CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 221: PHYSICAL CHEMISTRY II

STREAMS: BSc. CHEM **TIME: 2 HOURS**

DAY/DATE: TUESDAY 09/04/2024 **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS

- **Answer Question ONE and any other TWO Questions**

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^{8}	$\mathrm{m\ s^{-1}}$
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F=N_Ae$	9.648 53	10^{4}	$\mathrm{C\ mol^{-1}}$
Boltzmann's constant	k	1.380 65	10^{-23}	$\mathrm{J\ K^{-1}}$
Gas constant	$R=N_Ak$	8.314 47		$\mathrm{J\ K^{-1}\ mol^{-1}}$
		8.314 47	10^{-2}	$\mathrm{dm^3\ bar\ K^{-1}\ mol^{-1}}$
		8.205 74	10^{-2}	$\mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}}$
		6.236 37	10	$\mathrm{dm^3\ Torr\ K^{-1}\ mol^{-1}}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar=h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	$\mathrm{mol^{-1}}$
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0=1/c^2\mu_0$	8.854 19	10^{-12}	$\mathrm{J^{-1}\ C^2\ m^{-1}}$
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	$\mathrm{J^{-1}\ C^2\ m^{-1}}$
Vacuum permeability	μ_0	4π	10^{-7}	$\mathrm{J\ s^2\ C^{-2}\ m^{-1}\ (=T^2\ J^{-1}\ m^3)}$
Magneton				
Bohr	$\mu_B=e\hbar/2m_e$	9.274 01	10^{-24}	$\mathrm{J\ T^{-1}}$
nuclear	$\mu_N=e\hbar/2m_p$	5.050 78	10^{-27}	$\mathrm{J\ T^{-1}}$
g value	g_e	2.002 32		
Bohr radius	$a_0=4\pi\varepsilon_0\hbar^2/m_ee^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha=\mu_0e^2c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2=hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma=2\pi^5k^4/15h^3c^2$	5.670 51	10^{-8}	$\mathrm{W\ m^{-2}\ K^{-4}}$
Rydberg constant	$R=m_ee^4/8h^3c\varepsilon_0^2$	1.097 37	10^{5}	$\mathrm{cm^{-1}}$
Standard acceleration of free fall	g	9.806 65*		$\mathrm{m\ s^{-2}}$
Gravitational constant	G	6.673	10^{-11}	$\mathrm{N\ m^2\ kg^{-2}}$

**Exact value*

QUESTION ONE (30 MARKS)

a) Starting from the postulates of Kinetic theory of gases, derive the kinetic gas equation

$PV=\frac{1}{3}mn'c^{-2}$.Deduce from this

i. Boyle's law. (2 marks)

ii. Graham's law of diffusion. (2 marks)

iii. Dalton's law of partial pressures. (2 marks)

b) (i) Calculate the translational energy of gas molecules in a mole of nitrogen at 27°C. What will be the average kinetic energy of a single mole? (1 mark)

(ii)

I. State Maxwell's law of distribution of molecular speeds among the molecules of gas.

(1 mark)

II. Explain from this the effect of temperature on the distribution of speeds. (1 mark)

III. Can the molecules of a gas have high and almost zero speeds? Show that the most probable speed is given by $c_{mp}=\sqrt{\frac{2RT}{M}}$. (1mark)

(iii) In one litre container 10^{23} gas molecules each of mass 10^{-25} kg are present. The r.m.s velocity of the molecules is $1000 ms^{-1}$

I. What is the total K.E of the molecules? (1mark)

II. What is the temperature of the gas? (1mark)

c)

(i) An ideal gas at NTP has a more probable velocity $\overline{u} = 4.20\times 10^4$ cm/sec and a mean free path of 7.90×10^{-8} cm. Calculate the mean time between collision. (3 marks)

(ii) Explain the variation of compressibility factor Z with pressure for nitrogen and hydrogen

I. at the given temperature (3 marks)

II. at different temperatures (3 marks)

(iii) Deduce the law of corresponding states from the van der waals equation. What is the significance of the law? (3 marks)

(iv) Discuss the corrections made in the p and v factors of ideal gas equation to convert it into the van der waals' equation. (3 marks)

d) An electrolyte, A_xB_y, undergoes dissociation in a solution as

$A_xB_y \longrightarrow xA^{y+} + yB^{x-}$

Show that the degree of dissociation α, is given by

$$\alpha = \frac{i-1}{n-1}$$

where 'i' is the van't Hoff factor and n is the total number of ions produced by a molecule of A_xB_y in solution. (3 marks)

