

Mid Year Examination and Test Period 2007

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

Time Allowed: 2.5 HOURS

Number of pages: 18

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	Total
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1. (22 marks)

Use the following table of standard reduction potentials to answer the questions below:

<u>Reduction Half-reaction</u>	<u>E°/V</u>
(i) $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.358
(ii) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
(iii) $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.96
(iv) $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44

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

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

(c) Which of the species in the table will $\text{O}_2(\text{g})$ oxidise under acidic conditions?

(d) Write down the conventional cell diagram for a cell involving the oxygen and iron couples ((ii) and (iv) in the list above) which has a **positive** standard cell potential.

Question 1 continued on following page

Question 1 continued

- (e) Calculate the standard cell potential for the cell in (d).

- (f) Calculate the standard free energy change, ΔG° , for the reaction of $\text{O}_2(\text{g})$ with $\text{Fe}(\text{s})$ in acid.

- (g) Calculate the thermodynamic equilibrium constant, K , for the reaction of $\text{O}_2(\text{g})$ with $\text{Fe}(\text{s})$ in acid.

Question 1 continued on following page

Question 1 continued

- (h) Write down the Nernst equation for an electrochemical cell in which the cell reaction is the reaction of $O_2(g)$ and $Fe(s)$ under acidic conditions.

- (i) Describe one method of corrosion prevention and explain how it relates to the equation in part (h).

2. (10 marks)

(a) Provide definitions of the following terms in the context of acid-base equilibria:

(i) A Brønsted acid

(ii) A Brønsted base

(iii) A salt

(iv) A buffer solution

Question 2 continued on following page

Question 2 continued

- (b) A chemist discovers a new, water-soluble compound, exoticaine. A 1.5×10^{-6} mol L⁻¹ aqueous solution of exoticaine has a pH of 8.18. Circle, below, two words that best describe the acid-base properties of exoticaine:

STRONG

WEAK

ACID

BASE

3. (18 marks)

Formic acid (HCOOH) is an organic compound with $K_a = 1.8 \times 10^{-4}$.

- (a) What is the pK_a of formic acid?

- (b) What is the pH of a 0.0100 mol L⁻¹ solution of formic acid?

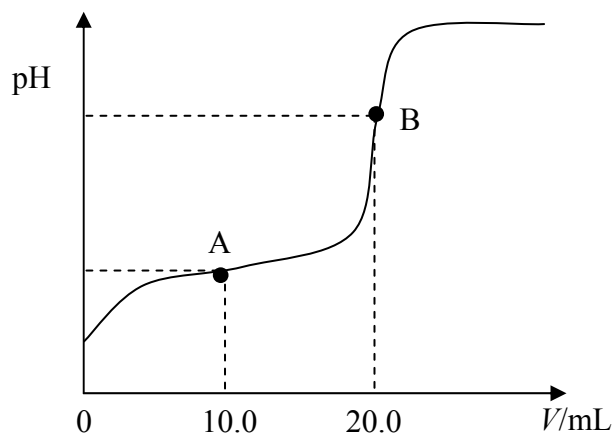
- (c) What is the pK_b of the formate anion (HCOO⁻)?

Question 3 continued on following page

Question 3 continued

(d) What is the pH of a $0.0050 \text{ mol L}^{-1}$ solution of sodium formate (HCOONa)?

(e) The plot below was obtained from a titration involving $0.0100 \text{ mol L}^{-1}$ solutions of formic acid and sodium hydroxide.



(i) Tick the box that correctly describes the titration:

Formic acid solution is being added to sodium hydroxide solution

OR sodium hydroxide solution is being added to formic acid solution

(ii) Indicate and clearly label the following on the above plot:

- The equivalence point
- The buffer region
- The approximate position of $\text{pH} = 7$ on the pH (y) axis

Question 3 continued on following page

Question 3 continued

- (iii) Using your answers to earlier parts of this question, what is the pH corresponding to point A of the plot? *Provide an explanation for your answer.*

- (iv) Using your answers to earlier parts of this question, what is the pH corresponding to point B? *Provide an explanation for your answer.*

- (v) 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)
Bromophenol blue	3.8
Brilliant yellow	7.2
Thymolphthalein	10.0
2,4,6-Trinitrotoluene	12.3

4. (28 marks)

- (a) For the combustion of ethane (1), use the thermodynamic data given below to calculate the following parameters at 298 K. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)



	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{C}_2\text{H}_6(\text{g})$	-84.7	-32.8	unknown
$\text{O}_2(\text{g})$	0	0	+205.1
$\text{CO}_2(\text{g})$	-393.5	-394.4	+213.7
$\text{H}_2\text{O}(\text{l})$	-285.8	-237.2	+69.9

(i) ΔH°

(ii) ΔG°

(iii) ΔS°

Question 4 continued on following page

Question 4 continued

(iv) S° for ethane ($C_2H_6(g)$)

(v) K (the thermodynamic equilibrium constant) at 298 K

(vi) K at 400 K (assume that ΔH° and ΔS° are constant between 298 and 400 K)

Question 4 continued on following page

Question 4 continued

- (b) By considering the phase and number of moles of each reaction component in reaction (1), comment on the sign you have obtained for ΔS° .

