Name: _____ Student number: _____

Chemistry 1A03 **Test 2** **November 7, 2008**

McMaster University **VERSION 1** **ANSWERS in BLUE**

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Duration: 120 minutes

This test contains 24 numbered pages printed on both sides. There are **30** multiple-choice questions appearing on pages numbered 3 to 21. Page 22 is extra space for rough work. Page 23 includes some useful data and equations, and there is a periodic table on page 24. You may tear off the last page 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.

Questions 1 to 23 are each worth 2 marks, questions 24 – 30 are each worth 3 marks; the total marks available are 67. There is **no** additional penalty for incorrect answers.
BE SURE TO ENTER THE CORRECT VERSION OF YOUR TEST (shown near the top of page 1), IN THE SPACE PROVIDED ON THE ANSWER SHEET.

ANSWER ALL QUESTIONS ON THE ANSWER SHEET, IN PENCIL.
Instructions for entering multiple-choice answers are given on page 2.
SELECT ONE AND ONLY ONE 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. Try to keep your eyes on your own paper – looking around the room may be interpreted as an attempt to copy.

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.

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OMR EXAMINATION – STUDENT INSTRUCTIONS

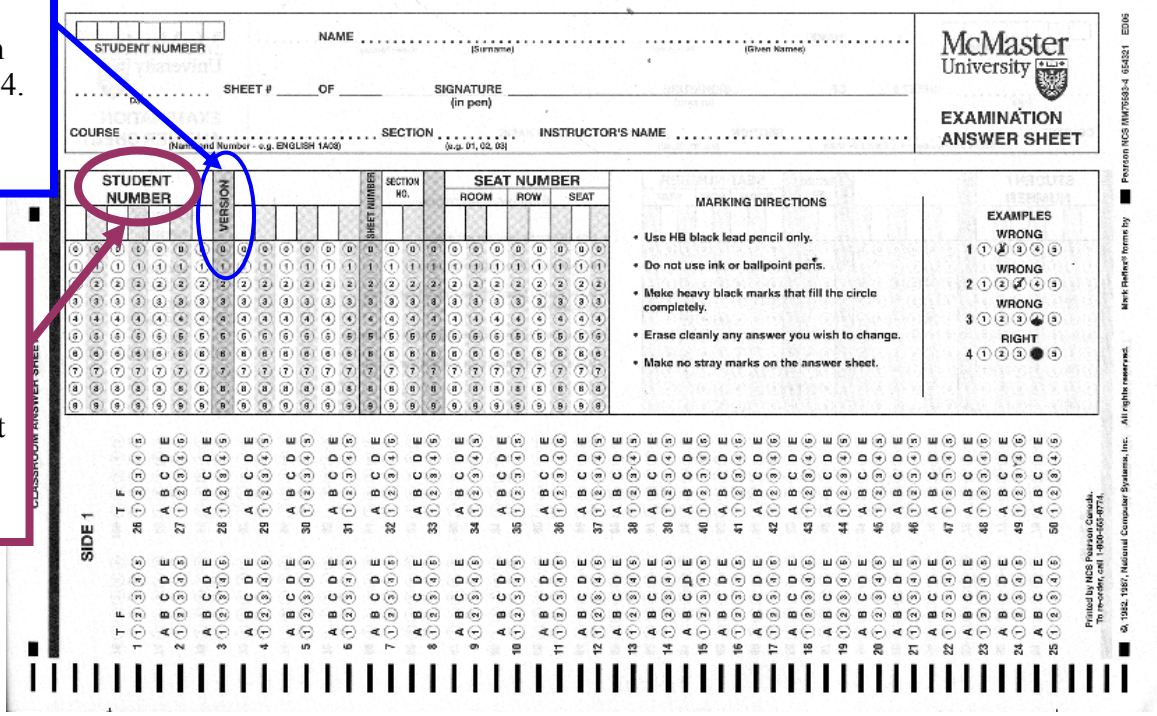
NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED: YOUR EXAMINIATION RESULT DEPENDS UPON PROPER ATTENTION TO THESE INSTRUCTIONS.

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. Do not use pen to bubble answers. 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, ~~(section number, instructor 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** (mark "1", "2", "3" or "4" and **do not** use the "0" bubble) (~~and course section number~~) in the space provided and fill in the corresponding bubble numbers underneath.
3. Answers: mark only **ONE** choice from the alternatives (~~1,2,3,4,5 or~~ A,B,C,D,E) provided for each question. ~~If there is a True/False question, enter response o 1 (or A) as True, and 2 (or B) as False.~~ 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".

Use this column for version number. Fill in only 1, 2, 3 or 4. Do not use the 0.

Make sure your student number is filled in, and that the correct numbers are bubbled in.



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See pages 1 and 2 of the test for instructions.

Questions 1-23 are worth two (2) marks each.

1. Most household plumbing is constructed from copper metal. While chemicals should never be emptied down the drain, which of the following would most likely chemically damage your pipes if dumped down the sink?

(A) Sodium hydroxide
(B) Hydrochloric acid
(C) Zinc metal
(D) Nitric acid
(E) Copper sulfate

In Lab 2 HNO_3 was used in the first step to digest Cu metal in a redox reaction, to produce $Cu^{2+}(aq)$ ions, with displacement of $NO_2(g)$.

