

FULL NAME:

STUDENT ID:

SIGNATURE:

University of Canterbury

Mid Year Examination and Test Period 2009

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

Time Allowed: 2.5 HOURS

Number of pages: 18 pages
2 pages (formulae and periodic table)

Answer **ALL** questions

Total marks = 120

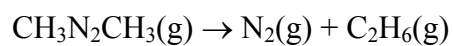
NOTE: There is a page of formulae and a periodic table with atomic masses at the end of this paper.

For examiners use only

1,2	3,4	5	6,7	8	9-11	Total/120

1. (13 marks)

Azomethane decomposes as follows:



At 305 °C this occurs with a rate constant of $k = 0.2310 \text{ min}^{-1}$.

- (a) The reaction is first-order. How could you have deduced this from the information above?

- (b) For an experiment at 305 °C, the partial pressure of azomethane is initially 317.5 mm Hg.

Calculate the following after 120 s:

- (i) The partial pressure of azomethane

- (ii) The change in the pressure of $\text{N}_2(\text{g})$

(iii) The change in the total pressure

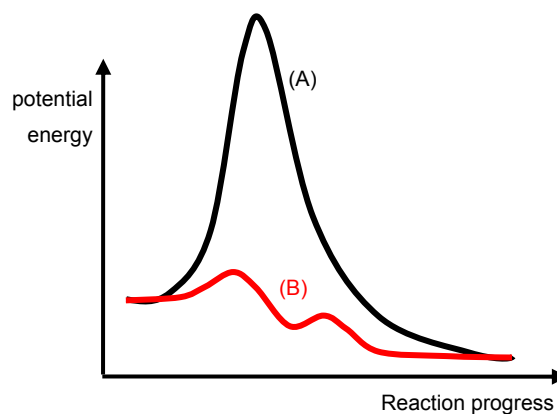
(c) How long would it take for half of the azomethane to have decomposed?

(d) At 325 °C the rate constant is found to have increased to $k = 0.5323 \text{ min}^{-1}$. What is the activation energy for the reaction?

[$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $0 \text{ }^\circ\text{C} = 273.15 \text{ K}$]

2. (7 marks)

The diagram below relates to two possible pathways for a reaction.



(a) Is pathway (A) that of an *elementary* or *complex* reaction? Explain your answer.

(b) Is pathway (B) that of an *elementary* or *complex* reaction? Explain your answer.

(c) Which of (A) or (B) represents the pathway of a *catalyzed* reaction? Explain your answer.

(d) Indicate the location of a *transition state* on the above diagram.

3. (14 marks)

Nitrous acid (HNO_2) is a weak acid with $K_a = 4.5 \times 10^{-4}$. [$K_w = 1.00 \times 10^{-14}$.]

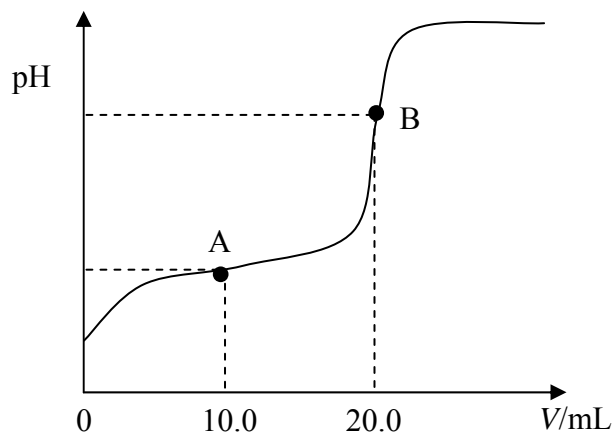
(a) What is the $\text{p}K_a$ of nitrous acid?

(b) What is the pH of a $0.0500 \text{ mol L}^{-1}$ solution of nitrous acid?

(c) What is the $\text{p}K_b$ of the nitrite anion (NO_2^-)?

