CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 120: PHYSICAL CHEMISTRY I

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

DAY/DATE: TUESDAY 19/12/2023 **2.30 P.M. – 4.30 P.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	$F = N_A e$	9.648 53	10^{4}	$\mathrm{C\ mol^{-1}}$
Boltzmann's constant	k	1.380 65	10^{-23}	$\mathrm{J\ K^{-1}}$
Gas constant	$R = N_A k$	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	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	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	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	10^{-8}	$\mathrm{W\ m^{-2}\ K^{-4}}$
Rydberg constant	$R = m_e e^4/8h^3 c\varepsilon_0^2$	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)

1. a i) A gas at 350 K and 12 atm has a molar volume 12 per cent larger than that calculated from the perfect gas law. Calculate [2 marks]

(a) The compression factor under these conditions

(b) The molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

ii) Deduce the relation between the pressure and mass density, of a perfect gas of molar mass *M*. Confirm graphically, using the following data on dimethyl ether at 25°C, that perfect behaviour is reached at low pressures and find the molar mass of the gas.

p/kPa	12.223	25.20	36.97	60.37	85.23	101.3
$\rho/(\mathrm{kg\ m^{-3}})$	0.225	0.456	0.664	1.062	1.468	1.734

iii) How many grams of ammonium chloride and how many millilitres 3.0 M Sodium hydroxide should be added to 200ml water and diluted to 500ml to prepare a buffer of pH 9.50 with a salt concentration of 0.10 M [2 marks]

iv) What weights of NaH_2PO_4 and Na_2HPO_4 would be required to prepare 1 L of a buffer solution of pH 7.45 that has an ionic strength of 0.100? [2 marks]

b.i) Calculate

a) The number of collisions per second per molecule (Z1)

b) The total number of collisions per second per cubic metre (Z11)

c) The mean free path (λ) at 1 atm pressure for oxygen molecules and 298K.

Given the coefficient of viscosity of oxygen as 2.08×10^{-5} pascal second.

ii) Why do real gases deviate from ideal gases' behaviour when

I) They are polar in character [0.5 mark]

II) Their pressure is high [0.5mark]

III) Their temperature is low [0.5mark]

iii) Discuss the corrections made in the P and V factors of the ideal gas equation to convert it into the van der Waals equation [3 marks]

iv) Two moles of ammonia are confined to a 5-litre flask at 27^0C. Calculate its pressure using the gas equation and Vander Waals equation. For ammonia a = 4.17atmdm^6 moles^{-2} and b = 0.0371dm^{3}mole^{-1} [2 marks]

c.i) What is meant by chemical equilibrium being a dynamic equilibrium? [2 marks]

ii) state le chatelier- Braun principle [0.5 marks]

iii) In the equilibrium

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$; $\Delta H = - 902$ kJ what would be the effect of

a) decrease in concentration of O_2? [0.5 mark]

b) increase in volume of vessel? [0.5 mark]

c) decrease in total pressure? [0.5 mark]

d) increase in temperature? [0.5 mark]

e) adding a catalyst? [0.5 mark]

d.i) Nerst and Holmann found that when one mole of dichloroacetic acid and 4.45 moles of amylene were heated together at 100^0C to the equilibrium state, the reaction mixture had a volume of 0.640 litres and contained 0.628 moles of ester. In another experiment one mole of the acid was heated at the same temperature with 8.16 moles of amylene and the equilibrium mixture had a volume of 1.062 litres. What amount of ester was formed in the second experiment? 2marks

ii) The dissociation of ammonium bisulphide is expressible by the equation :

$NH_4HS\ (g) \leftrightarrow NH3(g) + H_2S\ (g)$

At a certain temperature, the dissociation pressure of the solid is 500 mmHg. Calculate

a) K_p for it,

b) The total pressure of equilibrium when ammonia causing 300mm Hg pressure is introduced into the equilibrium mixture, with temperature remaining the same.

[2 marks]

QUESTION TWO (20 MARKS)

2. a. i) The following data are collected for a chemical reaction at a constant temperature, arbitrarily A + B → products. **[**2 marks]

[A] (M)	**[B] (M)**	**Initial rate (_ 10_{-7} M/s)**
0.00636	0.00384	2.91
0.0108	0.00384	4.95
0.00636	0.00500	4.95

What is the rate law for this reaction and what is the value of the rate constant

ii) Derive Arrhenius equation [2 marks]

iii) In a recent paper (Orkin et al., Phys. Chem 1997 101: 174) rate constants were determined for the reaction between the hydroxyl radical and chlorobromomethane.

