

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

**Part 0: Warmup. 4 points each**

1. A solution of sucrose (table sugar, a nonvolatile, non-dissociating solute) in water has a boiling point of 105°C. What would the boiling point be of a NaCl solution of the same concentration?

- a. 100°C
- b. 105°C
- c. 110°C
- d. 102.5°C
- e. not enough information to tell.

Answer   c  

2. The acids  $\text{HC}_2\text{H}_3\text{O}_2$  and HF are both weak but HF is a stronger acid than  $\text{HC}_2\text{H}_3\text{O}_2$ . HCl is a strong acid. Order the following according to base strength.

- a.  $\text{C}_2\text{H}_3\text{O}_2^- > \text{F}^- > \text{Cl}^- > \text{H}_2\text{O}$
- b.  $\text{Cl}^- > \text{F}^- > \text{C}_2\text{H}_3\text{O}_2^- > \text{H}_2\text{O}$
- c.  $\text{F}^- > \text{C}_2\text{H}_3\text{O}_2^- > \text{H}_2\text{O} > \text{Cl}^-$
- d.  $\text{C}_2\text{H}_3\text{O}_2^- > \text{F}^- > \text{H}_2\text{O} > \text{Cl}^-$
- e. none of these

Answer   d  

**Part I: Complete all of problems 3-6**

3. Define **three** of the following in a maximum of three sentences per item: (12 points)

a. buffer capacity: **The ability for a buffer to absorb acid or base without a change in pH**

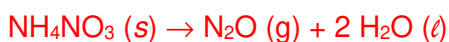
b. weak Brønsted base: **A proton acceptor that only partially undergoes hydrolysis in water.**

c. mole fraction: **The relative number of moles of one component in a mixture compared to the total number of moles of all components of the mixture.**

d. vapor pressure: **The pressure of vapor in equilibrium with its condensed phase in a closed system.**

4. Solid ammonium nitrate decomposes exothermically to dinitrogen oxide gas and liquid water. What is the  $\Delta G^\circ$  for the reaction at 298K? Is the reaction more spontaneous or less spontaneous at high temperatures? How do you know? (12 pts) **(Like quiz problems!)**

Species	$\Delta G^\circ_f$ (kJ/mol)	$\Delta H^\circ_f$ (kJ/mol)	$S^\circ_f$ (J/mol)
$\text{NH}_4\text{NO}_3$ (s)	-183.9	-365.6	151.1
$\text{N}_2\text{O}$ (g)	+104.2	+82.05	219.9
$\text{H}_2\text{O}$ (l)	-237.1	-285.8	69.91



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = \Delta G^\circ_f(\text{N}_2\text{O}) + 2\Delta G^\circ_f(\text{H}_2\text{O}) - [\Delta G^\circ_f(\text{NH}_4\text{NO}_3)]$$

$$\Delta G^\circ = [(+104.2) + 2(-237.1)] - [(-183.9)]\text{kJ}$$

$$\Delta G^\circ = \mathbf{-186.1 \text{ kJ}}$$

Since the reaction is exothermic,  $\Delta H^\circ$  must be negative. Since the reaction produces gaseous and liquid products from a solid,  $\Delta S^\circ$  must be positive. Since T is always positive,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  will be negative at all temperatures when  $\Delta H^\circ$  is negative and  $\Delta S^\circ$  is positive. Therefore the reaction is spontaneous at all temps, but more spontaneous at higher temperature (because delta G would become more negative).

