

Name: \_\_\_\_\_

Student number: \_\_\_\_\_

See page 2 of the exam for instructions.

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

1. Which of the following is the **conjugate base** of  $\text{H}_2\text{PO}_4^-$ ?

(A)  $\text{PO}_4^{3-}$

(B)  $\text{HPO}_4^{2-}$

(C)  $\text{H}_3\text{PO}_4$

(D)  $\text{H}_4\text{PO}_4^+$

(E)  $\text{OH}^-$

A conjugate base has a formula that is different by loss of  $\text{H}^+$ , so the conjugate base of  $\text{H}_2\text{PO}_4^-$  would be  $\text{HPO}_4^{2-}$ .

2. Equal sized pieces of sodium, magnesium, and cesium are placed in individual flasks containing water. **Predict the order** in which you think the metals would react, **from most reactive to least reactive**.

(A)  $\text{Cs} > \text{Na} > \text{Mg}$

(B)  $\text{Mg} > \text{Na} > \text{Cs}$

(C)  $\text{Mg} > \text{Cs} > \text{Na}$

(D)  $\text{Na} > \text{Cs} > \text{Mg}$

(E)  $\text{Cs} > \text{Mg} > \text{Na}$

Reactivity: Group 1 > Group 2 and increases down a group (follows the ionization energy (IE) trend, whereby the lower the IE, the more reactive the metal is. (Recall Lab 2).

5. Which one of the following **is an allowed set** of quantum numbers ( $n, l, m_l, m_s$ ) for an electron?

- (A) (2, 1, 0, 1)  
 (B) (3, 3, 1,  $-\frac{1}{2}$ )  
 (C) (2, 1, -1,  $-\frac{1}{2}$ )  
 (D) (3, -1, 1,  $+\frac{1}{2}$ )  
 (E) (4, 1, 2,  $+\frac{1}{2}$ )

Boundaries on  $n$ :  $n = 1, 2, 3, 4, \dots$   
 Boundaries on  $l$ :  $l = 0, 1, 2, 3, \dots, n-1$   
 Boundaries on  $m_l$ :  $m_l = -l, \dots, 0, \dots, +l$   
 Boundaries on  $m_s$ :  $m_s = +\frac{1}{2}, -\frac{1}{2}$   
 (A) incorrect  $m_s$  value  
 (B) incorrect  $l$  value  
 (C) correct  
 (D) incorrect  $l$  value  
 (E) incorrect  $m_l$  value

6. Both X-rays and electrons can form diffraction patterns when interacting with atoms in a solid. What would be the **momentum  $p$**  (in  $\text{kg m s}^{-1}$ ) of an electron that had the *same wavelength* as an X-ray photon with a frequency of  $1.5 \times 10^{18} \text{ Hz}$ ?

- (A)  $3.1 \times 10^7$   
 (B)  $3.3 \times 10^{-24}$   
 (C)  $2.6 \times 10^{-26}$   
 (D)  $1.3 \times 10^{-42}$   
 (E)  $3.5 \times 10^{-54}$

Refer to data page (p.25) for de Broglie equation ( $\lambda = h / mv = h / p$ ) and mass of an electron ( $m_e = 9.10 \times 10^{-31} \text{ kg}$ ).

$\lambda = h / p$  we need:  $p = h / \lambda$   
 Convert the given frequency into wavelength (recall that  $\nu$  and  $\lambda$  have an inverse relationship, related through the speed of light):

$$\lambda = c / \nu = 2.9979 \times 10^8 \text{ m/s} / 1.5 \times 10^{18} \text{ s}^{-1}$$

$$\lambda = 1.999 \times 10^{-10} \text{ m}$$

$$\text{Now } p = h / \lambda$$

$$p = (6.626 \times 10^{-34} \text{ J s}) / (1.999 \times 10^{-10} \text{ m})$$

$$p = 3.31 \times 10^{-24} \text{ J s m}^{-1} \text{ or } \text{kg m s}^{-1}$$

Note (data page):  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ , therefore  
 $\text{J s m}^{-1} = \text{kg m}^2 \text{ s}^{-2} \times \text{s m}^{-1} = \text{kg m s}^{-1}$

7. A beam of light with a frequency of  $5.00 \times 10^{14}$  Hz ionizes a hydrogen atom that is already in an excited state ( $n = 4$ ). The electron is ejected from the atom with a certain kinetic energy. What is the **kinetic energy (in J) of the ejected electron?**

- (A)  $1.95 \times 10^{-19}$  J  
 (B)  $1.36 \times 10^{-19}$  J  
 (C)  $1.18 \times 10^{-20}$  J  
 (D)  $3.26 \times 10^5$  J  
 (E)  $2.18 \times 10^{-18}$  J

This is like the photoelectric effect (an electron is ejected after excitation by a photon). The photon bears enough energy to (i) ionize an electron, and (ii) send it on its way with kinetic energy.

$$E_{\text{photon}} = \text{Ionization Energy} + \text{Kinetic Energy}$$

$$E_{\text{photon}} = h\nu = (6.626 \times 10^{-34} \text{ J s})(5.00 \times 10^{14} \text{ s}^{-1}) = 3.313 \times 10^{-19} \text{ J}$$

Ionization Energy = energy required to excite the electron from  $n = 4$  to  $n = \infty$ . From the data page,  $E_n = -R_H / n^2 = -2.178 \times 10^{-18} \text{ J} / n^2$

$$\text{I.E.} = 2.178 \times 10^{-18} \text{ J} (1/n_i^2 - 1/n_f^2) = 2.178 \times 10^{-18} \text{ J} (1/16 - 1/\infty^2)$$

$$\text{I.E.} = 1.36 \times 10^{-19} \text{ J}$$

Thus, Kinetic Energy =  $E_{\text{photon}} - \text{Ionization Energy}$

$$\text{Kinetic Energy} = 3.313 \times 10^{-19} \text{ J} - 1.36 \times 10^{-19} \text{ J} = 1.95 \times 10^{-19} \text{ J}$$

8. Select the statement that is **FALSE** regarding the perchlorate anion,  $\text{ClO}_4^-$ , and the chlorate ion,  $\text{ClO}_3^-$ , when they are drawn with charge minimized Lewis structures.

