Chemistry 104, Summer 2022
Exam 2 (100 points)

1. Which of the following statements are true and which – false? For the false statements, provide a brief explanation why they are false. (11 points)
   a. HI is a stronger acid than HBr.

   (1) True

   b. It is possible for K_C and K_P to have the same value for a given reaction at a certain temperature.

   (1) True

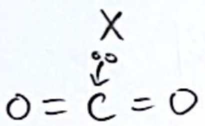
   c. $HClO_4$ and $NaClO_4$ make a good buffer system.

   (1) False. $HClO_4$ is a strong acid, so ClO_4^- is a weak base. (1)

   d. $PbCO_3$ is more soluble in pure water than in an acidic solution.

   (1) False. CO_3^{2-} is basic and will react with H_3O^+, improving $PbCO_3$ solubility. (1)

   e. CO_2 cannot act as an acid because it lacks protons.



   (1) False. CO_2 can accept an e^- pair, acting as a Lewis acid (1)

   f. In a reversible reaction A ⇔ B, if the rate constant of the forward reaction is greater than the rate constant of the reverse reaction, the process is product-favored as written.

   (1) True

   g. Adding a catalyst can force a reactant-favored reaction to become product-favored.

   (1) False. A catalyst will just increase both the rate of forward and reverse reactions and equilibrium will be reached faster. (1)

2. Classify the following 0.100 M aqueous salt solutions as acidic, basic or neutral. Justify your classification using appropriate chemical equations. No pH calculations are necessary. (10 points)

a. NaC_6H_5COO

Na^+ is neutral (0.5)

(1) $C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$

↓ basic (1)

b. $KHSO_4$

K^+ is neutral (0.5)

amphiprotic → $HSO_4^- + H_2O \rightleftharpoons H_2SO_4 + OH^-$ K_b very small (0.5)

$HSO_4 + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ $K_a = 1.2 \times 10^{-2}$ (0.5)

$K_a > K_b \Rightarrow$ acidic (1)

(1)

c. NH_4HCOO

$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ $K_a = 5.6 \times 10^{-10}$ (1)

$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^-$ $K_b = 5.6 \times 10^{-11}$ (1)

$K_a > K_b \Rightarrow$ acidic (1)

(1)

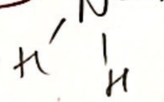
3. Explain the following observations in terms of the chemical structure of the relevant species.

a. H_3PO_4 is a stronger acid than $H_2PO_4^-$. (2 points)

$H_2PO_4^-$ has negative (1) charge, which strengthens its attraction to H^+, (1) making it harder to donate it.

b. NH_3 and NF_3 are Lewis bases. (2 points) (1)

Lewis bases donate an e^- pair. Both NH_3 and NF_3 have an e^- pair on N that can be donated. (1)



c. NH_3 is a stronger Lewis base than NF_3. (3 points) (1)

F is an electronegative (1) atom. It pulls away electron density from N, making it harder for N to donate its e^- pair. (1)

4. Consider the reaction

q + $MgCO_3$ (s) → MgO (s) + CO_2 (g) $\Delta H° = +118$ kJ/mol

State how each of the following interventions will affect the direction of the reaction. Briefly explain your answers. (8 points)

a. Increasing the volume of the container where the reaction takes place.

(1) V ↑ → P ↓. Shift will attempt to increase P, so will be towards the side with more gas moles → products. (1)

b. Adding more MgO (s).

(1) Solids are not in the equilibrium constant expression → no change (1)

c. Adding more CO_2 (g).

(1) Product side will be overloaded / Q will be > K shift towards reactants (1)

d. Decreasing the temperature.