5. Calculate the vapor pressure at 25° C of a solution containing 165 g of the nonvolatile solute, glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ), in 685 g water. The vapor pressure of water at 25° C is 23.8 mm Hg. (12 pts) **(Problem 13-49)**

$$P_{\text{soln}} = X_{\text{solvent}}P_{\text{solvent}}$$

First calculate the mole fraction of water:

$$\text{moles water: } 685 \text{ g H}_2\text{O} \times 1 \text{ mol}/18.02 \text{ g} = 38.01 \text{ mol H}_2\text{O}$$

$$\text{moles glucose: } 165 \text{ g C}_6\text{H}_{12}\text{O}_6 \times 1 \text{ mol}/180.2 \text{ g} = 0.916 \text{ mol}$$

so, the mole fraction of water is:

$$X_{\text{H}_2\text{O}} = \frac{\text{moles H}_2\text{O}}{\text{total moles}} = \frac{38.01}{38.01+0.916} = 0.976_4$$

And the vapor pressure is:

$$P_{\text{soln}} = X_{\text{solvent}}P_{\text{solvent}} = 0.976(23.8 \text{ mm Hg}) = 23.2 \text{ mm Hg}$$

6. A handbook lists various procedures for preparing buffer solutions. To obtain pH 9.50, the handbook says to mix 64.00 mL 0.200 M ammonia with 36.00 mL of 0.200 M  $\text{NH}_4\text{Cl}$ . The  $K_a$  for ammonium is  $5.6 \times 10^{-10}$ . **(Problem 17-25)**

- a. Show with a calculation that the expected pH of the resulting solution is 9.50. (8 pts)

Since this is a buffer solution, we expect the Henderson-Hasselbach equation to apply:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} = \text{p}K_a + \log \frac{\text{moles conjugate base}}{\text{moles weak acid}}$$

We are given a volume and concentration of both the acid ( $\text{NH}_4^+$ ) and conjugate base ( $\text{NH}_3$ ), and the  $K_a$  so we can calculate everything on the right-hand side of the equals sign.

$$\text{moles NH}_3 = 64.00 \text{ mL} \times 0.200 \text{ mol/L} = 12.8 \text{ mmol NH}_3$$

$$\text{moles NH}_4^+ = 36.00 \text{ mL} \times 0.200 \text{ mol/L} = 7.2 \text{ mmol NH}_4^+$$

$$\text{p}K_a = -\log K_a = -\log(5.6 \times 10^{-10}) = 9.25_2$$

Inserting into H-H equation:

$$\text{pH} = 9.25_2 + \log \frac{12.8 \text{ mmol NH}_3}{7.2 \text{ mmol NH}_4^+} = 9.50$$

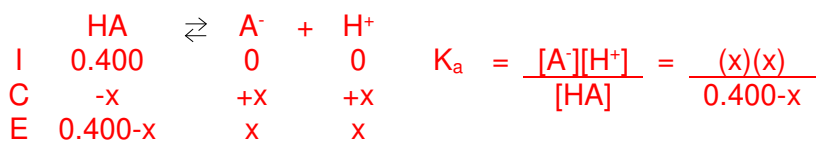
Therefore, we expect the pH of the solution to be 9.50.

- b. What would be pH be if 100 mL solution prepared using the recipe above were diluted to 1.00 L? (6 pts)

Since the pH of the solution depends on the **ratio** of  $\text{NH}_3$  to  $\text{NH}_4^+$  (in terms of moles or concentration), dilution of the solution will not change the ratio, because each species will become more dilute by the same amount. Therefore the ratio should remain unchanged and the pH should stay at 9.50.

7. Benzoic acid is a weak, monoprotic acid, often used as a food preservative. Consider a solution prepared by dissolving 0.200 moles of benzoic acid,  $\text{HC}_7\text{H}_6\text{O}_2$  (or HA), in 0.500 L of solution.  $K_a = 6.28 \times 10^{-5}$ . **(Like the HCN example we did in class!)**
- a. What is the pH of this solution? (8 pts)

