

CHM 1311-F

2nd Midterm

Nov. 21st 2017

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Your Name: _____

Student #: _____

1. The solution key will be posted today on the web. Solutions will be worked out in the next DGD.
2. You must respond to all exercises.
3. Periodic Table and relevant values are at the end.
4. A few scratch sheets are at the very end. Report in the booklet the minimum amount of calculations to show your reasoning.

Read carefully:

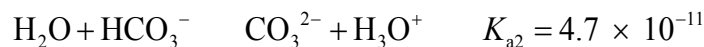
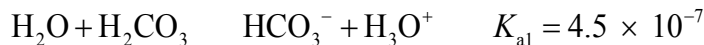
Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: academic fraud allegations will be filed which may result in your obtaining a 0 (zero) for the exam.

By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

Signature: _____

1. (4 points) Determine the concentrations of the ionic species present in a 1.55×10^{-2} M solution of the diprotic acid H_2CO_3 . ($K_{a1} = 4.5 \times 10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$)

Begin by analyzing the chemistry. H_2CO_3 is a diprotic acid with equilibria:



Every aqueous solution has the water equilibrium:



Thus, the ionic species present in the solution are HCO_3^- , CO_3^{2-} , H_3O^+ , and OH^- .

Set up concentration tables, write equilibrium expressions, and solve for the ionic concentrations.

Reaction: $\text{H}_2\text{O} +$	H_2CO_3	$\text{HCO}_3^- +$	H_3O^+
Initial concentration (M)	1.55×10^{-2}	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Final concentration (M)	$1.55 \times 10^{-2} - x$	x	x

$$K_{a1} = 4.5 \times 10^{-7} = \frac{x^2}{1.55 \times 10^{-2} - x}; \text{ assume that } x \ll 1.55 \times 10^{-2}:$$

$$4.5 \times 10^{-7} = \frac{x^2}{1.55 \times 10^{-2}}$$

$$x^2 = 6.98 \times 10^{-9}, \text{ so } x = 8.4 \times 10^{-5}; \text{ the assumption is valid.}$$

$$[\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 8.4 \times 10^{-5} \text{ M} \quad [\text{H}_2\text{CO}_3] = 1.55 \times 10^{-2} \text{ M}$$

Set up a concentration table for the second equilibrium:

Reaction: $\text{H}_2\text{O} +$	HCO_3^-	$\text{CO}_3^{2-} +$	H_3O^+
Initial concentration (M)	8.4×10^{-5}	0	8.4×10^{-5}
Change in concentration (M)	$-x$	$+x$	$+x$
Final concentration (M)	$8.4 \times 10^{-5} - x$	x	$8.4 \times 10^{-5} + x$

$$K_{a2} = 4.7 \times 10^{-11} = \frac{x(8.4 \times 10^{-5} + x)}{8.4 \times 10^{-5} - x}; \text{ assume that } x \ll 8.4 \times 10^{-5}:$$

$$x = 4.7 \times 10^{-11} \text{ M} = [\text{CO}_3^{2-}]$$

Use K_w to determine the concentration of hydroxide ions:

$$K_w = 1.00 \times 10^{-14} = (8.4 \times 10^{-5})[\text{OH}^-] \quad [\text{OH}^-] = 1.2 \times 10^{-10} \text{ M}$$

Ionic concentrations:

$$[\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 8.4 \times 10^{-5} \text{ M}$$

$$[\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M} \quad [\text{OH}^-] = 1.2 \times 10^{-10} \text{ M}$$

2. (1 point) The addictive painkiller morphine ($\text{C}_{17}\text{H}_{19}\text{NO}_3$) is the principal molecule in the milky juice that exudes from unripe poppy seed capsules. Calculate the pH of a 0.015 M solution of morphine, given that $K_b = 7.9 \times 10^{-7}$.

Follow the standard procedures to determine the pH. Begin by constructing a concentration table, write the equilibrium expression, and solve for the concentration of hydroxide ions.

