

FULL NAME:

STUDENT ID:

SIGNATURE:

University of Canterbury

Mid Year Examination and Test Period 2008

Prescription Number(s):	CHEM 113
Paper Title:	Engineering Chemistry

Time Allowed: 2.5 HOURS

Number of pages: 19 pages
2 pages (formulae and periodic table)

Answer **ALL** questions

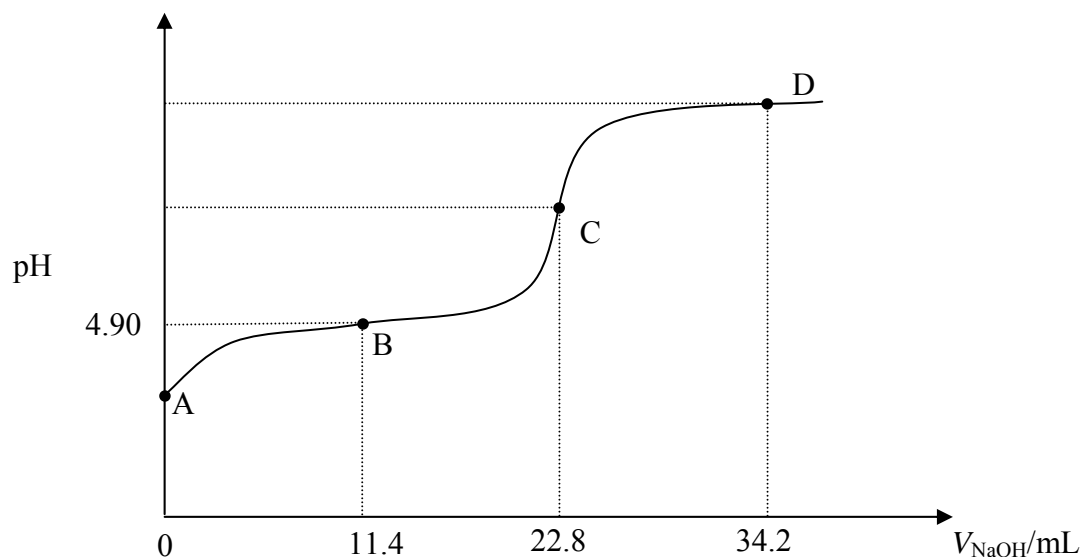
Total marks = 120

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

For examiners use only

1	2,3	4,5	6	7	8,9	Total/120
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1. (24 marks)



The figure above shows the titration curve obtained (using a pH meter) when a 25.0 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 0.108 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:

(i) the volume of HA solution?

(ii) the added volume of NaOH, V_{NaOH} ?

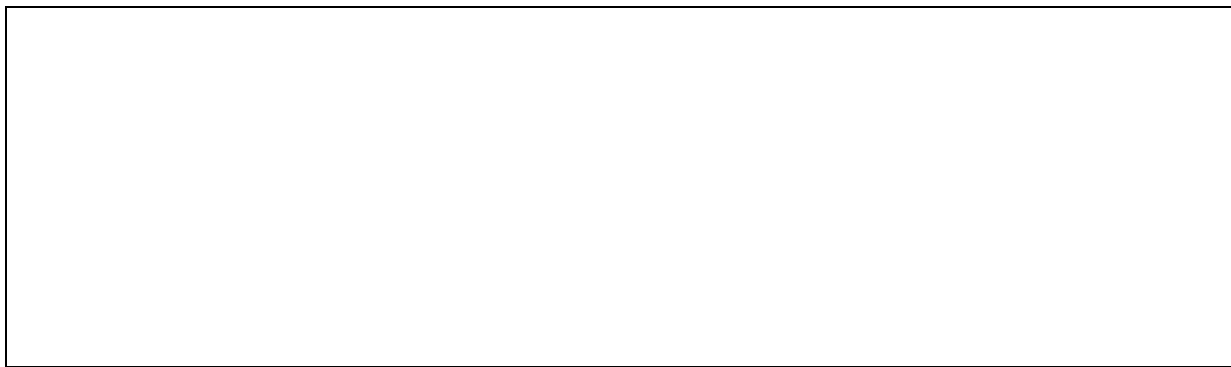
(b) **On the figure above**, clearly indicate and label the following:

(i) the equivalence point;

(ii) a buffer region.

