

PERIODIC TABLE OF THE ELEMENTS

IA		IIA		IIIB		IVB		VB		VIB		VIIB		VIII		IX		X		XI		XII		IIIA		IVA		VA		VIA		VIIA		0	
1 H 1.0079	3 Li 6.941	4 Be 9.0122	11 Na 22.98976	12 Mg 24.305	19 K 39.098	20 Ca 40.08	21 Sc 44.9559	22 Ti 78.94	23 V 50.9414	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.64	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	53 I 126.9054	54 Xe 131.29	81 Tl 204.37	82 Pb 207.2	83 Bi 208.9804	84 Po (210)	85 At (210)	86 Rn (222)	2 He 4.0026	10 Ne 20.179	18 Ar 39.948		
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9058	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc 98.9062	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 121.757	52 Te 127.60	55 Cs 132.9054	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.23	77 Ir 192.22	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967		
87 Fr (223)	88 Ra 226.0254	89 Ac (227)	LANTHANIDE SERIES					58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (147)	62 Sm 150.4	ACTINIDE SERIES					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 (260)									

TABLE OF ATOMIC NUMBERS AND WEIGHTS
IUPAC 1971

ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT	ELEMENT	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Aluminum	Al	13	26.9815	Mercury	Hg	80	200.59
Ammonium	Am	95	(243)	Nickel	Ni	28	58.71
Antimony	Sb	51	121.75	Neodymium	Nd	60	144.24
Argon	Ar	18	39.948	Neon	Ne	10	20.179
Arsenic	As	33	74.9216	Nepthunium	Np	93	237.0482
Astatine	At	85	(210)	Nickel	Ni	28	58.71
Barium	Ba	56	137.34	Niobium	Nb	41	92.9064
Berkelium	Bk	97	(247)	Nitrogen	N	7	14.0067
Beryllium	Be	4	9.0122	Nobelium	No	102	(254)
Bismuth	Bi	83	208.9804	Osmium	Os	76	190.2
Boron	B	5	10.81	Oxygen	O	8	15.9994
Bromine	Br	35	79.904	Palladium	Pd	46	106.4
Cadmium	Cd	48	112.40	Phosphorus	P	15	30.9738
Caesium	Cs	55	132.9054	Platinum	Pt	78	195.09
Cerium	Ce	58	140.12	Potassium	K	19	39.098
Chlorine	Cl	17	35.453	Promethium	Pm	61	(147)
Chromium	Cr	24	51.996	Protactinium	Pa	91	231.0359
Cobalt	Co	27	58.9332	Radium	Ra	88	226.0254
Copper	Cu	29	63.546	Radium	Ra	86	(222)
Curium	Cm	96	(247)	Rhenium	Rh	75	186.2
Dysprosium	Dy	66	162.50	Rhodium	Rd	45	102.9055
Einsteinium	Es	99	(249)	Rubidium	Rb	37	85.4678
Erbium	Er	68	167.26	Ruthenium	Ru	44	101.07
Europium	Eu	63	151.96	Samarium	Sm	62	150.4
Fermium	Fm	100	(255)	Sandwichium	Ss	21	44.5550
Fluorine	F	9	18.9984	Selenium	Se	34	78.96
Francium	Fr	87	(223)	Silicon	Si	14	28.086
Gadolinium	Gd	64	157.25	Silver	Ag	47	107.868
Gallium	Ga	31	69.72	Sodium	Na	11	22.98976
Germanium	Ge	32	72.59	Srrium	Sr	38	87.62
Gold	Au	79	196.9665	Sulfur	S	16	32.06
Hafnium	Hf	72	178.49	Tantalum	Ta	73	180.9179
Helium	He	2	4.0026	Tellurium	Te	43	127.60
Helium	He	67	164.9304	Terbium	Tb	65	158.9254
Hydrogen	H	1	1.0079	Thallium	Tl	81	204.37
Hydrogen	H	49	114.82	Thorium	Th	90	232.0381
Iodine	I	53	126.9045	Thulium	Tm	69	168.9342
Iridium	Ir	77	192.22	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.88
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.9055	Uranium	U	92	238.0289
Lanthanum	La	103	(257)	Vanadium	V	23	50.9414
Lavrencium	Lr	103	207.2	Xenon	Xe	54	131.30
Lithium	Li	3	6.941	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Zinc	Zn	30	65.38
Magnesium	Mg	12	24.305	Zirconium	Zr	40	91.22
Manganese	Mn	25	54.9380				
Mendelevium	Md	101	(258)				

