

Name: _____

Student number: _____

Chemistry 1AA3**First Test****February 4th, 2005****McMaster University****VERSION 1 - Solutions**

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Duration: 100 minutes

This test contains 16 numbered pages. There are **20** multiple-choice questions appearing on pages numbered 3 to 14. Page 15 includes some useful data and equations, and there is a periodic table on page 16. 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 15 are each worth 2 marks, questions 16 – 20 are each worth 3 marks; the total marks available are 45. 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.

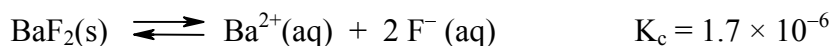
Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables or any aids, other than those provided, is not allowed.

Continued on next page...

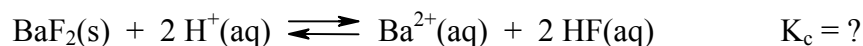
You are writing VERSION 1 of this test. Make sure you have correctly entered your version number ("1") in the correct column on your scan sheet (see p. 2 for details).

Questions 1 through 15 are worth two (2) marks each.

1. In the absence of acid, barium fluoride dissolves in water according to the equation:



The solubility of barium fluoride is affected by the acid-base chemistry of the fluoride ion. The acid dissociation constant, K_a , of HF is 7.1×10^{-4} . Find the **equilibrium constant, K_c** , for the overall reaction,



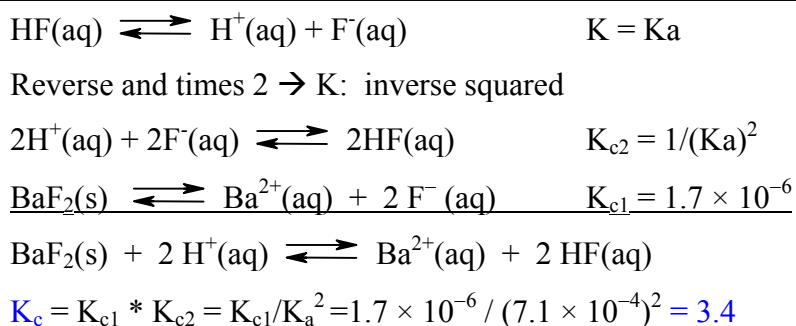
(A) 8.6×10^{-13}

(B) 1.2×10^{-9}

(C) 1.4×10^{-3}

(D) 2.4×10^{-3}

(E) 3.4



2. Equal volumes of 0.00400 M FeCl₃(aq) and 0.00100 M of KSCN(aq) were mixed.

The following reaction occurs at 25 °C:



The equilibrium concentration of FeSCN²⁺(aq) is equal to 1.26×10^{-4} M. What is the **equilibrium concentration of Fe³⁺(aq)?**

(A) 4.00×10^{-3} M

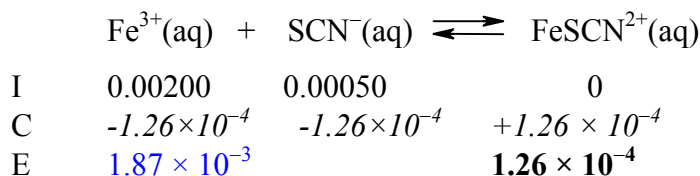
(B) 3.87×10^{-3} M

(C) 1.87×10^{-3} M

(D) 3.75×10^{-4} M

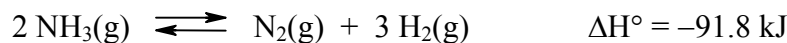
(E) 2.13×10^{-4} M

Divide initial concentrations by 2 for dilution upon mixing.



See lab 6

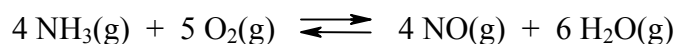
3. For the equilibrium reaction shown below:



Which one of the following changes will cause the equilibrium to shift to the **RIGHT** (*i.e.*, towards products)?