Reaction: $\text{H}_2\text{O} +$	Morphine	Morphine $\text{H}^+ +$	OH^-
Initial concentration (M)	0.015	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Final concentration (M)	$0.015 - x$	x	x

$$K_b = 7.9 \times 10^{-7} = \frac{[\text{morphineH}^+]_{\text{eq}} [\text{OH}^-]_{\text{eq}}}{[\text{morphine}]_{\text{eq}}} \text{ M} = \frac{x^2}{0.015 - x}; \text{ assume } x \ll 0.015:$$

$$7.9 \times 10^{-7} = \frac{x^2}{0.015}$$

$$x^2 = 1.1 \times 10^{-8}, \text{ so } x = 1.1 \times 10^{-4}; \text{ the assumption is valid.}$$

$$[\text{OH}^-] = 1.1 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log(1.1 \times 10^{-4}) = 3.96 \quad \text{pH} = 14.00 - 3.96 = 10.04$$

3. (2 points) What mass of ammonium chloride must be added to 1.25 L of 0.25 M ammonia to make a buffer solution of pH = 8.90? [$K_b(\text{NH}_3) = 1.8 \times 10^{-5}$]

This is a $\text{NH}_3/\text{NH}_4^+$ buffer. Use the buffer equation, Equation 16-1, to determine the amount of ammonium chloride needed:

$$M_{\text{NH}_4\text{Cl}} = 14.01 \text{ g/mol} + 4(1.01 \text{ g/mol}) + 35.45 \text{ g/mol} = 53.50 \text{ g/mol}$$

$$\log\left(\frac{n_{\text{NH}_3}}{n_{\text{NH}_4^+}}\right) = \text{pH} - \text{p}K_a = 8.90 - 9.25 = -0.35$$

$$\frac{n_{\text{NH}_3}}{n_{\text{NH}_4^+}} = 10^{-0.35} = 0.447$$

$$n_{\text{NH}_4^+} = \frac{n_{\text{NH}_3}}{0.447} = \frac{(1.25 \text{ L})(0.25 \text{ M})}{0.447} = 0.699 \text{ mol} = \text{moles of NH}_4\text{Cl}$$

$$m_{\text{NH}_4\text{Cl}} = (0.699 \text{ mol})(53.50 \text{ g/mol}) = 37 \text{ g}$$

4. (3 points) Calculate the pH at the second stoichiometric point when 250 mL of a 0.025 M solution of tartaric acid ($K_{a1} = 9.2 \times 10^{-4}$, $K_{a2} = 4.3 \times 10^{-5}$) is titrated with 1.00 M NaOH.

At the second stoichiometric point, all the weak acid (H_2T) has been converted into T^{2-} , so the major acid–base species present are T^{2-} and H_2O and the dominant equilibrium is



$$K_{\text{b1}} = \frac{K_{\text{w}}}{K_{\text{a2}}} = \frac{1.00 \times 10^{-14}}{4.3 \times 10^{-5}} = 2.3 \times 10^{-10}$$

Begin by determining the initial amount of T^{2-} (dilution effects may be considered negligible). Then construct an equilibrium table, write the equilibrium expression, and solve for the hydroxide ion concentration to determine the pH.

At the second stoichiometric point, $[\text{T}^{2-}]_{\text{initial}} = [\text{H}_2\text{T}]_{\text{before titration}} = 2.50 \times 10^{-2} \text{ M}$.

Here is the completed equilibrium table:

Reaction: $\text{H}_2\text{O} +$	T^{2-}	$\text{HT}^- +$	OH^-
Initial concentration (M)	0.0250	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Final concentration (M)	$0.0250 - x$	x	x

Now substitute into the equilibrium constant expression and solve for x :

$$K_{\text{eq}} = 2.3 \times 10^{-10} = \frac{[\text{HT}^-]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}{[\text{T}^{2-}]_{\text{eq}}} = \frac{x^2}{0.0250 - x}; \text{ assume that } x \ll 0.0250:$$

$x^2 = (2.3 \times 10^{-10})(0.0250) = 5.75 \times 10^{-12}$, so $x = 2.40 \times 10^{-6}$; the assumption is valid.