- (A) The formal charge of Cl in both ions is 0.  
 (B) The oxidation state of Cl in  $\text{ClO}_3^-$  is +5.  
 (C) The average Cl–O bond length is longer in  $\text{ClO}_4^-$  than in  $\text{ClO}_3^-$ .  
 (D) The shape of the  $\text{ClO}_4^-$  anion is tetrahedral.  
 (E) The  $\text{ClO}_3^-$  anion has 16 nonbonding valence electrons.

The charge-minimized Lewis structure of  $\text{ClO}_4^-$  has one Cl–O single bond, and 3 Cl=O double bonds. The average Cl–O bond order is 7/4 (1.75), and the average formal charge on O is -1/4. The formal charge on Cl is 0. The anion is  $\text{AX}_4$ , with tetrahedral shape. There are 9 lone electron pairs (in total) on all the atoms.

The charge-minimized Lewis structure of  $\text{ClO}_3^-$  has one Cl–O single bond, and 2 Cl=O double bonds, and a lone electron pair on Cl. The average Cl–O bond order is 5/3 (1.67), and the average formal charge on O is -1/3. The formal charge on Cl is 0. The anion is  $\text{AX}_3\text{E}$ , with trigonal pyramidal shape. There are 8 lone electron pairs (in total) on all the atoms. (Recall Q 24, Test 1 2007).

Oxidation numbers (O.N.): since for both ions the O.N. for O is -2, then let x be O.N. for Cl.

$$\text{For } \text{ClO}_4^- \text{ then } x + 4(-2) = -1, \text{ so } x = +7$$

$$\text{For } \text{ClO}_3^- \text{ then } x + 3(-2) = -1, \text{ so } x = +5$$

9. Which of the following statements is/are **TRUE**?

- (i)  $\text{TeCl}_4$  is a non-polar molecule.
- (ii)  $\text{TeCl}_2$  is a V-shaped (or “bent”) molecule.
- (iii) All of the atoms of  $\text{TeCl}_3^+$  are in the same plane.
- (iv)  $\text{TeCl}_4$  has one nonbonding pair of electrons on tellurium.

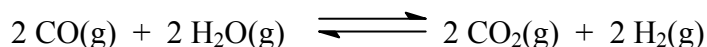
- (A) i, ii
- (B) ii, iv
- (C) iii
- (D) iv
- (E) i, iii

$\text{TeCl}_4$  has 4 single Te-Cl bonds, with a lone electron pair on Te. It is an  $\text{AX}_4\text{E}$  molecule, and therefore polar.  
 Statement (i) is FALSE.  
 Statement (iv) is TRUE.  
 $\text{TeCl}_2$  has 2 Te-Cl single bonds, with 2 lone electron pairs on Te. It is an  $\text{AX}_2\text{E}_2$  molecule, therefore bent.  
 Statement (ii) is TRUE.  
 The  $\text{TeCl}_3^+$  ion has 3 Te-Cl single bonds with a lone electron pair on Te. It is an  $\text{AX}_3\text{E}$  ion, therefore trigonal pyramidal shape.  
 Statement (iii) is FALSE.

10. From the following information:



determine  $K_c$  for



- (A)  $3.284 \times 10^3$
- (B) 7.318
- (C) 53.55
- (D) 0.1222
- (E)  $5.689 \times 10^{-4}$

The target reaction can be created from the two given equations by manipulating them (e.g. reverse a reaction, or multiply it by a factor). We must also change the K values as we change the reactions.

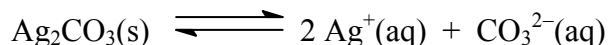
Take the first reaction, reverse it and multiply by 2. Therefore, we take  $K_1$ , we take its inverse and we square it.  
 Then take the second reaction, and multiply by 2. Therefore we take its K value and square it.

K for the overall reaction is thus  $= (1/K_1)^2 * (K_2)^2$   
 K overall = 53.55

11. At a certain temperature, solid  $\text{Ag}_2\text{CO}_3$  is dissolved in water to produce a solution that contains  $1.3 \times 10^{-4} \text{ M CO}_3^{2-}(\text{aq})$  ions and a certain concentration of  $\text{Ag}^+(\text{aq})$  ions.

What is the **value for the  $K_{\text{sp}}$**  that describes this equilibrium?

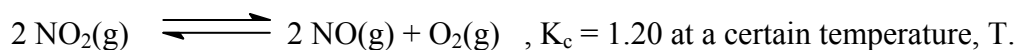
- (A)  $8.8 \times 10^{-12}$   
(B)  $1.2 \times 10^{-12}$   
(C)  $3.9 \times 10^{-9}$   
(D)  $2.2 \times 10^{-8}$   
(E)  $4.6 \times 10^{-7}$



When the  $\text{Ag}_2\text{CO}_3(\text{s})$  dissolves, it produces a 2:1 ratio of  $\text{Ag}^+(\text{aq})$ : $\text{CO}_3^{2-}(\text{aq})$  ions. If the concentration of  $\text{CO}_3^{2-}(\text{aq})$  is  $1.3 \times 10^{-4} \text{ M}$ , then the concentration of  $\text{Ag}^+(\text{aq})$  is two times that (according to the balanced reaction), thus  $2.6 \times 10^{-4} \text{ M}$ .

$$K_{\text{sp}} = [\text{Ag}^+(\text{aq})]^2[\text{CO}_3^{2-}(\text{aq})] = (2.6 \times 10^{-4})^2(1.3 \times 10^{-4}) = 8.79 \times 10^{-12}$$

12. For the equilibrium which describes the decomposition of  $\text{NO}_2(\text{g})$ , a major component of photochemical smog:



A 1.0 L reaction vessel contains 1.0 mole each of  $\text{NO}_2(\text{g})$ ,  $\text{NO}(\text{g})$  and  $\text{O}_2(\text{g})$  added at the same time. Identify the **CORRECT** statement.

- (A) The resulting system is in equilibrium.  
(B) The system is not at equilibrium and more  $\text{NO}(\text{g})$  will be formed.  
(C) The production of  $\text{NO}_2(\text{g})$  is favoured at temperature T.  
(D) The equilibrium concentration of  $\text{NO}(\text{g})$  will always be equal to that of  $\text{O}_2(\text{g})$ .  
(E) The equilibrium concentration of  $\text{NO}(\text{g})$  will always be equal to that of  $\text{NO}_2(\text{g})$ .