QUESTION TWO (20 MARKS)

a) i) Deduce Ostwald's dilution law equation for AB and A_2B types of electrolytes. What are its limitations? (2 marks) ii)The molar conductivities of ethanoic acid in various solutions (V is the volume containing 1 mole of solute) are given below:

V/dm^3	13.57	54.28	434.2	1737	6948	∞
Λ_0/Ω^{-1} cm^2mol^{-1}	6.09	12.09	33.22	63.60	116.8	387.9

Do these figures agree with Ostwald's dilution law? What conclusion would you draw from the figures as to the value of the dissociation constant of ethanoic acid? (3 marks)

iii) On what basic principles is the derivation of Ostwald's law, and its testing by the use of Λ_c/Λ_0 values, based? Which principle is it that is false so far a strong electrolytes are concerned? (1 mark)

b) i) Discuss the chemistry of confirmatory test of the following:

(I) Test for lead ion (pb^{2+}) in group I and II (5 ½ marks)

(II) Test for aluminium ions (Al^{3+}) in group III (2 ½ marks)

ii) Calculate the solubility of Zn $(OH)_2$ in 1M NH_3 at 298K.Given $K_{ins}=6.1\times10^{-11}$ and $K_{sp}=4.5\times10^{-17}$ (2 marks)

iii) Explain why the solutions of aluminium salts and of sodium hydrogen-sulphate(VI) are acidic whilst solutions of sodium sulphide, sodium phosphate (V) and sodium hydrogencarbonate are alkaline. (2 marks)

c) Write short notes on the Drawbacks in the Arrhenius theory of electrolytic dissociation. (2 marks)

QUESTION THREE (20 MARKS)

a)

i) Draw typical equilibrium diagrams showing the variation of the percentage composition of the vapour and liquid phases with boiling temperatures (at constant pressure) for mixtures of two completely miscible liquids A and B, which do not form a constant boiling mixture and of which A has the higher boiling point. Use the diagram to describe the changes which occur in the composition of the residual liquid and of the distillate when a 50 per cent mixture of A and B is distilled. Describe one useful practical application of constant boiling mixture formation. (W.) (3marks)

ii) Explain with the aid of diagrams how two liquids may be separated by distillation. What is the advantage of a fractionating column? In what circumstances is it not possible to separate a mixture of two liquids by fractional distillation? (2marks)

iii) An immiscible liquid A when steam distilled with water gave a distillate $0.200 dm^3$ of which contained $0.0572 dm^3$ of A. The observed boiling point for the distillation was 98.2°C and the atmospheric pressure was 758 mm Hg. The vapour pressure of water at 98.2°C was 712 mm Hg. The relative density of liquid was found to be 1.83. Calculate the molar mass of the unknown liquid. (2 marks)

b) i) The boiling point elevation constant for benzene and water are 3 and 0.5 $K.kg.mol^{-1}$. When 0.585 gm of NaCl is dissolved in 100 gm of water, it causes an elevation of 0.1°C in the boiling point. Calculate the molecular weight of NaCl. Will the elevation in boiling point of an NaCl solution (of the same molality) in benzene be higher? Assume that the solubility NaCl in benzene is 1% by weight. (2 marks)

ii) Liquid A and B form an ideal solution. In a binary solution of A and B the mole fraction of A is 0.33. Calculate the composition of the vapour in equilibrium with the solution, given $\overset{\circ}{p}_A$=75 mm of Hg and $\overset{\circ}{p}_B$=22 mm of Hg. (1.5 marks)

iii) A solution of KI is isotonic with a 0.01 M solution of I_2 at 27°C. When equal volume of two solutions were mixed together, the osmotic pressure dropped by 18.5% of that of the individual solutions. Calculate the percentage of conversion of I^- to I_3^-. Assume that the solutions behave ideally and the salts are completely dissociated. (1.5 marks)

c) i) x gm NaCl, y gm sucrose and z gm urea are dissolved in $0.5 dm^3$ of water. Suppose that no chemical reaction sets in, what should be the osmotic pressure of the solution. (2marks)

ii) A solution containing 3.0×10^{-4}kg of benzoic acid ($M=1.22\times10^{-1} kgmol^{-1}$) in 2.0×10^{-3}kg of benzene freezes at 0.317°C below the freezing point of the solvent. Calculate