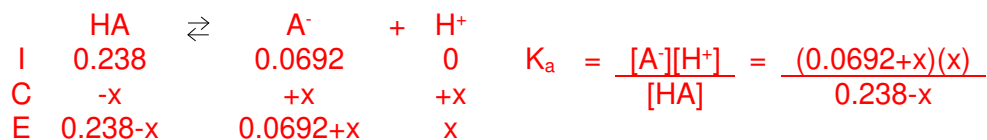
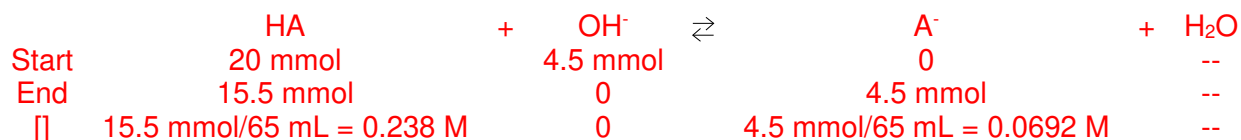
$$[\text{HA}] = (0.200 \text{ mol}) / (0.500 \text{ L}) = 0.400 \text{ M}$$



This leaves us with the equation  $x^2 + K_a x - 0.400 K_a = 0$  to solve for x.  
Solving gives  $x = [\text{H}^+] = 0.00498 \text{ M}$ , **pH = 2.30**

- b. What is the pH of a solution prepared by mixing 50.00 mL of the benzoic acid solution above with 15.00 mL of 0.300 M NaOH? (8 pts)

We first need to consider the reaction between the strong base NaOH and our weak acid HA. We initially have 15 mL x 0.300 mol/L = 4.5 mmol NaOH and 50 mL x 0.400 M = 20 mmol HA



Assuming  $x \ll 0.06$ ,

$$0.0692 + x \approx 0.0692 \text{ and } 0.238 - x \approx 0.238, \text{ leaving } x = [\text{H}^+] = (0.238 / 0.692) K_a = 2.16 \times 10^{-4} \text{ M}, \text{ pH} = 3.67$$

You may also skip any assumption and solve the quadratic, in which case you get **pH = 3.67!**

**Part II. Answer two (2) of problems 8-11. Clearly mark the problem you do not want graded. 14 points each.**

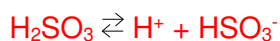
8. Explain why alcohols like methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) are very soluble in water, while octadecanol ( $\text{CH}_3(\text{CH}_2)_{17}\text{OH}$ ) is not. **(Like problems 13-1 through 13-5)**

Your discussion should address intermolecular interactions between solute molecules, solvent molecules, as well as those between solute and solvent molecules. Remember, dissolution requires that interactions between solutes be disrupted to that there can be an interaction between a solute molecule and solvent. This also requires that interactions between solute molecules be disrupted.

All three of these molecules are polar, however the long alkane chain on octadecanol decreases the overall polarity of the molecule and introduces a large number of dispersion forces between solute molecules. Your discussion should describe how this impacts its solubility in water.

9. What is the pH of a 0.15 M solution of sulfurous acid ( $\text{H}_2\text{SO}_3$ ,  $\text{p}K_{a1} = 1.82$ ,  $\text{p}K_{a2} = 7.00$ )? **(Like problems 16-47 through 16-52)**

Looking at the  $K_a$ 's,  $K_{a1} = 1.51 \times 10^{-2}$  and  $K_{a2} = 1.00 \times 10^{-7}$ , indicating that the  $\text{HSO}_3^-$  is a much weaker acid than  $\text{H}_2\text{SO}_3$ , therefore it will not appreciably contribute to the pH of the solution. So, we can treat this as a weak monoprotic acid.



Now we do the ICE thing:

	$\text{H}_2\text{SO}_3$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{HSO}_3^-$
I	0.15 M		0		0
C	-x		+x		+x
E	0.15-x		x		x

Inserting into the  $K_{a1}$  expression, we get:

$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = \frac{x^2}{0.15 - x}$$

Solving for x, we get  $x = [\text{H}^+] = [\text{HSO}_3^-] = \mathbf{0.0407 \text{ M}}$ , **pH = 1.39**.

(NOTE, since  $K_{a1}$  isn't extremely small, assuming  $x \ll 0.15$  is probably a bad idea.)