(c) Calculate C_{HA} .

(d) Using the given pH value for the solution at point B (4.90), calculate K_{a} (the acid ionisation constant) for HA.



(e) 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

$$K_b(X^-) = K_w/K_a(HX)$$



- (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)
Ethyl red	4.9
Brilliant yellow	7.2
<i>o</i> -Cresolphthalein	9.0
2,4,6-Trinitrotoluene	12.3

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

2. (10 marks)

(a) Give brief definitions of the following thermodynamic terms:

(i) system;

(ii) state function;

(iii) enthalpy;

(iv) second law of thermodynamics;

(v) third law of thermodynamics.

3. (14 marks)

The data in the following table pertain to reaction (1) at 25°C:



substance	ΔH°_f (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)
H ₂ O(g)	-241.8	188.72
Cl ₂ O(g)	80.3	266.1
HOCl(g)	-75.1	?

(a) Calculate ΔH° for reaction (1)

(b) Given $K = 0.090$ for reaction (1), calculate ΔG° for the reaction at that temperature. [$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.]

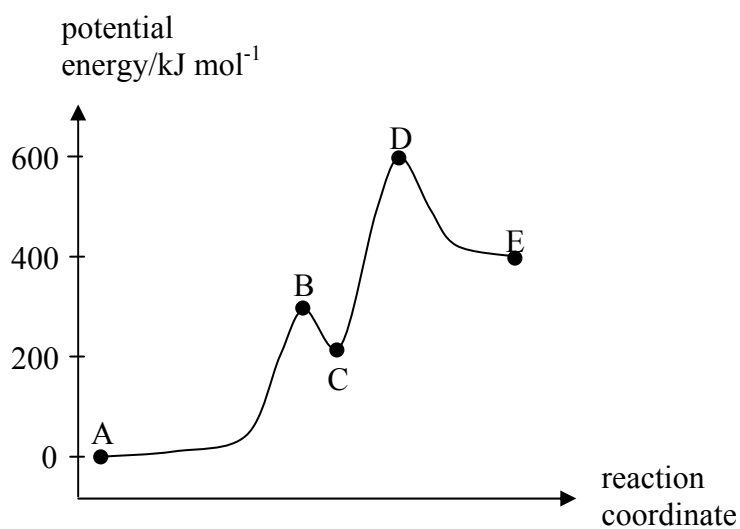
(c) From your answers in (a) and (b), calculate ΔS° for reaction (1). (If you were unable to obtain answers, use the **incorrect** values $\Delta H^\circ = 10.3 \text{ kJ mol}^{-1}$ and $\Delta G^\circ = 5.0 \text{ kJ mol}^{-1}$.)

- (d) From your answer in (c) and the data in the table, determine the absolute entropy of HOCl(g) at 298 K.

- (e) Calculate ΔG for reaction (1) under the following conditions:

$$P_{\text{H}_2\text{O}} = 0.24 \text{ atm}; \quad P_{\text{Cl}_2\text{O}} = 2.6 \times 10^{-3} \text{ atm}; \quad P_{\text{HOCl}} = 7.5 \times 10^{-3} \text{ atm}.$$

4. (8 marks)



Using the figure above, answer the following:

(a) Is the overall reaction mechanism elementary or complex? Explain.

(b) Is the overall reaction endothermic or exothermic? Explain.

(c) Indicate the point(s) (A-E) on the curve that correspond to:

(i) reactants

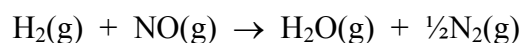
(ii) products

(iii) intermediates

(iv) transition states

5. (12 marks)

The rate data in the following table were obtained at 700°C for the reaction



Expt	Initial concentration (mol L ⁻¹)		Initial rate (mol L ⁻¹ s ⁻¹)
	[H ₂] ₀	[NO] ₀	
1	0.0100	0.0250	2.4 × 10 ⁻⁶
2	0.0050	0.0250	1.2 × 10 ⁻⁶
3	0.0100	0.0125	0.60 × 10 ⁻⁶

(a) Give a general rate-law expression for the reaction in terms of a rate constant and the concentrations of the reactants.

