1.10 Partial Pressures and Kp

If a reaction contains gases an alternative equilibrium expression can be set up using the partial pressures of the gases instead of concentrations.

Partial Pressure

The partial pressure of a gas in a mixture is the pressure that the gas would have if it alone occupied the volume occupied by the whole mixture.

If a mixture of gases contains 3 different gases then the total pressure will equal the 3 partial pressure added together

\[ P = p_1 + p_2 + p_3 \]

\[ \text{partial pressure} = \text{mole fraction} \times \text{total pressure of gas} \]

\[ p_j = x_j \times P \]

**Example**: A mixture contains 0.2 moles N\(_2\), 0.5 moles O\(_2\) and 1.2 moles of CO\(_2\). If the total pressure is 3kPa. What are the partial pressures of the 3 gases?

Total moles of gas = 0.5 + 1.2 + 0.2 = 1.9

<table>
<thead>
<tr>
<th>Gas</th>
<th>Moles</th>
<th>Mole Fraction</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>0.2</td>
<td>0.2/1.9 = 0.105</td>
<td>0.315</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.5</td>
<td>0.5/1.9 = 0.263</td>
<td>0.789</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1.2</td>
<td>1.2/1.9 = 0.632</td>
<td>1.896</td>
</tr>
</tbody>
</table>

Writing an expression for \(K_p\)

\[ \frac{p^2 \text{NH}_3}{p \text{N}_2 \times p \text{H}_2} \]  

\(p\) means the partial pressure of that gas 

\(K_p\) = equilibrium constant

Only include gases in the \(K_p\) expression. Ignore solids, liquids, and aqueous substances.

Working out the unit of \(K_p\)

Put the unit of pressure (kPa) into the \(K_p\) equation

\[ \text{Unit} = \frac{kPa^2}{kPa \times kPa^3} \]

However, if the equation is written the other way round, the value of \(K_p\) will be the inverse of above and the units will be kPa\(^2\).

It is important therefore to write an equation when quoting values of \(K_p\).
Example

For the following equilibrium

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

1 mole of \( \text{N}_2 \) and 3 moles of \( \text{H}_2 \) are added together and the mixture is allowed to reach equilibrium. At equilibrium 20% of the \( \text{N}_2 \) has reacted. If the total pressure is 2kPa what is the value of \( K_p \)?

<table>
<thead>
<tr>
<th></th>
<th>( \text{N}_2 )</th>
<th>( \text{H}_2 )</th>
<th>( \text{NH}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>1.0</td>
<td>3.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Equilibrium moles</td>
<td>0.80</td>
<td>2.40</td>
<td>0.40</td>
</tr>
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</table>

20% of the nitrogen had reacted = 0.2 \times 1.0 = 0.2 moles reacted. Using the balanced equation 3 x 0.2 moles of \( \text{H}_2 \) must have reacted and 2 x 0.2 moles of \( \text{NH}_3 \) must have formed.

Work out the moles at equilibrium for the reactants and products

moles of reactant at equilibrium = initial moles – moles reacted

moles of nitrogen at equilibrium = 1.0 – 0.2 = 0.8

moles of hydrogen at equilibrium = 3.0 – 0.20 \times 3 = 2.40

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.2 \times 2) = 0.4

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<td>0.80</td>
<td>2.40</td>
<td>0.40</td>
</tr>
<tr>
<td>Mole fractions</td>
<td>0.8/3.6 =0.222</td>
<td>2.40/3.6 =0.667</td>
<td>0.40/3.6 =0.111</td>
</tr>
<tr>
<td>Partial pressure</td>
<td>0.222 x2 = 0.444</td>
<td>0.667 x2 = 1.33</td>
<td>0.111 x2 = 0.222</td>
</tr>
</tbody>
</table>

Finally put concentrations into \( K_p \) expression

\[ K_p = \frac{p^2 \text{NH}_3 (g)}{p \text{N}_2 (g) \, p^3 \text{H}_2 (g)} \]

\[ K_p = \frac{0.222^2}{0.444 \times 1.33^3} = 0.0469 \text{ kPa}^{-2} \]

Heterogeneous equilibria for \( K_p \)

\( K_p \) expressions only contain gaseous substances. Any substance with another state is left out

\[ \text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g) \]

\[ K_p = p \text{CO}_2 \]

Unit kPa
Effect of changing conditions on value of $K_c$ or $K_p$

The larger the $K_c$ the greater the amount of products. If $K_c$ is small we say the equilibrium favours the reactants.

**Kc and Kp only change with temperature.**

It does not change if pressure or concentration is altered.

A catalyst also has no effect on $K_c$ or $K_p$.

Effect of Temperature on position of equilibrium and $K_c$

In this equilibrium which is exothermic in the forward direction

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$

If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of $K_c$ gets smaller as there are fewer products.

Effect of Pressure on position of equilibrium and $K_p$

In this equilibrium which has fewer moles of gas on the product side

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$$

If pressure is increased the reaction will shift to oppose the change and move in the forward direction to the side with fewer moles of gas. The position of equilibrium shifts right. The value of $K_p$ stays the same though as only temperature changes the value of $K_p$.

Increasing pressure does not change $K_p$. The increased pressure increases the pressure terms on bottom of $K_p$ expression more than the top. The system is now no longer in equilibrium so the equilibrium shifts to the right increasing mole fractions of products and decreases the mole fractions of reactants. The top of $K_p$ expression therefore increases and the bottom decreases until the original value of $K_p$ is restored.

<table>
<thead>
<tr>
<th>$K_p$</th>
<th>$K_p$ for $N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_p$</td>
<td>$\frac{P^2 NH_3}{P N_2 P^3 H_2}$</td>
</tr>
<tr>
<td>$K_p$</td>
<td>$\frac{x^2 NH_3 \cdot P^2}{x N_2 \cdot x^3 H_2 \cdot P^3}$</td>
</tr>
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Where $P$ is total pressure and $x$ mole fraction.