The other reagents shown do not react with Cu metal.

2. The Haber-Bosch reaction requires a feedstock of $H_2(g)$. One method for producing $H_2(g)$ involves the reaction of ethane gas (C_2H_6) with steam, to produce hydrogen gas and carbon monoxide. How many grams of $H_2(g)$ are produced when 45 grams of ethane, $C_2H_6(g)$, react with excess $H_2O(g)$?

(A) 15
(B) 5.0
(C) 9.0
(D) 7.5
(E) 18.0

Balanced reaction:
$C_2H_6(g) + 2\ H_2O(g) \rightarrow 2\ CO(g) + 5\ H_2(g)$

$$45\ g\ C_2H_6 \times \frac{1\ mol}{30.067\ g} = 1.50\ mol\ C_2H_6$$

$$mol\ H_2 = mol\ C_2H_6 \times 5 = 1.50\ mol \times 5 = 7.5\ mol$$

$$g\ H_2 = 7.5\ mol \times \frac{2.0158\ g}{1\ mol} = 15.1\ g \text{ or } 15\ g$$

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3. Both X-rays and electrons can form diffraction patterns when interacting with atoms in a solid. What would be the **speed (u, in m/s)** of an electron that had the *same wavelength* as an X-ray photon with a frequency of 1.5×10^{18} Hz?

(A) 3.6×10^{9} m/s

(B) 4.3×10^{-25} m/s

(C) 2.6×10^{15} m/s

(D) 1.4×10^{43} m/s

(E) 3.6×10^{6} m/s

$\lambda = h / mu$ and $\lambda = c/\nu$
So, speed $u = h / m\lambda$ and since $\lambda = c/\nu$
Then $u = h\nu / mc$

$$u = \frac{(6.626 \times 10^{-34}\ \text{Js})(1.5 \times 10^{18}\ \text{s}^{-1})}{(9.10 \times 10^{-31}\ \text{kg})(2.9979 \times 10^{8}\ \text{m/s})}$$

$u = 3.643 \times 10^{6}$ J s/kg m
1 J = 1 kg m^2 s^{-2} (data page)
$u = 3.643 \times 10^{6}$ kg m^2 s^{-2} s/kg m
$u = 3.643 \times 10^{6}$ m s^{-1}

4. Which one of the atoms listed below is described by all of the following statements?

(i) The atom is less electronegative than O.

(ii) The ground state of the atom contains at least one unpaired electron.

(iii) The atom is more electronegative than P.

(iv) The atom has a larger first ionization energy than arsenic.

(A) Ge

(B) Be

(C) Si

(D) Br

(E) F

(i) This statement eliminates F.
(ii) This statement eliminates Be.
(iii) This statement eliminates Si and possibly Ge
(Ge actually has the same electronegativity as Si!)
(iv) This statement eliminates Ge.

Br is the only choice that matches all statements.

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5. Which of the following molecules or ions have the **same VSEPR AX_nE_m class**?

BeH_2 H_2O NH_2^- SO_2

(A) H_2O, SO_2

(B) SO_2, NH_2^-

(C) NH_2^-, BeH_2

(D) H_2O, NH_2^-

(E) BeH_2, SO_2

BeH_2 is an AX_2 molecule.
H_2O is an AX_2E_2 molecule.
NH_2^- is an AX_2E_2 ion.
SO_2 is an AX_2E molecule.

6. Which ONE of the following pairs of reagents produces **no observable change** upon mixing together?

(A) $Cu(s) + HCl(aq)$

(B) $Cl_2(aq) + KBr(aq)$

(C) $KCl(aq) + AgClO_4(aq)$

(D) $Zn(s) + HI(aq)$

(E) $Na_2CO_3(s) + HCl(aq)$

Observable changes experienced in the labs include: gas forming, colour changes, precipitates forming. Any of these changes would be observable. Identify what happens in each reaction:
(A) No reaction will occur, as Cu will not displace $H_2(g)$ from HCl(aq).
(B) Cl_2 will oxidize Br^- - a brown colour will appear as $Br_2(l)$ is formed.
(C) A precipitate of AgCl(s) will form.
(D) Zn will displace $H_2(g)$ from an acid (as in Lab 2).
(E) The acid and base will react to produce NaCl(aq), as well as H_2CO_3 which quickly decomposes into $CO_2(g)$ and $H_2O(l)$: $Na_2CO_3(s) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + CO_2(g) + H_2O(l)$

7. Complete and balance the following redox equation in acidic solution. When balanced with the smallest whole number coefficients, the **coefficient of NO** is

$$H_2S + HNO_3 \rightarrow S + NO$$

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

Oxidation numbers: H_2S + HNO_3 → S + NO
+1 -2 +1 +5 -2 0 +2 -2
S is oxidized from -2 to 0 (loses 2 electrons)
N is reduced from+5 to +2 (gains 3 electrons)
Balancing in acid solution = add H^+ and H_2O to balance H and O.
Ox: $(S^{2-} \rightarrow S + 2\ e^-) \times 3$
Red: $(3\ H^+ + HNO_3 + 3\ e^- \rightarrow NO + 2\ H_2O) \times 2$
Add: $3\ S^{2-} + 6\ H^+ + 2\ HNO_3 + 6\ e^- \rightarrow 3\ S + 6\ e^- + 2\ NO + 4\ H_2O$
Simplifying: $3\ H_2S + 2\ HNO_3 \rightarrow 3\ S + 2\ NO + 4\ H_2O$

8. Assume that 1 mole of each of the substances below is placed into its own vessel containing 1 L of water. Which of the substances will be the **strongest electrolyte**? (Choose more than one if they are expected to be equally strong).