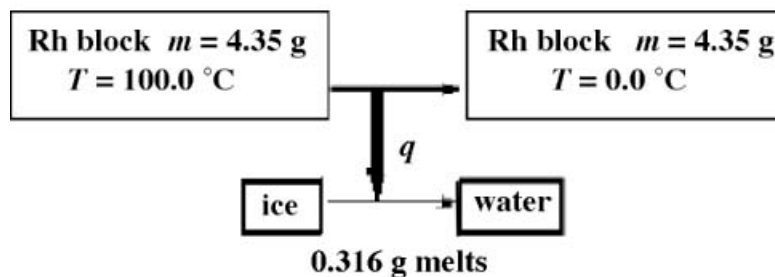
$$[\text{OH}^-] = 2.40 \times 10^{-6} \text{ M} \quad \text{pOH} = -\log(2.40 \times 10^{-6}) = 5.62$$

$\text{pH} = 14.00 - 5.62 = 8.38$; a suitable indicator for this titration is phenol red, $\text{p}K_{\text{in}} = 7.9$ (thymol blue, $\text{p}K_{\text{in}} = 8.9$, could also be used).

(If dilution is taken into account, $[\text{OH}^-] = 2.34 \times 10^{-6} \text{ M}$, $\text{pOH} = 5.63$.)

5. (4 points) A piece of rhodium metal whose mass is 4.35 g is heated to 100.0°C and then dropped into an ice calorimeter. As the Rh metal cools to 0.0°C , 0.316 g of ice melts (it takes 6.01 kJ of heat to melt exactly 1 mole of ice). What is the molar heat capacity of rhodium? $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$

To work a problem involving heat transfers, it is useful to set up a block diagram illustrating the process. In this problem, a rhodium block transfers energy to ice:



Thus, $q_{\text{ice}} = -q_{\text{Rh}}$ $q_{\text{Rh}} = n_{\text{Rh}} C \Delta T$, and $q_{\text{ice}} = n_{\text{ice}} \Delta H_{\text{fus}}$

Substituting gives $n_{\text{ice}} \Delta H_{\text{fus}} = -n_{\text{Rh}} C \Delta T$

Solve for C , the heat capacity of rhodium:

$$C = \frac{-n_{\text{ice}} \Delta H_{\text{fus}}}{n_{\text{Rh}} \Delta T}$$

Here are the data needed for the calculation:

$$n_{\text{Rh}} = \frac{m}{M} = \frac{4.35 \text{ g}}{102.91 \text{ g/mol}} = 0.04227 \text{ mol} \quad n_{\text{ice}} = \frac{m}{M} = \frac{0.319 \text{ g}}{18.01 \text{ g/mol}} = 0.01771 \text{ mol}$$

$$\Delta T = 0.0^\circ\text{C} - 100.0^\circ\text{C} = -100.0^\circ\text{C}$$

$$\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol} = 6.01 \times 10^3 \text{ J/mol}$$

Substitute and evaluate C :

$$C = \frac{-n_{\text{ice}} \Delta H_{\text{fus}}}{n_{\text{Rh}} \Delta T} = \frac{-(0.01771 \text{ mol})(6.01 \times 10^3 \text{ J/mol})}{(0.04227 \text{ mol})(-100.0^\circ\text{C})} = 25.2 \text{ J mol}^{-1} \text{ }^\circ\text{C}^{-1}$$

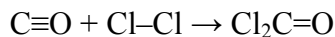
6. (1 point) In metric terms, a typical automobile averages 6.0 km/L of gasoline burned. Gasoline has an enthalpy of combustion of 48 kJ/g and a density of 0.68 g/mL. How much energy is consumed in driving an automobile 1.0 km?

First compute the quantity of gasoline consumed in travelling 1 km, and then determine the energy content of that quantity of gasoline:

$$\text{Mass of gasoline} = 1.0 \text{ km} \left(\frac{1 \text{ L}}{6.0 \text{ km}} \right) \left(\frac{10^3 \text{ mL}}{1 \text{ L}} \right) \left(\frac{0.68 \text{ g}}{1 \text{ mL}} \right) = 113 \text{ g}$$

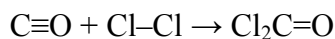
$$\text{Energy consumed} = 113 \text{ g} \left(\frac{48 \text{ kJ}}{1 \text{ g}} \right) = 5.4 \times 10^3 \text{ kJ}$$

7. (1 point) Phosgene ($\text{Cl}_2\text{C}=\text{O}$) is a highly toxic gas that was used for chemical warfare during World War I. Use the bond energies to estimate the energy change that occurs when carbon monoxide and chlorine combine to make phosgene.