(A) FALSE.  $Q = [\text{NO}]^2[\text{O}_2] / [\text{NO}_2]^2 = (1)^2(1) / (1)^2 = 1$ . This  $Q < K$ , the system is not at equilibrium.

(B) TRUE. Since  $Q < K$ , the equilibrium will shift to the right. More  $\text{NO}$  and  $\text{O}_2$  will be formed.

(C) FALSE. Since  $K > 1$ , products are slightly favoured, not reactants.

(D) This is not necessarily true, as  $\text{NO}$  and  $\text{O}_2$  are produced in a 2:1 stoichiometric ratio, and as in the  $K$  expression the concentrations will adjust to the values necessary to produce the ratio  $K$ .

(E) This is not necessarily true, as in the  $K$  expression the concentrations will adjust to the values necessary to produce the ratio  $K$ .

13. Dichromate ions,  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ , react with zinc metal in acid solution to produce  $\text{Cr}^{3+}(\text{aq})$  and  $\text{Zn}^{2+}(\text{aq})$  ions. When the reaction is balanced, such that the smallest possible integers appear as stoichiometric coefficients, **the coefficient for  $\text{Zn}^{2+}$  is:**

- |     |   |   |
|-----|---|---|
| (A) | 1 | Overall reaction: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{Zn}^{2+}(\text{aq})$ , in acidic solution.<br>Oxidation numbers:   |
| (B) | 4 | Reactants: Cr (+6), O (-2), Zn (0). Products: Cr (+3), Zn (+2).<br>Cr is reduced from +6 to +3. Zn is oxidized from 0 to +2.  |
| (C) | 2 | Half-reactions: Oxidation: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$  |
| (D) | 3 | Reduction: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{e}^- + 14\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$   |
| (E) | 6 | Multiply Oxidation by 3 (to make electrons balance):<br>Oxid: $3\text{Zn}(\text{s}) \rightarrow 3\text{Zn}^{2+}(\text{aq}) + 6\text{e}^-$<br>Red: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{e}^- + 14\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$<br>Overall: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{e}^- + 14\text{H}^+(\text{aq}) + 3\text{Zn}(\text{s}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) + 3\text{Zn}^{2+}(\text{aq}) + 6\text{e}^-$<br>Cancel out species which appear on both sides:<br>$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 3\text{Zn}(\text{s}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) + 3\text{Zn}^{2+}(\text{aq})$ |

14. In basic aqueous solution, the electrolysis of NaCl (the chloralkali process) leads to the production of chlorine gas, hydrogen gas and sodium hydroxide. The *unbalanced* equation, where sodium is a spectator ion, is:



Find the **FALSE** statement regarding the corresponding balanced reaction equation.

- (A) Water is the oxidizing agent.  
 (B) Each Cl atom loses 1 electron.  
 (C)  $\text{H}_2(\text{g})$  is the reduction product of  $\text{H}_2\text{O}$ .  
 (D) The oxidation number on O does not change.  
 (E) The oxidation of 1 mole of  $\text{Cl}^-$  produces 1 mole of  $\text{H}_2$ .

Balanced reaction:  $2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$   
 $\text{Cl}^-$  (O.N. -1) is oxidized to  $\text{Cl}_2$  (O.N. zero). H (O.N. +1) in  $\text{H}_2\text{O}$  is reduced to  $\text{H}_2$  (O.N. zero).  
 (A) TRUE: Since  $\text{H}^+$  from  $\text{H}_2\text{O}$  is reduced to  $\text{H}_2$ , then  $\text{H}_2\text{O}$  (or  $\text{H}^+$  from  $\text{H}_2\text{O}$ ) is the oxidizing agent.  
 (B) TRUE: Each  $\text{Cl}^-$  loses 1 electron.  
 (C) TRUE: see statement A.  
 (D) TRUE: O.N. is -2 for O on both sides of the reaction.  
 (E) FALSE: According to the balanced reaction, the oxidation of 2 moles of  $\text{Cl}^-$  produces 1 mole of  $\text{H}_2$ .

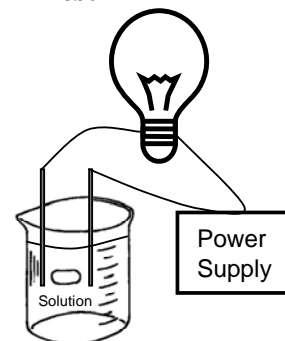
15. Choose the correct **net ionic equation** for the reaction of aqueous calcium chloride with aqueous potassium phosphate, in water:

- (A)  $3 \text{CaCl}_2(\text{aq}) + 2 \text{K}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{aq}) + 6 \text{KCl}(\text{aq})$   
 (B)  $3 \text{Ca}^{2+}(\text{aq}) + 2 \text{K}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 6 \text{K}^+(\text{aq})$   
 (C)  $3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$   
 (D)  $\text{K}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{KCl}(\text{s})$   
 (E) No net reaction occurs

The net ionic equation does not include any spectator ions; it shows only the participants in the precipitation, and the precipitate. Since a precipitate forms between  $\text{Ca}^{2+}(\text{aq})$  and  $\text{PO}_4^{3-}(\text{aq})$ , those are the only species which should appear. The  $\text{K}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  ions are the spectator ions.

16. You are asked to test the electrolyte performance of several aqueous solutions, using a light bulb-electrodes-electrolyte assembly, as shown below. Based on the trends of solubility and dissociation, **rank the following solutions from brightest to dimmest light bulb responses, i.e. from strongest to weakest electrolyte:**

- 1 M  $\text{Na}_2\text{CO}_3(\text{aq})$   
 1 M  $\text{HCOOH}(\text{aq})$  (Formic acid)  
 $\text{CH}_3\text{OH}(\text{l})$   
 $\text{H}_2\text{O}(\text{l})$   
 1 M  $\text{RbOH}(\text{aq})$