(i) hydrogen chloride
(ii) sodium iodide
(iii) magnesium chloride
(iv) ammonia
(v) lead iodide

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

(i) HCl (strong acid) will produce 2 moles of ions.
(ii) NaI (soluble salt) will produce 2 moles of ions.
(iii) $MgCl_2$ (soluble salt) will produce 3 moles of ions.
(iv) NH_3 (weak base) will produce a small amount of ions.
(v) PbI_2 (insoluble salt) will produce a very small amount of ions.

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9. Which one of the following reactions is **not a Bronsted-Lowry acid-base reaction**?

(A) $2\ HClO_4\ (aq) + Mg(OH)_2(s) \rightarrow 2\ H_2O(l) + Mg(ClO_4)_2(aq)$

(B) $CH_3COOH(l) + H_2O(l) \rightarrow CH_3COO^-(aq) + H_3O^+(aq)$

(C) $Na_2O(s) + H_2O(l) \rightarrow 2\ NaOH(aq)$

(D) $2\ Na(s) + H_2(g) \rightarrow 2\ NaH(s)$

(E) $NaNH_2(s) + NH_4Cl(aq) \rightarrow 2\ NH_3(aq) + NaCl(aq)$

(A) $HClO_4$ is the H^+ donor, OH^- is the H^+ acceptor.
(B) CH_3COOH is the H^+ donor, H_2O is the H^+ acceptor.
(C) O^{2-} is the H^+ donor, H_2O is the H^+ acceptor.
(D) This is a redox reaction with no H^+ donor and no acceptor.
(E) NH_4^+ is the H^+ donor, NH_2^- is the H^+ acceptor.

10. The steel-making process involves many different compounds of carbon. From the list below, identify the compound with **carbon in the most reduced form:**

(A) C(graphite)

(B) CO_2

(C) $H_2C{=}CH_2$

(D) CO

(E) CH_4

Oxidation number on C:
(A) 0 (element)
(B) +4 (O is usually -2)
(C) -2 (H with nonmetal is +1, and an element bonded to itself does not change oxidation number)
(D) +2 (O is usually -2)
(E) -4 (H with a nonmetal is +1)

11. When dilute solutions of the following reagents are mixed, for which mixtures **would a precipitate form**?

(i) $Pb(NO_3)_2(aq) + NH_4Cl(aq)$

(ii) $BaCl_2(aq) + NaOH(aq)$

(iii) $K_2SO_4(aq) + Ca(NO_3)_2(aq)$

(iv) $(NH_4)_2CrO_4 + NaCl(aq)$

(A) i, iii

(B) ii, iv

(C) iii, iv

(D) ii, iii

(E) i, ii

(i) YES – $PbCl_2$ is insoluble.
(ii) NO – all Na^+ salts are soluble, and $Ba(OH)_2$ is soluble.
(iii) YES – $CaSO_4$ is insoluble.
(iv) NO –all Na^+ salts are soluble, and all NH_4^+ salts are soluble.

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12. What is the **pH** of 125 mL of a 0.018 M solution of LiOH(aq)?

(A) 11.35
(B) 13.18
(C) 10.08
(D) 11.80
(E) 12.26

A strong base: $LiOH(aq) = Li^+(aq) + OH^-(aq)$

$[OH^-] = 0.018M$, $pOH = -\log(0.018) = 1.74$
$pH + pOH = 14.00$
$pH = 14.00 - pOH = 14.00 - 1.74 = 12.26$

pH = 12.26

13. Which of the following statements are **TRUE**?

(i) HF is a stronger acid than HI because the H-F bond is stronger than the H-I bond.

(ii) NO_2^- is a stronger base than NO_3^- because it is less stable than NO_3^- in deprotonated form.

(iii) A solution of $Ca(OH)_2(aq)$ can be used to remove $SO_2(g)$ from flue gas emissions by reaction to produce $CaSO_3(s) + H_2O(g)$.

(iv) The conjugate base of ascorbic acid ($pK_a = 4.2$) is a weak base.

(v) The dissolution of CO_2 in water results in the formation of a strong acid.

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

(i) FALSE – HF is a weaker acid than HI, because the HF bond is stronger than the HI bond.
(ii) TRUE - NO_3^- has 3 resonance structures as compared to only 2 for NO_2^-. The more resonance structures = more stable ion, thus less basic.
(iii) TRUE – $Ca(OH)_2$ is a base which reacts with the acidic SO_2.
(iv) TRUE – If $pK_a = 4.2$, then $K_a = 6.31 \times 10^{-5}$, therefore $K_b = K_w / K_a = 1.58 \times 10^{-10}$, which is less than 1.
(v) FALSE – Dissolution of CO_2 in water forms H_2CO_3 (carbonic acid), which is a weak acid.

