Name:_____ Student Number:_____

CHEM 1002 A, N and V Midterm Test #2
March 4, 2016
Calculators Allowed
Make sure this test has 7 pages. You may tear off the last page.

Part A. Answer each of the six questions with a few sentences or equations where necessary. (5 Marks each)

1. For the endothermic reaction $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$ initially at equilibrium, which direction will the reaction shift (left, right or no shift) when if we make the following changes? (Tick one box in each case.)

Change	Left	Right	No Shift
Increase the temperature at constant pressure		✓	
Add some $N_{2(g)}$ at constant volume			✓
Remove some $CO_{(g)}$ at constant volume		✓	
Reduce the volume	✓		
Add some $C_{(s)}$			✓

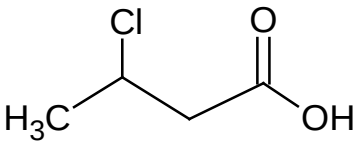
2. What is meant by the term “dynamic equilibrium?”

This refers to the fact that at equilibrium, the reaction has not stopped. But the forward and reverse reactions are going at the same rate, so concentrations do not change.

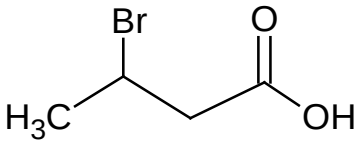
3. What is the conjugate acid of $H_2PO_4^-{}_{(aq)}$?

$H_3PO_{4(aq)}$

4. Which of the two molecules shown below would you expect to be a stronger acid? Why?



A



B

Structure A is the stronger acid. The more electronegative Cl atom attracts electrons towards itself more than the Br atom, including those in the O-H bond. This weakens the bond, allowing the H-atom to be pulled away by the base more easily.

5. Would the solubility of $NH_4NO_{3(s)}$ increase or decrease as the pH is increased? Show the relevant reactions and explain. $K_a(HNO_{3(aq)}) = 30$; $K_b(NH_{3(aq)}) = 1.8 \times 10^{-5}$.

The salt dissolves according to $NH_4NO_{3(s)} \rightarrow NH^+_{4(aq)} + NO^-_{3(aq)}$

The $NO_3^-{}_{(aq)}$ ion is a very weak base since $HNO_{3(aq)}$ is a very strong acid. Thus this ion has no effect on solution pH. But the $NH_4^+{}_{(aq)}$ ion is acidic because $NH_{3(aq)}$ is a weak base. Therefore:

$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$

Increasing the pH decreases $[H_3O^+_{(aq)}]$. This causes the equilibrium to shift right, $[NH_4^+{}_{(aq)}]$ to decrease, and so more $NH_4NO_{3(s)}$ dissolves to replace it. The solubility therefore increases.

6. If we add 50 mL of 0.10 M NaOH to 100 mL of 0.10 M HF, a buffer is created. Why? (show the relevant reaction and explain.

$OH^-_{(aq)} + HF \rightarrow F^-_{(aq)} + H_2O_{(l)}$ creates some $F^-_{(aq)}$, the conjugate base of the weak acid HF. A weak acid plus its conjugate base constitute a buffer.

Part B. **Answer any three of B1, B2, B3 and B4. If you answer all four, the best three will count. (20 marks each)**

B1. The reaction $H_{2(g)} + Br_{2(g)} \rightleftharpoons 2\ HBr_{(g)}$ has $K = 1.60 \times 10^5$ at 1024 K. 2.00 bar of $HBr_{(g)}$ is sealed in a vessel at 1024 K. Find the equilibrium partial pressures (in bar) of all three gases.

	$H_{2(g)}$	**$Br_{2(g)}$**	**$2\ HBr_{(g)}$**
Initial, bar	0	0	2.00
Change, bar	+x	+x	-2x
Equilibrium, bar	x	x	2.00 – 2x

At equilibrium,

$$K = \frac{p_{HBr}^2}{p_{H_2} p_{Br_2}} = \frac{(2.00 - 2x)^2}{x(x)}$$

$$\text{Thus, } K^{1/2} = \frac{2.00 - 2x}{x}$$

$$K^{1/2}x = 2.00 - 2x$$

$$(K^{1/2} + 2)x = 2.00$$

$$x = \frac{2.00}{K^{1/2} + 2} = \frac{2.00}{((1.60 \times 10^5)^{1/2} + 2)} = 0.004975$$

(Other solutions are possible, but noting that the expression for K is a perfect square makes the calculation easy.)