- (A)  $\text{Na}_2\text{CO}_3(\text{aq}) > \text{HCOOH}(\text{aq}) > \text{CH}_3\text{OH}(\text{l}) > \text{H}_2\text{O}(\text{l}) > \text{RbOH}(\text{aq})$   
 (B)  $\text{Na}_2\text{CO}_3(\text{aq}) > \text{RbOH}(\text{aq}) > \text{HCOOH}(\text{aq}) > \text{H}_2\text{O}(\text{l}) > \text{CH}_3\text{OH}(\text{l})$   
 (C)  $\text{RbOH}(\text{aq}) > \text{HCOOH}(\text{aq}) > \text{Na}_2\text{CO}_3(\text{aq}) > \text{H}_2\text{O}(\text{l}) > \text{CH}_3\text{OH}(\text{l})$   
 (D)  $\text{Na}_2\text{CO}_3(\text{aq}) > \text{HCOOH}(\text{aq}) > \text{RbOH}(\text{aq}) > \text{H}_2\text{O}(\text{l}) > \text{CH}_3\text{OH}(\text{l})$   
 (E)  $\text{H}_2\text{O}(\text{l}) > \text{CH}_3\text{OH}(\text{l}) > \text{Na}_2\text{CO}_3(\text{aq}) > \text{HCOOH}(\text{aq}) > \text{RbOH}(\text{aq})$

Strong electrolytes dissolve in water (or react with water) to form ions (e.g. the soluble salts  $\text{RbOH}$  and  $\text{Na}_2\text{CO}_3$  – use solubility table on data page to see that these are soluble salts). The difference between these 2 salts is in the number of moles of ions they produce. The  $\text{Na}_2\text{CO}_3$  produces 3 moles of ions when it dissolves, whereas the  $\text{RbOH}$  only produces 2 moles of ions.

Weak electrolytes only dissolve/ionize partially (e.g.,  $\text{HCOOH}(\text{aq})$ , a weak acid – we would know it is weak because it is not one of our 6 strong acids).

Water is an extremely weak electrolyte ( $K_w = 1.0 \times 10^{-14}$ ). Alcohols (e.g. methanol) are non-electrolytes.

Thus we have:  $\text{Na}_2\text{CO}_3(\text{aq}) > \text{RbOH}(\text{aq}) > \text{HCOOH}(\text{aq}) > \text{H}_2\text{O}(\text{l}) > \text{CH}_3\text{OH}(\text{l})$

17. Identify **two weak bases** produced on an industrial-scale which have been associated with increased **food productivity** and reduction of **water-borne** infectious diseases:

- (i) NaCl
- (ii) NH<sub>3</sub>
- (iii) NaOH
- (iv) Fe<sub>2</sub>O<sub>3</sub>
- (v) NaOCl

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

Of the substances shown:

NaCl = neutral salt

NH<sub>3</sub> = weak base

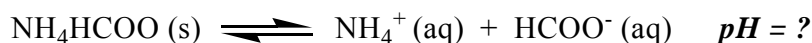
NaOH = strong base

Fe<sub>2</sub>O<sub>3</sub> = metal oxide (basic)

NaOCl = weak base salt

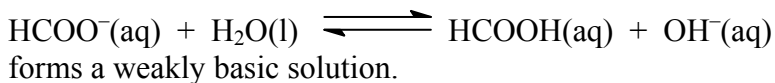
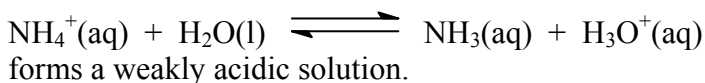
NH<sub>3</sub> (produced by the Haber-Bosch process) is a key component in fertilizer production, which supports increased food production. NaOCl (bleach) is a product of chlorine from the chloralkali process. Water sanitization is important for the reduction of water-borne diseases.

18. Predict the **pH** of a solution prepared from the dissolution of **ammonium formate salt** if the pK<sub>a</sub> (NH<sub>4</sub><sup>+</sup>) = 9.26 and pK<sub>a</sub> (HCOOH) = 3.74.



- (A) Strongly basic
- (B) Weakly acidic**
- (C) Strongly acidic
- (D) Weakly basic
- (E) Neutral

Consider the acid or base nature of each of the ions of this salt as they interact with water:



The overall solution pH will be governed by the relative strength of the weak acid and the weak base. The pK<sub>a</sub> of the weak acid is 9.26, and pK<sub>b</sub> for the weak base is 14-3.74 = 10.26. Since the pK<sub>a</sub> value is lower (i.e. K<sub>a</sub> for the acid is larger than K<sub>b</sub> for the base), then overall the solution will be acidic, but only weakly acidic.



19. **Select the examples of acid-base reactions** (whether Arrhenius, Brønsted-Lowry or Lewis reactions) from the following set of unbalanced chemical reactions:

- (i)  $\text{Zn (s)} + \text{Cu}^{2+} \text{ (aq)} \rightarrow \text{Zn}^{2+} \text{ (aq)} + \text{Cu (s)}$   
 (ii)  $\text{Mg(OH)}_2 \text{ (aq)} + 2 \text{ HCl (aq)} \rightarrow \text{MgCl}_2 \text{ (aq)} + 2 \text{ H}_2\text{O (l)}$   
 (iii)  $\text{BF}_3 \text{ (g)} + \text{NH}_3 \text{ (g)} \rightarrow \text{BF}_3 \cdot \text{NH}_3$   
 (iv)  $\text{Fe}_2\text{O}_3 \text{ (s)} + 2 \text{ Al (s)} \rightarrow 2 \text{ Fe (l)} + \text{Al}_2\text{O}_3 \text{ (s)}$   
 (v)  $\text{NaHCO}_3 \text{ (aq)} + \text{NH}_4\text{Cl (aq)} \rightleftharpoons \text{NaCl (aq)} + \text{NH}_3 \text{ (aq)} + \text{H}_2\text{CO}_3 \text{ (aq)}$

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

For Brønsted-Lowry acid-base reactions, look for transfer of a proton. Lewis acid-base reactions (where electrons are shared to form a new covalent bond) and to be distinguished from redox reactions (where oxidation numbers change because electrons are transferred).

(i) is a redox demonstration from class, and also the final step of the copper cycle from Lab 2. One usual clue for redox is to see an element in oxidation state zero.

(ii) is an acid-base reaction (by B-L or Lewis definition)

(iii) is a Lewis acid-base reaction

(iv) is a redox reaction (“thermite” reaction). One usual clue is to see an element in oxidation state zero.