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14. For the following pairs of acids, select the **stronger acid** from each pair.

(i) Cl_3COOH, CH_3COOH

(ii) H_2SO_4, H_2SeO_4

(iii) $HBrO_2$, $HBrO_4$

(iv) NH_4^+, NF_3H^+

(i) Cl_3COOH is stronger (inductive effect of Cl atoms weakens the O-H bond).
(ii) H_2SO_4 is stronger (S is more electronegative than Se, so stronger inductive effect).
(iii) $HBrO_4$ is stronger (more O atoms, so stronger inductive effect)
(iv) NF_3H^+ is sronger (F is more electronegative than H, so stronger inductive effect).

The stronger acids from the pairs are:

(A) (i) Cl_3COOH, (ii) H_2SO_4, (iii) $HBrO_4$ and (iv) NF_3H^+

(B) (i) CH_3COOH, (ii) H_2SeO_4, (iii) $HBrO_4$ and (iv) NH_4^+

(C) (i) CH_3COOH, (ii) H_2SO_4, (iii) $HBrO_2$ and iv) NF_3H^+

(D) (i) Cl_3COOH, (ii) H_2SeO_4, (iii) $HBrO_2$ and iv) NH_4^+

(E) (i) Cl_3COOH, (ii) H_2SO_4, (iii) $HBrO_4$ and iv) NH_4^+

15. Which of the following substances will form **alkaline (basic) solutions** when placed in water?

NaH K_3PO_4 HCOOH KBr CH_3NH_3Cl $LiNO_3$

(A) NaH, $LiNO_3$

(B) CH_3NH_3Cl, K_3PO_4

(C) NaH, K_3PO_4

(D) CH_3NH_3Cl, HCOOH

(E) KBr, $LiNO_3$, K_3PO_4

Species that have a basic anion (O^{2-}, PO_4^{3-}) can function as a strong or weak base to generate a basic solution, whereas CH_3COOH and $CH_3NH_3^+Cl^-$ are weak acids and KBr and $LiNO_3$ are neutral salts.

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16. The Haber-Bosch process is an important industrial process for generating **ammonia** (NH_3) that serves as a key fertilizer for agriculture. "Concentrated" ammonia is a saturated solution of gaseous ammonia in water with a concentration of 17.0 M. What is the **% ionization of ammonia** in this solution? $K_b = 1.8 \times 10^{-5}$ for ammonia.

(A) 0.0012
(B) 0.0014
(C) 0.10
(D) 0.016
(E) 0.080

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Initial	17.0 M		
Change	-x	+x	+x
Eqm	17.0-x M	x M	x M

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{(17.0\text{-}x)}$

Assume x << 17.0 (Check: $17.0 / 1.8 \times 10^{-5} = 9.4 \times 10^5$, valid assumption.

$x^2 = (1.8 \times 10^{-5})(17.0)$

$x = 0.0175$

$\%\text{ ionization} = \frac{[NH_4^+]eqm}{[NH_3]initial} \times 100\% = \frac{0.0175}{17.0} \times 100\% = 0.10\%$

17. After eating, you may develop acid reflux problems since your stomach (liquid volume = 0.250 L) has a pH of 1.20 from the presence of HCl. Milk of Magnesia™ contains $Mg(OH)_2$, which can neutralize acid. **What dosage (milligrams, mg) of $Mg(OH)_2$** (58.3 g/mol) do you need to use to completely neutralize the acid in your stomach as a way to alleviate the symptoms of acid reflux?

(A) 280 mg
(B) 11000 mg
(C) 460 mg
(D) 1100 mg
(E) 760 mg

Neutralization Reaction:
$Mg(OH)_2\,(aq) + 2HCl\,(aq) \rightarrow Mg^{2+}\,(aq) + 2Cl^-\,(aq) + 2H_2O\,(l)$

$[H_3O^+] = \text{antilog}(-1.20) = 0.063_1$ M
Moles of $H_3O^+ = 0.063_1$ mol/L x 0.25L = 0.0158 moles
Moles of $Mg(OH)_2$ = ½ x 0.0158 moles = 0.00789 moles
Amount of $Mg(OH)_2$ = 0.00789 moles x 58.3 g/mol = 0.46 g = 460 mg

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18. The partition coefficient K_{ow} describes the distribution of a persistent organic pollutant (POP) as shown by:

$$POP(aq) \rightleftharpoons POP(org)$$

Select the **TRUE** statements about K_{ow}. It is:

(i) a measure of the bond energy of the POP.
(ii) related to the dipole moment of the POP.
(iii) used to assess tendency of the POP to bio-accumulate in fatty tissue.
(iv) determined by mixing the POP with water and soap.

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

(i) FALSE: K_{ow} describes the partitioning of a molecule between a water phase and an octanol phase, so is related to intermolecular forces (e.g. dipoles), not intramolecular forces (bond energies).
(ii) TRUE – see (i).
(iii) TRUE – K_{ow} provides a measure of lipophilicity.
(iv) FALSE – mix the POP with water/octanol.

19. A system at equilibrium is described by the equation:

$$2\ C(s) + 2\ O_2(g) \rightleftharpoons 2\ CO_2(g)$$

Find the **FALSE** statement.

