

Full Name:

Student ID #:

UNIVERSITY OF CANTERBURY

Mid-Year Examinations 2005

Prescription Number(s): CHEM 111 & 113

Paper Title: General Chemistry A

Time Allowed: TWO HOURS

Number of pages: 24

Before commencing work, read the instructions on this page.

1. This is both your examination paper and your answer book. You may use the blank page opposite for any additional working pertaining to that question.
2. Please ensure that your name and student ID number have been entered in the appropriate spaces above.
3. ANSWER **ALL** QUESTIONS.

Total marks = 120: you should allocate about 1 minute per mark.

NOTE: There is a page of formulae and a periodic table with atomic masses at the end of this paper.

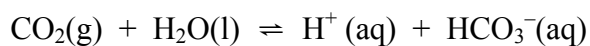
Please write your answers in the boxes provided

For examiners use only

1	2	3-4	5	6-7
8	9	Total		

1. (4 marks)

For the reaction



- (a) Give a mathematical expression for the thermodynamic equilibrium constant (K) in terms of the **activities** of the reaction components.

$$K =$$

- (b) Give the working rules for estimating the activities of the reaction components.

$$a_{\text{CO}_2} =$$

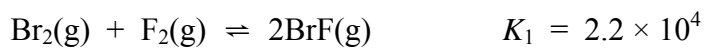
$$a_{\text{H}_2\text{O}} =$$

$$a_{\text{H}^+} =$$

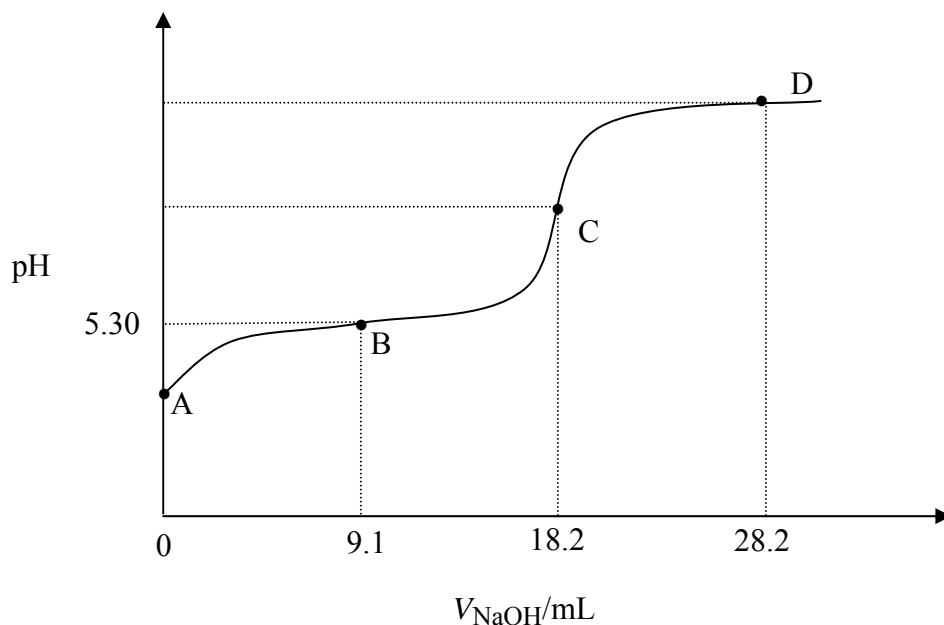
$$a_{\text{HCO}_3^-} =$$

2. (4 marks)

Use the data below to calculate the equilibrium constant (K_3) for the reaction



3. (24 marks)



The figure above shows the titration curve obtained (using a pH meter) when a 20.0 mL sample of a solution of weak acid, HA, of unknown concentration, C_{HA} , is titrated with standardised NaOH solution. The NaOH solution has a concentration of 0.110 mol L^{-1} and V_{NaOH} represents the volume in mL of NaOH which has been added. [Data: $K_{\text{w}} = 1.00 \times 10^{-14}$.]