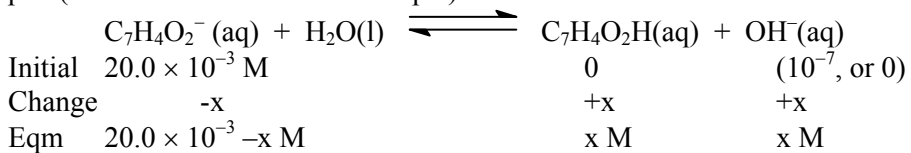
(v) is an acid-base reaction (by B-L or Lewis definition). We can identify a possible proton donor ( $\text{NH}_4^+$ ) and also a proton acceptor ( $\text{HCO}_3^-$ ).

20. **Sodium benzoate** is a widely used preservative in processed foods and beverages, such as Diet Coke™. Calculate the **pH** of a solution containing **20.0 mM** sodium benzoate ( $\text{NaC}_7\text{H}_5\text{O}_2$ ) assuming that no other acids are present.

( $K_a$  for benzoic acid =  $6.3 \times 10^{-5}$ )

- (A) pH = 11.05  
 (B) pH = 5.75  
 (C) pH = 8.25  
 (D) pH = 2.95  
 (E) pH = 7.0

Benzoate ion (the conjugate base of benzoic acid) is  $\text{C}_7\text{H}_4\text{O}_2^-$ . This ion will react with water to produce a small amount of  $\text{OH}^-$  ion, which will influence pH. (The  $\text{Na}^+$  ion has no effect on pH).



$$K_b = \frac{[\text{C}_7\text{H}_5\text{O}_2][\text{OH}^-]}{[\text{C}_7\text{H}_4\text{O}_2^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}}$$

$$1.59 \times 10^{-10} = x^2 / 20.0 \times 10^{-3} - x$$

Solve for x using the quadratic formula or the “small x approximation”.

$$x = 1.78 \times 10^{-6} = [\text{OH}^-], \text{ therefore } \text{pOH} = -\log_{10}[\text{OH}^-] = 5.75$$

$$\text{pH} = 14 - \text{pOH} = 8.25. \text{ The solution is weakly basic.}$$

*Note that on the data page the value of  $K_w$  is given, along with the conversion between mM and M.*

21. Which of the following statements about **ascorbic acid** ( $K_a = 5.0 \times 10^{-5}$ ) are

**FALSE?**

- (i) calcium ascorbate is a strong base
- (ii) ingestion of calcium ascorbate supplements is preferred over ascorbic acid since ascorbate increases stomach acidity
- (iii) ascorbic acid is a weak acid
- (iv) ascorbic acid is an anti-oxidant because it functions as an oxidizing agent when it converts hydroxyl radicals into water

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

Ascorbic acid was a molecule of the week, but we actually don't have to remember any of that material in order to answer this question. In the question we are given the  $K_a$  value, and it is less than one, so we know 2 things right away: (1) ascorbic acid is a weak acid, and (2) its conjugate base is also weak ( $K_b = K_w/K_a = 2.0 \times 10^{-10}$ ).  
Statement (i) is FALSE (see above).  
Statement (ii) is FALSE: addition of a weak base (ascorbate) to the stomach will DECREASE acidity, not increase it.  
Statement (iii) is TRUE (see above).  
Statement (iv) is FALSE: the oxidation number (O.N.) of O in a hydroxyl radical ( $\bullet\text{OH}$ ) is -1, and the O.N. of O in water is -2, thus O has been reduced, and so the ascorbic acid must be a reducing agent.

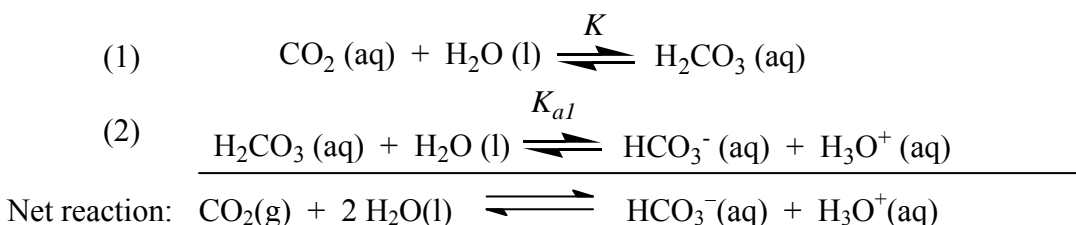
22. **Select** the chemical principle that **best explains why coke, C (s)** is used as a primary feedstock (reactant) in the industrial production of steel (pig iron, Fe(l)) from iron oxide ore ( $\text{Fe}_2\text{O}_3$ ):

- (A) C (s) is used as a salt to precipitate iron oxide ore
- (B) C (s) is used as an oxidizing agent to oxidize iron oxide ore
- (C) C (s) is used as an acid to neutralize iron oxide ore
- (D) C (s) is used as a reducing agent to reduce iron oxide ore
- (E) C (s) is used as a base to neutralize iron oxide ore

We can see from the iron formulae given that when  $\text{Fe}_2\text{O}_3$  ore is converted into Fe(l) that iron has undergone a reduction in oxidation number from +3 to 0.  
In order to have a redox process, the fundamental principles of redox chemistry tell us that C must get oxidized. If C gets oxidized, then it functions as a reducing agent.  
The steel-making example from class showed us that C is converted into CO or  $\text{CO}_2$  gases, but, even if we do not recall that example, the question is still answerable based on the information given.

23. **Acid-base titrations** are relevant in the treatment of acute health disorders for maintaining physiological blood pH, as they restore the relative concentration of  $\text{HCO}_3^-$  and pressure of  $\text{CO}_2$  required in the body.

Assume that in the blood there is a **two-step equilibrium process** described by (1) the dissolution of carbon dioxide ( $K = 3.39 \times 10^{-2}$ ), and (2) the first acid dissociation of carbonic acid ( $K_{a1} = 4.47 \times 10^{-7}$ ), governed by a net overall reaction as depicted below:



Based on the net reaction, determine the **equilibrium concentration of bicarbonate,  $[\text{HCO}_3^-]$**  of a patient after treatment for acidosis, if the final partial pressure of  $\text{CO}_2$  in the blood was measured to be 0.0502 atm, and the final blood pH was 7.35.