(d) What is the pH of a $0.0250 \text{ mol L}^{-1}$ solution of sodium nitrite (NaNO_2)?

- (e) The plot below was obtained from a titration involving $0.0500 \text{ mol L}^{-1}$ solutions of nitrous acid and sodium hydroxide.



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

Nitrous acid solution is being added to sodium hydroxide solution

OR sodium hydroxide solution is being added to nitrous acid solution

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

- The equivalence point
- The buffer region

- (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.*

4. (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

(b) A 0.10 mol L^{-1} solution of caffeine has a pH of 11.8. Circle, below, two words that best describe the acid-base properties of caffeine:

STRONG

WEAK

ACID

BASE

5. (12 marks)

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

(i) first law of thermodynamics;

(ii) entropy;

(iii) surroundings;

(iv) spontaneity;

(v) equilibrium.

(b) Give the names of the functions G , T and Q in the equation:

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

6. (12 marks)

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{H}_2\text{S}(\text{g})$	-20.6	205.8
$\text{O}_2(\text{g})$	0	205.1
$\text{SO}_2(\text{g})$	-296.8	248.2
$\text{H}_2\text{O}(\text{g})$	-241.8	188.8

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

(a) For the reaction: $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
use the thermodynamic data above to calculate the following:

(i) The standard molar enthalpy change, ΔH° ;

(ii) The standard molar entropy change, ΔS° ;

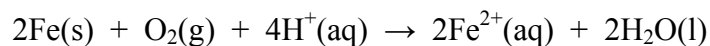
(iii) ΔG° for the reaction at 25°C ;

(iv) The equilibrium constant, K , for the reaction at 25°C .

(b) For the reaction in (a) predict, with an explanation of your reasoning, whether K would *increase*, *decrease*, or *remain unchanged* when the temperature is raised to 100°C .

7. (18 marks)

The corrosion of iron in seawater in an aerobic environment may be represented by the following overall equation:



(a) Write down the half-cell reaction for the oxidation process.

(b) Write down the half-cell reaction for the reduction process

(c) Draw a conventional cell diagram for the overall reaction. On the diagram, clearly indicate the *anode*, the *cathode* and the *positive electrode*.

(d) Calculate the standard voltage of the cell, E°_{cell} , given the following standard reduction potentials:

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}; \quad E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}; \quad E^\circ_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}} = +1.23 \text{ V}.$$

- (e) Calculate the voltage generated in a 'corrosion cell' when a piece of metallic iron dips into seawater with $[\text{Fe}^{2+}] = 2 \times 10^{-3} \text{ mol L}^{-1}$ at $\text{pH} = 5.5$, and is at the same time in contact with air at 1 atm. Assume that the mole fraction of O_2 in air is 0.2 and that $T = 298 \text{ K}$. [$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$]

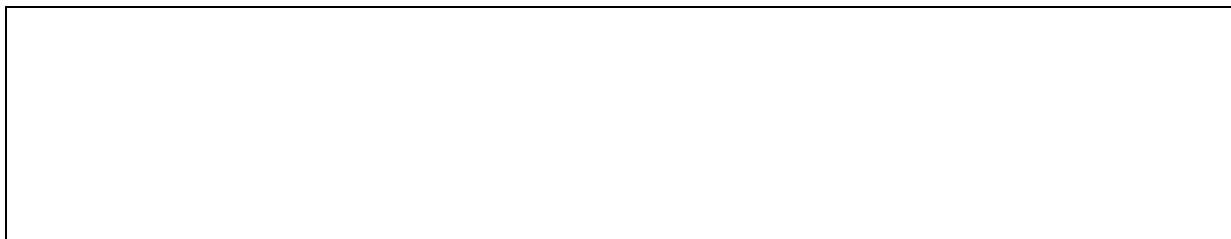
- (f) Describe two ways by which the above corrosion process might be prevented.