- (a) What pieces of laboratory equipment would be used to measure out:
- the volume of HA solution?
 - the added volume of NaOH, V_{NaOH} ?
- (b) **On the figure above**, clearly indicate and label the following:
- the equivalence point;
 - a buffer region.
- (c) Calculate C_{HA} .
- (d) Using the given pH value for the solution at point B (5.30), calculate K_{a} (the acid ionisation constant) for HA.
- What is the pH at point A?
- (f) Prove the **general result** that K_{b} (base ionisation constant) for the base X^{-} (i.e. conjugate base of the acid, HX) is given by

$$K_{\text{b}}(X^{-}) = K_{\text{w}}/K_{\text{a}}(\text{HX})$$

- (g) Calculate the pH at the equivalence point in the titration.
- (h) The endpoint of this titration could be detected using an indicator. Of the indicators listed below, which would be the most suitable? **Explain the reason for your choice.**

Indicator	pK_a (indicator)
Lacmoid	5.3
Brilliant yellow	7.2
<i>o</i> -Cresolphthalein	9.0
2,4,6-Trinitrotoluene	12.3

- (i) What is the pH at point D?

4. (12 marks)

Data: $K_{sp}(\text{BaCO}_3) = 8.1 \times 10^{-9}$

$K_{sp}(\text{MgCO}_3) = 4.0 \times 10^{-5}$

$K_{sp}(\text{PbCO}_3) = 3.3 \times 10^{-14}$

$K_{sp}(\text{SrCO}_3) = 1.6 \times 10^{-9}$

- (a) Which of the above four carbonate salts has the **greatest** molar solubility in water?
- (b) In **one sentence**, explain your answer for (a).
- (c) A solution contains a mixture of Ba^{2+} and Mg^{2+} ions obtained by adding $\text{Ba}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ to pure water: $[\text{Ba}^{2+}] = 0.12 \text{ mol L}^{-1}$ and $[\text{Mg}^{2+}] = 0.50 \text{ mol L}^{-1}$. Solid sodium carbonate (Na_2CO_3) is slowly dissolved into the mixed solution until a precipitate starts to form.

What is the **first solid to precipitate** (BaCO_3 or MgCO_3) and how many **moles of sodium carbonate** will have been added **per litre of solution** when this precipitate is **first** observed? (It may be assumed that there is negligible change to the solution volume as sodium carbonate is added.)

5. (4 marks)

Name **TWO** industrial applications of precipitation equilibria. For each of the named processes, write a balanced, central chemical equation which describes the precipitation of a solid from solution.

(a) **Name of process:**

Equation:

(b) **Name of process:**

Equation:

6. (6 marks)

(a) Provide a definition (in words) of a **state function**.

(b) Give the names of each of the state functions in the expression

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

G:

H:

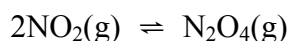
T:

S:

(c) What do the delta (Δ) signs in equation (1) represent?

7. (6 marks)

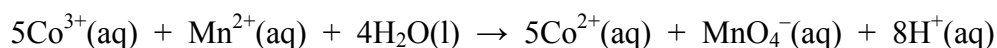
For the reaction

the equilibrium constant at 25°C is $K = 1.9 \times 10^{-4}$.

- (a) Calculate ΔG° at 25°C.
- (b) Given $P_{\text{NO}_2} = 0.1 \text{ atm}$ and $P_{\text{N}_2\text{O}_4} = 0.2 \text{ atm}$, calculate the value of ΔG at 25°C.

8. (16 marks)

An electrochemical cell comprising (i) a mixed solution of Co^{3+} and Co^{2+} ions and (ii) an acidified solution of potassium permanganate (MnO_4^-) and Mn^{2+} has the cell equation



For this cell, using the relevant data in the table below,

- (a) write down the **two** half-cell equations;
- (b) calculate the standard EMF of the cell, E° ;

Selected values of Standard Electrode Potentials at 25°C (aqueous species unless specified otherwise).