- (A) 17.0 mM
- (B) 148 mM
- (C) 6.78 mM
- (D) 0.0342 mM
- (E) 14.8 mM

$$K \text{ for the net reaction} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{P_{\text{CO}_2}} = K * K_{a1}$$

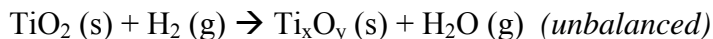
We are given the K values, as well as the partial pressure of  $\text{CO}_2$ , and pH. From pH we can get  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 4.47 \times 10^{-8}$

$$(3.39 \times 10^{-2})(4.47 \times 10^{-8}) = \frac{[\text{HCO}_3^-](4.47 \times 10^{-8})}{0.0502 \text{ atm}}$$

$[\text{HCO}_3^-] = 0.0170 \text{ M}$  or 17 mM (see conversion from mM to M on data page).

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

24. A sample of titanium dioxide ( $\text{TiO}_2$ ) weighing 1.598 g is heated in  $\text{H}_2$  gas to give water vapour and 1.438 g of *another* titanium oxide. What is the **formula of the oxide produced**?



- (A)  $\text{TiO}$
- (B)  $\text{TiO}_3$
- (C)  $\text{Ti}_2\text{O}$
- (D)  $\text{Ti}_2\text{O}_3$
- (E)  $\text{Ti}_3\text{O}_5$

All of the moles of Ti in the  $\text{TiO}_2$  end up in the  $\text{Ti}_x\text{O}_y$ .

If we calculate the number of moles of Ti in the starting material, then we will know moles of Ti in the product. Then we can convert that to a mass of Ti, and thus find the mass of O in the product by taking a difference. Then we can determine the molar ratio of Ti and O in the product. At every stage, use units to help with conversions.

$$1.598 \text{ g TiO}_2 \times \frac{1 \text{ mol TiO}_2}{79.878 \text{ g TiO}_2} \times \frac{1 \text{ mol Ti}}{1 \text{ mol TiO}_2} = 0.02001 \text{ mol Ti}$$

$$\text{mol Ti in TiO}_2 = \text{mol Ti in Ti}_x\text{O}_y$$

$$\therefore \text{mol Ti in Ti}_x\text{O}_y = 0.02001$$

$$\text{mass of Ti in Ti}_x\text{O}_y = 0.02001 \text{ mol Ti} \times \frac{47.88 \text{ g Ti}}{1 \text{ mol Ti}} = 0.9579 \text{ g Ti}$$

$$\text{mass of O in Ti}_x\text{O}_y = \text{mass of sample} - \text{mass Ti}$$

$$\text{mass of O in Ti}_x\text{O}_y = 1.438 \text{ g} - 0.9579 \text{ g} = 0.4801 \text{ g O}$$

$$\text{mol of O in Ti}_x\text{O}_y = 0.4801 \text{ g O} \times \frac{1 \text{ mol O}}{15.999 \text{ g O}} = 0.03001 \text{ mol}$$

Thus we have a molar ratio of:  $\text{Ti}_{0.02001}\text{O}_{0.03001}$

Divide each number by the smallest value:

$$\text{Ti}_{0.02001/0.02001}\text{O}_{0.03001/0.02001} = \text{Ti}_1\text{O}_{1.5} \text{ or, in whole numbers, Ti}_2\text{O}_3.$$

25. Based on Lewis structures in which all atoms obey the *octet rule as closely as possible*, which of the following species would be expected to have the **strongest** **nitrogen-oxygen bond**?



- (A)  $\text{NO}$   
(B)  $\text{NO}^+$   
(C)  $\text{NO}_2^+$   
(D)  $\text{NO}_2^-$   
(E)  $\text{NO}_3^-$

Draw the charge-minimized Lewis structures for all the species, calculate the average N-O bond order, and use the direct relationship between bond order and bond strength: for a given type of bond (e.g. N-O bond) the higher the bond order, the stronger the bond.

The following are descriptions of the charge-minimized Lewis structures:

$\text{NO}_2^-$  One N-O single bond, one N=O double bond. Lone electron pair on N. Two lone electron pairs on the doubly bonded O, and 3 lone electron pairs on the singly bonded O, along with a -1 formal charge. Average N-O bond order = 1.5.

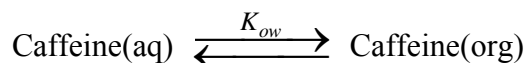
$\text{NO}_3^-$  Two N-O single bonds, one N=O double bond. Two lone electron pairs on the doubly bonded O, and 3 lone electron pairs on the singly bonded O atoms, along with -1 formal charges. Formal charge of +1 on N. Average N-O bond order = 1.33.

$\text{NO}$  Double N=O bond. Two lone electron pairs on O, one lone electron pair on N, plus a single electron on N (this is a radical, an odd-electron species). Average N-O bond order = 2.

$\text{NO}^+$  Triple N-O bond. One lone electron pair on O, along with a +1 formal charge, and one lone electron pair on N. Average N-O bond order = 3.

$\text{NO}_2^+$  Two N=O double bonds, formal +1 charge on N, 2 lone electron pairs on each O. Average N-O bond order = 2.

26. Decaffeination is accomplished using the partitioning of caffeine from coffee beans in water into an organic solvent, as expressed in the following equilibrium.

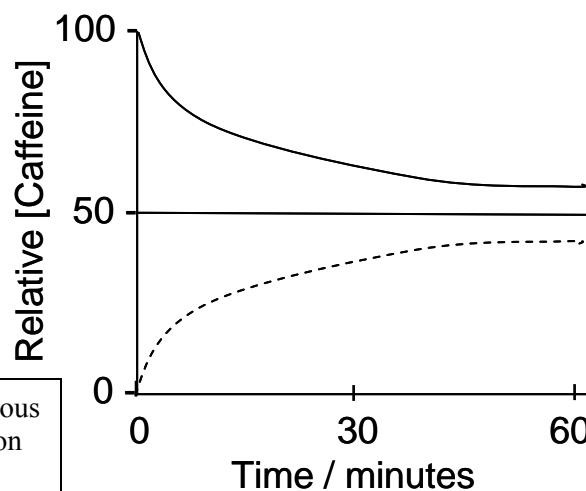


The time taken to establish equilibrium can be followed using the data set (graph) below, where we measure the changing concentration of caffeine in each solution.

