Name: ___________________ Student #: __________________

CHEMISTRY 1E03 9 NOVEMBER 2007

Instructors: J. Barbier, R. Dumont

MCMASTER UNIVERSITY - TERM TEST # 2 - DURATION: 120 minutes

This test contains **16** pages and **30** multiple-choice questions. The last four pages include two extra blank pages for rough work, a page with some useful data and equations, and a Periodic Table. You may tear off the last four pages. **You are responsible for ensuring that your copy of the question paper is complete**. Bring any discrepancy to the attention of your invigilator.

Questions 1-25 are each worth 2 marks, questions 26–30 are each worth 3 marks. There is no penalty for incorrect answers.

These question sheets must be returned with your answer sheet. However, no work written on the question sheets will be marked. You must enter your full name and student number on this question sheet, as well as on the answer sheet. **Your invigilator will be checking your student card for identification.**

Make sure to enter the correct version number of your test (shown at the bottom of each page) in the correct column on the answer sheet (see instructions on page 2).

Answer all questions on the answer sheet, in pencil. Instructions for entering multiple-choice answers are given on page 2. Select **one answer for each question** from the choices (A) through (E).

Only **Casio FX 991 electronic calculators** may be used; but they must NOT be transferred between students. Use of periodic tables or any aids other than those provided, is not allowed.

Note: Academic dishonesty may include, among other actions, communication of any kind (verbal, visual, etc.) between students, sharing of materials between students, copying or looking at other students' work. If a problem arises, please ask an invigilator to deal with it for you.

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QUESTIONS 1–25 ARE WORTH 2 MARKS EACH.

1. Ethanol, C_2H_5OH, is being promoted as a clean fuel and is used as an additive in many gasoline mixtures. Calculate the $\mathbf{\Delta H°_{rxn}}$ for the combustion of ethanol. $\Delta H°_f$ [$C_2H_5OH(l)$] = -277.7 kJ/mol; $\Delta H°_f$ [$CO_2(g)$] = -393.5 kJ/mol; $\Delta H°_f$ [$H_2O(g)$] = -241.8 kJ/mol

A) 357.6 kJ
B) -357.6 kJ 0.5 mark
C) 1234.7 kJ
D) -751.1 kJ 0.5 mark
E) -1234.7 kJ 2 marks

Combustion reaction of ethanol: $C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$
$\Delta H(rxn) = 2\ \Delta H_f^0(CO_2) + 3\ \Delta H_f^0(H_2O) - \Delta H_f^0(C_2H_5OH) = -1234.7$ kJ

2. How many mL of concentrated nitric acid (HNO_3, 16.0 *M*) should be diluted with water in order to make 2.00 L of 2.00 *M* solution?

A) 500. mL
B) 250. mL 2 marks
C) 62.5 mL
D) 32.0 mL
E) 125 mL

C_1V_1 (# moles HNO_3 in concentrated solution) = C_2V_2 ((# moles HNO_3 in dilute solution)
$V_1 = C_2V_2 / C_1 = 2.00 \times 2.00 / 16.0 = 0.250$ L = 250 mL

3. The minimum energy (in J) needed to ionize a hydrogen atom **from the *n* = 2 energy level** is

A) 1.64×10^{-18} J
B) 3.03×10^{-19} J
C) 2.18×10^{-18} J 0.5 mark
D) 5.45×10^{-19} J 2 marks
E) none of the above

Ionization corresponds to an electronic transition to the energy level n = ∞ (electron at an infinite distance from nucleus).
$\Delta E = -2.18 \times 10^{-18}\ J\ (1/\infty^2 - 1/2^2) = 5.45 \times 10^{-19}$ J

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4. In which one of the following reactions would you expect ΔH to be substantially **greater** than ΔU (i.e. $\Delta H > \Delta U$)?

A) $H_2O(s) \rightarrow H_2O(l)$
B) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
C) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
D) $CO_2(s) \rightarrow CO_2(g)$ 2 marks
E) $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$

From the definition of the enthalpy, $H = U + PV \rightarrow \Delta H = \Delta(U + PV) = \Delta U + \Delta(PV)$. ΔH will be larger than ΔU for reactions in which the volume of the chemical system increases significantly ($\Delta V > 0$), i.e. when there is a net production of gas.