Element	Reaction	E°/V
Cobalt (3d ⁷ 4s ²)	$\text{Co}^{3+} + \text{e} \rightleftharpoons \text{Co}^{2+}$	1.81
	$\text{Co}(\text{NH}_3)_6^{3+} + \text{e} \rightleftharpoons \text{Co}(\text{NH}_3)_6^{2+}$	0.1
	$\text{Co}^{2+} + 2\text{e} \rightleftharpoons \text{Co}(\text{s})$	-0.28
	$\text{Co}(\text{NH}_3)_6^{2+} + 2\text{e} \rightleftharpoons \text{Co}(\text{s}) + 6\text{NH}_3$	-0.43
Manganese (3d ⁵ 4s ²)	$\text{MnO}_4^- + \text{e} \rightleftharpoons \text{MnO}_4^{2-}$	0.564
	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e} \rightleftharpoons \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	1.70
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}(\text{l})$	1.51
	$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e} \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}(\text{l})$	1.23
	$\text{Mn}^{3+} + \text{e} \rightleftharpoons \text{Mn}^{2+}$ (in 7.5 mol L ⁻¹ H ₂ SO ₄)	1.49
	$\text{Mn}^{2+} + 2\text{e} \rightleftharpoons \text{Mn}(\text{s})$	-1.18

- (c) Draw a conventional cell diagram for the cell which has the given cell reaction. Show on your diagram which electrode is positive and the direction of electron flow in the external wires.
- (d) How many moles of electrons are transferred per mole of the cell reaction **as it is written above**?

$n =$

- (e) Calculate the EMF of the cell under reversible conditions at 25°C when $[H^+] = 1.20 \text{ mol L}^{-1}$; $[Co^{3+}] = 1 \times 10^{-2} \text{ mol L}^{-1}$; $[Co^{2+}] = 0.10 \text{ mol L}^{-1}$; $[MnO_4^-] = 0.50 \text{ mol L}^{-1}$ and $[Mn^{2+}] = 0.10 \text{ mol L}^{-1}$.

The following data may be useful: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $F = 96489 \text{ C mol}^{-1}$; $\frac{RT}{F} = 0.0257 \text{ V}$ at 25°C.

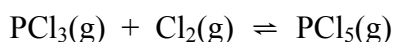
- (f) **Giving reasons**, predict whether the reaction will proceed spontaneously in the forward or reverse direction when the concentrations are as given in (e).

9. (12 marks)

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{ K}^{-1}$
PCl ₃ (g)	-320	-272	217
PCl ₅ (g)	-375	-305	365

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

- (a) For the reaction



predict the sign of ΔS° (do not attempt to calculate but provide an explanation).

- (b) Using the table above, calculate (at 298 K):

(i) ΔH° ;

(ii) ΔG° .

- (c) Use your answers in (b) to calculate:

(i) ΔS° (at 298 K);

(ii) $S^\circ(\text{Cl}_2(\text{g}))$ (at 298 K).

10. (6 marks) (111 only)

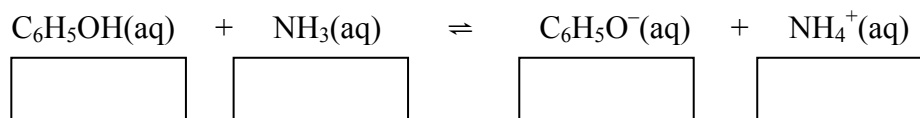
	$\Delta H^\circ_{\text{vap}}/\text{kJ mol}^{-1}$
CH ₄	9.2
NH ₃	23.3
H ₂ O	40.8
HF	27.2

With reference to the compounds listed in the table above answer the following.

- (a) Why does CH₄ have the lowest enthalpy of vaporisation?
- (b) Why is the enthalpy of vaporisation greater for H₂O than for NH₃ or HF?

