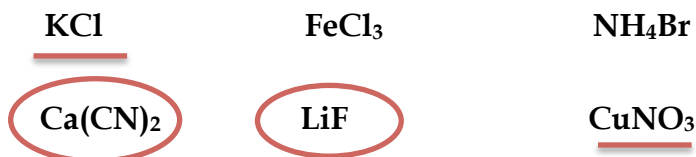


1. Short Answer Questions

- a. (0.5 pt) Bond breaking is always an exothermic process. TRUE FALSE
- b. (0.5 pt) A chemical equilibrium can be considered to be "going to completion" when the value of K is at least 10^{-10} 10^{-5} 10 10^5 or greater.
- c. (2 pts) From the list below, circle the basic salts and underline the neutral salts.

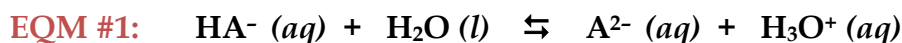


- d. (1 pt) For the reaction $2 A \rightleftharpoons B + 3 C$ the value of K is 44.5 at 25°C. The value of K for the reaction $2 B + 6 C \rightleftharpoons 4 A$ would be $K' = 1/K^2 = 5.05 \times 10^{-4}$.
- e. (1 pt) For the following three hydrofluoric acid solutions, underline the one with the highest percent ionization and circle the one with the lowest pH.
- 0.100 M HF 0.500 M HF 0.050 M HF 0.010 M HF

BONUS:

HA^- is an amphiprotic species. When added to water, the two equilibria below are possible. Circle the expected dominant equilibrium and determine if its equilibrium constant is less than or greater than 1. For H_2A , $\text{pK}_{\text{a}1} = 6.62$ and $\text{pK}_{\text{a}2} = 12.96$.

To receive all bonus points, show your reasoning.

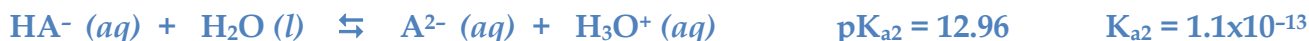


$K > 1$

$K < 1$

(BELOW IS A FULL-LENGTH EXPLANATION, THE KEY POINTS ARE IN BLUE)

Since H_2A is a diprotic acid, we can write two equilibria for its ionization:



So, EQM #1 above corresponds to the second ionization, with $K = K_{\text{a}2} = 1.1 \times 10^{-13}$

Therefore, A^{2-} is a diprotic base, and we can write two equilibria for its ionization:



So, EQM #2 above corresponds to the second ionization, with $K = K_{\text{b}2} = 4.2 \times 10^{-8}$

Comparing the two: EQM #1 $K_{\text{a}2} = 1.1 \times 10^{-13}$
 EQM #2 $K_{\text{b}2} = 4.2 \times 10^{-8}$

Since $K_{\text{b}2} > K_{\text{a}2}$, EQM #2 will dominate, and its value is less than 1!

2. Consider the following reaction: $A(g) + 2 B(g) \rightleftharpoons C(g)$

To a 2.40 L flask, A and B are added at initial pressures of 0.400 bar each. The mixture was allowed to equilibrate at 1000 K and the flask was found to contain 0.00444 mol of C.

THIS QUESTION IS FROM MIDTERM #1 2016

a) (4 pts) What is the value of K_P for the reaction?

$$P_C \text{ at EQM} = \frac{n_C RT}{V} = \frac{(0.00444 \text{ mol})(0.083145 \text{ L} \cdot \text{bar/mol} \cdot \text{K})(1000 \text{ K})}{2.40 \text{ L}}$$

$$= 0.154 \text{ bar}$$

	A(g) +	2 B(g)	\rightleftharpoons	C(g)
I	0.400	0.400		0
C	-0.154	-2(0.154)		+0.154
E	0.246	0.092		0.154

$$K_P = \frac{P_C}{(P_A)^2 \times P_B} = \frac{0.154}{(0.246)(0.092)^2} = 74.0$$

b) (2 pts) What is the percent yield of C?

$$? \text{ theoretical } P_C \text{ from A} = 0.400 \text{ bar A} \times \frac{1 \text{ bar C}}{1 \text{ bar A}} = 0.400 \text{ bar}$$

$$? \text{ theoretical } P_C \text{ from B} = 0.400 \text{ bar B} \times \frac{1 \text{ bar C}}{2 \text{ bar B}} = 0.200 \text{ bar}$$

Therefore, B is the LIMITING REAGENT.

$$\% \text{ yield} = \frac{0.154 \text{ bar}}{0.200 \text{ bar}} \times 100\% = 77.0\%$$

c) (1 pt) If the equilibrated gas mixture was then transferred to a container of smaller volume, what would be the resulting effect on the equilibrium?