(A) Addition of $CO_2(g)$ will shift the equilibrium to the left.
(B) Decreasing the total container volume will shift the equilibrium to the right.
(C) Addition of $O_2(g)$ will shift the equilibrium to the right.
(D) Adding the same number of moles of $O_2(g)$ and $CO_2(g)$ to the equilibrium mixture will shift equilibrium to the right.
(E) Adding solid carbon to the equilibrium mixture will not change the position of equilibrium.

Using the stoichiometry as written:
(A), (C), (E) TRUE, according to Le Châtelier's Principle.
(B) FALSE – decrease in V means P increases, so eqm. shifts to side with fewer moles gases (left).
(D) TRUE – since the gases were not added in a 1:2 ratio, eqm. shifts to adjust the ratio (build up more CO_2).
However the reaction is not balanced. If the reaction is properly balanced, then statements (B), (D) and (E) are FALSE. Full marks will be awarded to answers (B), (D) and (E), as a result.

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20. A self-contained breathing device uses the following chemical equilibrium:

$$4\ KO_2(s) + 2\ CO_2\ (g) \rightleftharpoons 2\ K_2CO_3\ (s) + 3\ O_2(g), \quad K_p = 28.5.$$

In order to simulate normal breathing conditions, the equilibrium partial pressure of $O_2(g)$ must equal 0.21 atm. What is the **equilibrium partial pressure of $CO_2(g)$** needed for these conditions?

(A) 0.048 atm
(B) 0.016 atm
(C) 0.0070 atm
(D) 0.021 atm
(E) 0.018 atm

$$K_p = 28.5 = \frac{P^3(O_2)}{P^2(CO_2)} = \frac{(0.21)^3}{x^2}$$

$$x = \sqrt{\frac{9.2610^{-3}}{28.5}} = 0.018$$

$P(CO_2)$ = 0.018 atm

21. In the process of decaffeinating coffee beans, a chemist with Melita Coffee Company measures the concentration of caffeine in the organic phase of her extraction to be 0.005M, whereas the concentration in the aqueous phase is 0.010M. The K_c for the extraction equilibrium is 0.83. What is the **best action** for her to take?

(A) Refresh the organic phase, as the mixture has already reached equilibrium.
(B) Allow the extraction to continue, because the organic phase has less caffeine than it will have at equilibrium.
(C) She does not have enough data to make a decision, and needs to measure the temperature of the liquids.
(D) K_c is less than 1, so it is not possible to decaffeinate coffee beans with this solvent.
(E) Add more coffee beans, to shift the equilibrium toward the organic phase.

In this equilibrium beans soaked in water are extracted with an organic phase.
At the time of measurement, $Q = \frac{[\text{caffeine}]org}{[\text{caffeine}]aq} = \frac{0.005\ M}{0.010\ M} = 0.5$ and $K_c = 0.83$ (given).
Since $Q < K$, the process will continue to shift to the right, as equilibrium has not been reached yet.
More caffeine will be extracted into the organic phase as the process continues towards equilibrium.

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22. In the Ostwald process for oxidizing ammonia, various nitrogen products are possible, depending on the conditions. One possibility is:

$$NH_3\,(g) + \frac{5}{4}O_2\,(g) \xrightleftharpoons{K_{P1}} NO(g) + \frac{3}{2}H_2O(g) \qquad (1)\ K_{P1} = 2.11 \times 10^{19} \text{ at } 700K$$

The NO product can also be formed by the decomposition of NO_2 at 700K,

$$2NO_2\,(g) \xrightleftharpoons{K_{P2}} 2NO(g) + O_2(g) \qquad (2)\ K_{P2} = 27.45 \text{ at } 700K$$

From these reactions, find K_{P3} for the further oxidation of ammonia to form $NO_2(g)$

$$2NH_3\,(g) + \frac{7}{2}O_2\,(g) \xrightleftharpoons{K_{P3}} 2NO_2(g) + 3H_2O(g) \qquad (3)\ K_{P3} = ?$$

(A) 1.89×10^{25}

(B) 3.58×10^{17}

(C) 5.73×10^{-18}

(D) 6.57×10^{33}

(E) 1.62×10^{37}

$$NH_3\,(g) + \frac{5}{4}O_2\,(g) \xrightleftharpoons{K_{P1}} NO(g) + \frac{3}{2}H_2O(g) \qquad (1)\ K_{P1} = 2.11 \times 10^{19} \text{ at } 700K$$

$$2NO_2\,(g) \xrightleftharpoons{K_{P2}} 2NO(g) + O_2(g) \qquad (2)\ K_{P2} = 27.45 \text{ at } 700K$$

2 x reaction 1 + reverse of reaction 2 gives the target:

$$2NH_3\,(g) + \frac{7}{2}O_2\,(g) \xrightleftharpoons{K_{P3}} 2NO_2(g) + 3H_2O(g) \qquad (3)\ K_{P3} =$$

$K_{P3} = (K_{P1})^2\,(1/K_{P2}) = (2.11 \times 10^{19})^2\,(1/27.45) = 1.62 \times 10^{37}$