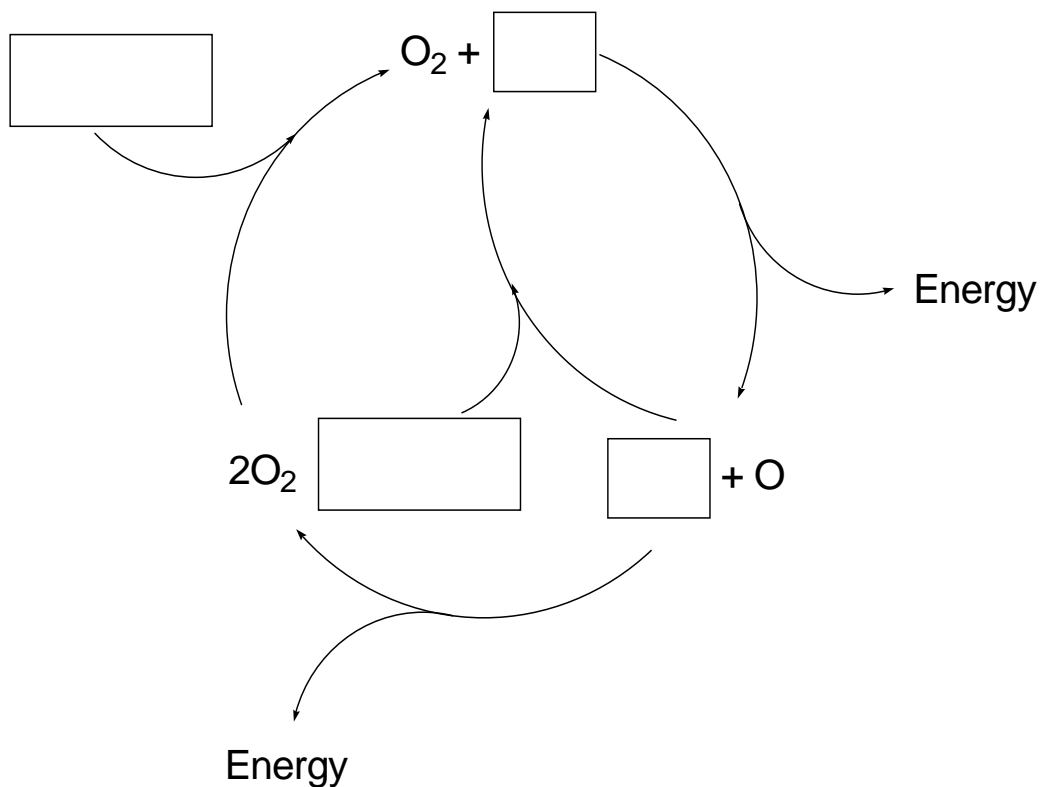
11. (6 marks) (111 only)

- (a) Define what is meant by a Brønsted acid.
- (b) Define what is meant by a Brønsted base.
- (c) In the following reaction, label the components as acids or bases:



12. (11 marks)

- (a) Complete the following diagram for the ozone cycle in the upper atmosphere by filling in the four blanks:

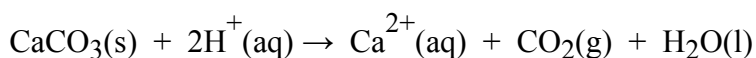


- (b) Draw a Lewis structure for ozone.
- (c) What is the class of compounds that are the major source of the chlorine atoms in the upper atmosphere which lead to ozone depletion? Provide the chemical formula for one of these compounds.
- (d) Show the mechanism of the series of reactions between chlorine-containing molecules or atoms and ozone that leads to ozone loss in the upper atmosphere.
- (e) In what months does the Antarctic ozone "hole" appear?

13. (9 marks)

- (a) List the name and approximate mole percent for each of the **four** most abundant gases in the atmosphere at sea level.
- (b) The pH scale is used to measure the acidity of the rainfall in those countries where acid rain is a problem. Unlike most such measures, a higher number (i.e. a higher pH) means less acid rain. Explain why a higher number is better.

- (c) Assume that new industrial pollution causes the average pH of the rain falling on a hectare of land to decrease from an expected value of 5.50 to 4.20. Assume also that the average annual rainfall is 1.00 m. Determine the mass of CaCO_3 that would be needed per hectare per year to neutralize the additional acid. The pertinent chemical reaction is



One hectare is $10,000 \text{ m}^2$ and one cubic metre contains $1000 \text{ L (dm}^3\text{)}$. The molar mass of CaCO_3 is 100.1 g mol^{-1} .

14. (14 marks)

- (a) (i) Using a **diagram**, explain the term: *triple point*. What is the state of a system at a *triple point*?
- (ii) Using a **diagram**, explain the term: *azeotrope*. State a property of an *azeotropic mixture*
- (b) Ethanol and methanol form very nearly ideal solutions. At 293 K, the vapour pressure of ethanol is 44.5 Torr, and that of methanol is 88.7 Torr.
- (i) Calculate the **partial** pressure at 293 K of ethanol above a mixture in which the mole fraction of ethanol is 0.80.
- (ii) Calculate the **total** pressure above this mixture at 293 K.
- (iii) Calculate the mole fraction of ethanol **in the vapour** above the mixture at 293 K.