(K ↑ as T ↑) ΔH > 0 → heat on reactants side. Reactant side will lose heat (T ↓, K ↓) → shift towards reactants. (1) (1)

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5. Methylamine, NH_2CH_3, is a weak base. Consider the titration of 75.0 mL of 0.250 M aqueous methylamine with 0.100 M HCl (aq). K_b of methylamine is 4.4×10^{-4}.
   a. The conjugate acid of methylamine is the ion methylammonium. What is its formula and what is its value of its K_a? (2 points)

$NH_3CH_3^{+}$ (1)

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{4.4\times10^{-4}} = 2.3\times10^{-11}$$ (1)

   b. Write the equation for the reaction between methylamine and HCl. Is this reaction reactant- or product-favored? Briefly justify your answer. (4 points)

(2) $NH_2CH_3(aq) + H_3O^+(aq) \rightarrow NH_3CH_3^+(aq) + H_2O(l)$ ($K_b = 4.4\times10^{-4}$; $K_b = 1.0\times10^{-14}$)

(or $NH_2CH_3 + HCl \rightarrow NH_3CH_3^+ + Cl^-$) → K_b very small

(1) NH_2CH_3 is a stronger base than H_2O/Cl^- – product-favored (1)
(can also compare acids in reactants and products)

   c. Calculate the pH of the resulting solution
      i. after 75.0 mL HCl are added. (7 points)

(1) $0.075\ L \times \frac{0.250\ mol\ CH_3NH_2}{1L} = 0.0188\ mol\ NH_2CH_3$

(1) $0.075\ L \times \frac{0.100\ mol\ HCl}{1L} = 0.0075\ mol\ HCl$

NH_2CH_3	+ HCl	→ $NH_3CH_3^+$	+ Cl^-
0.0188 mol	0.0075 mol	0	
−0.0075 mol	−0.0075 mol	+0.0075 mol	
(1) 0.0113 mol	0	0.0075 mol (1)	

(1)
$$pH = pK_a + \log\frac{[A^-]}{[HA]} = -\log(2.3\times10^{-11}) + \log\frac{0.0113\ mol/V}{0.0075\ mol/V}$$ (1)

pH = 10.82 (1)

all 0.0188 mol CH_3NH_2 converted to $CH_3NH_3^+$

ii. at the equivalence point. (7 points)

(1) $0.0188 \text{ mol} \times \frac{1 L}{0.100 \text{ mol HCl}} = 0.188 L$ need to be added

(0.5) $0.188 L + 0.075 L = V_{tot} = 0.263 L$

(0.5) $[CH_3NH_3^+] = \frac{0.0188 \text{ mol}}{0.263 L} = 0.0714 M$

$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$ (1)

	$CH_3NH_3^+$	CH_3NH_2	H_3O^+
I	0.0174M	0	0
C	~0	+x	+x
E	0.0174M	x	x

(1) $K_a = \frac{[H_3O^+][CH_3NH_2]}{[CH_3NH_3^+]} \Rightarrow 2.3 \times 10^{-11} = \frac{x^2}{0.0174}$ (1) $\Rightarrow x = [H_3O^+] = 1.3 \times 10^{-6} M$ (1)

$pH = -\log(1.3 \times 10^{-6} M) = $ **5.89 = pH** (1)

6. What is the molar solubility of $Zn_3(PO_4)_2$ ($K_{sp} = 9.0 \times 10^{-33}$)? (6 points)

(1) $Zn_3(PO_4)_2 (s) \rightleftharpoons 3 Zn^{2+} (aq) + 2 PO_4^{3-} (aq)$

	Zn^{2+}	PO_4^{3-}
I	0	0
C	+3x	+2x
E	3x	2x

(1) $K_{sp} = [Zn^{2+}]^3 [PO_4^{3-}]^2 \Rightarrow 9.0 \times 10^{-33} = (3x)^3 (2x)^2$ (1) $\Rightarrow$

(1) $9.0 \times 10^{-33} = 27 \cdot 4 x^5 \Rightarrow x^5 = 8.3 \times 10^{-35}$ (1) $\Rightarrow$

$x = 1.6 \times 10^{-7}$

$1.6 \times 10^{-7} M$ (1)

7. Silver carbonate (Ag_2CO_3) is a poorly soluble salt in pure water with $K_{sp} = 8.5 \times 10^{-12}$. Despite its low solubility in water, silver carbonate dissolves better in an ammonia solution due to the formation of the complex ion $Ag(NH_3)_2^+$ ($K_f = 1.7 \times 10^7$).
   a. Write the balanced equation describing the dissolution of Ag_2CO_3 (s) in pure water. (1 point)