5. Balance the following redox equation using the smallest integers possible and select the correct coefficient for the hydrogensulfite ion.
$MnO_4^-(aq) + HSO_3^-(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2O(l)$

A) 10 0.5 mark
B) 5 2 marks
C) 1
D) 3
E) 2

Mn is reduced from Mn(VII) to Mn(II) (gain of 5 electrons) and S is oxidized from S(IV) to S(VI) (loss of 2 electrons), so that 10 electrons must be transferred overall.

balance electron transfer: $2\ MnO_4^- + 5\ HSO_3^- \rightarrow 2\ Mn^{2+} + 5\ SO_4^{2-}$
balance ionic charges under acidic conditions: $H^+ + 2\ MnO_4^- + 5\ HSO_3^- \rightarrow 2\ Mn^{2+} + 5\ SO_4^{2-}$
balance masses with water: $H^+ + 2\ MnO_4^- + 5\ HSO_3^- \rightarrow 2\ Mn^{2+} + 5\ SO_4^{2-} + 3\ H_2O$

6. Select the correct set of quantum numbers (n, l, m_l, m_s) for the **highest-energy electron** in the ground state of indium, In.

A) 5 ,2, 0, ½
B) 5, 2, 1, ½
C) 5, 2, -1, -½
D) 5, 1, 2, -½
E) 5, 1, 0, ½ 2 marks

Indium (In) has Z = 49 $\rightarrow$ ground-state configuration is (Kr) $5s^2\ 4d^{10}\ 5p^1$.
The highest-energy electron is the 5p electron with $n = 5$, $l = 1$, $m_l = 0$ or ± 1, $m_s = \pm ½$.

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7. A system absorbs 21.6 kJ of heat while performing 6.9 kJ of work on the surroundings. If the initial internal energy, *U*, is 61.2 kJ, **what is the final value of *U***?

A) 75.9 kJ 2 marks
B) 32.7 kJ
C) 89.7 kJ
D) 46.5 kJ
E) 82.8 kJ

$\Delta U = U_{final} - U_{initial}$ = q (heat transferred) + w (work transferred) = + 21.6 kJ – 6.9 kJ = +14.7 kJ

U_{final} = 75.9 kJ

8. Select the **diamagnetic** ion.

A) V^{4+}
B) Cu^{2+}
C) Fe^{3+}
D) Ni^{2+}
E) Sc^{3+} 2 marks

A diamagnetic ion has no unpaired electrons. Scandium (Sc) has Z = 21 with a ground-state configuration of (Ar) $4s^2\ 3d^1$. Sc^{3+} has the Ar configuration ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) with all electrons paired.

9. Which of the following is a **basic** oxide?

A) SO_2
B) NO_2
C) CaO 2 marks
D) CO_2
E) H_2O

Oxides of metals from the s-block are all basic: $CaO + H_2O \rightarrow Ca(OH)_2$. Non-metal oxides are typically acidic (e.g. $SO_2 + H_2O \rightarrow H_2SO_3$, sulfurous acid).

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10. The successive ionization energies of a certain element are $I_1 = 577.9$ kJ/mol, $I_2 = 1820$ kJ/mol, $I_3 = 2750$ kJ/mol, $I_4 = 11{,}600$ kJ/mol, and $I_5 = 14{,}800$ kJ/mol. **Based on the shell structure of atoms**, this pattern of ionization energies suggests that the unknown element is

A) Kr
B) K 1 mark
C) Se
D) Al 2 marks
E) Cl

The successive ionization energies increase because it becomes more and more difficult to extract an electron as the cation charge increases. However, the I_4 and I_5 values are much larger than the I_1, I_2 and I_3 values indicating that the first 3 electrons are removed from the same shell (shell *n*) and the last 2 electrons are removed from a "deeper" shell of lower (more negative) energy (shell *n-1*). This is consistent with the ground-state configuration of Al (Z = 13) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$. The smaller jump from I_1 to I_2 and I_3 corresponds to the smaller energy difference between the 3p and the 3s sub-shells.

