Lesson 3 Changes to an equilibrium

Le Chatelier's principle states *"**If a system at equilibrium is subjected to a change then the system will adjust to <u>partially</u> oppose the effect of the change**"*
If a system at equilibrium is thrown momentarily out of equilibrium due to a change the system partially opposes the change by moving in a net backward or forward direction to re-establish equilibrium once more.

- Addition of product -> results in a net backward reaction.
- Addition of reactant -> results in a net forward reaction.
- An increase in concentration or pressure due to a decrease in volume -> results in a net movement in the direction which produces less particles.
    Eg $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ a net forward reaction will occur.
    Eg $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ no net change because there are two particles on both sides, the system cannot respond.
- A decrease in concentration or pressure due to an increase in volume -> results in a net movement in the direction which produces more particles.
- An increase in pressure due to the addition of an inert gas -> no change.
- An increase in temperature -> net movement in the direction which will use energy.
    eg $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ΔH = -ve an increase in temperature will result in a net backward reaction

    eg $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ ΔH = +ve an increase in temperature will result in a net forward reaction
- A decrease in temperature -> net movement in the direction which will produce energy.
    eg $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ΔH = -ve a decrease in temperature will result in a net forward reaction

    eg $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ ΔH = +ve a decrease in temperature will result in a net backward reaction
- An increase in temperature -> net movement in the direction which will absorb energy.
    eg $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ΔH = -ve a net backward reaction
    eg $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ ΔH = +ve a net forward reaction

Addition of a catalyst -> no response to the equilibrium position of the system as the rate of the backward and forward reactions are effected equally. A catalyst only causes a reaction to reach equilibrium quicker than it would without a catalyst. Some reactions are so slow in reaching a dynamic equilibrium that it may take days.

<u>***It is important to note that the value of the equilibrium constant (K_c), which is the value of the reaction quotient when the reaction is at equilibrium, does not change unless there is a change in temperature.***</u>
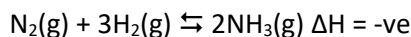For example take the following reaction. $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$
It's reaction quotient is shown on the right. When the reaction, at equilibrium, is disturbed by the addition of, say, H_2 gas the value of the reaction quotient decreases and the reaction responds in a way as to restore its value back to K_c.
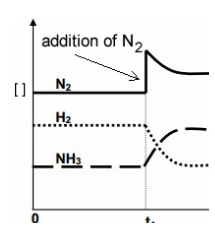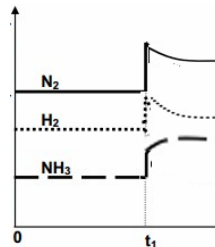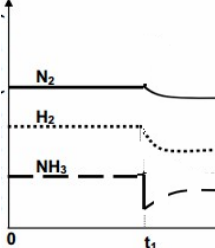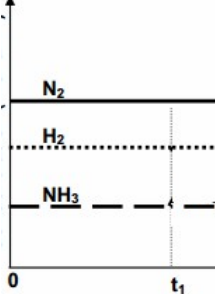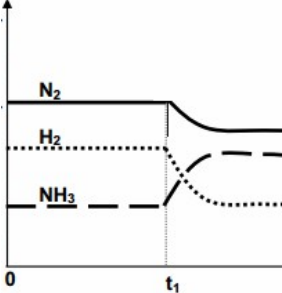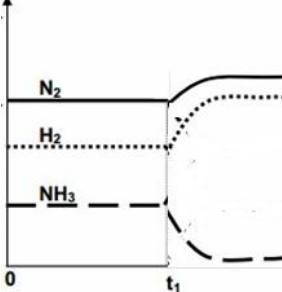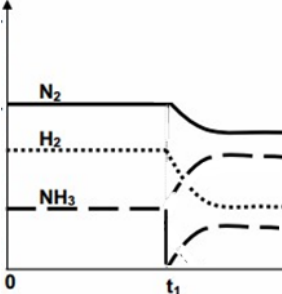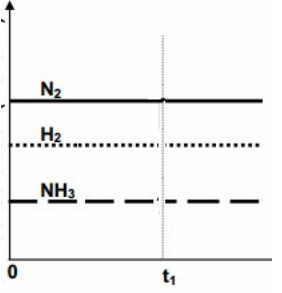
$$\frac{[NH_3]^2}{[H_2]^3\,[N_2]}$$

Remember K_c is the value of the reaction quotient at equilibrium and this does not change when the reaction is at equilibrium at a given temperature.