SHIFT TOWARDS REACTANTS

SHIFT TOWARDS PRODUCTS

NO EFFECT

3. Your lab TA asks you to prepare a buffer solution with a pH of 5.10. The following reagents are all available to you: 500 mL of 0.250 M hydrofluoric acid, 500 mL of 0.250 M acetic acid, solid sodium fluoride and solid sodium acetate.

THIS IS A SLIGHTLY MODIFIED VERSION OF AN EXAMPLE IN THE COURSE NOTES

a) (1 pt) Which 2 ingredients will you use to prepare the desired buffer?



b) (2 pts) What is the base/acid ratio in the desired buffer?

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\right)$$

$$\therefore \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 10^{\text{pH} - \text{pK}_a} = 10^{5.10 - 4.74} = 2.29$$

c) (3 pts) What mass (in g) of solid base must you dissolve in the corresponding acid solution to achieve the desired buffer pH?

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 2.29$$

$$\therefore [\text{CH}_3\text{COO}^-] = 2.29 \times [\text{CH}_3\text{COOH}] = 2.29 \times 0.250 \text{ M} = 0.573 \text{ M}$$

$$? \text{ g CH}_3\text{COONa} = 0.500 \text{ L} \times \frac{0.573 \text{ mol OCl}^-}{\text{L}} \times \frac{1 \text{ mol CH}_3\text{COONa}}{1 \text{ mol CH}_3\text{COOH}} \times \frac{82.03 \text{ g CH}_3\text{COONa}}{\text{mol CH}_3\text{COONa}}$$

$$= 23.5 \text{ g}$$

d) (3 pts) If 5.00 mL of 1.00 M HCl is added to the buffer solution, what will be the new pH?

$$? \text{ mol H}_3\text{O}^+ \text{ added} = 0.00500 \text{ L} \times \frac{1.00 \text{ mol H}_3\text{O}^+}{\text{L}} = 0.0050 \text{ mol}$$

$$? \text{ mol CH}_3\text{COOH initial} = 0.500 \text{ L} \times \frac{0.250 \text{ mol OCl}^-}{\text{L}} = 0.1250 \text{ mol}$$

$$? \text{ mol CH}_3\text{COO}^- \text{ initial} = 0.500 \text{ L} \times \frac{0.573 \text{ mol HOCl}}{\text{L}} = 0.2865 \text{ mol}$$

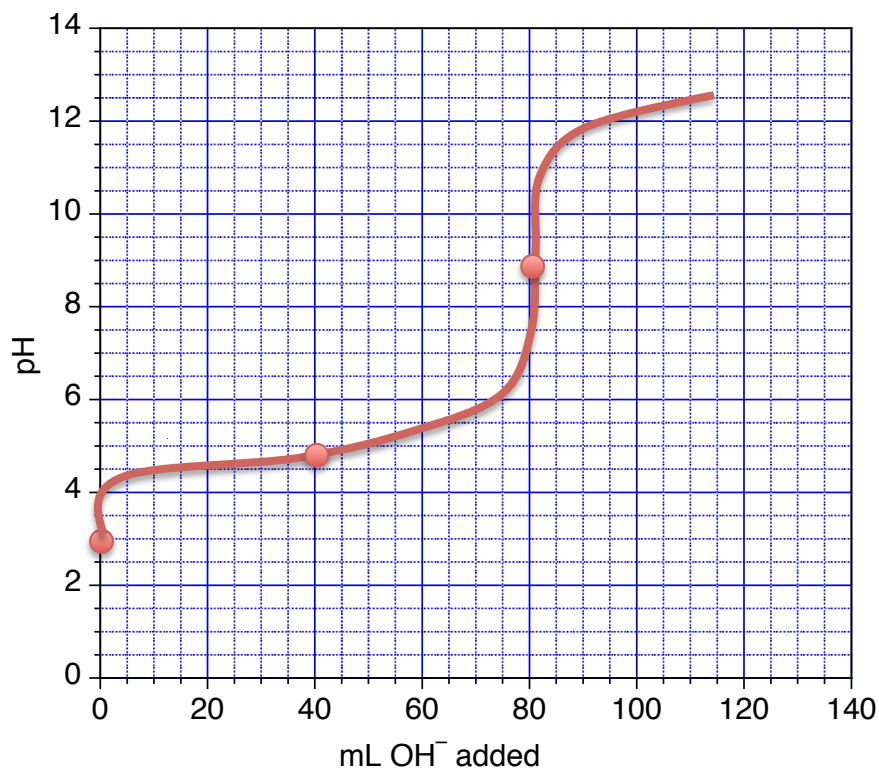
	A ⁻	+ H ₃ O ⁺	⇌	HA	+ H ₂ O
B	0.2865			0.1250	-
A		0.0050			-
M	-0.0050	-0.0050		+0.0050	-
A	0.2815	0		0.1300	-