11. Which one of the following is most likely to be a **covalent** compound?

A) $CaSO_4$
B) KF
C) $CaCl_2$
D) SF_4 2 marks
E) Al_2O_3 0.5 mark

Covalent bonds form between non-metal atoms when the difference in electronegativity is small.

12. Which of the following elements has the **smallest** first ionization energy?

A) Na
B) Be
C) K 2 marks
D) As
E) Cl

Ionization energy decreases down a group and increases across a period (left → right).

13. Calculate the energy required for the gas phase process represented by
$Na(g) + Br(g) \rightarrow Na^{+}(g) + Br^{-}(g)$

Given:
First ionization energy (Na) = +496 kJ/mol
First ionization energy (Br) = +1140 kJ/mol
Electron affinity (Br) = – 324 kJ/mol
Electron affinity (Na) = – 53 kJ/mol

A) +172 kJ/mol 2 marks
B) –172 kJ/mol
C) +1636 kJ/mol
D) –820 kJ/mol
E) +820 kJ/mol

The reaction corresponds to the first ionization of Na (loss of one electron) combined with the capture of an electron by bromine (electron affinity).

$\Delta H = +496 \text{ kJ} - 324 \text{ kJ} = +172 \text{ kJ}$

14. The total number of **lone pairs** (or non-bonding electron pairs) in NCl_3 is

A) 1
B) 10 2 marks
C) 6
D) 9
E) 20 0.5 mark

The Lewis structure of NCl_3 contains 26 valence electrons: 3 N-Cl single bonds, 3 lone pairs on each Cl atom, one lone pair on the N atom. All formal charges are zero.

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15. Which one of the following molecules has a **zero** molecular dipole moment?

A) SO_2
B) CO
C) SF_4
D) XeF_4 2 marks
E) CH_2Cl_2 0.5 mark

XeF_4 (32 valence electrons) is an AX_4E_2 VSEPR molecule, with a geometry derived from the AX_6 (octahedral) shape. The molecule contains 4 Xe-F single bonds, 3 lone pairs on each F and 2 lone pairs on Xe. All formal charges are zero. The two lone pairs on Xe are as far apart as possible, i.e. occupy opposite positions. The Xe and F atoms form a square planar molecule. The four dipole moments of the polar (δ+)Xe-F(δ–) bonds sum up to zero as a result of the symmetrical geometry.

CH_2Cl_2 has an irregular (unsymmetrical) tetrahedral geometry in which the dipole moments of the C-H and C-Cl bonds do not cancel out.

16. Predict the geometry and polarity of the $\mathbf{CS_2}$ molecule.

A) linear, nonpolar 2 marks
B) tetrahedral, nonpolar
C) bent, polar
D) linear, polar
E) bent, nonpolar

The Lewis structure of the CS_2 molecule contains 16 valence electrons: S = C = S with 2 lone pairs on each S atom. The molecule is an AX_2 VSEPR type with a linear geometry, similar to CO_2. The dipole moments of the two polar (δ+)C=S(δ–) bonds cancel out.

17. The bond angle in Cl_2O is expected to be **closest** to

A) 120°
B) 90° 0.5 mark
C) 180°
D) 109.5° 2 marks
E) 145°

The Lewis structure of Cl_2O (Cl-O-Cl) contains 20 valence electrons, 2 Cl-O single bonds, 3 lone pairs on each Cl and 2 lone pairs on O. It is an AX_2E_2 VSEPR type with a bend or angular geometry derived from the tetrahedral AX_4 shape. The Cl-O-Cl bond angle is close to 109.5^o (smaller due to repulsion from the lone pairs).

