Question 2

This question carries 18% of the marks for this assignment, and tests Objectives 1, 2, 3, 4, 11, 12, 13 and 14 of Block 7.

This question is concerned with a metal M. At 298.15 K, the standard electrode potential of the ($M^{2+}|M$) couple is:

$$M^{2+}(aq) + 2e^- = M(s);\ E^\ominus = -0.62\ V$$

Thermodynamic data at 298.15 K for metal M are as follows:

	$\Delta H_f^\ominus$ / kJ mol^{-1}	$\Delta G_f^\ominus$ / kJ mol^{-1}	$S^\ominus$ / J K^{-1} mol^{-1}
M(s)	0	0	43.8

Any other information you need should be taken from Block 7 and the S342 *Data Book*.

(a) (*3 marks*) Calculate the value of $\Delta G_f^\ominus$ (M^{2+}, aq) at 298.15 K.

(b) (*15 marks*) Metal M forms a *soluble* chloride, MCl_2, which is fully dissociated in aqueous solution as follows:

$$MCl_2(s) = M^{2+}(aq) + 2Cl^-(aq) \qquad (5)$$

An electrochemical cell is constructed by suspending a metal M electrode and a silver/silver chloride electrode in an aqueous solution of MCl_2. The cell is represented by the following cell diagram:

$$Ag(s)\,|\,AgCl(s)\,|\,MCl_2(aq)\,|\,M(s) \qquad (6)$$

(i) Write the implied cell reaction for cell diagram 6.

(ii) If the concentration of the MCl_2 solution is 0.05 mol dm^{-3}, calculate the emf (E) of the cell at 298.15 K. *State carefully any assumptions or approximations that you make.*

What is the spontaneous cell reaction under these conditions? Identify the anode and cathode, and state which will be the negative electrode.

How would you account for any difference between your calculated value of E and the *measured* emf of the cell?

The marks for part (c) will be awarded as follows: (i) 2 marks; (ii) 10 marks; (iii) 3 marks.

Question 3

This question carries 23% of the marks for this assignment, and tests Objectives 1, 4, 11, 13, 14 and 16 of Block 7, and Objectives 1, 11, 12, 13 and 14 of Block 8.

Sodium perchlorate, $NaClO_4$, can be prepared electrolytically by the anodic oxidation of aqueous chlorate ions, ClO_3^-, as follows:

$$ClO_3^-(aq) + H_2O(l) = ClO_4^-(aq) + 2H^+(aq) + 2e \qquad (7)$$

Hydrogen evolution takes place at the cathode, so the overall cell reaction can be represented as:

$$ClO_3^-(aq) + H_2O(l) = ClO_4^-(aq) + H_2(g) \qquad (8)$$

(a) (*12 marks*) One type of diaphragm cell uses an electrolyte feed containing ClO_3^- and ClO_4^- at concentrations of 4.5 mol dm^{-3} and 1.5 mol dm^{-3}, respectively. The electrolysis is run at 60 °C.

Use information from the S342 *Data Book* to determine:

(i) the values of $\Delta G_m^\ominus$, and hence $E^\ominus$, for the overall cell reaction (equation 8) at 60 °C; and hence

(ii) the minimum potential for the desired electrolysis under the conditions specified above.

State, and comment on, any assumptions or approximations involved in your calculations.

(b) (*11 marks*) In practice, the type of cell outlined in part (a) uses platinum anodes and steel cathodes. When run such that the current efficiency for perchlorate production is 90%, the applied cell potential is typically in the range 4–4.5 V.

(i) What other product is likely to be formed at the anode, and why would this be expected to affect the current efficiency for perchlorate production? (*two or three sentences*)

(ii) With reference to the general expression for cell potential (Block 8, equation 46, p. 38), identify and discuss *briefly* the factors that probably contribute to the difference between the actual applied potential and your theoretical estimate in part (a). (*About 100–150 words*)

Question 4

This question carries 32% of the marks for this assignment, and tests Objectives 1 and 2 of Topic Study 3.

(a) (*27 marks*) Use graph paper to construct an Evans diagram (potential difference versus $\log|i|$ type) to determine which of the cathodic reactions (equation 10 or 11) is likely to couple with the anodic reaction in equation 9 for the uniform corrosion of metal Z at pH 3 and 298.15 K, under (i) agitated conditions and (ii) unagitated conditions. Estimate the corresponding corrosion current densities.

Use the following information (all at 298.15 K) taking any further data or information required from the S342 *Data Book* and Topic Study 3.

Anodic reaction

$$Z(s) = Z^{2+}(aq) + 2e;\ E^\ominus(Z^{2+}|Z) = -1.00\ V \qquad (9)$$

Under standard concentration conditions at pH 0 on a surface composed of metal Z:

$$\alpha_{ox,\,an} = 2.0;\ i_e = 10^{-7}\ A\ m^{-2}$$

The value of i_e is proportional to both $[Z^{2+}]$ and $[OH^-]$.

Cathodic reactions

(i) $H^+(aq) + e = \frac{1}{2}H_2(g)$ (10)

Under standard concentration conditions on a surface composed of metal Z:

$$\alpha_{red,\,ca} = 1.0;\ i_e = 10^{-8}\ A\ m^{-2}$$

The value of i_e is proportional to $[H^+]^{\frac{1}{2}}$.