- (c) Calculate the changes of entropy of the surroundings ($\Delta S_{\text{surr}}^\circ$) and of the universe ($\Delta S_{\text{univ}}^\circ$) induced by reaction (1) under standard thermodynamic conditions.

- (d) Comment on the direction of spontaneous change for reaction (1) under standard thermodynamic conditions.

5. (24 marks)

- (a) Barium metal crystallizes in a body-centred cubic lattice. The density of the metal is 3.50 g cm^{-3} . Calculate the radius (**in pm**) of a barium atom.

$$M(\text{Ba}) = 137.3 \text{ g mol}^{-1}; N_A = 6.022 \times 10^{23} \text{ mol}^{-1}; 1 \text{ pm} = 10^{-12} \text{ m}.$$

Question 5 continued on following page

Question 5 continued

(b) Using **diagrams** briefly explain the following terms:

(i) Hexagonal close-packed structure;



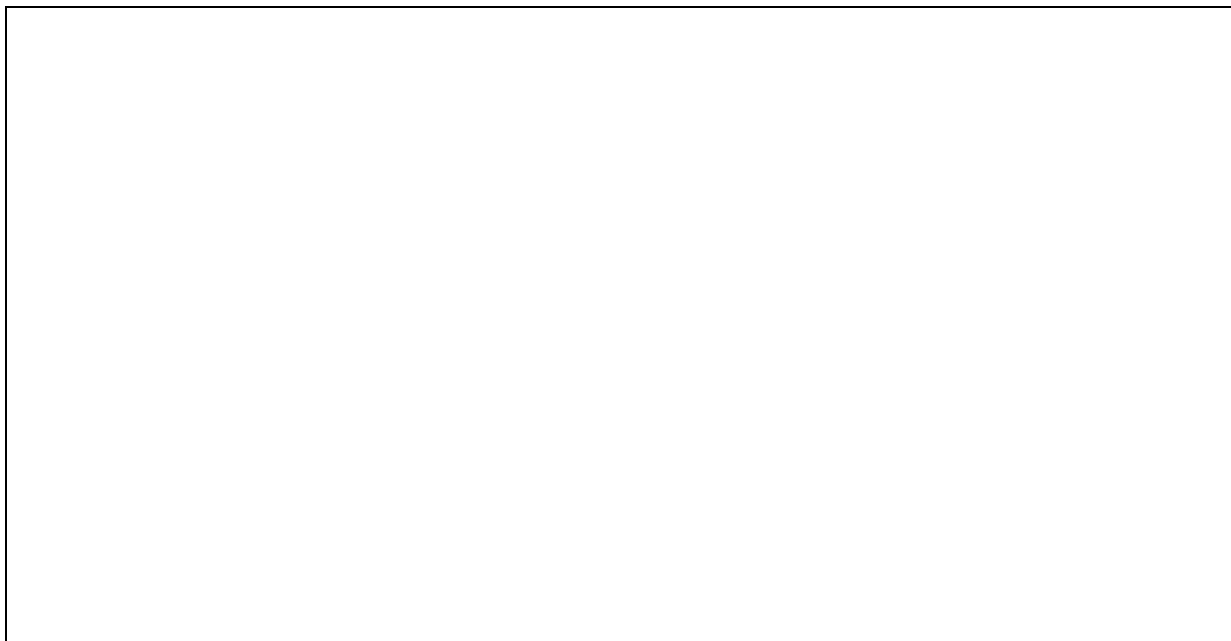
(ii) interstitial impurity;