8. (12 marks)

- (a) (i) Sketch the phase diagram (p - T) for carbon dioxide, labelling the triple and critical points, and indicating, on the pressure axis, where 1.0 atmosphere lies.



- (ii) What do the lines on the phase diagram represent?

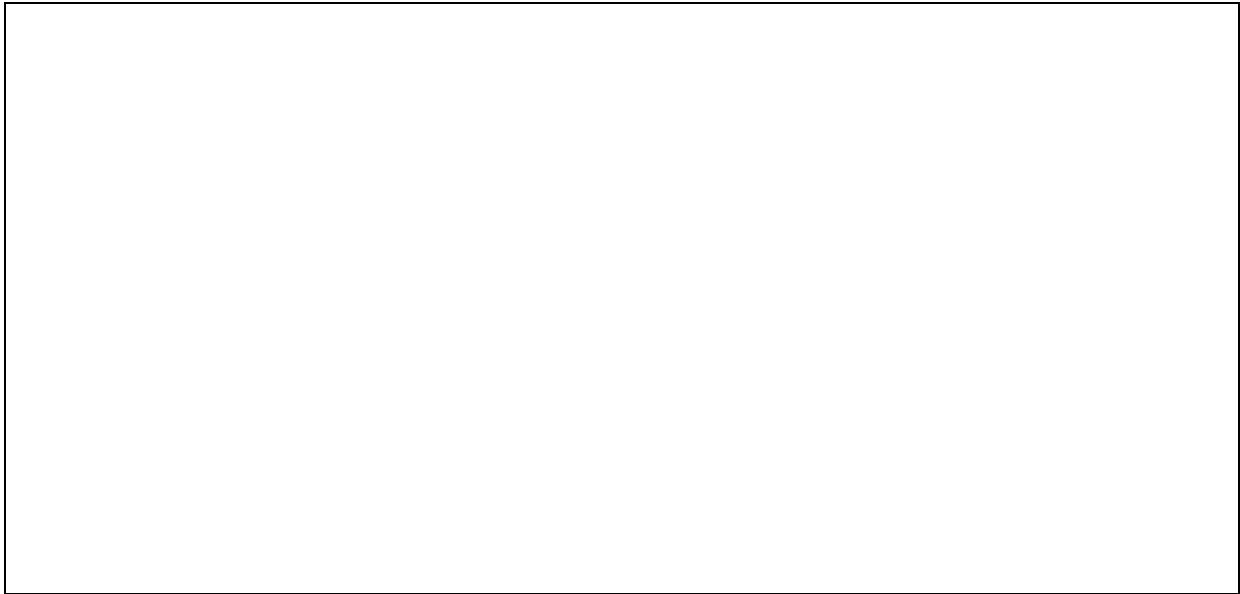


- (b) At 35°C, the vapour pressure of pure water is 42 Torr and the vapour pressure of pure dioxane ($C_4H_8O_2$) is 60 Torr.

- (i) Calculate the total vapour pressure above a liquid mixture of water and dioxane with a mole fraction of dioxane of 0.6, assuming that they formed an ideal solution.



- (ii) The total vapour pressure AT 35°C above a mixture of water and dioxane, with a mole fraction of dioxane equal to 0.6, is measured to be 80 Torr. Do water and dioxane form an ideal solution?
- (iii) The composition of the vapour in equilibrium with a liquid mixture with a mole fraction of dioxane of 0.50 is also 0.50. Sketch the boiling point diagram (T - X) for water-dioxane mixtures, labelling all lines and axes.



- (iv) What is the composition of the distillate (from the top of the distillation column) and the residue (from the bottom of the distillation column) when a liquid mixture, initially with a mole fraction of 0.70, is distilled in an efficient distillation column?