18. Use a Born-Haber cycle to calculate the **lattice energy of NaBr(s)** given the following data:

Enthalpy of sublimation (ΔH_{sub}) of Na(s) = +177.8 kJ/mol
First ionization energy of Na = +495.9 kJ/mol
Bond energy (Br–Br) = +192.5 kJ/mol
Electron affinity of Br = – 325 kJ/mol
Enthalpy of formation (ΔH_f) of NaBr(s) = – 361.1 kJ/mol
Enthalpy of vaporization (ΔH_{vap}) of Br_2(l) = +30.9 kJ/mol

A) –450 kJ/mol
B) –1456 kJ/mol
C) –821 kJ/mol 2 marks
D) –709 kJ/mol 0.5 mark
E) –806 kJ/mol 1 mark

Apply Hess's law to the Born-Haber cycle based on the reaction of formation of NaBr(s):

$Na(s) + \frac{1}{2} Br_2(liq) \rightarrow NaBr(s)$

ΔH^0_f (NaBr(s)) = ΔH_{subl}(Na) +1/2 $\Delta H_{vap}(Br_2)$ + 1/2 BE (Br-Br) + ΔH_{ion}(Na) + EA(Br) + $\Delta H_{lattice}$(NaBr)

19. According to the VSEPR theory, what is the shape of a molecule with the general formula $\mathbf{AX_2E_3}$?

A) T-shaped
B) trigonal pyramidal
C) bent 0.5 mark
D) linear 2 marks
E) trigonal planar

The AX_2E_3 geometry is derived from the AX_5 trigonal bipyramidal geometry. The 3 lone pairs occupy the 3 equatorial positions so as to minimize the repulsions between them (with angles of 120^0 rather than 90^0). The symmetrical arrangement of the 3 lone pairs does not lead to angular distortion of the molecule.

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20. Which of the following molecules have the **same** geometries?

A) PCl_3 and $BrCl_3$
B) N_2O and NO_2 0.5 mark
C) BeF_2 and H_2O
D) SF_4 and CH_4
E) CO_2 and BeH_2 2 marks

E) CO_2 (O=C=O) and BeH_2 (H-Be-H) both correspond to the AX_2 VSEPR type with a linear geometry.
B) N_2O is linear whereas NO_2 is bent due to the single electron present on N.

21. Use the following bond energies to estimate the **enthalpy of formation** of HBr(g).
D(H–H) = 436 kJ/mol
D(Br–Br) = 192 kJ/mol
D(H–Br) = 366 kJ/mol

A) –52 kJ/mol 2 marks
B) +104 kJ/mol
C) +262 kJ/mol 0.5 mark
D) +52 kJ/mol
E) –104 kJ/mol 1 mark

The reaction of formation of HBr is: $1/2\ H_2(g) + 1/2\ Br_2(liq) \rightarrow HBr(g)$. *Note that, with the data given, one has to ignore the fact that bromine is a liquid at standard T, P, i.e., ignore the small enthalpy of vaporization of bromine (31 kJ/mol Br_2).*

$\Delta H(rxn) = ½\ D(H\text{-}H) + ½\ D(Br\text{-}Br) – D\ (H\text{-}Br) = –52$ kJ/mol

22. The equilibrium constant, K_p, for the reaction $CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$ at 986°C is equal to 0.63. A rigid cylinder at that temperature contains 1.2 atm of carbon monoxide, 0.20 atm of water vapor, 0.30 atm of carbon dioxide, and 0.27 atm of hydrogen. Is the system at equilibrium?

A) No, the forward reaction must proceed to establish equilibrium. 2 marks
B) Need to know the starting concentrations of all substances before deciding.
C) Yes.
D) No, the reverse reaction must proceed to establish equilibrium.
E) Need to know the volume of the container before deciding.

The reaction quotient $Q = [P(CO_2) \times P(H_2)] / [P(CO) \times P(H_2O)] = 0.34$.
$Q \neq K_p$, therefore the reaction is not at equilibrium.
$Q < K_p$, therefore the reaction will shift in the forward direction to increase Q.

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23. Consider the following reaction at equilibrium: $2\ SO_2(g) + O_2(g) \leftrightarrow 2\ SO_3(g)$, with $\Delta H^o_{rxn} = -198$ kJ/mol.
If the volume of the system is decreased at constant temperature, what change will occur in the position of the equilibrium?