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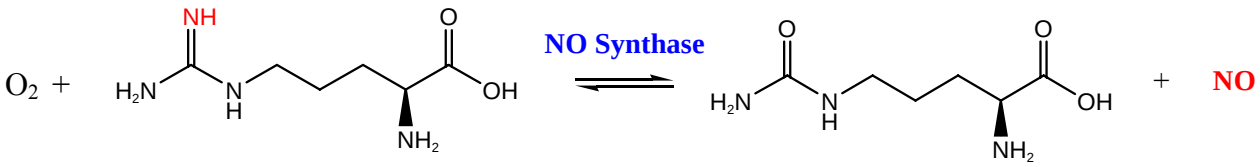
23. For the equilibrium which generates the signalling gas molecule, NO, in our bodies, NO synthase is an enzyme, or catalyst. Select the **TRUE** statements regarding this reaction:



Arginine (Arg) **Citrulline (Cit)**

(i) The product, NO, is a free radical, which will react quickly where it is produced.

(ii) The catalyst, NO Synthase, shifts the equilibrium in the forward direction.

(iii) $K_c = \frac{[Cit][NO]}{[Arg][O_2]}$ for the reaction.

(iv) Outside of the body NO can be produced by high temperature combustion of $N_2(g)$.

(v) Under "hypoxic" conditions, where oxygen is not available to the body, more NO will be produced.

(A) i, ii, v

(B) i, iii, iv

(C) ii, iv

(D) iii, v

(E) ii, iii

(i) TRUE – NO is an 11 valence electron molecule.
(ii) FALSE – a catalyst does not alter the position of equilibrium.
(iii) TRUE – based on law of mass action
(iv) TRUE – $N_2 + O_2(g) \rightarrow 2\ NO(g)$
(v) FALSE – if oxygen is not available, the equilibrium will shift to the left.

Name: _____ Student number: _____

Questions 24 to 30 are worth three (3) marks each.

24. Rank the species CO_2, CO, CO_3^{2-} and CH_3COO^- in order of **increasing bond energy of the carbon-oxygen bonds** (from lowest bond energy to highest bond energy):

(A) $CO < CO_2 < CH_3COO^- < CO_3^{2-}$

(B) $CO < CO_3^{2-} < CH_3COO^- < CO_2$

(C) $CO_3^{2-} < CH_3COO^- < CO < CO_2$

(D) $CH_3COO^- < CO_3^{2-} < CO_2 < CO$

(E) $CO_3^{2-} < CH_3COO^- < CO_2 < CO$

Higher bond energy can be predicted by higher bond order, when comparing the same bond (C-O) for a series.

Average C-O bond orders in each species:

CO = 3
CO_2 = 2
CH_3COO^- = 1.5 (2 resonance structures)
CO_3^{2-} = 1.3 (3 resonance structures)

Thus order of increasing bond energy:
$CO_3^{2-} < CH_3COO^- < CO_2 < CO$

Name: _____ Student number: _____

25. Identify the **TRUE** statement(s) concerning the following redox reaction carried out in **basic solution**, once it is balanced using the smallest integer stoichiometric coefficients:

$MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow MnO_2(s) + CO_3^{2-}(aq)$ (unbalanced)

(i) 2 moles of OH^- are consumed per mole of MnO_4^-.

(ii) 3 moles of $C_2O_4^{2-}$ are consumed.

(iii) The total number of electrons transferred is twelve.

(iv) The oxidation number of C in $CO_3^{2-}(aq)$ is –4.

(v) $C_2O_4^{2-}(aq)$ is the reducing agent.

(A) ii, iv

(B) iii, v

(C) i, iii, iv

(D) i, ii, v

(E) ii, iii

$MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow MnO_2(s) + CO_3^{2-}(aq)$

Oxidation numbers: +7 -2 +3 -2 +4 -2 +4 -2

Reduction: $(2\ H_2O(l) + MnO_4^-(aq) + 3\ e^- \rightarrow MnO_2(s) + 4\ OH^-) \times 2$

Oxidation: $(4\ OH^- + C_2O_4^{2-}(aq) \rightarrow 2\ CO_3^{2-}(aq) + 2\ e^- + 2\ H_2O(l)) \times 3$

Overall: $2\ MnO_4^-(aq) + 3\ C_2O_4^{2-}(aq) \rightarrow 2\ MnO_2(s) + 4\ OH^- + 6\ CO_3^{2-}(aq) + 2\ H_2O(l)$

Therefore:

(i) TRUE – they are in a 2:4 or 1:2 ratio.

(ii) TRUE – refer to balanced reaction.

(iii) FALSE – there are 6 electrons transferred, as shown in each half-reaction.

(iv) FALSE –the oxidation number is +4.

(v) TRUE = C in $C_2O_4^{2-}(aq)$ is oxidized, and so it is the reducing agent.

Name: _____ Student number: _____

26. Morphine is widely used alkaloid (**weak base**, represented by R_2NH, and with $K_b = 1.6 \times 10^{-6}$) drug used in patients after major surgeries to manage pain. Calculate the **pH** of an intravenous (IV) sack containing a 0.015 M of morphine-HCl ($R_2NH_2^+Cl^-$) **salt** solution.

