heat of the reaction is (positive/negative).
### 2A(g) + B(g) ⇌ 3C(g) + D(g) \[\Delta H < 0\]

### Le Chatelier's Principle:
The system reacts to... 

<table>
<thead>
<tr>
<th>Disturbance</th>
<th>A added</th>
<th>B removed</th>
<th>D added</th>
<th>Volume doubled</th>
<th>Temperature increased</th>
<th>Temperature decreased</th>
<th>Catalyst added</th>
</tr>
</thead>
<tbody>
<tr>
<td>A and B in a container</td>
<td>[A]↑</td>
<td>[B]↓</td>
<td>[D]↑</td>
<td>P↓</td>
<td>T↑</td>
<td>T↓</td>
<td></td>
</tr>
<tr>
<td>A and B in a container</td>
<td>[A]↓</td>
<td>[B]↑</td>
<td>[D]↓</td>
<td>P↑</td>
<td>T↓</td>
<td>T↑</td>
<td></td>
</tr>
<tr>
<td>A and B in a container</td>
<td>forward</td>
<td>reverse</td>
<td>reverse</td>
<td>more mol gas forward</td>
<td>endothermic reverse</td>
<td>exothermic forward</td>
<td></td>
</tr>
<tr>
<td>A and B in a container</td>
<td>[C] will</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
<td></td>
</tr>
<tr>
<td>A and B in a container</td>
<td>constant</td>
<td>constant</td>
<td>constant</td>
<td>constant</td>
<td>↓</td>
<td>↑</td>
<td>constant</td>
</tr>
</tbody>
</table>

*Both reactions equally faster*