$OH + Cl_2 BrCl \rightarrow$ products

Data that were obtained included the following values of the rate constant k for the following temperatures

T(k)	K(cm^3/ molecule second)
298	1.11×10^{-13}
313	1.34×10^{-13}
330	1.58×10^{-13}

I) Determine A [3.5 marks]

II) Estimate the rate constant at 370 K [1 mark]

III)Compare it with the experimentally determined value of 2.10×10^{-13} cm3/ molecule second [1.5 marks]

b. Explain the following statements

i) The second dissociation constant of an acid is lower in magnitude than the first dissociation constant [2 marks]

ii) Methyl orange is a suitable indicator for the titration of strong acids and weak bases. [2 marks]

c. i) A solution at 25^0C contains 0.01 Molar propionic acid (Ka = 1.39×10^{-5}) and 0. 03 molar HCl. Calculate α for propionic acid and the pH of the mixture.

3marks

ii) If the final Volume is 1 litre, how many moles of HCl will have to be added to 500cc i0.1 (M) $Na_2 CO$ to adjust the pH to 10 (Given for H_2CO_3, $K_1 = 4.52 \times10^{-7}$, $K_2 = 4.69 \times10^{-11}$).3marks

QUESTION THREE (20 MARKS)

3.a.i) Write short notes on the following

a) Buffer capacity [2 marks]

ii) Explain how you can Prepare a 100 cc buffer solution of pH = 9. You are supplied with 0.1(N) NH_4OH and 0.1 (N) HCl. Given that K_b for $NH_4OH = 2\times 10^{-5}$.

[2.5 marks]

iii) 300 cc of a solution of HOAc (m.wt. = 60) containing 10 gm/l ($K_a = 1.86\times 10^{-5}$) is mixed with 200 cc of solution of phenylacetic acid (m.wt. = 136) containing 5gm/l ($K_a = 5.42 \times 10^{-5}$). Calculate the pH of the mixture. [3 marks]

iv) What weight of NA_2HPO_4 and KH_2PO_4 would be required to prepare 200ml of a buffer solution of pH 7.40 that has an ionic strength of 0.20? [2 marks]

b. i) Discuss Ostwald dilution law [2 marks]

ii) A solution of ammonia gives the following values of equivalent conductivities at different dilutions

V in L	8	16	32
A_v	3.20	4.45	6.32oh^{-1}cm^2

If equivalent Conductivity at infinite dilution of NH_4OH is 237 Ohm^{-1}cm^2. Show that the above-given data establish the truth of Ostwald's dilution Law. [2 marks]

c. i) Calculate the lattice enthalpy of $MgBr_2$ from the following data: [3 marks]

	ΔH/(kJ mol−1)
Sublimation of Mg(s)	+148
Ionization of Mg(g) to Mg^{2+}(g)	+2187
Vaporization of Br_2(l)	+31
Dissociation of Br_2(g)	+193
Electron attachment to Br(g)	−331
Formation of $MgBr_2$(s) from Mg(s) and Br_2(l)	−524

ii) When 2.25 mg of anthracene, $C_{14}H_{10}$(s), was burned in a bomb calorimeter the temperature rose by 1.35 K. Calculate the calorimeter constant. By how much will the temperature rise when

135 mg of phenol, $C_6H_5OH(s)$, is burned in the calorimeter under the same conditions? ($\Delta_c H^{\varnothing}$ ($C_{14}H_{10}$,s) = −7061 kJ mol^{-1}.) [3.5 marks]

QUESTION FOUR (20 MARKS)

4. a. i) Describe using a suitable diagram how you can measure the standard electrode potential of zinc using a Calomel electrode. [4 marks]

ii) Predict whether Zinc and silver will react with 1N sulphuric acid to give out hydrogen gas or not. Given that the Standard reduction potentials of Zinc and Silver are -0.76 and 0.80 Volt respectively. [2 marks]

iii) A cell employs the following half-reactions [2 marks]

$Ni^{2+}_{(aq)} + 2e^- \leftrightarrow Ni_{(s)}$ $\qquad E^\circ_{Ni^{2+}} = -0.25V$

