Name: _____   Student number: _____

Chemistry 1E03   **Test 2**   **Nov. 13, 2015**

McMaster University   *VERSION 1*

Instructors: Drs. R.S. Dumont, P. Kruse & L. Davis

Duration: 120 minutes

This test contains 18 numbered pages printed on both sides. There are **25** multiple-choice questions appearing on pages numbered 3 to 13. Pages 14 and 15 provide extra space for rough work. Page 16 includes some useful data and equations, and there is a periodic table on page 17. You may tear off the last pages to view the periodic table and the data provided.

You must enter your 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.

You are responsible for ensuring that your copy of the question paper is complete. Bring any discrepancy to the attention of your invigilator.

All questions are worth 1 mark; the total marks available are 25. There is **no** additional penalty for incorrect answers.

BE SURE TO ENTER THE CORRECT VERSION NUMBER OF YOUR TEST (shown near the top of page 1), IN THE SPACE PROVIDED ON THE ANSWER SHEET.

<u>**ANSWER ALL QUESTIONS**</u> **ON THE ANSWER SHEET, IN PENCIL.**
Instructions for entering multiple-choice answers are given on page 2.
SELECT <u>ONE AND ONLY ONE</u> **ANSWER FOR EACH QUESTION** from the answers **(A)** through **(E). No work written on the question sheets will be marked**. The question sheets may be collected and reviewed in cases of suspected academic dishonesty.

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 you have a problem please ask the invigilator to deal with it for you. Do not make contact with other students directly. Keep your eyes on your own paper – looking around the room may be interpreted as an attempt to copy answers.

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.

Name: _____   Student number: _____

OMR EXAMINATION – STUDENT INSTRUCTIONS

NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED: YOUT EXAMINIATION RESULT DEPENDS UPON PROPER ATTENTION TO THESE INSTRUCTIONS.

The scanner, which reads the sheets, senses the bubble shaded areas by their non-reflection of light. A heavy mark must be made, completely filling the circular bubble, with an HB pencil. Marks made with a pen will **NOT** be sensed. Erasures must be thorough or the scanner will still sense a mark. Do **NOT** use correction fluid on the sheets. Do **NOT** put any unnecessary marks or writing on the sheet.

1. On SIDE 1 (**red side**) of the form, in the top box, *in pen*, print your student number, name, course name, and the date in the spaces provided. Then you **MUST** write your signature, in the space marked SIGNATURE.

2. In the second box, *with a pencil*, mark your student number, **exam version number** in the space provided and **fill in the corresponding bubble numbers underneath**.

3. Answers: mark only **ONE** choice from the alternatives (A,B,C,D,E) provided for each question. The question number is to the left of the bubbles. Make sure that the number of the question on the scan sheet is the same as the number on the test paper.

4. Pay particular attention to the Marking+ Directions on the form.

5. Begin answering the question using the first set of bubbles, marked "1".

1. The O–H bond energy in water is approximately 467 kJ mol^{-1}. What is the **wavelength** of the photon with just enough energy to break one O–H bond?

   .
   A) 467 nm
   B) 213 nm
   C) 256 nm
   D) 4130 nm
   E) 23.7 nm

E = 467 kJ/mol / 6.022 x 10^{23} mol^{-1} = 7.755 x 10^{-19} J = h c / λ. So we can solve for λ.

2. Which one of the following atoms has the **largest** first ionization energy? (Hint: consider the ground state electron configurations for these atoms.)

   .
   A) Al
   B) Si
   C) S
   D) K
   E) P

All options are 3rd row elements. As a general trend, the first ionization energies increase left to right across the periodic table. However, P ([Ne]3s^{2}3p^3) has a half-filled 3p shell, and therefore there is a local exception to this trend where the first ionization energy of P is slightly higher than the element to the right, S ([Ne]3s^{2}3p^4).

3. Identify the **incorrect** combination of quantum numbers (n,ℓ,m_ℓ) for the given atomic orbitals:

   .
   A) 2p   (2, 1, –1)
   B) 4s   (4, 0, 0)
   C) 2p   (2, 1, 0)
   D) 3s   (3, 0, 1)
   E) 3d   (3, 2, –2)

The rules for the quantum numbers include that n>l, which all options fulfill, n>0 and l≥0, which all options also fulfill, and l≥|ml|, which is violated by (3, 0, 1).

4. Which of the following statements are **TRUE**?
   (i)   Br atoms are smaller than As atoms.
   (ii) O has a higher first ionization energy than N.
   (iii) Li has a higher magnitude of electron affinity than O.
   (iv) Ba is easier to ionize than Sr.
   (v) Cl^- is a larger ion than Ca^{2+}.
   .