(I) the degree of association assuming that the acid exists as dimer in benzene, (1mark)

(II) The apparent molar mass of the acid; K_f of benzene is 5.1 (2 marks)

iii) A solution of 3.0×10^{-4}kg of camphor ($C_{10}H_{16}O$) in 2.53×10-2kg of chloroform boils at 334.3 K. Boiling point of chloroform is 334.0 K. Calculate $\Delta H_{vap,m}$ and K_b for chloroform. (1.5 marks)

iv) A 0.5 aqueous solution of potassium chloride is found to freeze at -0. 24°C.Calculate the van't Hoff factor and degree of dissociation of the solute at the concentration. [K_f =1.86 $K.kg.mol^{-1}$] (1.5 marks)

QUESTION FOUR (20 MARKS)

a) (i) Explain the terms: phase, number of components and degrees of freedom. Derive the phase rule ,P+F=C+2 (3marks)

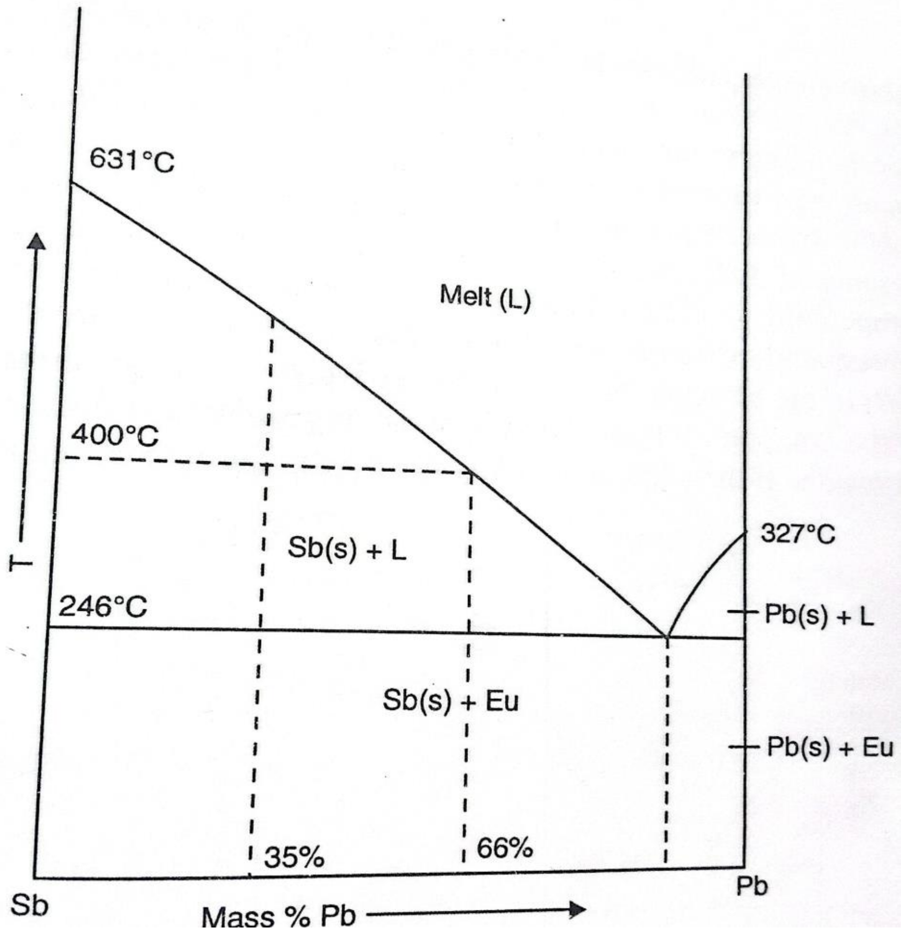
(ii) The system Pb (m .pt. 327°C) and Sb (m .pt. 631°C) exhibits a simple eutectic at 86% Pb (by mass) and 246°C. Breaks in the cooling curves in thermal analysis were found for the following compositions.