Distillate $X_{\text{Dioxane}} =$

Residue $X_{\text{Dioxane}} =$

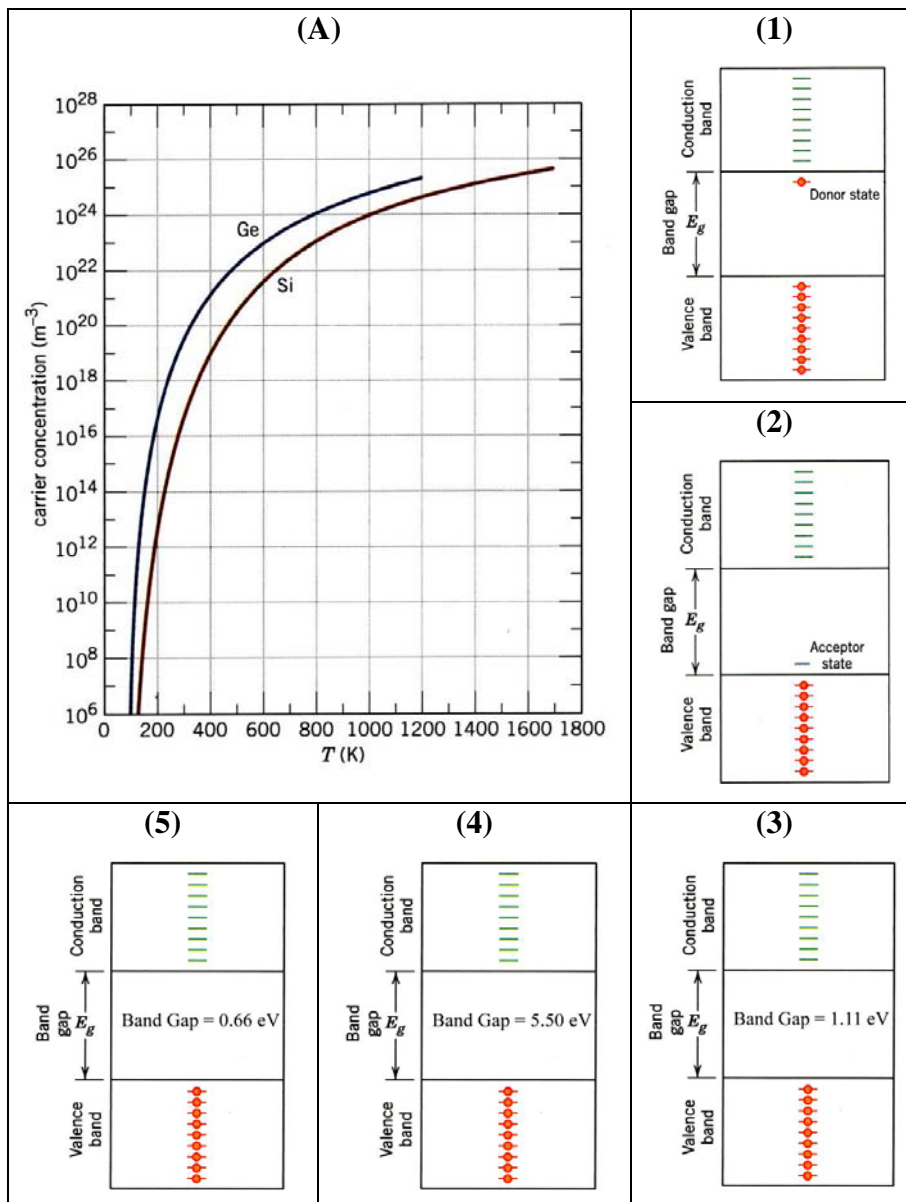
9. (6 marks)

Figure A below shows carrier concentrations for Ge and Si as a function of temperature. Figures 1 to 5 below show schematic band structures of different materials.

(a) Which Figure (from 1 to 5 below) shows the band structure of Si?