A) i, iv, v
B) i, iii, v
C) ii, iii, v
D) i, ii, iv
E) all

Statement (ii) is wrong. Similarly to question 2, N ([He]2s²2p³) has a relatively stable half-filled 2p shell, and therefore the first ionization energy of N is slightly higher than O ([He]2s²2p⁴).

Statement (iii) is wrong, because as a general trend, the magnitudes of the electron affinities increase from left to right across the periodic table.

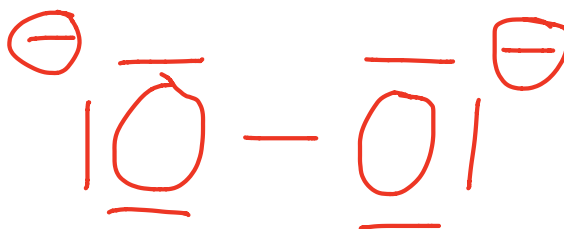5. Choose the **FALSE** statement about the Lewis structure of the peroxide anion, O_2^{2-}:
   .
A) Each oxygen atom has 3 nonbonding electron pairs.
B) Each oxygen atom carries a formal charge of -1.
C) The oxygen-oxygen bond is a single bond.
D) Each oxygen atom obeys the octet rule.
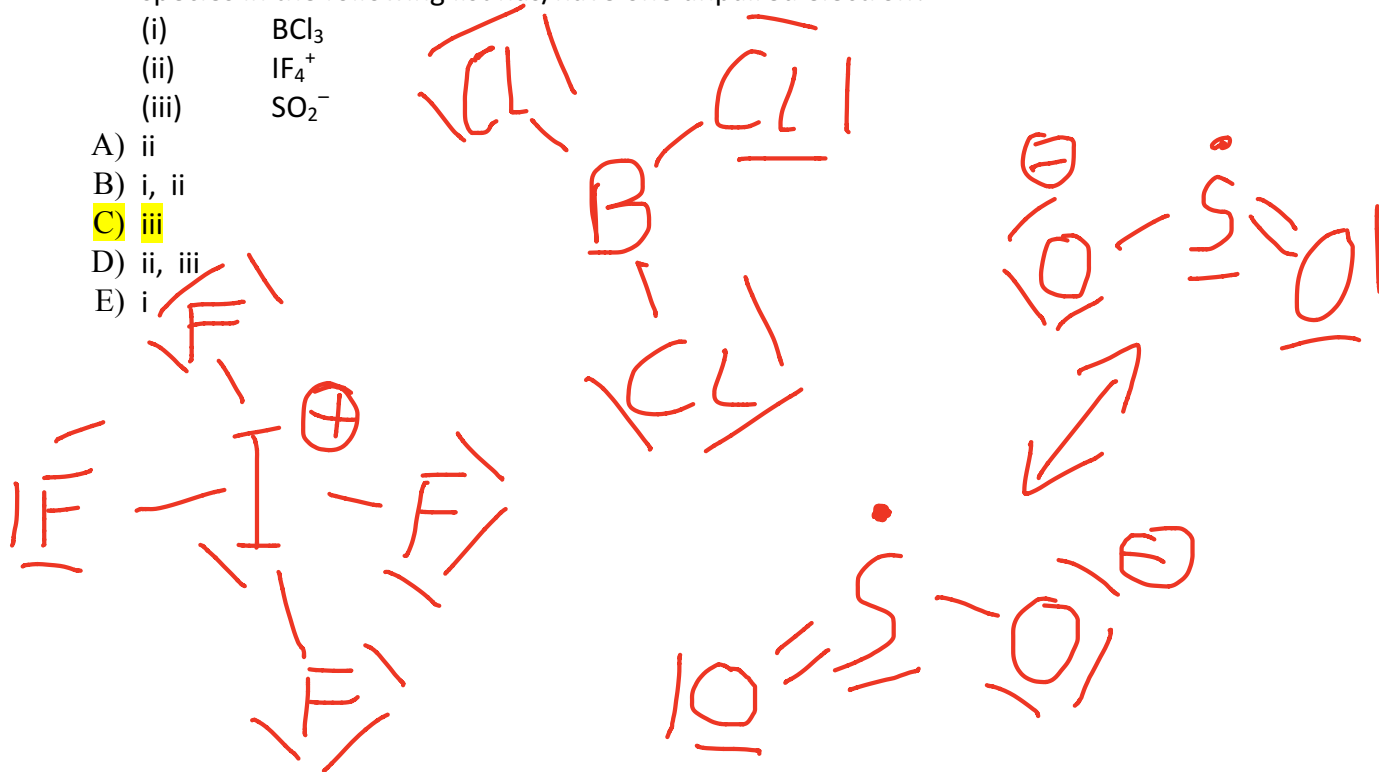E) Two resonance forms are required to describe bonding in this anion.

