- Consider the image of the Downs cell shown on the right. This cell produces a reactive metal in commercial quantities when continuously supplied with an electrolyte composed of a mixture of NaCl and CaCl₂.
- a. What is the metal formed in this electrolytic cell? <u>Na</u>
- b. Justify your answer to question a. above. The only oxidants present are Na⁺ and Ca^{2+.} Na⁺ is a stronger oxidant and will preferentially react at the cathode.



- c. A current of 30,000 amps flows through the cell keeping the electrolyte in the molten state.
 - i. Write the balanced reaction taking place at the anode. (2 marks)

 $2Cl^{-}(l) \rightarrow 2e^{-} + Cl_{2}(g)$ 1 mark balanced equation, 1 mark for states_

- ii. Calculate the mol of electrons passing through the cell per hour.(2 marks) $Q = It => 30,000 \times 1.00 \times 60 \times 60 = 1.08 \times 10^8 C - 1 mark$ $=> n_e = 108,000,000/96500 = 119 - 1 mark$
- iii. Calculate the mass, in kg, of metal formed in one hour of operation.

 $Na^{+}(l) + e^{-} \rightarrow Na(l) --- 1$ mark for correct stoichiometric ratio between mol of metal and electrons. Consequential marks can be given depending on answer given in a. above.

=> 119 X 23,0 = 0.741 kg ---- 1 mark for correct units and amount.

d. What would be the consequences of an iron anode being used in the cell? Justify your answer.

The iron electrode will be consumed or Cl_2 gas will not be formed.--- 1 mark Fe is a stronger reductant than Cl^- and will undergo oxidation according to the equation below $Fe(s) \rightarrow Fe^{2+}(l) + 2e^{-}$.

e. NaCl and MgCl₂ can be obtained in high concentrations and copious quantities in the form of brine. Can this provide a cheap source of reactive metals for the Downs cell? Explain *No.*

 $H_2O(I)$ is a stronger oxidant than either Ca²⁺ or Na⁺ and will be preferentially oxidised

2. The oceans hold 50 times more CO_2 than the atmosphere. So it is logical to start CO_2 capture and sequestration in the oceans. A new method is being developed that involves the electrolysis of sea water. Ocean carbon capture and sequestration involves the following interrelated equilibria.

- 1. $CO_2(g) \rightleftharpoons CO_2(aq)$
- 2. $CO_2(aq) + H_2O(I) \rightleftharpoons H_2CO_3(aq)$
- 3. $H_2CO_3(aq) \rightleftharpoons HCO_3^{2-}(aq) + H^+(aq)$
- 4. HCO3⁻ (aq) \rightleftharpoons H⁺(aq) + CO₃²⁻(aq)
- 5. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(aq)$
- 6. $CaCO_3(aq) \rightleftharpoons CaCO_3(s)$



Using your knowledge of electrolysis and le Chatelier's principle answer the following questions.

- a. During cell operation:
 - *i.* identify the products formed at the cathode. $H_2(g)$ and OH(aq)
- **b.** using le Chatelier's principle give an explanation as to how the product formed at the cathode promotes sequestration of carbon.

The OH⁻(aq) will react with H⁺ driving both the equilibria below to the right, thus producing a greater yield of $CO_3^{2-}(aq)$

 $H_2CO_3(aq) \rightleftharpoons HCO_3^{2-}(aq) + H^+(aq)$

 $HCO3^{-}(aq) \rightleftharpoons H^{+}(aq) + CO_{3}^{2-}(aq)$

An increase of $CO_3^{2^2}$ will drive the equilibrium, below, to the right thus sequestering more CO_2 .

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(aq)$

1 ----- mark for mentioning the removal of H^+ by the OH^- ions.