10. You are given 250.0 mL of a 0.100 M propionic acid solution (HP,  $K_a = 1.35 \times 10^{-5}$ ). What volume of 1.00 M sodium propionate (NaP) would you add to raise the pH to 4.00?

**(Like problems 17-13 through 17-20)**

For HP,  $pK_a = -\log(1.35 \times 10^{-5}) = 4.87_0$

$$4.00 = 4.87_0 + \log \frac{\text{mol } P^-}{\text{mol HP}}$$

We can determine the ratio of moles (or concentration) of  $P^-$  to HP:

$$10^{4.00-4.87_0} = 0.135 = \frac{\text{mol } P^-}{\text{mol HP}}$$

Therefore, at equilibrium: **mol  $P^-$  = 0.135(mol HP)**

We also know that we have 250.0 mL x 0.100 M = 25.0 mmol of HP to start with.

So, we need to introduce 0.135(25.0)mmol  $P^-$  = 3.37 mmol

In order to deliver 3.37 mmol  $P^-$ , we need to add:

$$3.37 \text{ mmol } P^- \times \frac{1 \text{ L}}{1.00 \text{ mol } P^-} = \mathbf{3.37 \text{ mL}}$$

11. A forensic chemist is given a white solid that is expected of being pure cocaine ( $C_{17}H_{21}NO_4$ , 303.36 g/mol). She dissolves 1.22 g of the solid in 15.60 g of benzene and determines that the freezing point is lowered by 1.32°C. Assuming a 1% uncertainty in her measurements, can the chemist state that the substance is likely to be cocaine? **(Like problem 13-65)**

$$\Delta t_{fp} = k_{fp}m$$

$$1.32^\circ\text{C} = (5.12^\circ\text{C kg mol}^{-1})m \quad \text{or} \quad m = 1.32^\circ\text{C}/(5.12^\circ\text{C kg mol}^{-1}) = 0.257_8 \text{ m}$$

$$\frac{0.257_8 \text{ mol "cocaine"}}{\text{kg benzene}} \times 0.0156 \text{ kg benzene} = 0.00402_2 \text{ mol "cocaine"}$$

$$\frac{1.22 \text{ g "cocaine"}}{0.00402_2 \text{ mol "cocaine"}} = \frac{\mathbf{303.4 \text{ g}}}{\mathbf{mol}}$$

Since the expected molar mass of cocaine is 303.4 g/mol, it is likely that the sample is cocaine.

### Possibly Useful Information

$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$	$^{\circ}\text{C} = \text{K} - 273.15$	$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$
$\Delta t_{\text{fp}} = k_{\text{fp}}m$	$\Delta t_{\text{bp}} = k_{\text{bp}}m$	$\Pi = MRT$
$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RT\ln K$	$\Delta G = \Delta G^{\circ} - RT\ln Q$	$P_{\text{soln}} = X_{\text{solvent}}P^{\circ}_{\text{solvent}}$
$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{conjugate base}]}{[\text{weak acid}]}\right)$	$\text{pH} + \text{pOH} = 14$	$K_a K_b = K_w = 1.00 \times 10^{-14}$
$1 \text{ atm} = 760 \text{ mm Hg}$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$	

### Selected Constants

Solvent	Boiling Point ( $^{\circ}\text{C}$ )	$K_b$ ( $^{\circ}\text{C kg/mol}$ )	Freezing Point ( $^{\circ}\text{C}$ )	$K_f$ ( $^{\circ}\text{C kg/mol}$ )
Water	100.0	0.51	0	1.86
Benzene	80.1	2.53	5.5	5.12
Ethyl Ether	34.5	2.02	-116.2	1.79
Chloroform	61.2	3.63	-63.5	4.70

1 1A											18 8A						
1 H 1.00794	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	18 8A 2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 9B	10 10B	11 11B	12 12B	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)							

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	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)

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