It is not even possible to distribute the electrons in any other way...

6. Free radicals and radical ions are species with one **unpaired electron**. Which of the species in the following list has/have one unpaired electron?
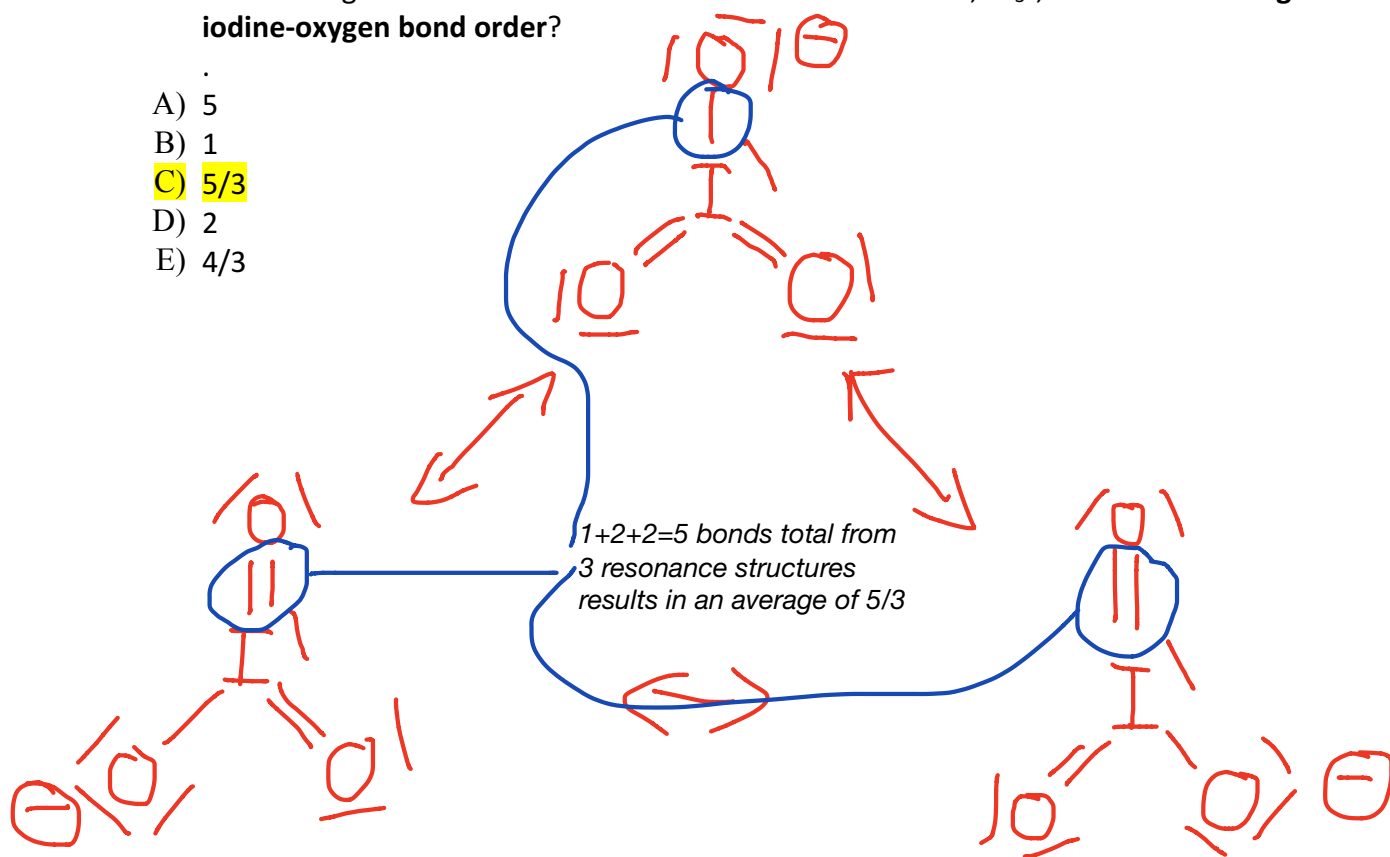   (i) BCl_3
   (ii) IF_4^+
   (iii) SO_2^-