- | | | |
|-----|--|-------------------------------------|
| (A) | Adding a catalyst. | <i>No effect</i> |
| (B) | Increasing the temperature. | <i>Shifts endothermic (left)</i> |
| (C) | Adding Ne(g) to the reaction. | <i>No effect</i> |
| (D) | Increasing the concentration of NH ₃ (g). | <i>to remove NH₃</i> |
| (E) | Reducing the volume of the reaction vessel. | <i>Shifts to fewer moles (left)</i> |

4. For the equilibrium reaction shown below:



Choose the statements that are **TRUE**:

- | | | |
|-------|---|--------------------------------------|
| (i) | Addition of NO(g) shifts the equilibrium to the left. | <i>T</i> |
| (ii) | Addition of H ₂ O(g) has no effect on the equilibrium. | <i>F – shifts left</i> |
| (iii) | Addition of HCl(g) shifts the equilibrium to the left. | <i>T – make NH₃</i> |
| (iv) | K _p = K _c (RT) for this equilibrium. | <i>T, dn = 10 – 9 = +1</i> |
| (v) | K _c = [NO] ⁴ / [NH ₃] ⁴ [O ₂] ⁵ for this equilibrium. | <i>F – missing H₂O(g)</i> |
-
- | | |
|-----|-------------------|
| (A) | i, ii, v |
| (B) | <i>i, iii, iv</i> |
| (C) | i, iv |
| (D) | ii, iii |
| (E) | ii, iv, v |

5. Choose the **FALSE** statements regarding chemical equilibrium.

- (i) When the reaction quotient is greater than the equilibrium constant, the reaction will proceed in the reverse direction.
 - (ii) Increasing the temperature always increases the equilibrium constant.
 - (iii) When the system has reached equilibrium, the molecules stop reacting.
 - (iv) When the system has reached equilibrium, the concentrations of the products and reactants remain constant.
- (A) i, ii
 (B) i, iii
 (C) ii, iii
 (D) ii, iv
 (E) iii, iv

6. What is the **pOH** of a 100 mL solution of 0.00059 M HNO_3 ?

- (A) 3.23
 (B) 4.23
 (C) 7.00
 (D) 9.77
 (E) 10.77

A strong acid dissociates completely,
 $[\text{H}^+] = 0.00059\text{M}$
 $\text{pH} = -\log[\text{H}^+] = 3.23$
 $\text{pOH} = 14.00 - \text{pH} = 10.77$

7. Your stomach (volume = 2.5 L) has a pH of 1.00 because of the presence of HCl.

How many grams of $\text{Mg}(\text{OH})_2$ (58.3 g/mol) do you need to add to completely neutralize the acid in your stomach?

- (A) 2.9 g
 (B) 5.8 g
 (C) 7.3 g
 (D) 15 g
 (E) 21 g

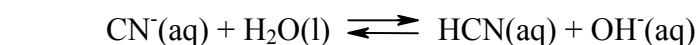
$\text{Mg}(\text{OH})_2 + 2\text{HCl} \rightarrow \text{MgCl}_2 + 2\text{H}_2\text{O}$
 Strong base + strong acid
 $[\text{H}^+] = 10^{-1.00} = 1.0 \times 10^{-1} = 0.10 \text{ mol/L}$
 $n(\text{HCl}) = 0.10 \text{ M} \times 2.5 \text{ L} = 0.25 \text{ mol}$
 $n(\text{Mg}(\text{OH})_2) = n(\text{HCl})/2 = 0.125 \text{ mol}$
 $m(\text{Mg}(\text{OH})_2) = 0.125 \text{ mol} \times (58.3 \text{ g/mol})$
 $= 7.3\text{g}$

8. You prepare 250 mL of a solution that is 0.200 M in KCN(aq) and 0.100 M in HCN(aq). You measure the pH of the solution and find that it is 9.70. What is the **base dissociation constant, K_b** , for CN^- ?

- (A) 1.0×10^{-4}
 (B) 2.5×10^{-5}
 (C) 7.3×10^{-8}
 (D) 4.0×10^{-10}
 (E) 1.0×10^{-10}

A basic solution, so OH^- is produced.

$$\text{pOH} = 14.00 - 9.70 = 4.30, [\text{OH}^-] = 10^{-4.30} = 5.0 \times 10^{-5} = x$$



I	0.200	0.100	0
C	-x	+x	+x
E	0.199 ₉₅	0.099 ₉₅	5.0×10^{-5}

Use Henderson Hasselbalch (can use small x) or

$$K_b = [\text{HCN}][\text{OH}^-] / [\text{CN}^-] = (0.099_{95})(5.0 \times 10^{-5}) / (0.199_{95}) = 2.5 \times 10^{-5}$$

9. If each of the solutions below are 0.10 M, which of the following mixtures will result in the formation of a **buffer solution**?