T°C	550	500	400	300	296
Mass % Pb	30	44	66	80	96

I. Draw a tentative phase diagram for the system and label it. (2 marks)

II. Calculate the amount of antimony that crystallizes out from 20 kg of a melt containing 35% Pb by mass after cooling it to a temperature of 400°C . (2 marks)

III. How much is the maximum amount of Sb that can be recovered from this melt? (2 marks)



b) Write down the number of components, number of phases and evaluate the degrees of freedom for the following equilibria:

i. A dilute solution of sulphuric acid in water. (1.5 marks)

ii. An aqueous solution saturated with respect to both sodium chloride and potassium chloride and in equilibrium with the vapour phase (1.5 marks)

iii. An aqueous solution with a mixture of sodium chloride and potassium bromide and in equilibrium with the vapour phase (1.5 marks)

iv. Reduction of $Fe_2O_3(s)$ by CO in the presence of (a)air and (b) oxygen alone (1.5 marks)

c) (i) why does air free water freeze at a higher temperature than water saturated with air? How high is this freezing point? (1.5 marks)

ii) State the usefulness of phase rule for study of equilibria. What are its limitations? (1.5 marks)

iii) Latent heat of fusion of water in 6025 joules per mole and can be treated as constant. Normal melting point of ice is 0°C. What will be the melting point of ice if the pressure on it is

I. reduced to 0.006 atmosphere (1 mark)

II. Increased to 5 atmospheres? (1 mark)

Specific volumes (volumes per gram) of ice and water at 0°C are 1.0907ml and 1.0001 ml respectively.

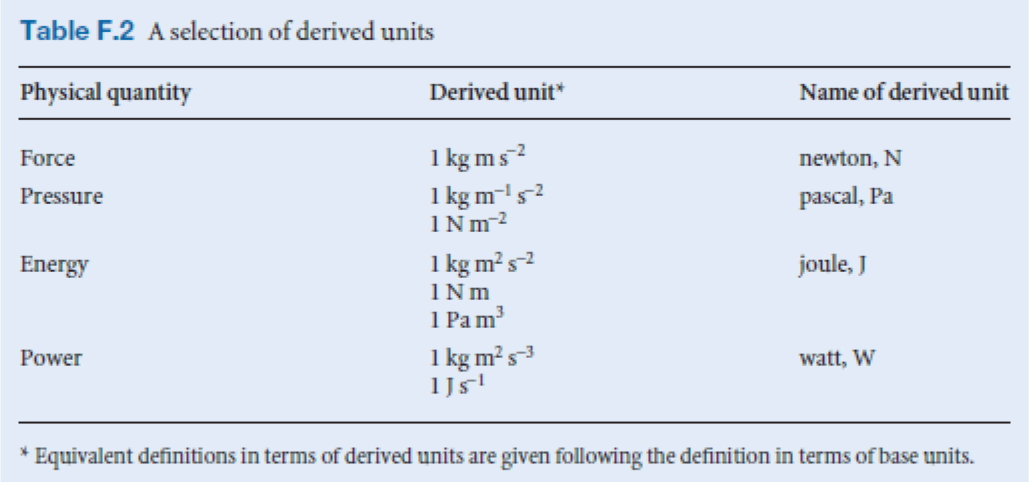


Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	1 kg m^{-1} s^{-2} 1 N m^{-2}	pascal, Pa
Energy	1 kg m^2 s^{-2} 1 N m 1 Pa m^3	joule, J
Power	1 kg m^2 s^{-3} 1 J s^{-1}	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

