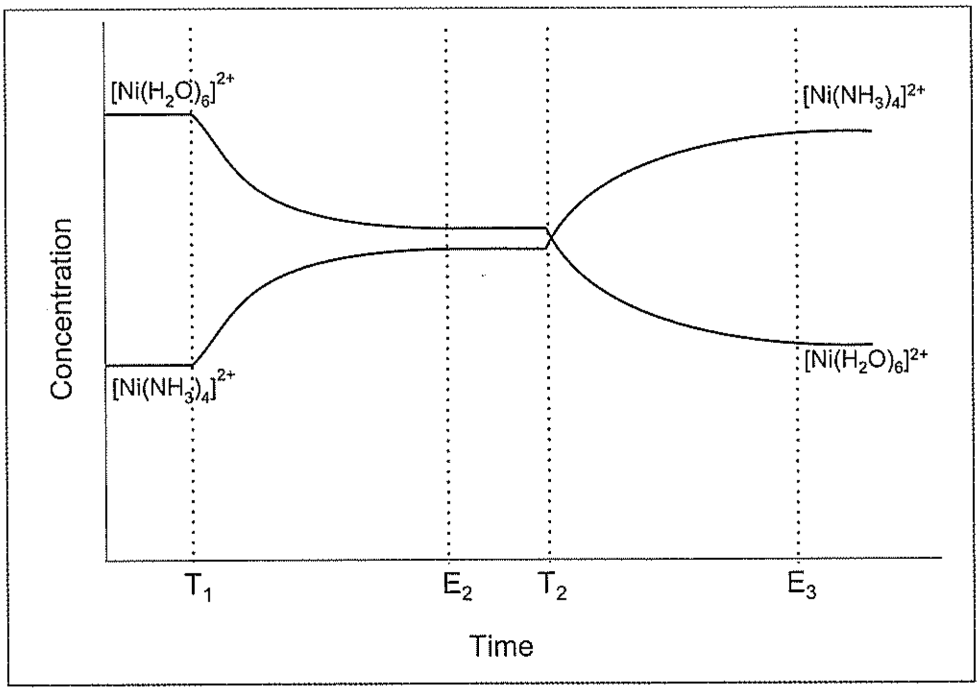
Question 33 **(8 marks)**

The following aqueous equilibrium system represents a ligand-exchange reaction between the green hexaaquanickel(II) complex ion, $[Ni(H_2O)_6]^{2+}$, and the blue tetraamminenickel(II) complex ion, $[Ni(NH_3)_4]^{2+}$.

$$[Ni(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Ni(NH_3)_4]^{2+}(aq) + 6H_2O(l)$$

The system was allowed to establish equilibrium and then various changes were made. The effects of these changes are shown in the concentration graph below.



(a) Assuming the value of K_c remains unaffected, suggest what change could have been imposed on the system at T_1. (1 mark)

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(b) At E_2 the system re-establishes equilibrium. Explain how this is known. (1 mark)

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At T_2 the temperature of the system is increased.

(c) Is the above reaction endothermic or exothermic as written? (1 mark)

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(d) Explain in terms of reaction rates, the effect of a temperature increase on this equilibrium between T_2 and E_3. (3 marks)

(e) At E_3 would the value of K_c be higher, lower or the same? (1 mark)

(f) What observations would be noted as the temperature was increased? (1 mark)

Question 33

(a) Some ammonia solution was added thus increasing the concentration of $NH_3(aq)$.

(b) The concentration of all species is constant from E_2 to T_2.

(c) Endothermic

(d) Effect: The graph shows that beyond T_2 the product $[Ni(NH_3)_4]^{2+}(aq)$ is favoured.
Explanation: Increasing temperature increases the average kinetic energy of all of the particles in a system, and therefore the rate of both the forward and reverse reactions will increase. However, when temperature is raised the rate of the endothermic reaction; in this case the forward reaction; increases by a greater factor than the exothermic reaction, in this case the reverse reaction. Consequently in forming a new equilibrium the products are favoured and thus when equilibrium is re-established the concentration of $[Ni(NH_3)_4]^{2+}(aq)$ has increased as is shown by the graph.

(e) Higher, since more products are present

(f) The solution would become bluer in colour

Question 38 **(20 marks)**

Ammonia is an extremely versatile inorganic compound. Current worldwide production exceeds 130 million tonnes annually. Western Australia is a significant ammonia producer with a major ammonia plant situated in the Pilbara region. This plant, on the Burrup Peninsula, uses natural gas as one of its raw materials. The following reactions, Step 1 and 2, show how methane from natural gas can be used to produce hydrogen.

Step 1: $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +206$ kJ

Step 2: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H = -41$ kJ

To produce ammonia, the hydrogen from Step 1 and 2 is then reacted with nitrogen gas that has been extracted from air. This process, known as the Haber-Bosch process, is shown in Step 3. The Haber-Bosch process uses an iron/iron oxide catalyst, high gas pressure and a moderately high temperature to produce ammonia.