A) ii
B) i, ii
C) iii
D) ii, iii
E) i

7. In the charge-minimized Lewis structures for the iodate ion, IO_3^-, what is the **average iodine-oxygen bond order**?
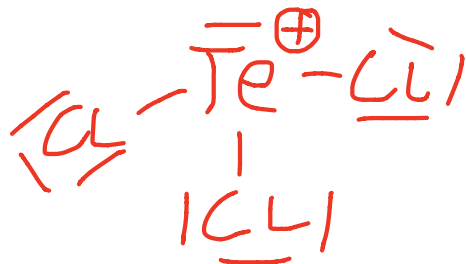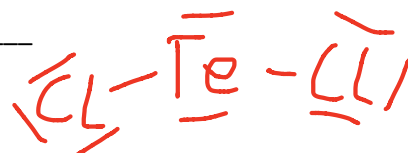   .
A) 5
B) 1
C) 5/3
D) 2
E) 4/3

1+2+2=5 bonds total from 3 resonance structures results in an average of 5/3

8. Which of the following statements is(are) **TRUE**?
   (i) $TeCl_2$ is a bent molecule.
   (ii)   All of the atoms of $TeCl_3^+$ are in the same plane.
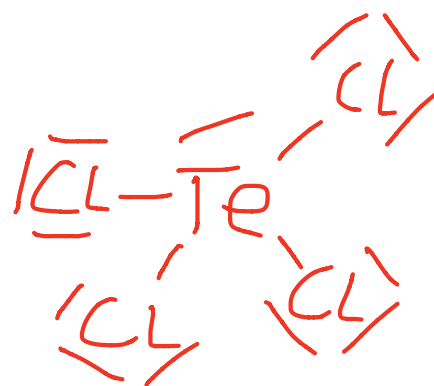   (iii) $TeCl_4$ has one nonbonding pair of electrons on tellurium.

A) i, ii
B) i, iii
C) ii
D) iii
E) i

4 domains around the central atom, 2 bonds and 2 lone pairs: the resulting shape is bent.

4 domains around the central atom, 3 bonds and one lone pair: the resulting shape is a trigonal pyramid.
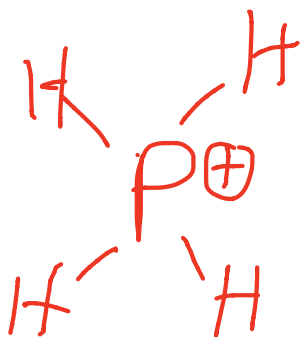
Indeed, there is a nonbonding electron pair...

9. Identify the cation(s) with a non-zero molecular dipole moment from among the following (the central atom is underlined):
   (i) $\underline{P}H_4^+$
   (ii) $H_3\underline{O}^+$
   (iii) $\underline{N}O_2^+$
   (iv) $\underline{Cl}F_2^+$
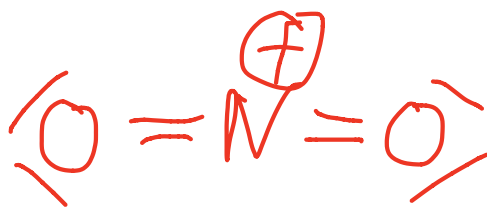
A) iii
B) ii, iv
C) i, iii
D) ii
E) none

tetrahedral, symmetric, no dipole
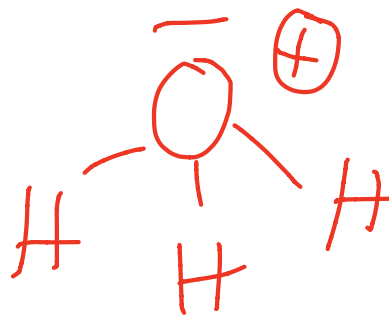
trigonal pyramid, polar covalent, dipole

linear, symmetric, no dipole
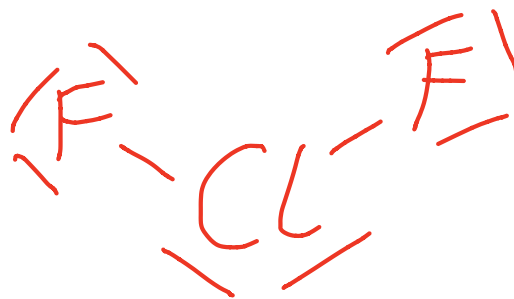
bent, polar covalent, dipole

10. Rank the species CO_2, CO, CO_3^{2-} and HCO_2^- in order of **increasing bond order** of the carbon-oxygen bonds.
.

A) $HCO_2^- < CO_3^{2-} < CO_2 < CO$
B) $CO_3^{2-} < HCO_2^- < CO < CO_2$
C) $CO < CO_2 < HCO_2^- < CO_3^{2-}$
D) $CO < CO_3^{2-} < HCO_2^- < CO_2$
E) $CO_3^{2-} < HCO_2^- < CO_2 < CO$