Consider a mixture of H_2 and N_2 which was placed in a sealed container and allowed to reach equilibrium. The reaction took place according to the equation below.
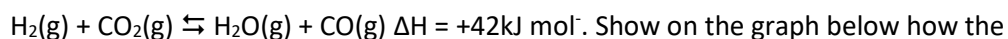
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = \text{-ve}$$

Fill in the blank boxes.

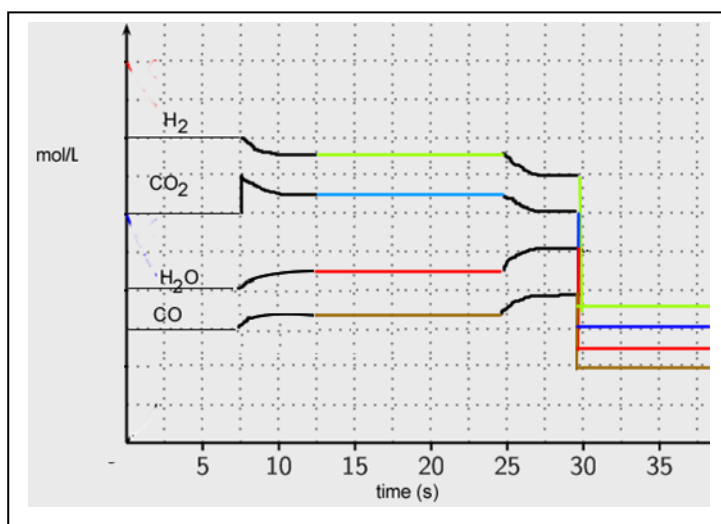| Change	Final change when it returns to equilibrium	What the graph looks like	Value of K_c	Response
Addition of reactant, N_2 gas	$[N_2]$ = ↑ $[H_2]$= ↓ $[NH_3]$ = ↑		No change	Net forward reaction
Increase the pressure by a volume decrease	$[N_2]$ = ↑ $[H_2]$= ↑ $[NH_3]$ = ↑		No change	Net forward reaction
Removal of product, NH_3 gas	$[N_2]$ = ↓ $[H_2]$= ↓ $[NH_3]$ = ↓		No change	Net for forward reaction
Catalyst added to the equilibrium mixture	No change		No change	Effects backward and forward rates equally

Temperature decrease	$[N_2] = \downarrow$ $[H_2] = \downarrow$ $[NH_3] = \uparrow$		increase	Net forward reaction
Temperature increase	$[N_2] = \uparrow$ $[H_2] = \uparrow$ $[NH_3] = \downarrow$		Decrease	Net backward reaction
Removal of product (NH_3 gas)	$[N_2] = \uparrow$ $[H_2] = \uparrow$ $[NH_3] = \downarrow$		No change	Net forward reaction
Increase in pressure by the addition of helium gas	No change		No change	No change. *In order to shift the equilibrium position increase in pressure must result from a change in volume.*

1) Consider a sealed container with a gaseous mixture of H_2O and CO_2 . This mixture was allowed to react and reach equilibrium according to the equation below.

$H_2(g) + CO_2(g) \leftrightarrows H_2O(g) + CO(g)$ $\Delta H = +42kJ\ mol^-$. Show on the graph below how the system responds to the following changes. If the system responds equilibrium is established within 5 seconds of the change.

a) CO_2 gas is added at 7.5 s
b) Helium gas is added at 15 s
c) Temperature is increased at 25s
d) Volume is doubled at 30 s
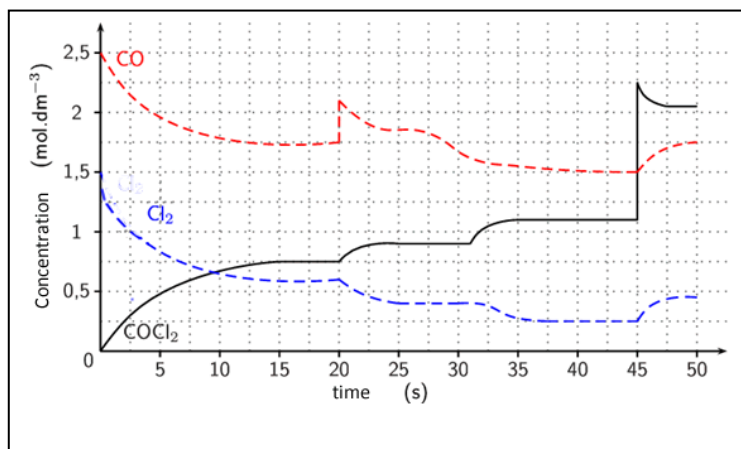
e) Calculate K_c at 5s *No units*

$$K_c = \frac{[H_2O]\,[CO]}{[H_2]\,[CO_2]} = \frac{1 \times 0.75}{1.5 \times 2} = \frac{1}{4}$$