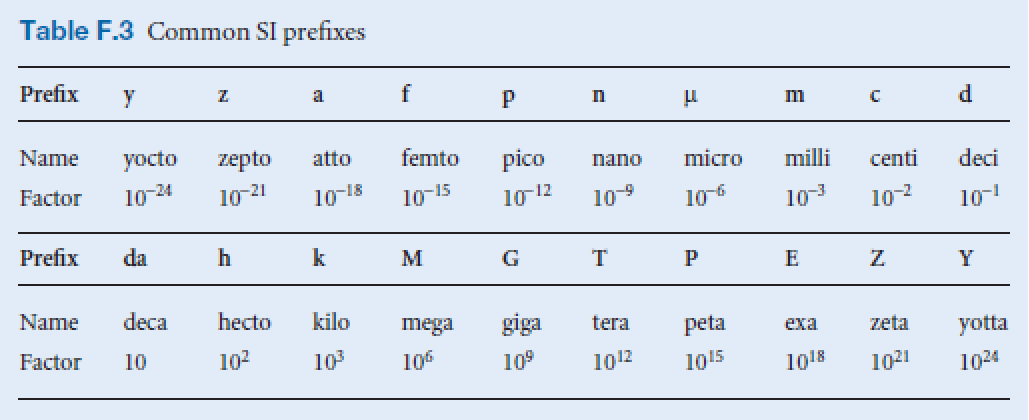
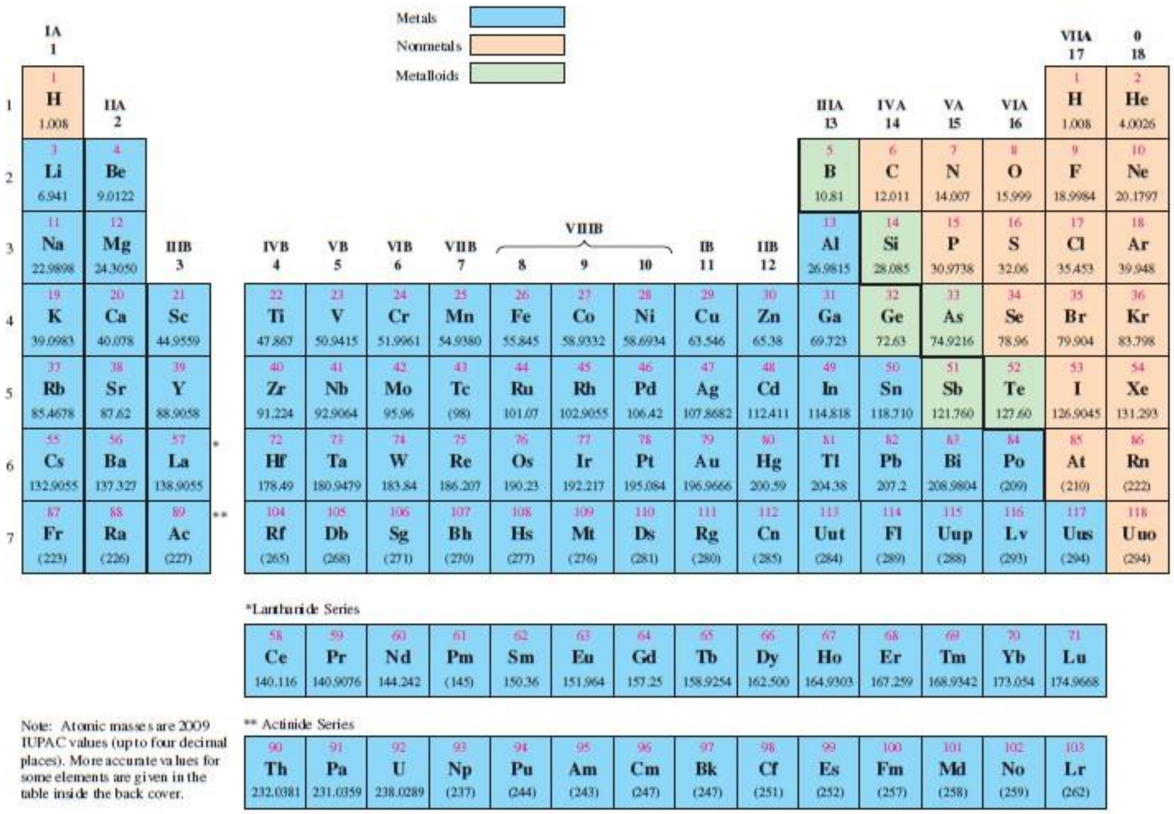


Table F.3 Common SI prefixes

Prefix	y	z	a	f	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}

Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^2	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

PERIODIC TABLE OF THE ELEMENTS



Metals 🟦
Nonmetals 🟧
Metalloids 🟩

	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIIIB 8	9	10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	0 18
1	1 **H** 1.008																1 **H** 1.008	2 **He** 4.0026
2	3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.9984	10 **Ne** 20.1797
3	11 **Na** 22.9898	12 **Mg** 24.3050											13 **Al** 26.9815	14 **Si** 28.085	15 **P** 30.9738	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9380	26 **Fe** 55.845	27 **Co** 58.9332	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.63	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9058	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.96	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.293
6	55 **Cs** 132.9055	56 **Ba** 137.327	57 **La** 138.9055 *	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.9666	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227) **	104 **Rf** (265)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 **Uut** (284)	114 **Fl** (289)	115 **Uup** (288)	116 **Lv** (293)	117 **Uus** (294)	118 **Uuo** (294)

*Lanthanide Series

58 **Ce** 140.116	59 **Pr** 140.9076	60 **Nd** 144.242	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.500	67 **Ho** 164.9303	68 **Er** 167.259	69 **Tm** 168.9342	70 **Yb** 173.054	71 **Lu** 174.9668

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.

** Actinide Series

90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)