Thus

$$p_{H_2} = x = 0.00497 \text{bar}$$

$$p_{Br_2} = x = 0.00497 \text{bar}$$

$$p_{HBr} = 2.00 - 2(0.00497) = 1.99 \text{ bar}$$

Check: $K = \frac{p_{HBr}^2}{p_{H_2} p_{Br_2}} = \frac{(2.00 - 2x)^2}{x(x)} = \frac{(2.00 - 2(0.00497))^2}{0.00497(0.00497)} = 1.60 \times 10^5$

B2. (a) [8 marks] Calculate the pH of a solution made by dissolving 50.0 g of formic acid (HCOOH, K_a = 1.80×10^{-4}) in 2.50 L of water.

$$\frac{50.0\,\text{g}}{46.0\,\text{g mol}^{-1}} = 1.09\,\text{mol HCOOH}$$

[HCOOH] = 1.09 mol / 2.50 L = 0.436 M

$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$

	$[HCOOH_{(aq)}]$	$[H_3O^+_{(aq)}]$	$[HCOO^-_{(aq)}]$
Initial	0.436	0	0
Change	–x	+x	+x
Equilibrium	0.436–x	x	x

$$\frac{x(x)}{0.436 - x} = 1.80 \times 10^{-4} \approx \frac{x^2}{0.436}$$

$$x^2 = 0.436(1.80 \times 10^{-4})$$

$$x = 0.00886$$

$$pH = -\log_{10}(0.0089) = 2.05$$

(b) [12 marks] Calculate the pH of s solution made by dissolving 50.0 g of sodium formate ($NaHCOO_{(s)}$) in 2.50 L of water.

$$\frac{50.0\,\text{g}}{68.0\,\text{g mol}^{-1}} = 0.735\,\text{mol NaHCOO}$$

$[HCOO^-_{(aq)}]$ = 0.735 mol / 2.50 L = 0.294 M

$$K_b(HCOO^-_{(aq)}) = \frac{K_w}{K_a(HCOOH)} = \frac{1.00 \times 10^{-14}}{1.80 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$HCOO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCOOH_{(aq)} + OH^-_{(aq)}$

	$[HCOO^-_{(aq)}]$	$[HCOOH_{(aq)}]$	$[OH^-_{(aq)}]$
Initial	0.294	0	0
Change	–x	+x	+x
Equilibrium	0.294–x	x	x

$$\frac{x(x)}{0.294 - x} = 5.56 \times 10^{-11} \approx \frac{x^2}{0.294}$$

$$x^2 = 0.294(5.56 \times 10^{-11})$$

$$x = 4.04 \times 10^{-6}$$

$$pOH = -\log_{10}(4.04 \times 10^{-6}) = 5.39$$

$$pH = 14 - pOH = 14 - 5.39 = 8.61$$

B3. [20 marks] Calculate the concentrations of all species present (in M) and the pH in a 0.500 M solution of fumaric acid, $H_4C_4O_{4(aq)}$. For this acid, $K_{a1} = 8.85 \times 10^{-4}$ and $K_{a2} = 3.21 \times 10^{-5}$.
Please put your answers in the boxes at the bottom of this page.

$H_4C_4O_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_3C_4O_4^-{}_{(aq)}$

	$[H_4C_4O_{4(aq)}]$	$[H_3O^+_{(aq)}]$	$[H_3C_4O_4^-{}_{(aq)}]$
Initial	0.500	0	0
Change	–x	+x	+x
Equilibrium	0.500–x	x	x

$$\frac{[H_3O^+_{(aq)}][H_3C_4O^-_{4(aq)}]}{[H_4C_4O_{4(aq)}]} = K_{a_1} = 8.85\times10^{-4}$$

$$\frac{x(x)}{0.500-x} = 8.85\times10^{-4}$$

$$x^2 = 8.85\times10^{-4}(0.500-x)$$

$$x^2 + 8.85\times10^{-4}x - 4.42\times10^{-4} = 0$$

$$x = \frac{-8.85\times10^{-4} \pm \sqrt{(8.85\times10^{-4})^2 - 4(1)(-4.42\times10^{-4})}}{2(1)}$$

$$= \frac{-8.85\times10^{-4} \pm 0.0420}{2} = 0.0206 \text{ or } -0.0214$$

Choosing the positive root, x = 0.0206
Thus, $[H_4C_4O_{4(aq)}] = 0.500 - x = 0.500 - 0.0206 = 0.479$ M
$[HC_2O_4^-{}_{(aq)}] = x = 0.0206$ M
$[H_3O^+_{(aq)}] = x = 0.0206$ M
$pH = -\log_{10}[H_3O^+_{(aq)}] = -\log_{10}(0.0206) = 1.69$