- (i) 100 mL HF and 100 mL NaOH
 (ii) 50 mL NaF and 100 mL HCl
 (iii) 100 mL NaF and 50 mL HCl
 (iv) 100 mL HF and 50 mL NaF
 (v) 100 mL NaCl and 50 mL HCl

Need **weak/weak pair** for buffer
 At completion have:

- (i) NaF + water
 (ii) HF, HCl + NaCl
 (iii) NaF + HF
 (iv) HF + NaF
 (v) NaCl + HCl

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

10. Calculate the **pH** of the solution that results when the solutions below are mixed

together: (K_a for $\text{HNO}_2 = 4.5 \times 10^{-4}$)

- (i) 25.0 mL of 0.100 M NaNO_2
- (ii) 10.0 mL of 0.100 M HNO_3
- (iii) 35.0 mL of 0.100 M HNO_2

3. Use H-H eq'n or

$$K_a = x \text{ (0.0214 / 0.0643)}$$

$$[\text{H}^+] = x = 4.5 \times 10^{-4} * (3.0)$$

$$\text{pH} = -\log(1.35 \times 10^{-4}) = 2.87$$

(A) 2.87

(B) 2.98

(C) 3.21

(D) 3.52

(E) 3.82

1. First react strong with weak to completion (HNO_3 is limiting):

	HNO_3	+ NaNO_2	\rightarrow	NaNO_3	+ HNO_2
I	0.00100 mol	0.00250 mol		0	0.00350
F	0	0.00150 mol	(ignore)		0.00450

2. Divide by total volume to get initial concentrations for ICE table.

Ignore the neutral spectator ions, Na^+ and NO_3^- . Remaining weak reacts with water to equilibrium. $K_a > K_b$ so the buffer is acidic.

	$\text{HNO}_2 + \text{H}_2\text{O}$	\rightleftharpoons	NO_2^-	+	H_3O^+
I	0.0642 ₉		0.0214 ₃		0
C	-x		+x		+x
E	~0.0643		~0.0214		x ($x < 1\%$ of 0.02)

11. You are given 1.50 L of a solution that is 0.149 M hypochlorous acid (HOCl ,

$K_a = 3.5 \times 10^{-8}$). **What mass of NaOCl(s)** must be added to produce a solution with $\text{pH} = 6.90$? Assume no volume change on addition of solid NaOCl .

(A) 1.2 g

(B) 3.1 g

(C) 3.2 g

(D) 4.6 g

(E) 6.0 g

Ignore the neutral spectator ion, Na^+ . Buffer is acidic, so HOCl reacts with water. Equilibrium and initial concentrations of weak pair are approximately equal. Find $[\text{OCl}^-]$ from known pH.

	$\text{HOCl} + \text{H}_2\text{O}$	\rightleftharpoons	OCl^-	+	H_3O^+
I	0.149		Y		$10^{-7.00}$
C	-x		+x		+x
E	~0.149		~Y		$10^{-6.90}$

$$[\text{H}_3\text{O}^+] = 10^{-6.90} = 1.26 \times 10^{-7} \quad x \text{ is very small } (3 \times 10^{-8})$$

$$K_a = 3.5 \times 10^{-8} = [\text{OCl}^-][\text{H}_3\text{O}^+] / [\text{HOCl}] = Y(1.26 \times 10^{-7}) / (0.149)$$

$$[\text{OCl}^-] = Y = 0.041_4 \text{ mol/L}$$

$$m(\text{NaOCl}) = 0.041_4 \text{ mol/L} * 1.50 \text{ L} * (75.5 \text{ g/mol}) = 4.6 \text{ g}$$

12. In the titration of an aqueous solution of a weak base with aqueous HCl, which of the following statements is **FALSE** at the **half-equivalence point**?