(A) 5.01

(B) 3.52

(C) 11.2

(D) 7.00

(E) 8.86

	$R_2NH_2^+ \rightarrow$	R_2-NH	H^+
I	0.015	0	0
C	-x	+x	+x
E	0.015- x	x	x

$$K_a = \frac{[R_2NH][H^+]}{[R_2NH_2^+]} = \frac{K_w}{K_b}$$

$K_a = 6.25 \times 10^{-9}$

$$6.25\times10^{-9} = \frac{x^2}{0.015 - x} \approx \frac{x^2}{0.015}$$

$$[H^+] = x \approx \sqrt{(6.25\times10^{-9})(0.015)}$$

$$[H^+] \approx 9.682\times10^{-6} M$$

$$pH = -\log(9.682\times10^{-6}) = 5.01$$

Small x assumption is valid, since:

$\frac{(0.015)}{6.25 \times 10^{-9}} = 2.4 \times 10^6$, >100

 Continued on next page

27. Select the **FALSE** statement(s) from the following:

(i) $AlCl_3$ is a Lewis acid and will react with Cl^- to form the adduct $AlCl_4^-$.

(ii) The dilution of acetic acid decreases the % ionization of the acid.

(iii) Ingestion of high dosages of Vitamin C (ascorbic acid) supplements in the form of calcium ascorbate does not further acidify stomach acid.

(iv) The hydroxide ion is both a Lewis base and a Bronsted base in its reaction with $B(OH)_3$ to form $B(OH)_4^-$.

(v) A solution of ammonium nitrite, NH_4NO_2, has neutral pH (pH = 7); (K_a $HNO_2 = 7.2 \times 10^{-4}$; K_b $NH_3 = 1.8 \times 10^{-5}$).

(A) ii, iii

(B) i, iii, iv

(C) i, iv

(D) ii, iv, v

(E) iv, v

(i) TRUE – the Cl^- ion shares an electron pair with the electron deficient Al atom to form the adduct.
(ii) FALSE – % ionization increases with dilution (even though acidity decreases).
(iii) TRUE – ingesting the Vitamin C in weak base form will not increase pH.
(iv) FALSE – the OH^- functions as a Lewis base (electron pair donor) to the electron deficient B atom, but does not function as a proton acceptor (Bronsted base).
(v) FALSE – the K_a for NH_4^+ is $K_w / K_b = 5.6 \times 10^{-10}$, and the K_b for NO_2^- is $K_w / K_a = 1.4 \times 10^{-11}$, thus since K_a is larger we would expect the solution to be weakly acidic.

Name: _____ Student number: _____

28. With respect to the fluorapatite solubility equilibrium below, choose the **TRUE** statements.

$$Ca_5(PO_4)_3F\ (s) \overset{K_{sp}}{\rightleftharpoons} 5Ca^{2+}\ (aq) + 3PO_4^{3-}\ (aq) + F^-\ (aq) \qquad K_{sp} = 1.0 \times 10^{-60}$$

(i) $K_{sp} = [Ca^{2+}]^5\,[PO_4^{3-}]^3\,[F^-]$

(ii) The activity of the ions can be considered to be equal to their molarities, as the *K* value is very small.

(iii) The addition of fluoride ion, for example from toothpaste, will shift the equilibrium to the right.

(iv) Based on the above stoichiometry, the molar solubility of $Ca_5(PO_4)_3F$ is 6.11×10^{-8}M.

(v) Fluorapatite is less water-soluble than hydroxyapatite ($K_{sp} = 1.0 \times 10^{-36}$) because F^- is a stronger base than OH^-.

Note: to take the nth root (n) of a number, x, using the CASIO fx—991MS calculator:
Enter: **n** **Shift** **^** **x** (3 key strokes, then the number, in this sequence).

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

(i) TRUE – no pure solids included in *K*.
(ii) TRUE – small *K* implies very dilute concentrations of ions.
(iii) FALSE – addition of F^- will shift the equilibrium to the left.
(iv) TRUE – Let x be the concentration of F^-.
$K_{sp} = 1.0 \times 10^{-60} = (5x)^5(3x)^3(x) = 84375x^9$
$x^9 = 1.19 \times 10^{-65}$
$x = 6.11 \times 10^{-8}$M
(v) FALSE – F^- is a weaker base than OH^-, so this cannot be the reason why fluorapatite is less soluble.

Name: _____ Student number: _____

29. Air typically has a mole ratio of N_2 to O_2 of 79:21. When drawn into an internal combustion engine, under ideal conditions, the oxygen reacts completely with gasoline to form CO_2 and water. However, life is not as simple as that. The otherwise stable nitrogen molecules can react to form pollutant gases (NO_x), from the reaction of oxygen and nitrogen under the high temperatures of the engine:

e.g. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.

For example, consider the following data. A sample of air is heated to 2500K. When equilibrium is established in a closed container, with air initially at 1.00 atm, the mole percent of NO is found to be 1.8%. **Calculate K_p** for the reaction at 2500 K.