Identify the **TRUE** statement(s) with respect to this process and the graph below.

- (i) The magnitude of  $K_{ow}$  for this process is less than one, since the  $[\text{Caffeine}]_{\text{aq}} > [\text{Caffeine}]_{\text{org}}$  at equilibrium
- (ii) At  $t = 0$ ,  $Q < K_{ow}$
- (iii) At  $t = 60$  minutes, equilibrium is achieved, and there is no further exchange of caffeine molecules between the two phases.
- (iv) The dotted line represents the change in concentration of caffeine in the water phase with time.

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



Statement (i) is TRUE: We start with only caffeine in the aqueous phase, so the solid line on the graph represents the concentration of caffeine in the aqueous layer, and the dashed line represents the concentration of caffeine in the organic layer. There is a greater concentration in the aqueous layer, so the  $K$  will be less than 1.  $K = [\text{caffeine}]_{\text{org}} / [\text{caffeine}]_{\text{H}_2\text{O}}$

Statement (ii) is TRUE: At time zero we have only caffeine in the aqueous layer, so  $Q$  is less than  $K$ .

Statement (iii) is FALSE: equilibrium is dynamic, and so molecules continue to exchange between the phases, however no change in relative concentration is observed.

Statement (iv) is FALSE: see above, for statement (i).

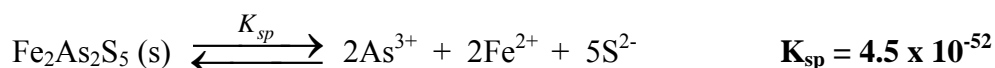
Name: \_\_\_\_\_

Student number: \_\_\_\_\_

**Use the following information for questions 27 and 28**

Many communities in Bangladesh suffer from high levels of arsenic ( $\text{As}^{3+}$ ) in their ground water. The source of this arsenic is a mineral called arseno-pyrite, which can be represented as  $\text{Fe}_2\text{As}_2\text{S}_5$ .

If the ground water concentration of  $\text{As}^{3+}$  is governed by the following equilibrium,



then use this information to answer the **following 2 questions**.

27. The World Health Organization guideline for  $[\text{As}^{3+}]$  is 0.01 mg/L. What is the **concentration of  $\text{As}^{3+}$  in the ground water, relative to the guideline concentration?** (Assume the water is otherwise free of salts).

*Note:* to take the nth root (n) of a number, x, using the CASIO fx—991MS calculator:  
Enter: **n Shift ^ x** (4 key strokes, in this sequence).

- (A) 200× greater
- (B) 10× greater
- (C) 5× greater
- (D) 400× greater
- (E) 2× greater

$$\begin{aligned}
 K_{sp} &= [\text{As}^{3+}]^2 [\text{Fe}^{2+}]^2 [\text{S}^{2-}]^5 \\
 \text{To solve for } [\text{As}^{3+}], \text{ let } [\text{As}^{3+}] &= 2x \\
 \text{Then } [\text{Fe}^{2+}] &= 2x \text{ and } [\text{S}^{2-}] = 5x \\
 K_{sp} &= [2x]^2 [2x]^2 [5x]^5 \\
 4.5 \times 10^{-52} &= [2x]^2 [2x]^2 [5x]^5 \\
 4.5 \times 10^{-52} &= (4x^2)(4x^2)(3125x^5) \\
 4.5 \times 10^{-52} &= 50,000 x^9 \\
 (4.5 \times 10^{-52}) / (50,000) &= x^9 \\
 9.0 \times 10^{-57} &= x^9 \\
 x &= (9.0 \times 10^{-57})^{1/9} \\
 x &= 5.925 \times 10^{-7} \text{ mol/L} \\
 \text{But } [\text{As}^{3+}] &= 2x, [\text{As}^{3+}] = 1.185 \times 10^{-6} \text{ mol/L} \\
 \text{W.H.O. guideline} &= (0.01 \text{ mg/L} \times 10^{-3} \text{ g/mg}) / 74.922 \text{ g/mol} \\
 &= 1.33 \times 10^{-7} \text{ mol/L} \\
 \text{Relative concentration} &= (1.185 \times 10^{-6} \text{ mol/L}) / (1.33 \times 10^{-7} \text{ mol/L}) \\
 &= 8.9 \text{ times greater, or } 10 \times \text{ greater.}
 \end{aligned}$$

Use also the information on the previous page to answer this question.

28. Water purification by removal of  $\text{As}^{3+}$  can be accomplished using a filtration process, which takes advantage of the low solubility of an arsenic-iron hydroxide complex. Water contaminated with  $\text{As}^{3+}$  is passed through an iron hydroxide ( $\text{Fe}(\text{OH})_2$ ) filter, which causes the precipitation of a complex that can be represented by  $\text{As}_2\text{Fe}(\text{OH})_8$ . Which of the following statements is **TRUE**?

- (i) The sum of the exponents in the  $K_{\text{sp}}$  expression for  $\text{Fe}_2\text{As}_2\text{S}_5$  is three, and the solid does not appear in the expression of the equilibrium constant.
- (ii) The presence of another sulfide-containing mineral in the soil, with a  $K_{\text{sp}}$  comparable to  $K_{\text{sp}}$  for  $\text{Fe}_2\text{As}_2\text{S}_5$ , would act to suppress the concentration of  $\text{As}^{3+}$  because of the common ion effect.
- (iii)  $K_{\text{sp}}(\text{Fe}_3\text{As}_2\text{S}_5) > K_{\text{sp}}(\text{As}_2\text{Fe}(\text{OH})_8)$  to ensure the removal of arsenic from the ground water

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

(i) FALSE: From previous page,  $K_{\text{sp}} = [\text{As}^{3+}]^2[\text{Fe}^{2+}]^2[\text{S}^{2-}]^5$

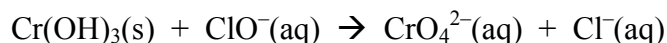
(ii) TRUE: Addition of sulfide ion ( $\text{S}^{2-}$ ) to the equilibrium shown on the previous page would shift the equilibrium to the left (Le Châtelier's principle).