A) A shift to produce more SO_3 2 marks
B) A shift will occur in the endothermic direction
C) A shift to produce more O_2
D) No change
E) A shift to produce more SO_2

A decrease in volume is equivalent to an increase in pressure of the gas mixture. The system responds by reducing the amount of gas present (to maintain a constant pressure), i.e. by shifting in the forward direction.

24. Hydrogen sulfide will react with water as shown in the following reactions. What is the value of $\mathbf{K_2}$?

$H_2S(g) + H_2O(l) \leftrightarrow H_3O^+(aq) + HS^-(aq)$ $K_1 = 1.0 \times 10^{-7}$
$HS^-(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + S^{2-}(aq)$ $K_2 = ?$
$H_2S(g) + 2\ H_2O(l) \leftrightarrow 2\ H_3O^+(aq) + S^{2-}(aq)$ $K_3 = 1.3 \times 10^{-20}$

A) 7.7×10^{12} 0.5 mark
B) 1.3×10^{-27}
C) 7.7×10^{26}
D) 1.3×10^{-13} 2 marks
E) 2.3×10^{-7}

reaction 2 = reaction 3 – reaction 1 $\rightarrow$ $K_2 = K_3 / K_1$. This can be also derived by writing the expressions of K_1, K_2 and K_3.

25. When the following reaction is at equilibrium, which of these relationships is **always true**?

$$2\ NOCl(g) \leftrightarrow 2\ NO(g) + Cl_2(g)$$

A) $p(NOCl) = p(NO)$
B) $p(NO) = 2\ p(Cl_2)$
C) $K_p\ p(NO)^2\ p(Cl_2) = p(NOCl)^2$
D) $p(NO)^2\ p(Cl_2) = K_p\ p(NOCl)^2$ 2 marks
E) $p(NO)\ p(Cl_2) = p(NOCl)$

D) Simply from the definition of K_p (always written for the forward reaction).
B) True only in experiments where one starts with pure NOCl gas.

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QUESTIONS 26-30 ARE WORTH 3 MARKS EACH.

26. Which ones of the following statements are **TRUE**?

i) Copper metal does not react with hydrochloric acid.
ii) Zinc metal reacts with hydrochloric acid and chlorine gas is evolved.
iii) An oxidation-reduction reaction takes place between zinc metal and copper(II) ions in aqueous solution.
iv) Copper metal reacts with nitric acid producing copper nitrate and hydrogen gas.
v) When aqueous sodium hydroxide is added to aqueous copper(II) sulfate and the solution is heated, copper(II) oxide is formed.

A) i, iii, v 3 marks
B) ii, iv
C) iii, v 2 marks
D) i, ii, iii 1 mark
E) i, iv

Refer to the lab experiments # 2 and 3.
Note the following:
ii) When Zn reacts with HCl(aq), H_2 gas is produced.
iv) When copper reacts with HNO_3(aq), the oxidizing agent is NO_3^- (not H^+) and NO or NO_2 gas is formed.
v) Cu(II) sulfate reacts like Cu(II) nitrate used in lab #3, both salts yield Cu^{2+}(aq) that forms a precipitate of $Cu(OH)_2$ when NaOH(aaq) is added.

27. A **pure** sample of NO_2(g) is introduced in an evacuated container at 1000 K. NO_2(g) decomposes according to the reaction $2\ NO_2(g) \leftrightarrow 2\ NO(g) + O_2(g)$, with an equilibrium constant $K_p = 158$ at 1000 K. When equilibrium is reached, the partial pressure of O_2(g) = 0.25 atm. What are the equilibrium partial pressures (in atm) of NO(g) and NO_2(g) (in that order)?