$:C\equiv O:$ B.O. = 3

$O = C = O$ B.O. = 2

B.O. = 3/2

B.O. = 4/3
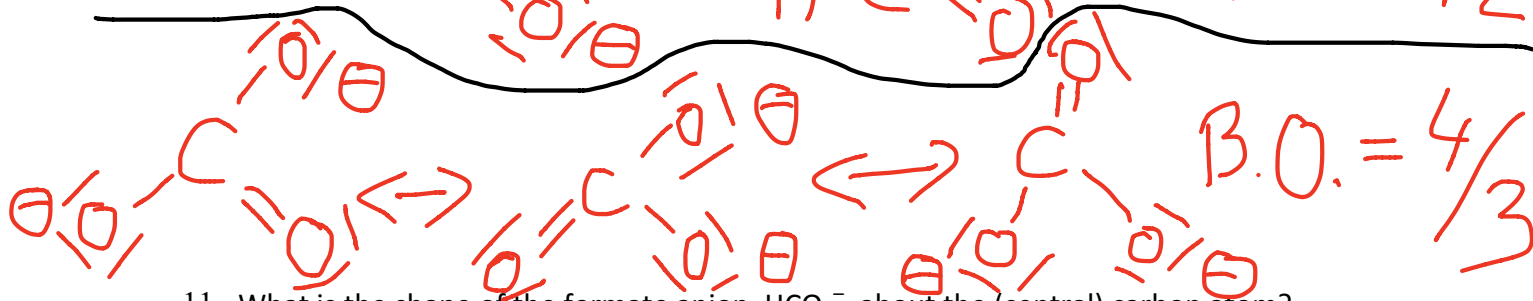
11. What is the shape of the formate anion, HCO_2^-, about the (central) carbon atom?
.

A) triangular pyramidal
B) tetrahedral
C) triangular planar
D) T-shaped
E) linear
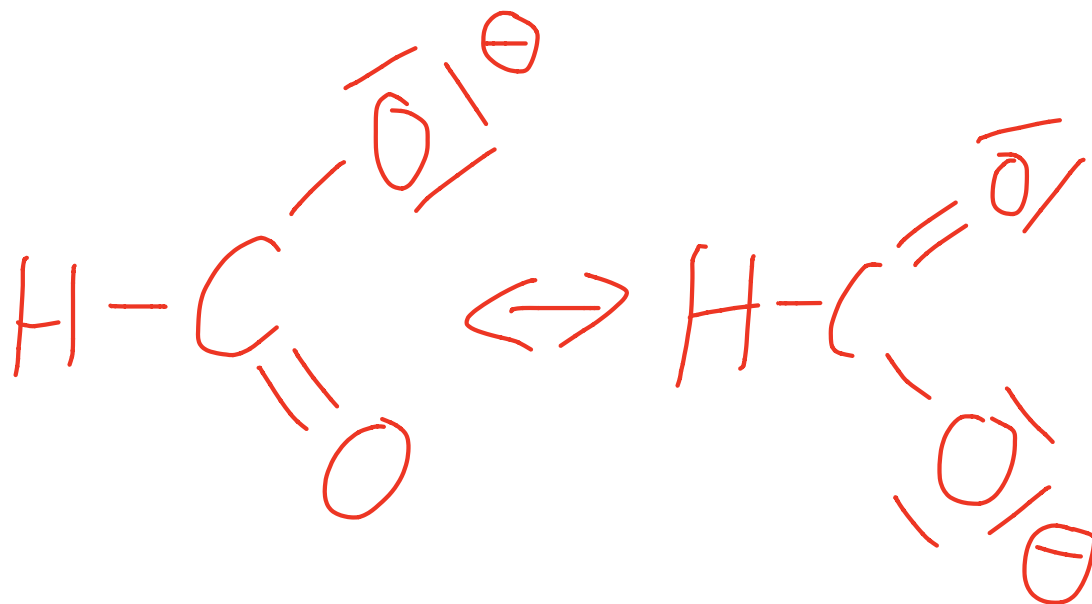
12. During experiment 2, Cycles of Copper, a student obtains a percent yield of 108%. What is the most likely source of error?
.
A) 108% is a valid yield as the atomic weight of copper at the end of the experiment is higher than at the start.
B) The student accidently added too much nitric acid in the first step.
C) There was residual solvent left within the copper precipitate at the end of the experiment.
D) Not all of the zinc reacted with the Cu^{2+} (aq) to yield Cu(s).
E) Copper oxide was lost during the decanting step.

The atomic weight is constant and does not change. Loosing copper oxide will decrease the yield. A yield above 100% is the result from contaminated product, e.g. with residual solvent.