DEPARTMENT OF CHEMISTRY

Examiner: Dr. C Morrison

Instructions

Read through *all* the instructions and questions

Answer all questions

Do not use pencil or red pen; all pencil work will be ignored

All answers must be clearly indicated by a vertical line in the box of your choice on the answer sheet as indicated below:



If you make a mistake cross it out, as indicated below:



There is only one correct answer per question

There is no penalty for a wrong answer

If more than one box is filled per question (except to cross out mistakes), then that question will not be graded

You cannot be graded for telepathic responses - write it down!

You will be told when there are 10 minutes left

Do not ask questions after the first half hour

Do not talk, share pens, calculators or anything else - you will get a zero grade if caught

Constants and Data

$$R = 8.314 \text{ J/K.mol} = 0.0821 \text{ L.atm/K.mol}$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1} \text{ or AMU/g}$$

$$k = 1.38 \times 10^{-23} \text{ J/K.molecule}$$

$$\epsilon^{\circ} = 8.85 \times 10^{-12} \text{ F.m}^{-1}$$

$$\mu^{\circ} = 4\pi \times 10^{-7} \text{ s}^2\text{m}^{-1}\text{.F}^{-1}$$

$$h = 6.63 \times 10^{-34} \text{ J.s}$$

$$c = 3 \times 10^8 \text{ m.s}^{-1}$$

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$F = 96484.6 \text{ C.mol}^{-1}$$

$$m_e = 9.1 \times 10^{-31} \text{ Kg}$$

$$m_n = m_p = 1.67 \times 10^{-27} \text{ Kg}$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Nm}^{-2} = 760 \text{ mm Hg}$$

$$R_H = 109677.58 \text{ cm}^{-1}$$

$$R_{\infty} = 109737.32 \text{ cm}^{-1}$$

Molar volume of Ideal gas at STP = 22.41L

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$J = C.V$$

$$F = C.V^{-1}$$

For the quadratic equation $ax^2 + bx + c = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Activity Series for Metals: Metals are arranged according to their ability to displace Hydrogen from an acid or water. Lithium is the most reactive metal, and Gold the least reactive.

Li K Ba Ca Na Mg Al Zn Cr Fe Cd Co Ni Sn Pb H Cu Hg Ag Pt Au

$$^{12}\text{C} = 12.000 \text{ g.mol}^{-1}$$

$$^{13}\text{C} = 13.003 \text{ g.mol}^{-1}$$

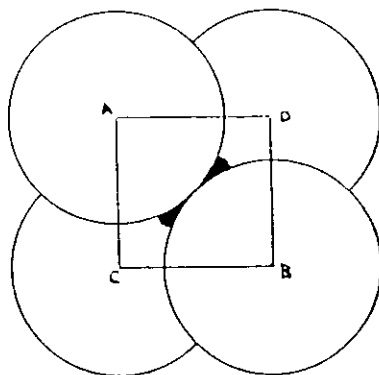
Do not remove pages: grades will be deducted!

(NB: In this exam take $\text{MX}_{(s)} \rightarrow \text{M}^+(\text{g}) + \text{X}^-(\text{g})$ to be endothermic)

- Q1 An analysis of 227 compounds indicated that the radius ratio rule worked about two-thirds of the time. Which factor(s) contribute to the failure of this rule?
 (a) covalency (b) electronegativity (c) small atoms can form stronger covalent bonds than larger ones
 (d) Madelung constant (e) bond directionality (f) the rule assumes that ions are packed as hard spheres in a lattice without structural imperfections (g) all of the above, except (b) (h) all of the above, except (d)
 (i) all of the above, except (f) (j) (c), (d), (e)

The following two questions refer to NaF.