(b) From the data in the table, determine:

(i) the order of reaction with respect to H₂;

(ii) the order of reaction with respect to NO;

(iii) the overall order of reaction.

(c) From your answers in (b) and the data in the table, determine the value of the rate constant at 700°C, specifying its units.

(d) From your results, is it possible to tell whether this reaction is elementary or complex? *Explain.*

6. (18 marks)

- (a) Use the following table of standard reduction potentials to answer the questions below:

Reduction Half-reaction	E° / V
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89

- (i) Which of the species in the table is the strongest oxidising agent?

- (ii) Which of the species in the table is the strongest reducing agent?

- (iii) Which of the ions in the table will $\text{Zn}(\text{s})$ reduce?

- (iv) Write down the conventional cell diagram for a cell that involves the zinc and copper half reactions above, and has a positive cell potential.

Calculate the standard cell potential for that cell.

- (v) Calculate the equilibrium constant for the reaction of $\text{Zn}(\text{s})$ with $\text{Cu}^{2+}(\text{aq})$.

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

- (vi) Calculate the standard free energy change, ΔG° , for the reaction of Zn(s) with $\text{Cu}^{2+}(\text{aq})$.

- (b) Give two methods that may be used to protect iron against corrosion. Briefly explain how they protect the iron from corrosion.

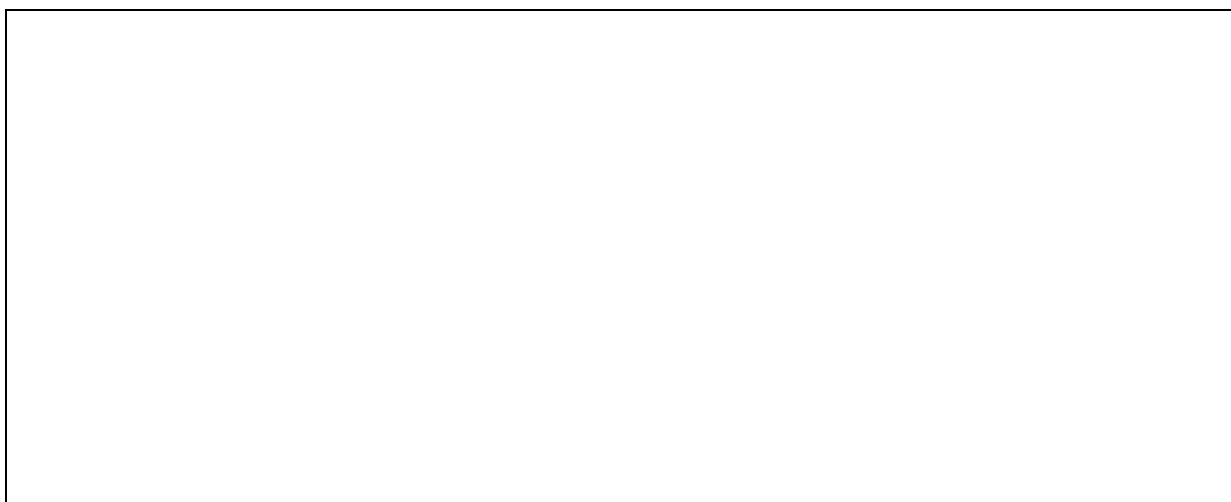
- (a) Sketch the phase diagram for a system, such as CO_2 , for which $\Delta V(\text{solid} \rightarrow \text{liquid})$ is positive. Indicate on the diagram: (i) the triple point; (ii) the critical point, and (iii) where sublimation occurs.



- (b) Two liquids, A and B, form mixtures that exhibit **positive** deviations from Raoult's law. The boiling point of A is 105°C and that of B is 153°C .

(i) Which of A and B will have the higher vapour pressure at 95°C ?

(ii) Sketch the boiling point ($T-x_A$) diagram for A and B. Indicate on the diagram the azeotropic composition.



- (c) Dibromoethene and dibromopropene form an ideal mixture.

The vapour pressure of dibromoethene is 172 Torr, and that of dibromopropene is 128 Torr at 358 K.

A **liquid** mixture of dibromoethene and dibromopropene is prepared in which the mole fraction of dibromoethene is 0.40.