- (A) Half of the weak base has reacted.
- (B) The solution is classified as a buffer.
- (C) All of the HCl added to this point has reacted.
- (D) The indicator should have begun to noticeably change colour.
- (E) The pH at this point can be calculated from the K_b of the weak base.

Indicator should begin to change colour near the equivalence point.

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

- (i) When reacting with H_2O , BCl_3 will act as a Lewis base.
- (ii) The conjugate base of HCO_3^- is CO_3^{2-} .
- (iii) CaO dissolves to give a solution with $pH < 7$.
- (iv) F_3CCOOH is a weaker acid than Cl_3CCOOH .

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

- i) BCl_3 is a Lewis acid, it has less than an octet around B, and so would like to accept a pair of electrons. The O of H_2O is the electron donor (the base).
- ii) True, has one less H^+
- iii) False, metal oxides give basic solutions.
- iv) False, the electronegative F atoms help spread the charge in the conjugate base, since the base is weaker (more stable) the acid is stronger.

14. The **relative acid strengths** of four series of substances are shown below, listed from strongest to weakest. Examine each series and **decide whether each ordering is correct** and pick the answer below that matches your assessment.

- (i) $\text{HOCl} > \text{HOBr} > \text{HOI}$
- (ii) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2$
- (iii) $\text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$
- (iv) $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$

Which of the orderings above is **incorrect** (false)?

- (A) i
- (B) ii
- (C) iii
- (D) iv
- (E) none; *i.e.*, all correct

For oxoacids (i & ii), strength increases as # O atoms increases and as central atom becomes more electronegative. For hydrides (iii, & iv) strength increases from left to right (electronegativity) and down a group (atomic size).

15. From the following three chemical equilibria identify those reactions that can **only** be described using **the Lewis acid-base concept** and no other acid-base definition.

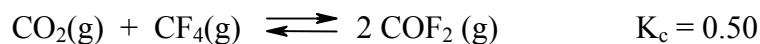
- (i) $\text{BCl}_3 + \text{CH}_3\text{OCH}_3 \rightleftharpoons \text{Cl}_3\text{B}-\text{O}(\text{CH}_3)_2$
- (ii) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{OH}_2^+ \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{CH}_3\text{OH}$
- (iii) $\text{AlCl}_3 + \text{CH}_3\text{Cl} \rightleftharpoons \text{AlCl}_4^- \text{CH}_3^+$

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

(ii) is a proton transfer, thus a Bronsted acid-base reaction (as well as Lewis). In (i) the bond is formed from O to B, in (iii) the bond is formed from Cl to Al. Neither water (Arrhenius) nor protons (Bronsted) are involved.

Questions 16 through 20 are worth three (3) marks each.

16. Carbon dioxide and tetrafluoromethane react at 1000°C according to the equation:



A flask is filled with $\text{COF}_2(\text{g})$ at a concentration of 0.040 mol/L. When the reaction reaches **equilibrium**, what is the **concentration of $\text{COF}_2(\text{g})$** ?

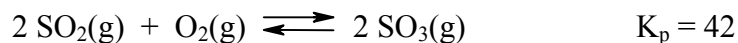
- (A) 0.010 M
- (B) 0.015 M
- (C) 0.020 M
- (D) 0.025 M
- (E) 0.030 M

	$\text{CO}_2(\text{g})$	+	$\text{CF}_4(\text{g})$	\rightleftharpoons	$2 \text{COF}_2(\text{g})$
I	0		0		0.040
C	+x		+x		-2x
E	x		x		0.040-2x

$K_c = 0.50 = [\text{COF}_2]^2 / ([\text{CO}_2][\text{CF}_4]) = (0.040-2x)^2/x^2$
 Take square root of both sides
 $0.707 = (0.040 - 2x) / x$
 $0.707x = 0.040 - 2x$
 $2.707x = 0.040$
 $x = 0.040 / 2.707 = 0.0147$
 At equilibrium,
 $[\text{COF}_2] = 0.040 - 2x = 0.040 - 0.0296 = 0.0104 \text{ M}$

Continued on next page...