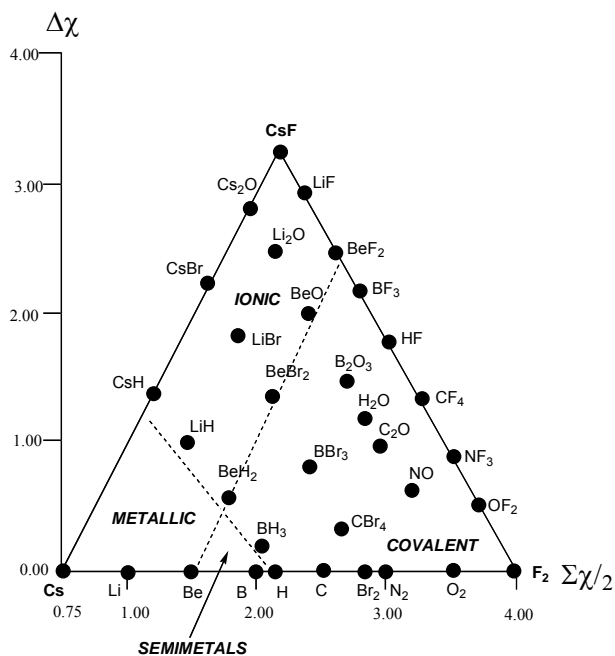
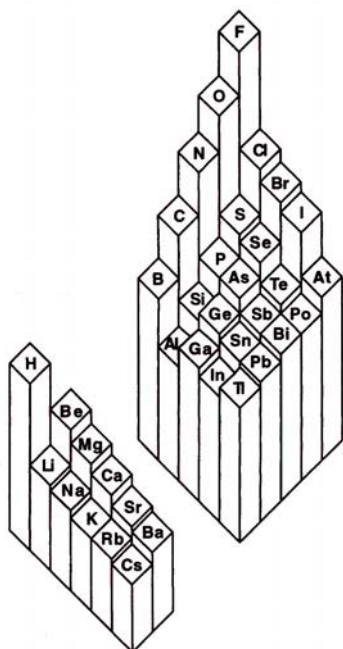
(b) Which Figure (from 1 to 5 below) shows the band structure of Ge?

(c) Explain Figure A below in the light of the band structures of Si and Ge.



10. (5 marks)

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 the periodic table (below right) predict the type of bonding for the following materials: Rb-Ba, N-Cl, O-F, Al-Mg, Mg-O.



Material	Nature of Bonding
Rb-Ba	
N-Cl	
O-F	
Al-Mg	
Mg-O	

11. (11 marks)

- (a) Name four general types of crystalline solids that differ from each other in the nature of the chemical bonding;

- (b) Three substances A to C (below) crystallise to give solids with melting points of X, Y or Z (below).

(A) water (H ₂ O);	(X) -224 °C;
(B) oxygen difluoride (OF ₂);	(Y) 0 °C;
(C) diethyl ether (CH ₃ -CH ₂ -O-CH ₂ -CH ₃);	(Z) -116 °C

- (i) Which type of crystalline solid (*as in 11(a)*) is formed by all of these substances?

- (ii) Assign the correct melting point (X, Y or Z) to each of the substances (A, B and C).

Substance	Melting Point
(A) water (H ₂ O)	
(B) oxygen difluoride (OF ₂)	
(C) diethyl ether(CH ₃ -CH ₂ -O-CH ₂ -CH ₃)	

- (iii) Explain your assignment of melting points in (ii) above in the light of the strength and type of intermolecular interactions present in the crystalline lattice of each substance.

END OF PAPER

(Physical Chemistry Formulae and Periodic Table on following pages)

Physical Chemistry Formulae

$$PV = nRT$$

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

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

$$P_A = X_A P_A^\circ$$

$$P_B = (k_H)_B X_B$$

$$\Delta U = q + w$$

$$w_P = -P\Delta V$$

$$H = U + PV$$

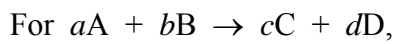
$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{when } \Delta T = 0$$

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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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