Bond	No.	Energy (kJ/mol)	Bond	No.	Energy (kJ/mol)
$\text{C}\equiv\text{O}$	1	1070	$\text{C}-\text{Cl}$	2	330
$\text{Cl}-\text{Cl}$	1	240	$\text{C}=\text{O}$	1	750

To estimate the energy change in a reaction, determine Lewis structures to obtain types of bonds, list the number of bonds of each type in reactants and products, and subtract the sum of average bond energies for products from the sum of average bond energies for reactants, using values from Table 3-2 of your textbook.



Reactants			Products		
Bond	No.	Energy (kJ/mol)	Bond	No.	Energy (kJ/mol)
$\text{C}\equiv\text{O}$	1	1070	$\text{C}-\text{Cl}$	2	330



$$\Delta E_{\text{reaction}} \cong [1 \text{ mol}(1070 \text{ kJ/mol}) + 1 \text{ mol}(240 \text{ kJ/mol})] - [2 \text{ mol}(330 \text{ kJ/mol}) + 1 \text{ mol}(750 \text{ kJ/mol})] = 1310 \text{ kJ} - 1410 \text{ kJ} = -100 \text{ kJ}$$

BONUS (5 points)

How many grams of PbCl_2 ($K_{\text{sp}} = 1.7 \times 10^{-5}$) will dissolve in 0.750 L of 0.650 M $\text{Pb}(\text{NO}_3)_2$ solution?

This problem describes a solution containing a common ion. To determine concentrations of ions at equilibrium, follow the five-step procedure for working equilibrium problems:

1. Species present initially are Pb^{2+} , NO_3^- , and PbCl_2
2. Reaction is a solubility process: $\text{PbCl}_2 (s) \rightleftharpoons \text{Pb}^{2+} (aq) + 2 \text{Cl}^- (aq)$
3. $K_{\text{sp}} = [\text{Pb}^{2+}]_{\text{eq}} [\text{Cl}^-]_{\text{eq}}^2 = 1.7 \times 10^{-5}$
4. Set up and complete a concentration table, letting x be the increase in $[\text{Pb}^{2+}]$:

Reaction:	$\text{PbCl}_2 (s)$	$\text{Pb}^{2+} (aq) +$	$2 \text{Cl}^- (aq)$
Initial concentration (M)	Solid	0.650	0
Change in concentration (M)	Solid	+ x	+ $2x$
Final concentration (M)	Solid	$0.650 + x$	$2x$

5. Substitute into the equilibrium constant expression and solve for x :

$$1.7 \times 10^{-5} = (0.650 + x)(2x)^2; \text{ assume } x \ll 0.650:$$

$$4x^2 = \frac{1.7 \times 10^{-5}}{0.650}$$

$$x^2 = 6.54 \times 10^{-6}, \text{ so } x = 2.56 \times 10^{-3}$$

$$2.56 \times 10^{-3} < 5\% \text{ of } 0.650, \text{ so the assumption is valid.}$$

The increase in lead ions is $\Delta[\text{Pb}^{2+}] = 2.56 \times 10^{-3} \text{ M}$.

To convert to moles Pb^{2+} that dissolve, multiply by the solution volume:

$$n = cV = (2.56 \times 10^{-3} \text{ M})(0.750 \text{ L}) = 1.92 \times 10^{-3} \text{ mol}$$

The amount of PbCl_2 that dissolves is determined by the amount of increase in Pb^{2+} ; convert to mass by multiplying by the molar mass of PbCl_2 :

$$m = nM = (1.92 \times 10^{-3} \text{ mol})(278.1 \text{ g/mol}) = 0.53 \text{ g}$$