17. A flask contains oxygen gas with an initial pressure of 0.20 atm at 900 K. Sulfur dioxide is added to the flask and it is sealed. The following reaction proceeds:

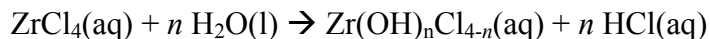


If the equilibrium partial pressure of $\text{SO}_3(\text{g})$ is 0.30 atm, what was **the initial partial pressure of $\text{SO}_2(\text{g})$** ?

- (A) 0.51 atm
 (B) 0.36 atm
 (C) 0.34 atm
 (D) 0.21 atm
 (E) 0.043 atm

	$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$		
I	Y	0.20	0
C	-2x	-x	+2x
E	Y-2x	0.20-x	0.30
$2x = 0.30 \text{ atm} \rightarrow x = 0.15 \text{ atm}$			
$K_p = 42 = P_{\text{SO}_3}^2 / (P_{\text{SO}_2}^2 * P_{\text{O}_2})$			
At equilibrium $(Y-2x)^2 = P_{\text{SO}_2}^2 = P_{\text{SO}_3}^2 / (K_p * P_{\text{O}_2})$			
$(Y-0.30)^2 = (0.30)^2 / (42 * 0.05) = 0.0429$			
$Y - 0.30 = 0.207$			
Initial pressure of $\text{SO}_2 = Y = 0.21 + 0.30 = 0.51 \text{ atm}$			

18. When placed in water, zirconium tetrachloride (ZrCl_4 , 233 g/mol) undergoes a complex reaction producing a number of zirconium-containing species and one HCl molecule for each Cl atom lost from ZrCl_4 , as shown in the reaction below:



Calculate the **pH** of the solution that would result from the addition of 0.50 g ZrCl_4 to 0.100 L of water if 90.0 percent of the Cl atoms in ZrCl_4 had reacted.

- (A) 1.07
 (B) 1.11
 (C) 2.07
 (D) 2.11
 (E) 2.67

$0.50 \text{ g ZrCl}_4 * (1 \text{ mol} / 233 \text{ g}) * (4 \text{ mol Cl} / \text{mol ZrCl}_4) = 8.58 \times 10^{-3} \text{ mol Cl}$
 $8.58 \times 10^{-3} \text{ mol Cl} * (90 \text{ reacted} / 100) = 7.725 \times 10^{-3} \text{ mol Cl reacted.}$
 1 mol HCl per mole Cl reacted
 $7.725 \times 10^{-3} \text{ mol HCl formed} = 7.725 \times 10^{-3} \text{ mol H}_3\text{O}^+ \text{ formed.}$
 $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.725 \times 10^{-3} \text{ mol} / 0.100 \text{ L}) = -\log (7.725 \times 10^{-2})$
pH = 1.11

19. An aqueous solution (volume = 25.0 mL) of 0.125 M butylated hydroxytoluene (BHT), a common anti-oxidant, was titrated with a 0.100 M NaOH solution. BHT and NaOH react in a 1:1 mole ratio. The pH at the equivalence point was 11.13. What is the pK_a of BHT to one decimal place?

- (A) 2.9
 (B) 9.2
 (C) 9.5
 (D) 9.7
 (E) 11.1

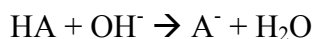
We are seeking a pK_a , so BHT is a weak acid, call it HA.

At the equivalence point,

$$\text{moles NaOH} = \text{moles HA} = 0.125 \text{ M} \times 0.025 \text{ L} = 3.125 \times 10^{-3}$$

$$\text{volume NaOH} = 3.125 \times 10^{-3} \text{ mol} / 0.100 \text{ M} = 0.03125 \text{ L}$$

$$\text{total volume} = 0.025 \text{ L} + 0.03125 \text{ L} = 0.05625 \text{ L}$$

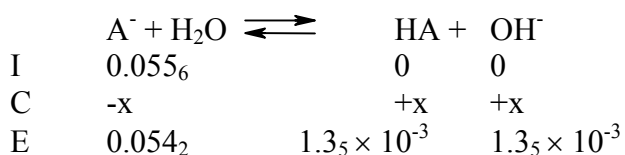


Strong base reacts to completion, and uses up all of the HA, producing 3.125×10^{-3} mol conjugate base, A^-