$Cr^{3+}_{(aq)} + 3e^- \leftrightarrow Cr(s)$ $\qquad E^o_{Cr^{3+}} = -0.74V$

Calculate the potential if $[Ni^{2+}] = 1.0 \times 10^{-4}M$ and $[Cr^{3+}] = 2.0 \times 10^{-3}M$

b. i) Set up a thermodynamic cycle for determining the enthalpy of hydration of Ca^{2+} ions using the following data: enthalpy of sublimation of Ca(s), +178.2 kJ mol^{-1}, First and second ionization enthalpies of Ca(g), 589.7 kJ mol^{-1} and 1145 kJ mol^{-1}, enthalpy of vapourization of bromine, 30.91kJ mol^{-1} dissociation enthalpy of $Br_2(g)$, 192.9 kJ mol^{-1}, electron gain enthalpy of Br(g), -331.0 kJ mol^{-1}, enthalpy of solution of $CaBr_2(s)$, -103.1 kJ mol^{-1}, enthalpy of hydration of $Br^-(g)$, -97.5kJ mol^{-1} [3 marks]

ii) A galvanic cell was constructed using electrodes made of lead and lead (IV) oxide (PbO_2) with sulfuric acid as the electrolyte. The half-reactions and their reduction potentials in this system are

PbO2 (s) + 4H+ SO_4^{2-} (aq) + 2e ↔ PbSO4 (s) + 2H2O $\qquad E^o_{PbO2} = 1.69$ V

PbSO4 (s) + 2e ↔ Pb (s) + SO_4^{2-} (aq) $\qquad E^o_{PbSO4} = -0.36$ V

What is the cell reaction, and what is the standard potential of the cell? [2 marks]

c. i) Set up a thermodynamic cycle for determining the enthalpy of hydration of Ca^{2+} ions using the following data: enthalpy of sublimation of Ca(s), +178.2 kJ mol−1; first and second ionization enthalpies of Ca (g), 589.7 kJ mol^{-1} and 1145 kJ mol^{-1}; enthalpy of vaporization of bromine,30.91 kJ mol^{-1}; dissociation enthalpy of Br_2(g), +192.9 kJ mol^{-1}; electron gain enthalpy of Br(g), −331.0 kJ mol^{-1}; enthalpy of solution of $CaBr_2$(s), −103.1 kJ mol^{-1}; enthalpy of hydration of Br^-(g), −97.5 kJ mol^{-1}. [4 marks]

ii) A sample of the sugar d-ribose ($C_5H_{10}O_5$) of mass 0.727 g was placed in a constant-volume calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is −3251 kJ mol−1, gave a temperature rise of 1.940 K. Calculate the internal energy of combustion of d-ribose and its enthalpy of formation. [3 marks]

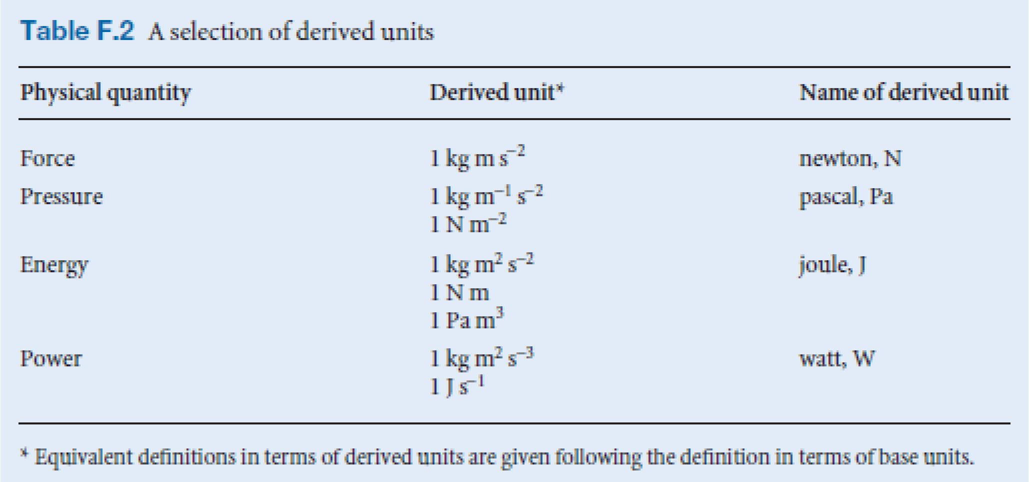


Table F.2 A selection of derived units

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.