- Q2 The effective nuclear charges at Na^+ and F^- , using Slater's screening rules, are respectively:
 (a) 6.5 and 4.5 (b) 7.35 and 5.35 (c) 6.85 and 4.85 (d) 6.15 and 4.15 (e) 5.65 and 3.65
- Q3 What are the radius of Na^+ and F^- , respectively, given that the internuclear distance is 231pm, as measured by X-ray diffraction?
 (a) 97.3pm and 133.7pm (b) 135.3pm and 95.7pm (c) 95pm and 136pm (d) 93pm and 138pm (e) none of these
- Q4 The diagram below represents four anions arranged tetrahedrally, with a cation (black sphere) at the center, touching all the anions. What is the radius of the cation, given that the cube side = d?
 (a) $(\sqrt{3} - \sqrt{2})d/\sqrt{2}$ (b) $(\sqrt{3} - \sqrt{2})d/2$ (c) $d\sqrt{3}/\sqrt{2}$ (d) $(\sqrt{2} - 1)d$ (e) $(\sqrt{3} - 1)d$ (f) $(\sqrt{3} - 1)d/\sqrt{2}$



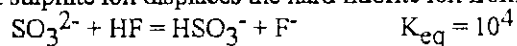
- Q5 For KClO_4 , $U=591\text{kJ/mol}$. Calculate the thermochemical radius for the ClO_4^- ion.
 (a) 369pm (b) 38pm (c) 236pm (d) 502pm (e) 464pm

$$U = 1.202 \times 10^{-7} (v_{z+} z_- / r) (1 - 3.45 \times 10^{-11} / r)$$

- Q6 What is the internuclear distance in KCl (which has an NaCl type structure) given that its density is 2.004g/cm^3 ?
 (a) 498pm (b) 249pm (c) 627.6pm (d) 313.8pm (e) it is not possible to determine from the information available
- Q7 Which of each of the following pairs *might* be expected to be more ionic?
 1 CaCl_2 or MgCl_2 2 NaCl or CaCl_2 (similar radii) 3 NaCl or CuCl (similar radii) 4 TiCl_3 or TiCl_4
 (a) 1 CaCl_2 ; 2 NaCl ; 3 NaCl ; 4 TiCl_3 (b) 1 CaCl_2 ; 2 NaCl ; 3 CuCl ; 4 TiCl_4
 (c) 1 MgCl_2 ; 2 CaCl_2 ; 3 CuCl ; 4 TiCl_4 (d) 1 MgCl_2 ; 2 CaCl_2 ; 3 NaCl ; 4 TiCl_3
- Q8 Which one of the following statements is correct about CaCl_2 and CdCl_2 ?
 (a) CaCl_2 is softer than CdCl_2
 (b) CdCl_2 is more ionic than CaCl_2 because Cd^{2+} causes less polarization than Ca^{2+} since the d electrons are more efficient in screening the nuclear charge
 (c) CdCl_2 is more covalent than CaCl_2 because Cd^{2+} causes more polarization than Ca^{2+}
 (d) none of the above choices

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- Q9** Generally, a hard acid will react with a hard base and a soft acid with a soft base. However, the reaction below shows that the soft sulphite ion displaces the hard fluoride ion from the hard H^+ ion:



Why does the above hard-soft rule appear to break down?

- (a) the strength of $SO_3^{2-} > F^-$ (b) the strength of $SO_3^{2-} < F^-$ (c) F^- is smaller, making the Madelung constant larger (d) F^- is smaller, making the Madelung constant smaller (e) the reaction is impossible
- Q10** Which argument given below rationalizes the following melting and boiling point data on alkali and alkaline earth halides?

	MP/ $^{\circ}C$	BP/ $^{\circ}C$
KBr	734	1435
CaBr ₂	730	812
CsF	682	1251
BaF ₂	1355	2137

- (a) The change from 1:1 to 1:2 structure in the fluorides lowers the lattice energy, hence increasing the MP and BP of these compounds
 (b) London dispersion forces are more important in the bromides than in the fluorides
 (c) The change from 1:1 to 1:2 structure in the fluorides increases the lattice energy, hence increasing the MP and BP of these compounds
 (d) covalency allows some of the above species to be more stable in the liquid and gas phases
 (e) choice (a) and (d)
 (f) choice (c) and (d)
 (g) choice (a), (b) and (d)
 (h) choice (b), (c) and (d)
- Q11** Which one of the ions below would have the smallest hydration energy?

	ionic radius/nm	ionic charge
(a)	0.06	+1
(b)	0.08	+2
(c)	0.12	-1
(d)	0.16	-2
(e)	0.18	+1