13. Which statement is **FALSE** regarding the following three product-favored reactions?
   (i) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
   (ii) $H_2SO_3(aq) + NaOCl(aq) \rightarrow NaHSO_3(aq) + HOCl(aq)$
   (iii) $KH_2PO_4(aq) + KOH(aq) \rightarrow H_2O(l) + K_2HPO_4(aq)$
   .
A) All of these reactions are Brønsted-Lowry acid-base reactions.
B) In reaction (ii), H_2SO_3 is acting as a Brønsted-Lowry acid.
C) NH_4^+ is the conjugate acid of NH_3.
D) HOCl is the conjugate acid of OCl^-.
E) HOCl is a stronger acid than H_2SO_3.

If HOCl was a stronger acid than H_2SO_3, then the reaction would be going the other way, because the stronger acid is the stronger proton donor.

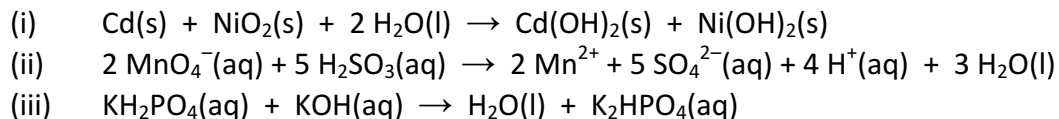14. Dichromate ions, $Cr_2O_7^{2-}$(aq), react with zinc metal in acid solution to produce Cr^{3+}(aq) and Zn^{2+}(aq) ions. When the reaction is balanced, such that the smallest possible integers appear as stoichiometric coefficients, what is the **coefficient** of Zn^{2+}?
.

A) 2
B) 1
C) 6
D) 4
E) 3

$3\ Zn + Cr_2O_7^{2-} + 14\ H^+\ \rightarrow\ 2\ Cr^{3+} + 3\ Zn^{2+} + 7\ H_2O$
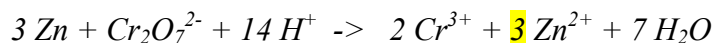
15. Which statement is **TRUE** regarding the following three reactions?
   (i) $Cd(s) + NiO_2(s) + 2\ H_2O(l) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$
   (ii) $2\ MnO_4^-(aq) + 5\ H_2SO_3(aq) \rightarrow 2\ Mn^{2+} + 5\ SO_4^{2-}(aq) + 4\ H^+(aq) + 3\ H_2O(l)$
   (iii) $KH_2PO_4(aq) + KOH(aq) \rightarrow H_2O(l) + K_2HPO_4(aq)$
   .

A) In reaction (iii), $H_2PO_4^-$ is acting as a Brønsted-Lowry base.
B) In reaction (iii), HPO_4^{2-} is the conjugate acid of $H_2PO_4^-$.
C) In reaction (i), Cd(s) is oxidized.
D) In reaction (ii), sulfur is reduced.
E) In reaction (i), NiO_2 is the reducing agent.

$H_2PO_4^-$ is acting as an acid during this particular reaction, because it is loosing a proton.
HPO_4^{2-} is hence the conjugated base to $H_2PO_4^-$, not its conjugated acid.
In (ii), sulfur goes from the +4 to the +6 oxidation state, i.e. it is further oxidized.
In (i) nickel is reduced from the +4 to the +2 oxidation state, i.e. it is the oxidizing agent here.

16. An unknown aqueous solution contains either KNO_3 or K_3PO_4. Addition of which **one** of the following aqueous solutions provides a simple visual test that identifies the unknown?
   .

A) LiBr
B) Na_2SO_4
C) RbOH
D) NaCl
E) $CaBr_2$

Calcium nitrate, like other nitrates, is soluble (see solubility rule 2), while alkali metal phosphates are also soluble (see solubility rule 8), leaving calcium phosphate as the only possible non-soluble combination (see solubility rule 8) from the given ions. It will precipitate out and give an easy visual indication of the contents of the unknown solution.

17. For the heterogeneous reaction,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g),$$
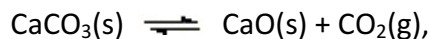
the equilibrium constant at 112°C is $K_p = 0.220$.   If the partial pressure of $CO_2(g)$ is 0.50 bar at this same temperature, which one of the following statements is **TRUE**?

.

A) $Q > K$, the reaction will proceed to the left.
B) $Q = K$, the system is at equilibrium.
C) $Q < K$, the reaction will proceed to the right.
D) $Q < K$, the reaction will proceed to the left.
E) $Q > K$, the reaction will proceed to the right.

Because $CaCO_3$ and CaO are both solids, their activities are 1, and $Q = P_{CO2} = 0.5$. Hence $Q>K$. The only way to decrease Q in order to approach equilibrium is by reducing the activity of the products and/or increasing the activity of the reactants, meaning that the reaction needs to proceed to the left.