- (i) Calculate the **partial** pressures of dibromoethene and dibromopropene above this mixture at 358 K.

- (ii) Calculate the **total** pressure above this mixture at 358 K.

- (iii) Calculate the mole fraction of dibromoethene **in the vapour** above the mixture at 358 K.

8. (7 marks)

Europium forms crystals with a body-centred cubic structure. The density of crystalline europium is 5.244 g cm^{-3} . Calculate the atomic radius of europium in angstroms (\AA).

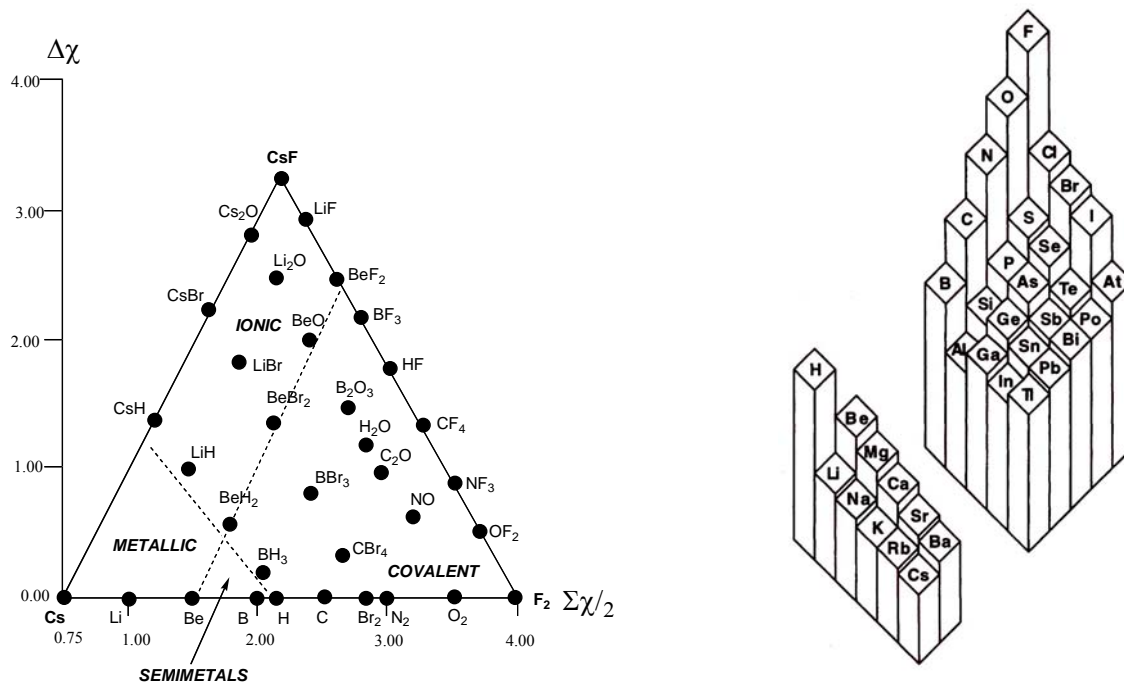
$$M_r(\text{Eu}) = 152.0$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ \AA} = 10^{-8} \text{ cm}$$

9. (12 marks)

- (a) Electronegativity can be used to predict the nature of bonding in materials composed of two elements. Using the provided van Arkel diagram (below left) and a 3-D chart of the trends in electronegativity across periodic table (below right) predict type of bonding for the following materials: Na-Rb, Na-Br, N-Cl, B-H.