2) Consider the reaction
$CO(g) + Cl_2(g) \leftrightarrows COCl_2(g)$ ΔH = -108kJ/mol
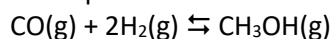Indicate what happens at
20S *CO is added*
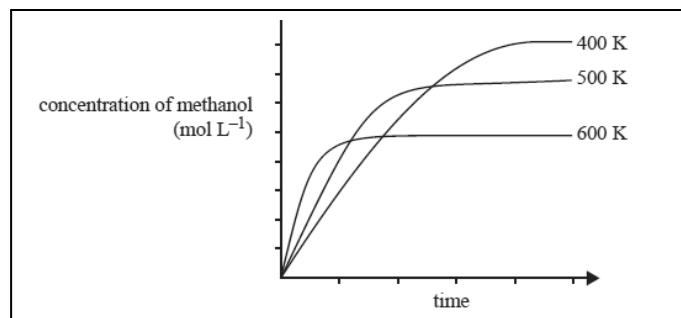30s *Reaction is cooled*
45s *COCl₂ is added*

3) Methanol is produced on an industrial scale by the catalytic conversion of a mixture of hydrogen and carbon monoxide gases at a temperature of 520 K and a pressure of 50 to 100 atmospheres. The reaction that occurs in the methanol converter is
$CO(g) + 2H_2(g) \leftrightarrows CH_3OH(g)$
Carbon monoxide gas and hydrogen gas are mixed in a reaction vessel and equilibrium is established. The graph on the right shows how the concentration of methanol in this vessel changes with time at three different temperatures. The pressure is the same at each temperature.

i) Is the reaction exothermic or endothermic? Explain *Exothermic. As temperature decreases more product is formed when equilibrium is established.*

ii) Explain why a moderately high temperature of 520 K is used although the equilibrium concentration of methanol is greater at lower temperatures.
At high temperatures, such as 600 K equilibrium is established quickly but with less product than at temperatures of 400 K. A temperature of 520 K is acompromise between rate and yield (amount of product formed). In industrial applications the rate and the amount of product formed is crucial. The highest yield at the fastest rate is always what industrial chemists strive for.

iii) Explain why, at a given temperature, the use of high pressures results in a greater equilibrium concentration of methanol.
High pressure will drive the equilibrium position to the right, hence producing a higher yield.
iv) A catalyst consisting of a mixture of copper, zinc and aluminium is used to increase the rate of this reaction. Explain how a catalyst can increase reaction rate.

Provides an alternative reaction pathway that requires less activation energy which leads to more reactant particles per unit time undergoing fruitful collisions.

4) At room temperature an unknown amount of moles of SO_2 and 0.40 moles of O_2 were introduced into a sealed 10.00 L vessel and allowed to come to equilibrium.

a) Write the equilibrium constant expression and calculate the value for the equilibrium constant at time A.
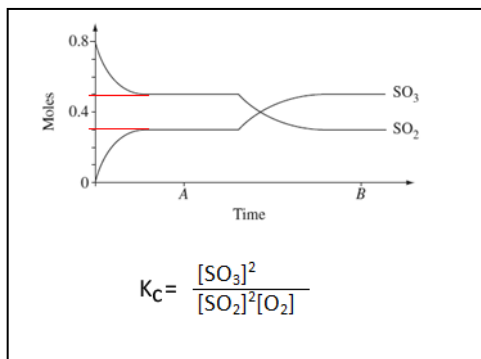
$2SO_3(g) + O_2(g) \leftrightarrows 2SO_3(g)$
The amount in mol of O_2 left at equilibrium is,
according to the reaction ratio, if 0.3 mol of SO_3 is formed then 0.15 mol of O_2 is used. Hence 0.40 – 0.15 = 0.25 mol of O_2 is present at equilibrium.
$[O_2]$ = 0.25/10.00 L = 0.025 M
$[SO_3]$ = 0.3 / 10.00L = 0.03 M
$[SO_2]$ = 0.5 / 10.00L = 0.05 M
K_c = $(0.03)^2$ / $((0.05)^2(0.025))$ = 14. 4 M⁻ (sig figs not taken into account)

$$K_c= \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

b) Explain why a new equilibrium position was established at time B.
Temperature change occurred. The concentration of all species present gradually changed indicating that a temperature change had occurred.