18. A student creates a calibration curve relating the absorbance of $FeSCN^{2+}(aq)$ to the concentration of $FeSCN^{2+}(aq)$. The slope of this plot is 1.68. If a student mixes 10.0 mL of 0.20 M $Fe^{3+}(aq)$ with 10.0 mL of 0.40 M $SCN^-(aq)$ an absorbance of 0.084 is observed. What is the **equilibrium constant** for the reaction?

.

A) 120
B) 44
C) 3.2
D) 6.7
E) 12

Mixing the two solutions of equal volumina will double the total volume and hence half the initial concentration of each reactant. To 0.1 M for Fe^{3+} and 0.2 M for SCN^- respectively. From a final (equilibrium) absorbance of 0.084 and the slope of the calibration curve of 1.68 we know that the equilibrium concentration of $FeSCN^{2+}$ is 0.05 M. Due to the 1:1 stoichiometry, the equilibrium concentrations of the reactants have to be 0.1 M - 0.05 M = 0.05 M for Fe^{3+} and 0.2 M – 0.05 M = 0.15 M for SCN^-. The equilibrium constant can be calculated to be $K = 0.05 / (0.05 * 0.15) = 6.7$.

19. 1.41 bar of $PCl_5(g)$, 7.95 bar of $PCl_3(g)$ and 7.95 bar of $Cl_2(g)$ are at equilibrium in a reaction vessel. Calculate the **equilibrium constant** K_p for
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
at the temperature of the equilibrium mixture.

.

A) 28.6
B) −1.30
C) 44.8
D) 51.8
E) 9.71

$K_P = P_{Cl2} * P_{PCl3} / P_{PCl5} = (7.95)^2 / 1.41 = 44.8$

20. The equilibrium constant K_p for
$$C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$$
is 1.52 at 700°C. If the partial pressure of CO in an equilibrium mixture at 700°C is 1.30 bar, what is the **partial pressure** of CO_2 (in bar)?

.

A) 1.11
B) 0.860
C) 0.900
D) 1.30
E) 1.17

$K_P = P_{CO}^2 / (1 * P_{CO2})$ => $P_{CO2} = P_{CO}^2 / K_P = (1.3)^2 / 1.52 = 1.11$

21. Select the one **false** statement concerning the equilibrium,
$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$
for which $\Delta H° = 100.6$ kJ.
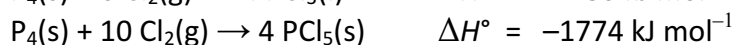
.

A) Removing $CO_2(g)$ increases the amount of MgO(s).
B) Doubling the amount of all three species (with the volume of the reaction vessel fixed) has no effect on the equilibrium.
C) Increasing the temperature increases the amount of MgO(s).
D) Adding MgO(s) does not change the amount of $MgCO_3(s)$.
E) Halving the size of the reaction vessel increases the amount of $MgCO_3(s)$.

Doubling the amount of all 3 species will not affect the activities of $MgCO_3$ and MgO because the are pure solids and have activities of 1, but it will the partial pressure of CO_2 will double at constant volume, which does impact the equilibrium. All other statements are indeed correct.

22. $PCl_5(s)$ can be prepared by the reaction,

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s).$$
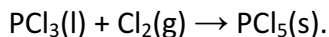
Calculate the **enthalpy change** (in kJ) that accompanies the production of 100.0 g of $PCl_5(s)$ by the above reaction, given the following data.

$P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(l)$	$\Delta H° =$	-1280 kJ mol^{-1}
$P_4(s) + 10\ Cl_2(g) \rightarrow 4\ PCl_5(s)$	$\Delta H° =$	-1774 kJ mol^{-1}

.
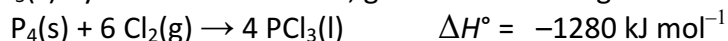
A) −124.7
B) +124.7
C) −258.1
D) −59.31
E) +59.31

$\Delta H°_f (PCl_3) = (-1280\ kJ / mol) / 4 = -320.0\ kJ / mol$
$\Delta H°_f (PCl_5) = (-1774\ kJ / mol) / 4 = -443.5\ kJ / mol$
$\Delta H°_{rxn} = -443.5\ kJ / mol - (-320.0)\ kJ / mol = -123.5\ kJ / mol$
Molar mass of PCl_5 is $31.0 + 5 * 35.5 = 208.5$ g / mol. 100.0 g of PCl_5 therefore corresponds to to 0.480 mol, the production of which is accompanied by a ΔH of about -59.3 kJ.