(i) Na-Rb

(ii) Na-Br

(iii) N-Cl

(iv) B-H

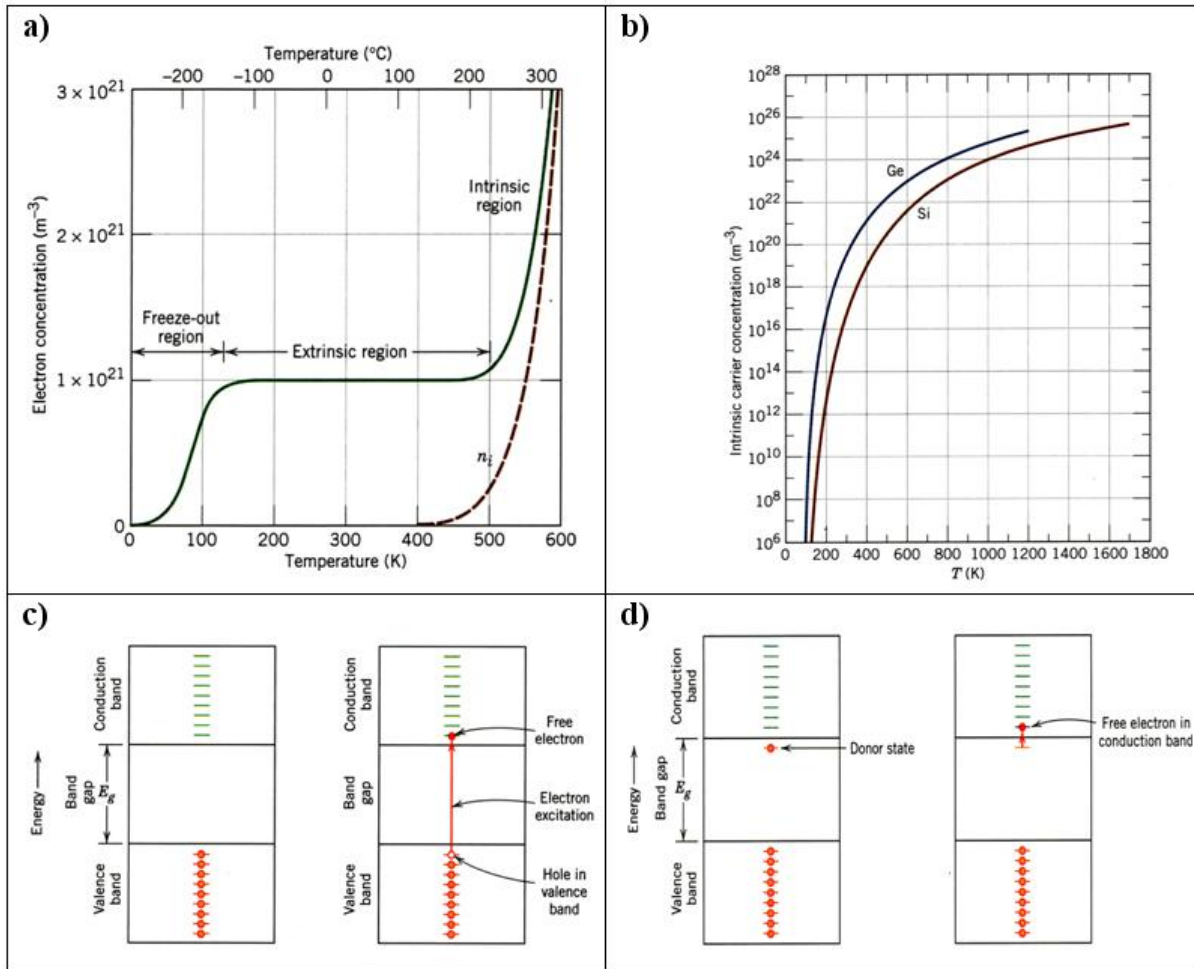
- (b) You are making an n-type semiconductor using very high purity (10^{-7} atomic %) silicon (Si). Choose all possible dopants you could use out of the following list:

B, C, N, Ti, Ga, Ge, As and briefly explain your answer.

- (c) (i) What is the difference between a homopolymer and a copolymer?

- (ii) Why does syndiotactic polypropylene melt at 270 °C whereas atactic polypropylene melt at 90 °C?

- (d) There are four diagrams (a-d) presented below describing conductivity in semiconductors. Group these four diagrams into two pairs describing the same type of semiconductor. Briefly explain your choice.



END OF PAPER

Physical Chemistry Formulae

$$PV = nRT$$

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

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

$$P_A = X_A P_A^\circ$$

$$P_B = (k_H)_B X_B$$

$$\Delta U = q + w$$

$$w_P = -P\Delta V$$

$$H = U + PV$$

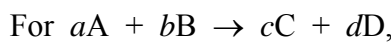
$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{when } \Delta T = 0$$

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

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

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

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



$$\text{Rate} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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)

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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