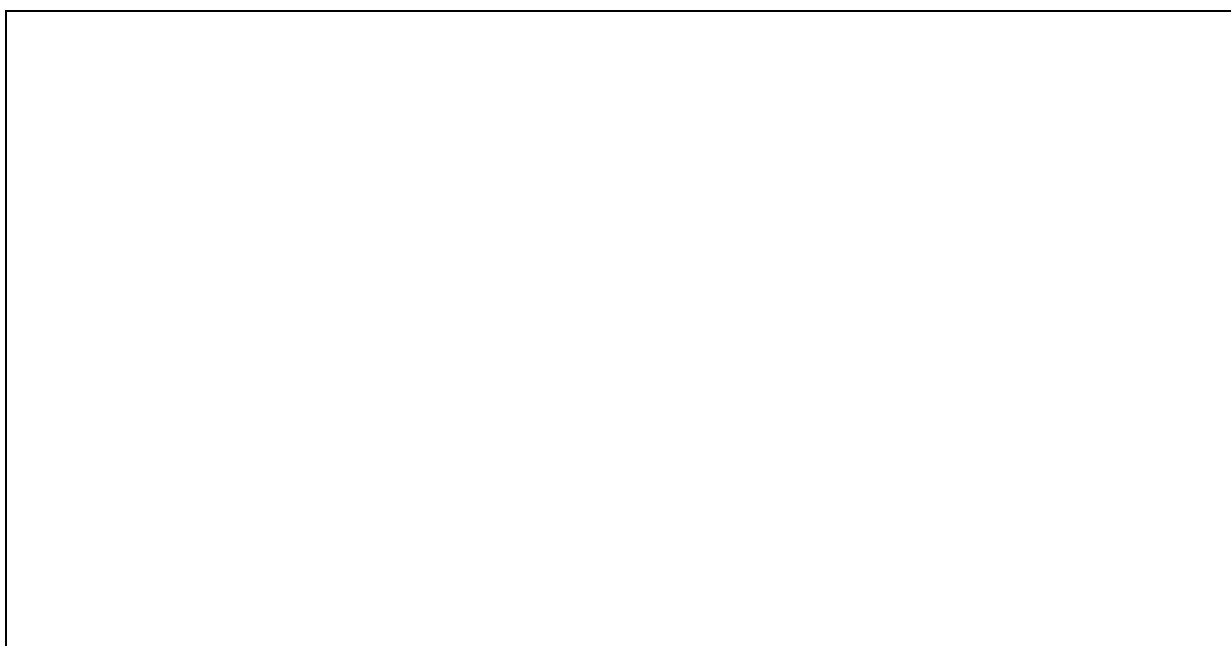
Question 5 continued on following page

Question 5 continued

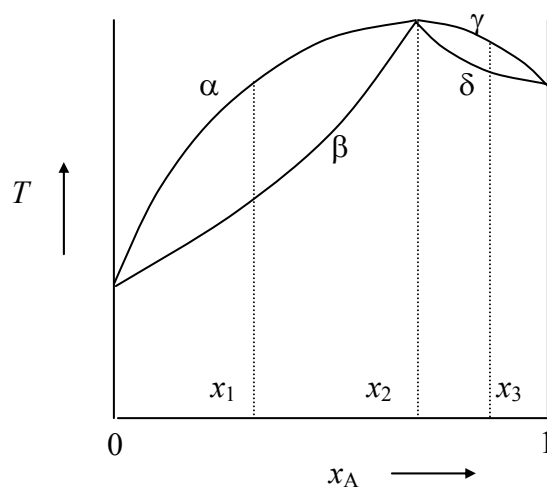
- (iii) n-type semiconductor (give an **example** of an n-type semiconductor);



- (iv) condensation polymer (give an **example** of a condensation polymer).



6. (18 marks)



The boiling point-composition ($T - x_A$) diagram for a mixture of A and B is given above.

- (a) Of the four curve segments labelled as α , β , γ and δ in the diagram above, which **two** segments indicate the composition of the **vapour**, in equilibrium with the liquid? (Tick **one** of the following boxes.)

α and β

β and γ

α and δ

β and δ

α and γ

γ and δ

- (b) Which pure liquid, A or B, would you expect to have the **higher** vapour pressure at a particular temperature? (Tick **one** of the following boxes.)

A

B

- (c) Which of the following occurs when the two liquids are mixed? (Tick **one** of the following boxes.)

Heat is absorbed
(endothermic process)

No heat is absorbed
or released

Heat is released
(exothermic process)

Question 6 continued on following page

Question 6 continued

- (d) What is the composition of the distillate formed when **each** of the following liquid mixtures is distilled in an efficient distillation column?

	liquid mixture	distillate composition
(i)	x_1	$x_A =$ <input type="text"/>
(ii)	x_2	$x_A =$ <input type="text"/>
(iii)	x_3	$x_A =$ <input type="text"/>

- (e) What is the composition of the residue left when **each** of the following liquid mixtures is boiled in an efficient distillation column until the boiling point is constant?

	liquid mixture	residue composition
(i)	x_1	$x_A =$ <input type="text"/>
(ii)	x_2	$x_A =$ <input type="text"/>
(iii)	x_3	$x_A =$ <input type="text"/>

Question 6 continued on following page

Question 6 continued

- (f) Ethanol and methanol form an ideal solution. At 293 K, the vapour pressure of ethanol is 44.5 Torr, and that of methanol is 88.7 Torr. Consider a mixture of these liquids where the mole fraction of ethanol is 0.60 and the temperature is 293 K.

- (i) Calculate the **partial** pressure of ethanol above the mixture.