Step 3: $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ

(a) Comment on the conditions used in the Haber-Bosch process, in terms of the effect on reaction rate and yield of ammonia. (6 marks)

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The current annual ammonia production at the Burrup plant is 7.60×10^5 tonnes.

(b) What minimum volume of air, measured at S.T.P. must be used to provide sufficient nitrogen gas for a single day's production of ammonia? You may assume air is 78% nitrogen and that the Haber-Bosch process has a yield of exactly 100%. (6 marks)

(c) Calculate the minimum mass of methane that must be used to produce sufficient hydrogen for a single day's production of ammonia. You may assume all reaction steps have a yield of exactly 100%. (4 marks)

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On a particular day the plant uses sufficient nitrogen and hydrogen to produce 2.500×10^3 tonnes of ammonia. The production data for that day reveals that only 2.351×10^3 tonnes of ammonia were actually produced.

(d) Determine the yield of ammonia for that day. (1 mark)

(e) Suggest why industrial processes can never actually have a yield of 100% and comment on some of the specific factors that would contribute to a loss of yield in the production of ammonia. (3 marks)

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Question 38

(a) Use of an iron/iron oxide catalyst will increase the rate at which $NH_3$is produced. The catalyst would provide an alternate pathway with a lower activation energy, allowing a greater proportion of particles to overcome the activation energy barrier. Catalysts reduce costs because they can be recycled and also allow a lower temperature to be used. However a catalyst will have no effect on the yield of NH_3 produced.
Use of high pressure will increase both the rate and yield of NH_3 production. A higher pressure will result in more collisions between reactant particles and therefore a higher reaction rate. A high pressure will also favour the forward reaction as the system adjusts to reduce the pressure by favouring the direction which produces fewer gas molecules (4 mol → 2 mol). This will in turn increase the yield of NH_3.
Use of a moderate temperature is a compromise between a high rate and a high yield. A high rate would be obtained by using a high temperature, thereby increasing the average kinetic energy of the reaction particles and allowing a larger proportion to overcome the activation energy barrier. A high yield would be obtained by using a low temperature, as this would result in the forwards exothermic reaction being favoured. Therefore a moderate temperature is used as a compromise between maximising yield and rate.

(b) $m(NH_3 \text{ produced per day}) = \dfrac{m(NH_3 \text{ produced per year})}{365} = \dfrac{7.60 \times 10^5}{365} = 2.08 \times 10^3$ t per day

$n(NH_3 \text{ produced per day}) = \dfrac{m}{M} = \dfrac{2.08 \times 10^3 \times 10^6}{17.034} = 1.22 \times 10^8$ mol **Note:** 1 tonne = 1×10^6 g

$n(N_2 \text{ required}) = \dfrac{n(NH_3)}{2} = \dfrac{1.22 \times 10^8}{2} = 6.11 \times 10^7$ mol

$V(N_2) = 22.71 \times n(N_2) = 22.71 \times 6.11 \times 10^7 = 1.39 \times 10^9$ L

$V(\text{air}) = \dfrac{1.39 \times 10^9 \times 100}{78} = 1.8 \times 10^9$ L (2SF) [Note: Air is given as 78% (2SF) by volume N_2.]

(c) $n(H_2 \text{ required}) = n(NH_3) \times \dfrac{3}{2} = 1.22 \times 10^8 \times \dfrac{3}{2} = 1.83 \times 10^8$ mol

Adding Step 1 and 2 shows that 1 mole of CH_4 produces 4 moles of H_2, as shown in the equation below.

$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$

$n(CH_4 \text{ required}) = n(H_2) \times \dfrac{1}{4} = 1.83 \times 10^8 \times \dfrac{1}{4} = 4.58 \times 10^7$ mol

$m(CH_4) = n \times M = 4.58 \times 10^7 \times 16.042 = 7.35 \times 10^8$ g or 735 t (3SF)

(d) $\% \text{ yield} = \dfrac{\text{actual}}{\text{theoretical}} \times 100 = \dfrac{2.351 \times 10^3}{2.500 \times 10^3} \times 100 = 94.04\%$ (4SF)

(e) Some general reasons why industrial processes can never achieve 100% yield include:

- Loss of reagent due to unwanted side reactions that unnecessarily consume reagents.
- Physical loss of product, e.g. due to the inability to completely separate or purify the product from the final reaction mixture.
- Equilibrium reactions that do not go to completion.
- Presence of impurities in the reagents meaning the amount of reagent added is less than the amount measured.

In particular, all three stages of this process (production of hydrogen and then ammonia) are reversible, so it would be difficult to get any of the steps to go to completion and obtain a 100% yield. Particularly when considering which conditions would produce a high yield and which would produce a fast reaction rate. These conditions do not always match and therefore compromises need to be made. A higher yield may be possible, however this would involve a reaction rate that would be uneconomically slow.
Also, both the reagents, N_2 and H_2 are unlikely to be completely pure. This means the amounts introduced into the reaction system are actually a little less than thought. Thus the amount of product, ammonia, obtained will also be a little less than expected.