15. [18 marks]

- (a) Nickel has a face-centred cubic structure with a unit-cell edge length of 3.524 \AA .
- (i) Explain why the unit cell contains the equivalent of four nickel atoms.
- (ii) Calculate the atomic radius of nickel.
- (iii) Calculate the density of crystalline nickel in g cm^{-3} .
- $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; $M(\text{Ni}) = 58.69 \text{ g mol}^{-1}$; $1 \text{ \AA} = 10^{-8} \text{ cm}$.

(b) Using **diagrams**, explain the following four terms:

- (i) *interstitial*
- (ii) *hexagonal close packed*
- (iii) *n-type semiconductor*
- (iv) *copolymer*

END OF PAPER

Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)
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Physical Chemistry Formulae

$$PV = nRT$$

$$P_A = x_A P_{\text{total}}$$

$$\text{where } P_{\text{total}} = P_A + P_B \quad \text{and} \quad x_i = \frac{n_i}{\sum_i n_i}$$

$$P_A = X_A P_A^\circ$$

$$P_B = (k_H)_B X_B$$

$$\Delta U = q + w$$

$$w_P = -P\Delta V$$

$$H = U + PV$$

$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{when } \Delta T = 0$$

$$\Delta H(T_2) = \Delta H(T_1) + \Delta C_P(T_2 - T_1)$$

$$C_P = dH/dT \quad (\text{when } \Delta P = 0)$$

$$C_V = dU/dT \quad (\text{when } \Delta V = 0)$$

$$\Delta H_{\text{reaction}} = \sum_{\text{prods}} \nu_{\text{prod}} \Delta H_f(\text{prod}) - \sum_{\text{reacts}} \nu_{\text{react}} \Delta H_f(\text{react})$$

$$\text{For } aA + bB \rightarrow cC + dD, \quad \text{Rate} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

$$\text{For Rate} = \frac{-d[A]}{dt} = k,$$

$$[A] = [A]_0 - kt$$

$$\text{For Rate} = \frac{-d[A]}{dt} = k[A],$$

$$[A] = [A]_0 e^{-kt} \quad \text{and} \quad t_{1/2} = (1/k) \log_e(2)$$

$$k = A e^{-E_a/RT}$$

$$\log_e \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$\text{pH} = -\log_{10}[H^+]$$

$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[A^-]}{[HA]} \right) = \text{p}K_a + \log_{10}(n(A^-)/n(HA))$$

$$\Delta S = \sum_{\text{prods}} \nu_{\text{prod}} S(\text{prod}) - \sum_{\text{reacts}} \nu_{\text{react}} S(\text{react})$$

$$\Delta S_{\text{phase change}} = \frac{\Delta H_{\text{phase change}}}{T_{\text{critical}}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \sum_{\text{prods}} \nu_{\text{prod}} \Delta G_f(\text{prod}) - \sum_{\text{reacts}} \nu_{\text{react}} \Delta G_f(\text{react})$$

$$\Delta G = \Delta G^\circ + RT \log_e Q$$

$$\Delta G^\circ = -RT \log_e K$$

$$\log_e K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\log_e \left(\frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$w_{\text{elect}} = \Delta G = -nFE$$

$$\Delta G^\circ = -RT \log_e K = -nFE^\circ$$

$$E^\circ = \frac{RT}{nF} \log_e K = \frac{2.303RT}{nF} \log_{10} K$$

$$\text{At } 25^\circ\text{C: } E^\circ = \frac{0.0591 \text{ V}}{n} \log_{10} K$$

$$E = E^\circ - \frac{RT}{nF} \log_e Q = E^\circ - \frac{2.303RT}{nF} \log_{10} Q$$

$$\text{At } 25^\circ\text{C: } E = E^\circ - \frac{0.0591 \text{ V}}{n} \log_{10} Q$$

R Gas constant (8.314 J mol⁻¹ K⁻¹ or 0.082 L atm mol⁻¹ K⁻¹)

F Faraday Constant (96489 C mol⁻¹)