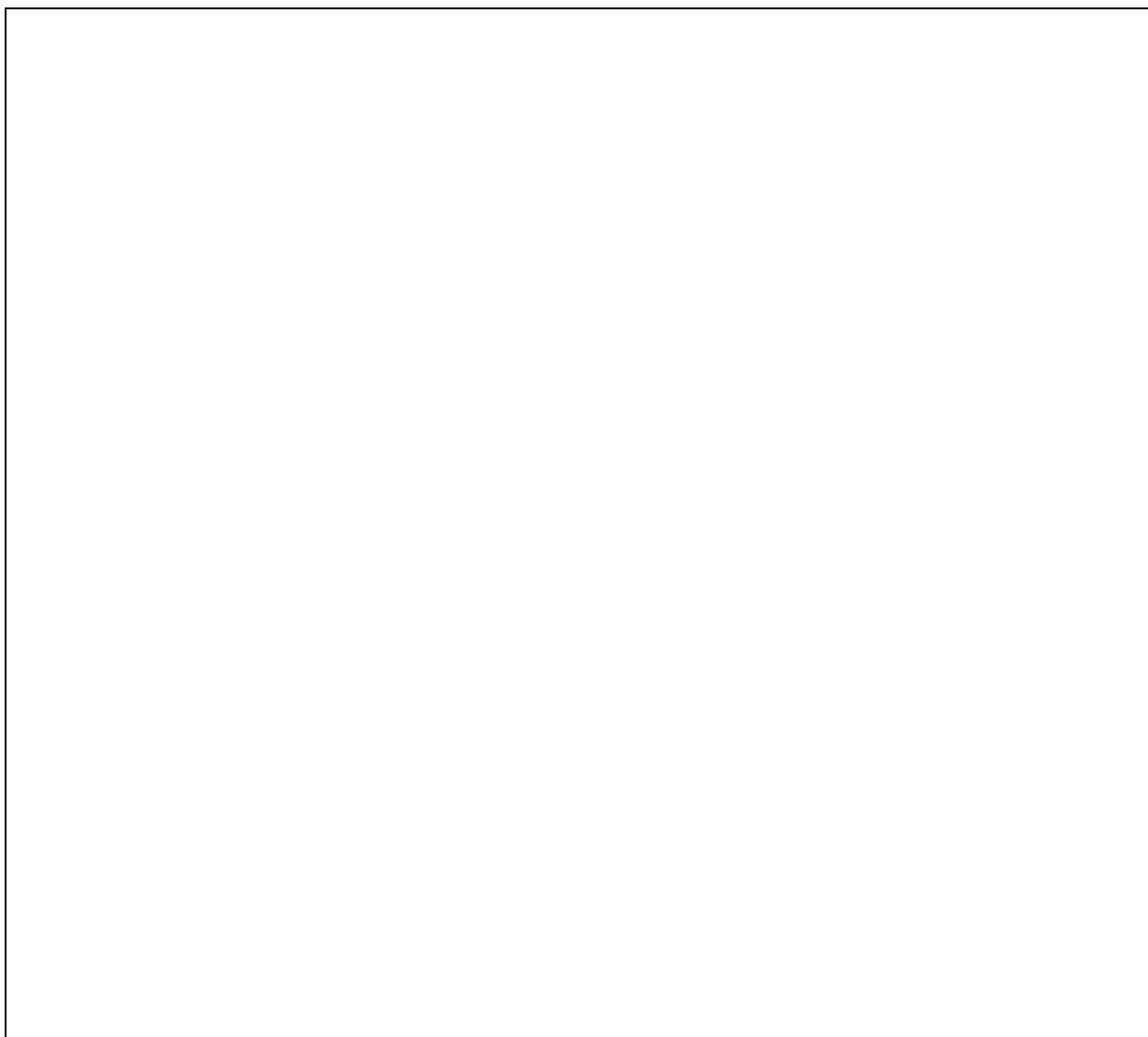
- (ii) Calculate the **total** pressure above this mixture.

- (iii) Calculate the mole fraction of ethanol **in the vapour** above the mixture.

Question 6 continued on following page

Question 6 continued

- (g) Sketch the p - T phase diagram for a pure substance (one-component) whose normal boiling point is 80.1°C and whose normal freezing point is 5.5°C .
- (i) Indicate on the diagram the positions of the triple point and the critical point.
- (ii) Indicate where sublimation would occur rather than melting or boiling.



END OF PAPER

Physical Chemistry Formulae

$$PV = nRT$$

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

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

$$P_A = X_A P_A^\circ$$

$$P_B = (k_H)_B X_B$$

$$\Delta U = q + w$$

$$w_P = -P\Delta V$$

$$H = U + PV$$

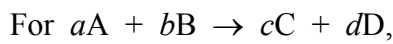
$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{when } \Delta T = 0$$

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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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