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\right) = 4.74 + \log\left(\frac{0.2815}{0.1300}\right) = 5.08$$

4. You are performing a titration of 80.0 mL of 0.120 M HN_3 with 0.120 M NaOH. Determine the pH of the solution:

- (3 pts) initially
- (2 pts) at the half-equivalence point
- (4 pts) at the equivalence point
- (1 pt) Use these values to sketch a titration curve on the graph provided.

THIS QUESTION IS FROM THE 2015 FINAL EXAM



a) initial pH:

	HA	+ H ₂ O	⇌	H ₃ O ⁺	+ A ⁻
I	0.120	-		0	0
C	-x	-		+x	+x
E	0.120 - x	-		x	x

$$\text{pH} = -\log(0.00151) = 2.82$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$1.9 \times 10^{-5} = \frac{x^2}{0.120 - x} \approx \frac{x^2}{0.120}$$

$$\therefore x \approx 0.00151 \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{Check: } \frac{0.00151}{0.120} \times 100\% = 0.04\% \longrightarrow \text{PASSES}$$

b) At the $\frac{1}{2}$ equivalence point: $\text{pH} = \text{p}K_a = -\log(1.9 \times 10^{-5}) = 4.72$ (after 40 mL added)

c) At the equivalence point:

mol HA = mol OH⁻ added = 0.0096 mol (this corresponds to adding 80.0 mL of base)
 new [A⁻] = 0.0096 mol / (0.080 L + 0.080 L) = 0.060 M

Azide (N_3^-) is the conjugate base of a weak acid, so it hydrolyzes:

	A ⁻	+ H ₂ O	⇌	HA	+ OH ⁻
I	0.060	-		0	0
C	-x	-		+x	+x
E	0.060 - x	-		x	x

$$\text{pOH} = -\log(5.6 \times 10^{-6}) = 5.25$$

$$\text{pH} = 14 - 5.25 = 8.75$$

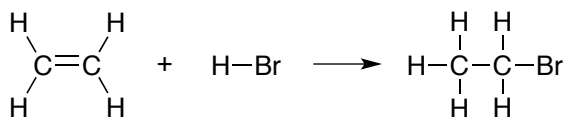
$$K_b = \frac{K_w}{K_a} = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$\frac{1.0 \times 10^{-14}}{1.9 \times 10^{-5}} = 5.2 \times 10^{-10} = \frac{x^2}{0.060 - x} \approx \frac{x^2}{0.060}$$

$$\therefore x \approx 5.6 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{Check: } \frac{5.6 \times 10^{-6}}{0.060} \times 100\% = 0.2\% \longrightarrow \text{PASSES}$$

5. (4 pts) With the table of bond energies, estimate the energy change of the following reaction:



Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
C-C	348	H-H	436
C=C	612	O-H	463
C-O	360	O=O	494
C=O	743	H-Br	363
C-H	412	C-Br	276

THIS IS SILBERBERG SUGGESTED PROBLEM 8.50

BROKEN:

1 x C=C	1 x 612 kJ	612 kJ
1 x H-Br	1 x 363 kJ	363 kJ
TOTAL		+ 975 kJ

FORMED:

1 x C-C	1 x 348 kJ	348 kJ
1 x C-H	1 x 412 kJ	412 kJ
1 x C-Br	1 x 276 kJ	276 kJ
TOTAL		-1036 kJ

$$\Delta E = +975 \text{ kJ} + (-1036 \text{ kJ}) = -61 \text{ kJ}$$

Question	Points Possible	Points Earned	TA Initial
1	5		
2	7		
3	9		
4	10		
5	4		
TOTAL	35		