1 ----- mark for relating the loss of H^+ to the increase in $\text{CO}_3{}^{2\text{-}}$ yield and hence $\text{CaCO}_3(\text{aq})$ increase

c. Explain why Cl⁻ ions are removed from the sea water before it passes into the electrolytic cell? (*1 mark*)

 $Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$ $H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$

H₂ and Cl₂ may react spontaneously.

d. With reference to one of the equilibria mentioned above explain the purpose of adding Ca²⁺ ions to the water as it enters the electrolytic cell?
(1 mark)

 Ca^{2+} ions will react to form $CaCO_3$ and sequester carbon pushing the equilibrium below to the right. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(aq)$

e. Would Cu(NO₃)₂ be as effective as adding Ca(NO₃)₂ to the incoming sea water? Justify your response. (*2 marks*)

 Cu^{2+} will react at the cathode rather than H_2O . Cu(s) will deposit on the cathode. OH and H_2 will not be produced at that cathode. Hence the following equilibria will not be pushed to the right. $H_2CO_3(aq) \rightleftharpoons HCO_3^{2-}(aq) + H^+(aq)$ $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

f. This method is energy intensive and releases more CO₂ into the atmosphere than it currently removes. Under what conditions does this method of carbon capture become viable in capturing more carbon than it produces? (1 mark)

Renewable energy source, wind, solar. Any other viable renewable energy source or low carbon emission energy source such as nuclear will suffice.

g. Energy costs are very high when using this cell. Describe how these costs can be offset with reference to one product produced at the cathode during operation of the electrolytic cell. Identify the product and suggest one specific use. (*2 marks*)

Production of hydrogen which can be stored and used as a fuel in a hydrogen fuel cell to generate electricity.

3. Phosgene COCl₂ became important in the 19th century in dye manufacturing. It is also a critical industrial reagent in the synthesis of pharmaceuticals and other organic compounds. The reaction below shows the production of phosgene.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \Delta H = positive$$

Carbon monoxide gas and chlorine gas are placed in a 4.00 litre reaction vessel and are allowed to react. The graph below shows the change in concentration of the reactants and product over time.



a. Write the expression for the reaction quotient (Q) for the synthesis of phosgene gas (COCL₂) (1 mark)

<u>[COCl₂]</u> = Q [CO] [Cl₂]

b. What is the value of the reaction quotient at t=10 s? Give the answer to the right number of significant figures and the appropriate units. (2 marks)

 $\frac{[COCl_2]}{[CO] [Cl_2]} = Q$

[1.50] = Q = 0.679 M⁻ [0.700] [0.800] c. Give the most likely stress applied to the system at the following times and justify your answer.

i. T = 4 (assume constant temperature) Catalyst added. Rate of reaction increase. Since temperature is kept constant, this can only be achieved with the addition of a catalyst.

ii. T = 26

Addition of CO. A sudden spike in [CO] indicates CO is added and the system responds by moving in the forward direction to partly undo the increase in CO.

iii. T = 36

Temperature increase. The system moves in the forward direction without a change in the concentration of reactants or product. Being an endothermic reaction, addition of heat will cause the system to move in the forward direction to partly absorb the energy provided.

- d. At t = 10 the system had an unknown substance added to it. Using the response of the system, as seen in the concentration vs time graph, give two plausible suggestions as to what the product may have been and justify each suggestion. (2+2=4 marks)
 - *i.* Inert gas. A gas that does not take part in the reaction, hence the concentrations of reactants and product remain unchanged.

ii. Catalyst. A catalyst added to the system once it has reached equilibrium will have no impact as the catalyst increases the forward and reverse rates equally.

4. Consider the concentration vs time graph of a closed gas system, shown below.



- a. A change occurs at t4. Indicate how the system responds to the change at t4 by clearly <u>drawing</u>, in the box placed the graph above, the concentration changes observed for A, B and C. (1 mark)
- b. How does the value of the equilibrium constant(K) at t1 compare with the value of K at t3? Explain your reasoning. (2 marks)

 $K_{t1} = K_{t3}$ No temperature change is observed.

c. Three mol of gas A and three mol of gas B were placed in a 10.00 litre reaction chamber and allowed to reach equilibrium. The reaction chamber is surrounded by a heat exchanger that keeps the reaction temperature constant. The amount of heat absorbed by the heat exchanger in order to keep the temperature constant was measured at 26.5 kJ. Calculate the equilibrium constant (K).