23. Determine the **enthalpy of formation** (in kJ mol^{-1}) of hydrogen chloride gas using the following bond energy data:

Cl-Cl	243 kJ mol^{-1}
H-H	436 kJ mol^{-1}
H-Cl	431 kJ mol^{-1}

.

A) −53.4
B) 17.1
C) 91.5
D) −17.1
E) −91.5

$0.5\ H_2 + 0.5\ Cl_2 \rightarrow HCl$, because the enthalpy of formation is defined as 1 mole of products from the elements in their most stable form under standard conditions.
Hence
$\Delta H°_f (HCl) = 0.5 * 243\ kJ/mol + 0.5 * 436\ kJ/mol - 431\ kJ/mol = -91.5\ kJ/mol$
Note that because of the sign convention of bond energies the products are subtracted from the reactants in this case.

24. A chemical reaction with an enthalpy change $\Delta H° = -400$ kJ is carried out in a calorimeter containing 1500 cm^3 of pure water initially at 25.0°C. What is the **final temperature** (in °C) of the water?

.

A) 336.7
B) -28.7
C) 69.3
D) 67.5
E) 88.8

*Assuming a density of 1.00 g/mL and a specific heat capacity of 4.18 J K^{-1} g^{-1} for water, the heat capacity of the calorimeter containing 1500 mL of water is approximated to be 1500 * 4.18 J / K. A ΔH of -400 kJ indicates exothermicity and will therefore lead to a temperature rise of 4 x 10^5 / (1500 * 4.18) K = 63.8 K. Since we start at 25°C, this gets us up to a final temperature of 88.8°C.*

25. Dissolving 4.24 g of CaF$_2$ in 50.0 mL of pure water at 20.00°C results in a solution with temperature 16.79°C. What is the **enthalpy of dissolution of CaF$_2$ (in kJ mol^{-1})?** Assume that the specific heat of the solution equals 4.18 J K^{-1} g^{-1}.

.

A) +1.05
B) +13.4
C) -1.05
D) -671
E) -13.4

*We end up with 54.24 g of a solution with a specific heat capacity of 4.18 J K^{-1} g^{-1}. The temperature decreased by 3.21 K. Therefore the enthalpy of dissolution of 4.24 g of CaF$_2$ is 54.24 * 4.18 * 3.21 J = 727.8 J. The molar mass of CaF$_2$ is 40.1 + 2 * 19.0 = 78.1 g/mol, with 4.24 g of the material corresponding to 0.0543 mol. Hence the molar enthalpy of dissolution of CaF$_2$ is 727.8 / 0.0543 J/mol = 13.4 kJ/mol*

Name: _____   Student number: _____

Extra space for rough work:

Name: _____   Student number: _____

Extra space for rough work:

Name: _____   Student number: _____

- **Some general data are provided on this page.**

- **A Periodic Table with atomic weights is provided on the next page.**

$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$

$c = 2.9979 \times 10^8 \text{ m s}^{-1}$

$m_e = 9.10 \times 10^{-31} \text{ kg}$

$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$h = 6.6256 \times 10^{-34} \text{ Js}$

1 bar = 100.0 kPa

$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = 0.01 \text{ L bar} = 1 \text{ Pa m}^3$

$1 \text{ cm}^3 = 1 \text{ mL}$

1 Hz = 1 cycle/s

0°C = 273.15 K

$1 \text{ m} = 10^9 \text{ nm} = 10^{10} \text{ Å}$

$1 \text{ g} = 10^3 \text{ mg}$

De Broglie wavelength:

$\lambda = h / mv = h / p$

Hydrogen atom energy levels:

$E_n = -R_H / n^2 = -2.178 \times 10^{-18} \text{ J} / n^2$

Density of water:

1.00 g mL^{-1}

Specific heat capacity of water:

$4.18 \text{ J K}^{-1} \text{ g}^{-1}$

Solubility Guidelines for Common Ionic Solids

1. Alkali metal and ammonium salts are *soluble*.
2. Nitrate, chlorate, perchlorate, hydrogen carbonate and ethanoate salts are *soluble*.
3. Sulfate salts are *soluble*, *except* for the calcium, strontium, barium and lead salts which are *insoluble*.
4. Chloride, bromide and iodide salts are *soluble*, *except* for the silver, lead and mercury I salts which are *insoluble*.
5. Silver, lead and mercury I salts are *insoluble*, unless deemed soluble by rule 2 or 3.
6. Sulfide salts are *insoluble*, *except* for the alkali metal, ammonium, and alkaline earth salts which are *soluble*.
7. Oxide and hydroxide salts are *insoluble*, *except* for the alkali metal, ammonium, calcium, strontium and barium salts which are soluble.
8. Carbonate and phosphate are *insoluble*, *except* for the alkali metal and ammonium salts.

END OF EXAM