(iii) TRUE: The  $K_{\text{sp}}$  (extent of ionization) of  $\text{As}_2\text{Fe}(\text{OH})_8$  must be less than  $K_{\text{sp}}$  of  $\text{Fe}_3\text{As}_2\text{S}_5$  in order for the filter to work effectively. The  $\text{As}^{3+}$  ion is present in the water because it comes from the dissolution of  $\text{Fe}_3\text{As}_2\text{S}_5$ . In order to precipitate the  $\text{As}^{3+}$  ion, we want to capture it in a less soluble complex,  $(\text{As}_2\text{Fe}(\text{OH})_8)$ , smaller  $K_{\text{sp}}$ .



Name: \_\_\_\_\_

Student number: \_\_\_\_\_

29. **Balance** the following redox reaction in **aqueous basic** solution.

When the reaction has been balanced correctly, the **stoichiometric coefficients for Cr(OH)<sub>3</sub>, ClO<sup>-</sup>, and OH<sup>-</sup>**, given in order from **left to right** are:

(A) 3, 4, 5

(B) 2, 3, 7

(C) 2, 3, 4

(D) 2, 4, 6

(E) 1, 2, 3

Oxidation numbers:

Reactants: Cr (+3), O(-2), H(+1), Cl(+1), O(-2)

Products: Cr(+6), O(-2), Cl(-1).

Cr is oxidized from +3 to +6.

Cl is reduced from +1 to -1.

Half-reactions:

Oxidation:  $5 \text{OH}^-(\text{aq}) + \text{Cr(OH)}_3(\text{s}) \rightarrow \text{CrO}_4^{2-}(\text{aq}) + 3 \text{e}^- + 4 \text{H}_2\text{O}(\text{l})$

Reduction:  $\text{H}_2\text{O}(\text{l}) + \text{ClO}^-(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq})$

Multiply Oxidation by 2, Reduction by 3 (to make electrons balance):

Oxid:  $10 \text{OH}^-(\text{aq}) + 2 \text{Cr(OH)}_3(\text{s}) \rightarrow 2 \text{CrO}_4^{2-}(\text{aq}) + 6 \text{e}^- + 8 \text{H}_2\text{O}(\text{l})$

Red:  $3 \text{H}_2\text{O}(\text{l}) + 3 \text{ClO}^-(\text{aq}) + 6 \text{e}^- \rightarrow 3 \text{Cl}^-(\text{aq}) + 6 \text{OH}^-(\text{aq})$

Overall:

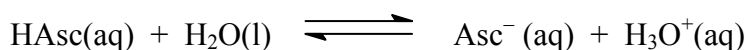
$10 \text{OH}^-(\text{aq}) + 2 \text{Cr(OH)}_3(\text{s}) + 3 \text{H}_2\text{O}(\text{l}) + 3 \text{ClO}^-(\text{aq}) + 6 \text{e}^- \rightarrow 2 \text{CrO}_4^{2-}(\text{aq}) + 6 \text{e}^- + 8 \text{H}_2\text{O}(\text{l}) + 3 \text{Cl}^-(\text{aq}) + 6 \text{OH}^-(\text{aq})$

Cancel out species which appear on both sides:

$4 \text{OH}^-(\text{aq}) + 2 \text{Cr(OH)}_3(\text{s}) + 3 \text{ClO}^-(\text{aq}) \rightarrow 2 \text{CrO}_4^{2-}(\text{aq}) + 5 \text{H}_2\text{O}(\text{l}) + 3 \text{Cl}^-(\text{aq})$

30. Linus Pauling, two-time individual winner of both the Nobel Prize in Chemistry and Nobel Prize for Peace was a long-time advocate of **high dosage** usage of **ascorbic acid** ( $\text{C}_6\text{H}_8\text{O}_6$ , shown below as **HAsc**) as a way to prevent various chronic diseases during ageing.

What is the **final pH** in the stomach after ingestion of a **1000 mg** dose of ascorbic acid ( $K_a = 5.01 \times 10^{-5}$ )? Assume the stomach is “empty” and the stomach volume is only **5.0 mL** of aqueous HCl, at **initial pH = 2.50**.



- (A) pH = 3.08
- (B) pH = 2.50
- (C) pH = 2.21
- (D) pH = 2.03
- (E) pH = 1.87

We have the ionization of a weak acid in a solution which already has acid present, thus we have initial concentrations of weak acid and also of  $\text{H}_3\text{O}^+$ . The initial concentration of ascorbic acid is needed, in mol/L.

$$\text{mol C}_6\text{H}_8\text{O}_6 = 1000 \text{ mg C}_6\text{H}_8\text{O}_6 \times \frac{10^{-3} \text{ g}}{\text{mg}} \times \frac{1 \text{ mol C}_6\text{H}_8\text{O}_6}{176.1232 \text{ g C}_6\text{H}_8\text{O}_6} = 5.68 \times 10^{-3} \text{ mol}$$

concentration  $\text{C}_6\text{H}_8\text{O}_6 = n/V = 5.68 \times 10^{-3} \text{ mol} / 5.0 \times 10^{-3} \text{ L} = 1.136 \text{ M}$

concentration of  $\text{H}_3\text{O}^+$  from stomach acid =  $10^{-\text{pH}} = 3.16 \times 10^{-3} \text{ M}$

	$\text{HAsc(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Asc}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	
Initial	1.136 M	0 $3.162 \times 10^{-3} \text{ M}$
Change	-x	+x      +x
Eqm	$1.136 - x \text{ M}$	x M $3.162 \times 10^{-3} + x \text{ M}$

$$K_a = \frac{[\text{Asc}^-][\text{H}_3\text{O}^+]}{[\text{HAsc(aq)}]} = 5.01 \times 10^{-5} = \frac{(x)(3.16 \times 10^{-3} + x)}{(1.136 - x)}$$

We have a quadratic to solve. The quadratic equation comes out to be:

$$x^2 + 3.212 \times 10^{-3} x - 5.6936 \times 10^{-5} = 0$$

Solving for x with the use of the quadratic formula gives us:

$$x = 6.11 \times 10^{-3} \text{ M.}$$

To find pH, we need the equilibrium concentration of  $\text{H}_3\text{O}^+$ , which is

$$3.162 \times 10^{-3} + x = 3.162 \times 10^{-3} + 6.11 \times 10^{-3} \text{ M} = 9.27 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} [9.27 \times 10^{-3}] = 2.03.$$