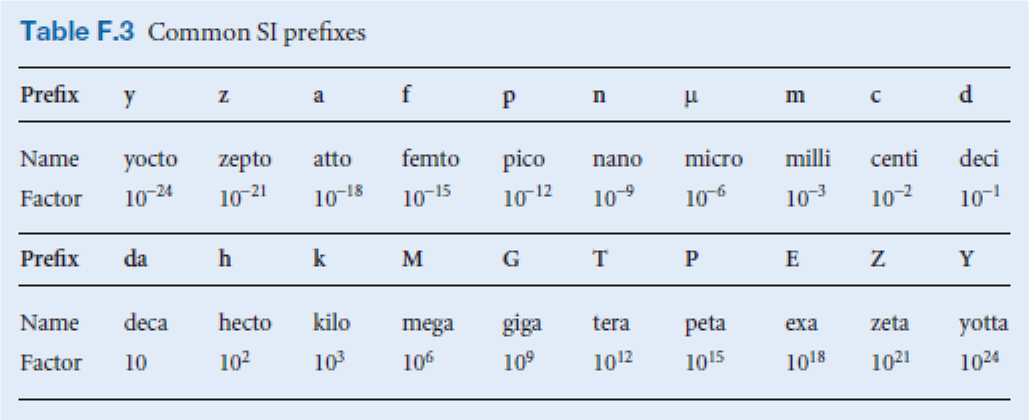
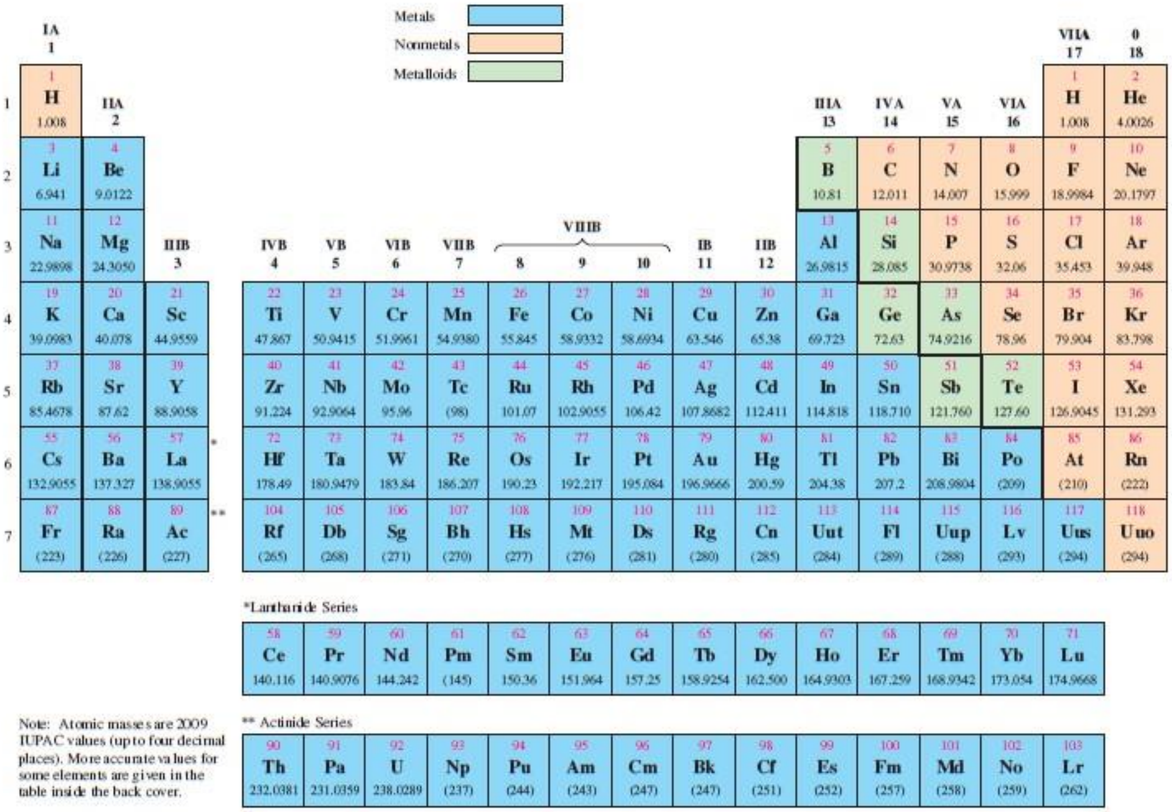


Table F.3 Common SI prefixes

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	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	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

** 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)

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.

……