$H_3C_4O_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2C_4O_4^{2-}{}_{(aq)}$

$$\frac{[H_3O^+_{(aq)}][H_2C_4O^{2-}_{4(aq)}]}{[H_3C_4O^-_{4(aq)}]} = K_{a_2} = 3.21\times10^{-5}$$

$$[H_2C_4O^{2-}_{4(aq)}] = \frac{K_{a_2}[H_3C_4O^-_{4(aq)}]}{[H_3O^+_{(aq)}]} = \frac{K_{a_2}(x)}{(x)} = K_{a_2} = 3.21\times10^{-5}\,\text{M}$$

$$[OH^-_{(aq)}] = \frac{K_w}{[H_3O^+_{(aq)}]} = \frac{1.0\times10^{-14}}{0.0206} = 4.85\times10^{-13}\,\text{M}$$

$[H_4C4O_{4(aq)}]$, M	$[H_3C_4O_4^-{}_{(aq)}]$, M	$[H_3O^+_{(aq)}]$, M	$[H_2C_4O_4^{2-}{}_{(aq)}]$, M	$[OH^-_{(aq)}]$, M	pH
0.479 M	0.0206 M	0.0206 M	3.21×10^{-5} M	4.85×10^{-13} M	1.69
[4 marks]	[4 marks]	[4 marks]	[3 marks]	[3 marks]	[2 marks]

B4. (a) [10 marks] Calculate the pH of a solution made by dissolving 100 g NaHCOO, and 20.0 g HCOOH in 2.5 L of water. K_a for HCOOH is 1.8×10^{-4}.

$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$

$NaHCOO_{(s)} \rightarrow Na^+_{(aq)} + HCOO^-_{(aq)}$

$$[HCOOH_{(aq)}] \approx \left(\frac{\frac{20.0\ \text{g}}{46.0\ \text{g mol}^{-1}}}{2.5\ \text{L}} \right) = 0.174\ \text{M}$$

$$[HCOO^-_{(aq)}] \approx \left(\frac{\frac{100\ \text{g}}{68.0\ \text{g mol}^{-1}}}{2.5\ \text{L}} \right) = 0.588\ \text{M}$$

$$pK_a = -\log_{10}(K_a) = -\log_{10}(1.8 \times 10^{-4}) = 3.74$$

$$pH = pK_a - \log_{10}\left(\frac{[\text{acid}]}{[\text{base}]}\right)$$

$$= pK_a - \log_{10}\left(\frac{[HCOOH_{(aq)}]}{[HCOO^-_{(aq)}]}\right)$$

$$= 3.74 - \log_{10}\left(\frac{0.174\ \text{M}}{0.588\ \text{M}}\right)$$

$$= 3.74 - (-0.53)$$

$$= 4.27$$

(b) [10 marks] 0.050 mol $NaOH_{(s)}$ is dissolved in 1.00 L of the above buffer solution. Calculate the new pH.

$OH^-_{(aq)} + HCOOH_{(aq)} \rightarrow HCOO^-_{(aq)} + H_2O_{(aq)}$

Thus in 1.00 L of solution, $[HCOOH_{(aq)}]$ decreases by 0.050 mol/L, and $[HCOO^-_{(aq)}]$ increases by 0.050 mol/L

The new concentrations are therefore $[HCOOH_{(aq)}] = 0.174 - 0.050 = 0.124$ M and $[HCOO^-_{(aq)}] = 0.588 + 0.050 = 0.638$ M

$$pH = 3.74 - \log_{10}\left(\frac{0.124\ \text{M}}{0.638\text{M}}\right)$$

$$= 3.74 - (-0.71)$$

$$= 4.45$$

Part A	B1	B2	B3	B4	Total / 90

Some Useful Constants

$N_{Av} = 6.02 \times 10^{23}\ mol^{-1}$

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

$0^{o}C = 273.15\ K$

$K_w = 1.00 \times 10^{-14}$

IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	(8)	VIIIB (9)	(10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3.	57 La 138.9	72. Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 Ds (269)	111 Rg (280)	112 Cp (277)		114 Fl (289)		116 Lv (293)		

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	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 (260)