- Q12** Solute-solute and solute-solvent interactions in non-polar solute/solvent systems are most probably:
 (a) ion-dipole (b) dipole-dipole (c) ion-induced dipole (d) dipole-induced dipole (e) London dispersion
- Q13** All potassium salts are water soluble and all perchlorates are water soluble. Why is $KClO_4$ essentially insoluble in water at room temperature (1.7g/100ml)?
 (a) ΔH_{soln} = positive; ΔS = large; U = small (b) ΔH_{soln} = positive; ΔS = small; U = large
 (c) ΔH_{soln} = negative; ΔS = large; $U < \Delta H_{soln}$
 (d) ΔH_{soln} = positive; ΔS = small; Madelung constant = small (e) none of these choices
- Q14** In ammonia the bond length is 102pm, the bond angle is 106.7° and the dipole moment is $4.88 \times 10^{-30} C.m$. Calculate the percentage covalent character of the NH bond.
 [The angle between bonds (θ) and the trigonal axis angle (ϕ) are related by: $\phi = \sin^{-1} \{2\sin(\theta/2)/\sqrt{3}\}$]
 (a) 78.9% (b) 73.6% (c) 34.6% (d) 26.4% (e) 11.5% (f) none of these choices
- Q15** In $H_2C=SF_4$ which position is the double bond in and what plane are the two hydrogens in respectively?
 (a) axial; axial (b) axial; equatorial (c) equatorial; equatorial (d) equatorial; axial

The following two questions refer to CaF.

- Q16** Calculate the lattice energy of CaF, given that the Madelung constant = 1.763, $r_{Ca-F} = 251$ pm and the Born exponent = 8.
 (a) 976kJ/mol (b) -976kJ/mol (c) 853kJ/mol (d) -853kJ/mol

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Q17 Find ΔH°_f for CaF. The following data may be helpful.

	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$
$\text{Ca}_{(s)} \rightarrow \text{Ca}_{(g)}$	172
$\text{Ca}_{(g)} \rightarrow \text{Ca}^+_{(g)} + e$	589
$\text{F}_{2(g)} \rightarrow 2\text{F}_{(g)}$	160
$\text{F}_{(g)} + e \rightarrow \text{F}^-_{(g)}$	-352

(a) -284kJ/mol (b) -364kJ/mol (c) -407J/mol (d) -407kJ/mol (e) -487kJ/mol

Q18 Using the following relationship for ionization energy:

$$IE = (m_e e^4 / 8h^2 e^2) (Z^* / n^*)^2$$

where all the constants have their usual values, with Z^* and n^* being the *effective nuclear charge* and *effective principle quantum number* respectively, find the first ionization energy of potassium.

$[n =$	1	2	3	4	5	6]
$[n^* =$	1	2	3	3.7	4	4.2]

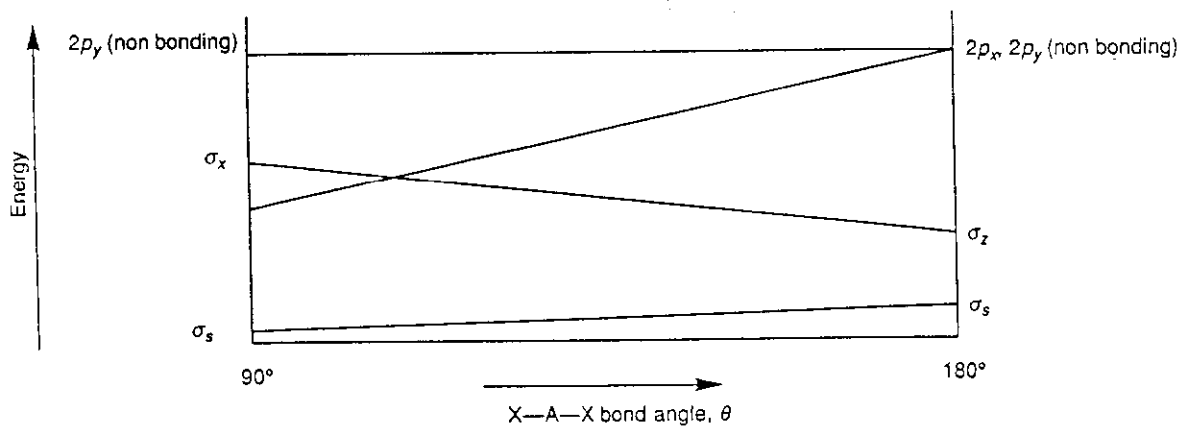
(a) 1.81eV (b) 464J/mol (c) 4.81eV (d) 175J/mol (e) 7.32eV

Q19 If the bond angle in NH_3 is 107.2° , what is the percentage s character of the lone pair?