A) 0.250, 2.0×10^{-2}
B) 0.50, 2.0×10^{-2} 3 marks
C) 0.125, 4.0×10^{-4}
D) 0.50, 4.0×10^{-4} 1.5 marks
E) 0.125, 2.0×10^{-2}

According to the reaction, if one starts with pure NO_2 gas, the NO and O_2 gases are always present in a 2:1 mole ratio, i.e. $p(NO) = 2 \times p(O_2) = 0.50$ atm.

$K_p = p(NO)^2 \times p(O_2) / p(NO_2)^2 \rightarrow p(NO_2) = [(0.50)^2 \times (0.25) / 158]^{1/2} = 0.02$ atm

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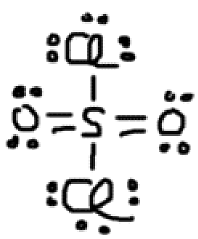
28. Which of the following statements are **TRUE** about SO_2Cl_2? (S is the central atom and is bonded to 2 O and 2 Cl atoms.)

(i) The molecule has a permanent dipole moment.
(ii) The molecule has a square pyramidal geometry about S.
(iii) There is one lone pair of electrons on S.
(iv) All the atoms have a formal charge of zero in the charge-minimized Lewis structure.
(v) The oxidation number of sulfur is +4.
(vi) The molecule belongs to the AX4 VESPR class.

A) iii, iv 0.5 mark
B) i, iv, vi 3 marks
C) iv, vi 2 marks
D) ii, vi 0.5 mark
E) i, v 0.5 mark

The Lewis structure contains 32 valence electrons:

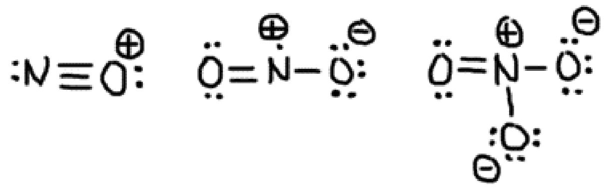


i) true: AX_4 irregular tetrahedral geometry with different dipole moments for the S=O and S-Cl bonds → polar molecule
ii) false
iii) false
iv) true
v) false, S is in the +VI oxidation state
vi) true, double and single bonds are equivalent in the VSEPR model

29. For the molecular ions NO^+, NO_2^- and NO_3^-, what is the correct order of **decreasing bond length**?

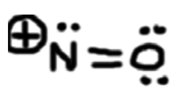
A) $NO_3^- > NO_2^- > NO^+$ 3 marks
B) $NO_2^- > NO_3^- > NO^+$ 1.5 marks
C) $NO_3^- > NO^+ > NO_2^-$ 1 mark
D) $NO^+ > NO_2^- > NO_3^-$
E) $NO_2^- > NO^+ > NO_3^-$

The Lewis structures contain 10, 17 and 24 valence electrons for NO^+, NO_2^- and NO_3^-:



Bond length decreases when the (average) bond order increases:
4/3 = 1.33 in NO_3^-, 3/2 = 1.5 in NO_2^-, 3 in NO^+.

Note that one can write a resonance Lewis structure for NO^+ that avoids the formal (+) charge on the more electronegative O:



Considering the two resonance forms, the average bond order in NO^+ is 2.5, still the largest of all three species.

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30. Which of the following statements about periodic trends are **TRUE**?

(i) The correct sequence for decreasing ionic radius is: $Br^{-} > Rb^{+} > Sr^{2+}$.
(ii) The ground-state electron configuration of bromine has no unpaired electrons.
(iii) The oxide of strontium is a basic oxide.
(iv) Rubidium is oxidized more easily than sodium.
(v) The electronegativity of chlorine is smaller than that of phosphorus.

A) i, iv 2 marks
B) ii, v
C) iii, iv, v
D) i, ii, iv 1.5 marks
E) i, iii, iv 3 marks

i) True, Br^{-}, Rb^{+} and Sr^{2+} are isoelectronic ions and their size decreases with increasing atomic number (nuclear charge).
ii) False, Br (Z = 35) has a configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
iii) True, like for all metals of the s block
iv) True, ionization energy decreases and/or reactivity increases down group I
v) False, electronegativity increases with nuclear charge (Z) from left to right across a period.