(A) 6.4×10^{-6}

(B) 3.5×10^{-3}

(C) 2.1×10^{-3}

(D) 8.8×10^{-5}

(E) 9.2×10^{-3}

Initially P_{air} = 1.00 atm, and so P_{N2} = 0.79 atm and P_{O2} = 0.21 atm

	$N_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2NO(g)$
Initial	0.79 atm	0.21 atm	0
Change	-x	-x	+2x
Eqm	0.79 –x	0.21 –x	2x

At eqm, $P_{TOTAL} = (0.79\text{-}x) + (0.21 - x) + 2x = 1.00$ atm

If the mole % NO is 1.8%,
therefore $P_{NO} = (1.00 \text{ atm})(1.8/100) = 0.018 = 2x$, and $x = 0.0090$ atm

$$K_P = \frac{(P_{NO})^2}{P_{N2}\,P_{O2}} = \frac{(0.018)^2}{(0.79 - 0.0090)(0.21 - 0.0090)} = 2.06 \times 10^{-3}$$

Name: _____ Student number: _____

30. Adding gallium trichloride (**$GaCl_3$**) to an iminophosphine (represented by formula **RNPCl**) sets up an equilibrium reaction to form the iminophosphenium gallate salt (**$RNP^+GaCl_4^-$**), which absorbs light with a wavelength of 555 nm (absorbance is directly proportional to concentration). Neither the iminophosphine nor gallium trichloride absorb light at this wavelength. In the presence of > 10 times mole excess of gallium trichloride, the equilibrium can be shifted completely to the right. Using the data below, **determine the value of *Kc*** for the equilibrium reaction. (Assume solutions of RNPCl and $GaCl_3$ are already mixed).

$$\mathbf{RNPCl + GaCl_3 \rightleftharpoons RNP^+GaCl_4^-}$$

Trial	Initial [RNPCl] M	Initial [$GaCl_3$] M	Absorbance at 555 nm
1	0.030	0.32	0.10
2	0.060	0.73	0.20
3	0.090	0.97	0.30
4	0.12	0.080	0.20

(A) 50.
(B) 0.30
(C) 130
(D) 0.060
(E) 28

In trials 1, 2 and 3 the reaction is shifted entirely to products, and so the concentration of $RNP^+GaCl_4^-$ is the same as the starting concentration of the limiting reagent (RNPCl) (in other words, we assume 100% completion).

Trial 4 (where 1 reagent is not in huge excess) is then an equilibrium situation. The absorbance in Trial 4 is the same value as in Trial 2. Since we know the concentration of product in Trial 2, we then know the equilibrium concentration of product in Trial 4. Let us apply these ideas to a table:

	RNPCl + $GaCl_3$ ⇌		$RNP^+GaCl_4^-$
Initial	0.12	0.080	0
Change	-x	-x	+x
Eqm	0.12 – x	0.080-x	x

Except that we know the x value: it is 0.060 M (comparing absorbance values from Trials 2 and 4).

Thus, $K_c = \dfrac{(x)}{(0.12-x)(0.080-x)} = \dfrac{(0.060)}{(0.12-0.060)(0.080-0.060)} = 50.$

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Name: _____ Student number: _____

This page is for rough work only.

Name: _____ Student number: _____

Some general data are provided on this page and the next page. Other data appear with the questions.

A periodic table is provided on the next page.

STP = 273.15 K, 1 atm

F = 96485 C/mol

R = 8.3145 J/K·mol = 0.08206 L·atm/K·mol

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

1 atm = 760 mm Hg = 101.325 kPa

0°C = 273.15 K

1 J = 1 kg m^2 s^{-2} = 1 kPa·L = 1 Pa·m^3

1 m = 10^9 nm = 10^{10} Å

1 cm^3 = 1 mL

1 g = 10^3 mg = 10^{-3} kg

1 Hz = 1 cycle/s

$c = 2.9979 \times 10^8$ m/s

$h = 6.6256 \times 10^{-34}$ J·s

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

$\lambda = h / mu = h / p$

$E_n = -R_H / n^2 = -2.179 \times 10^{-18}$J / n^2 ($R_H$ is the energy form of the Rydberg constant for H)

$K_w = 1.0 \times 10^{-14}$ (25 °C)

Solubility guidelines for Common Ionic Solids

Follow the lower-numbered guideline when two guidelines are in conflict. This leads to the correct prediction in most cases.

1. Salts of group 1 cations (with some exceptions for Li^+) and the NH_4^+ cation are soluble.
2. Nitrates, acetates, and perchlorates are soluble.
3. Salts of silver, lead, and mercury(I) are insoluble.
4. Chlorides, bromides, and iodides are soluble.
5. Carbonates, phosphates, sulfides, oxides, and hydroxides are insoluble (sulfides of group 2 cations and hydroxides of Ca^{2+}, Sr^{2+}, and Ba^{2+} are slightly soluble).
6. Sulfates are soluble except for those of calcium, strontium, and barium.

Name: ____________________ Student number: ______________

PERIODIC TABLE OF THE ELEMENTS

I 1	II 2	3	4	5	6	7	8	9	10	11	12	III 13	IV 14	V 15	VI 16	VII 17	VIII 18
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 105.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra 226.03	89 **Ac 227.03	104 Unq [261]	105 Unp [262]	106 Unh [263]												

Transition Metals: groups 3–12

Atomic weights are based on $^{12}C = 12$ and conform to the 1987 IUPAC report values rounded to 5 significant digits.
Numbers in [ ] indicate the most stable isotope.

* Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
** Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	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]

 END OF TEST