A^- then reacts with water to reach equilibrium. The 'initial' concentration of A^- is $3.125 \times 10^{-3} \text{ mol} / 0.05625 \text{ L} = 0.0556 \text{ M}$

The equilibrium concentration of OH^- is found from the pH.

$$\text{pOH} = 14.00 - 11.13 = 2.87; [\text{OH}^-] = 10^{-2.87} = 1.35 \times 10^{-3} \text{ M} = x$$



$$\text{K}_b = (1.35 \times 10^{-3})^2 / 0.0542 = 3.36 \times 10^{-5}$$

$$\text{pK}_b = 4.47; \quad \text{pK}_a = 14.00 - 4.47 = 9.53$$

20. Pentachlorophenol ($\text{C}_6\text{Cl}_5\text{OH}$), is a toxic compound used as a wood preservative and in pressure-treated lumber, and has a $K_a = 3.5 \times 10^{-9}$. An aqueous solution of pentachlorophenol (50.0 mL, 0.75 M) was titrated with 0.12 M KOH(aq). Which of one the following **indicators** would be the **best** to use for this titration?

	<u>Indicator</u>	<u>pH Range for Colour Change</u>
(A)	Bromphenol Blue	3.0 – 4.6
(B)	Bromthymol Blue	6.0 – 7.5
(C)	Cresol Red	7.2 – 8.8
(D)	Phenolphthalein	8.2 – 10.0
(E)	Alizarin Yellow R	10.0 – 12.0

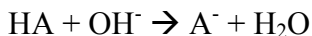
We want to find the indicator that changes colour as close as possible to the **equivalence point**. Call the weak acid HA

At the equivalence point,

$$\text{moles KOH} = \text{moles HA} = 0.75 \text{ M} \times 0.050 \text{ L} = 0.0375$$

$$\text{volume KOH} = 0.0375 \text{ mol} / 0.12 \text{ M} = 0.3125 \text{ L}$$

$$\text{total volume} = 0.050 \text{ L} + 0.3125 \text{ L} = 0.3625 \text{ L}$$



Strong base reacts to completion, and uses up all of the HA, producing 0.0375 mol conjugate base, A^-

A^- then reacts with water to reach equilibrium. The ‘initial’ concentration of A^- is $0.0375 \text{ mol} / 0.3625 \text{ L} = 0.103 \text{ M}$

	$\text{A}^- + \text{H}_2\text{O} \rightleftharpoons$	$\text{HA} + \text{OH}^-$
I	0.10 ₃	0 0
C	-x	+x +x
E	~0.10 ₃	x x

$$K_b = K_w / K_a = 1.00 \times 10^{-14} / 3.5 \times 10^{-9} = 2.86 \times 10^{-6}$$

$$2.86 \times 10^{-6} = x^2 / 0.103 \rightarrow x^2 = 2.94 \times 10^{-7}$$

$$[\text{OH}^-] = x = 5.42 \times 10^{-4} \quad (0.5\% \text{ of } 0.10)$$

$$\text{pOH} = -\log(5.42 \times 10^{-4}) = 3.27$$

$$\text{pH} = 14.00 - 3.27 = 10.73$$

Alazirin Yellow R will be changing colour at this pH

DATA PAGE

Some useful data are provided on this page. Other data appears with the questions.

$$R = 8.314 \text{ J/(K}\cdot\text{mol)} = 0.08206 \text{ L}\cdot\text{atm/(K}\cdot\text{mol)}$$

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

$$1 \text{ atm} = 760 \text{ mm Hg} = 101.325 \text{ kPa}$$

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$K_w = 1.0 \times 10^{-14}$$

$$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$$

$$K_a(\text{HF}) = 7.1 \times 10^{-4}$$

$$K_a(\text{HNO}_2) = 4.5 \times 10^{-4}$$

$$K_a(\text{HOCl}) = 3.5 \times 10^{-8}$$

$$K_a(\text{pentachlorophenol}) = 3.5 \times 10^{-9}$$

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