(a) 23% (b) 25% (c) 31% (d) 69% (e) 77%

Q20 On a simplified Walsh diagram for XH_2 , as shown below, why does the σ_s molecular orbital energy decrease on changing angle from 180° to 90° ?

- (a) the overlap of the 1s-1s H orbitals with that of the X $2p_z$ increases
 (b) the X $2p_x$ and H 1s orbital overlap decreases
 (c) the overlap of the 1s-1s H orbitals increases



Q21 VSEPR works less well for transition metal compounds compared to main group compounds because:

- (a) main group elements do not deform to prolate and oblate shapes
 (b) orbital directionality is ineffective in transition metals for lone pairs
 (c) there are a large number of electrons in transition metals
 (d) d orbitals are too diffuse to make lone-pair repulsions effective

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- Q22** π bonding can be formed from which combinations of orbitals?
(a) $p_x + p_x$ (b) $p_y + p_y$ (c) $p_x + d_{xz}$ (d) $d_{xz} + d_{xz}$
(e) all except choice (d), because this forms δ bonds (f) all except choice (e)
- Q23** For PF_5 which of the following statements is correct?
(a) resonance structures are only required when d orbitals are invoked
(b) if resonance has to be invoked, then the axial bonding will be weaker than the equatorial bonding
(c) a planar resonance structure can be invoked involving sp^2 hybridization
(d) a non-planar PF_3 structure is not possible
(e) choices (a) and (b) (f) choices (b) and (c) (g) choices (c) and (d)
- Q24** BeH_2 is linear (from VSEPR and Walsh diagram) in the *ground state*. What happens to the shape if an electron is promoted to a higher molecular orbital? (Hint: draw the MO diagram)
(a) nothing (b) it becomes bent (c) it breaks up (d) none of these choices
- Q25** Which statement is false about hybridization?
(a) orbitals must be of the same symmetry (b) similar orbital energies are required
(c) hybridization of atomic centers cannot be treated independently of one another
(d) hybrid orbitals are formed from different orbitals and have new shapes
(e) none of the above choices
- Q26** In Slater's rules the 3s and 3p electrons each contribute 1.00 (100%) to the shielding of a d electron. Why is this?
(a) the principle quantum number is the same (b) it is easier to ionize a 3d electron
(c) there is a higher probability of finding the 3s or 3p electron near the nucleus
(d) 3d electrons are more diffuse
- Q27** From *Bent's rule*, which states "*More electronegative substituents "prefer" hybrid orbitals having less s character, and more electropositive substituents "prefer" hybrid orbitals having more s character,*" we may infer that:
(a) p character tends to concentrate in orbitals with weak covalency
(b) s character tends to concentrate in orbitals with weak covalency
(c) electronegative substituents will prefer axial sites in trigonal bipyramidal structures
(d) electronegative substituents will not prefer axial sites in trigonal bipyramidal structures
(e) only two of the above choices are correct (f) only three of the above choices are correct
- Q28** In VSEPR, when determining the number of electron-pairs, a triple bond is counted as -2. Why?
(a) only σ bonds count toward the framework (b) both σ and π bonds count toward the framework
(c) triple bonds are more repulsive than σ bonds (d) two more electrons than in a σ bond contribute to the count
- Q29** In N_2 the σ_p molecular orbital may lie *below* the π orbitals because:
(a) mixing is allowed between the 2s and 2p orbitals
(b) the technique used to measure the MO energies (PES) ionizes the N_2 , leading to the change
(c) the energy difference between 2s and 2p $> 1600\text{kJ/mol}$ (d) none of these choices
- Q30** When atomic orbitals of the same symmetry interact:
(a) Their energies are allowed to cross.
(b) Their energies never cross.
(c) They form non-bonding molecular orbitals.
(d) No molecular orbitals are formed.
(e) None of these.

Note: $r_{\text{K}^+} = 133\text{pm}$