(1) $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$

   b. Write the balanced equation describing the formation of the complex ion $Ag(NH_3)_2^+$. (1 point)

(1) $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+$

   c. Write the balanced equation describing the dissolution of Ag_2CO_3 (s) in NH_3 (aq) and calculate the equilibrium constant for this process. (5 points)

(2) $Ag_2CO_3(s) + 4NH_3(aq) \rightleftharpoons 2Ag(NH_3)_2^+(aq) + CO_3^{2-}(aq)$

net of

(1) $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq) \quad K = 8.5 \times 10^{-12}$

(1) $2Ag^+(aq) + 4NH_3(aq) \rightleftharpoons 2Ag(NH_3)_2^+(aq) \quad K = (1.7 \times 10^7)^2$

$$K = (8.5 \times 10^{-12})(1.7 \times 10^7)^2$$

(1) K = 2.5×10^3 (~2500)

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8. The equilibrium constant for the reaction

$N_2 (g) + 3 H_2 (g) \Leftrightarrow 2 NH_3 (g)$

is $K_P = 4.34 \times 10^{-3}$ at 300 °C. Pure NH_3 is placed in a 1.00-L flask and allowed to reach equilibrium at this temperature. There are 1.05 g NH_3 in the equilibrium mixture. What is the total pressure in the flask (in atmospheres) once equilibrium has been reached? (10 points)

(1) $1.05 \text{ g } NH_3 \times \frac{1 \text{ mol}}{17.031 \text{ g}} = 0.0616 \text{ mol } NH_3$

(1) $PV = nRT \Rightarrow P_{NH_3} = \frac{(0.0616 \text{ mol})(0.08206 \text{ L atm mol}^{-1} K^{-1})(573 K)}{(1.00 L)}$ (1)

$= 2.90 \text{ atm}$

	N_2 +	$3H_2$ ⇌	$2NH_3$
I	0	0	A
C	+x	+3x	−2x
E	x	3x	A − 2x = 2.90 atm

(2)

$P_{tot} = 14.54 \text{ atm}$

$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$ (1) $\Rightarrow 4.34 \times 10^{-3} = \frac{(2.90 \text{ atm})^2}{x (3x)^3}$

(1)

$27x^4 = 1.94 \times 10^3 \Rightarrow x = 2.91 \text{ atm} = P_{N_2}$ (1)

$P_{H_2} = 3P_{N_2} = 3(2.91 \text{ atm}) = 8.73 \text{ atm}$ (1)

(1)

$P_{tot} = P_{NH_3} + P_{N_2} + P_{H_2} = (2.90 + 2.91 + 8.73) \text{ atm} = 14.54 \text{ atm}$

10

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9. A solution contains 2.0×10^{-4} M Ag^+ and 1.5×10^{-3} M Pb^{2+}. Solid NaI, a soluble source of iodide (I^-) ion, is added to this solution to separate the two ions.
   a. What should be the I^- concentration that would create a saturated AgI solution? K_{sp} of AgI is 8.3×10^{-17}. (3 points)

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \quad (1)$$

$$K_{sp} = [Ag^+][I^-] \Rightarrow 8.3\times10^{-17} = (2.0\times10^{-4}\,M)[I^-] \quad (1)$$

$$\boxed{[I^-] = 4.2\times10^{-13}\,M} \quad (1)$$

   b. What should be the I^- concentration that would create a saturated PbI_2 solution? K_{sp} of PbI_2 is 7.9×10^{-9}. (4 points)

$$(1) \quad PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \quad (1)$$

$$K_{sp} = [Pb^{2+}][I^-]^2 \Rightarrow 7.9\times10^{-9} = (1.5\times10^{-3}\,M)[I^-]^2 \Rightarrow \quad (1)$$

$$\boxed{[I^-] = 2.3\times10^{-3}\,M} \quad (1)$$

   c. As NaI is added, will AgI or PbI_2 precipitate first? (1 point)

$$\boxed{AgI} \quad (1)$$

   d. What will be the concentration of the first ion that precipitates (Ag^+ or Pb^{2+}) when the second salt just begins to precipitate? (3 points)

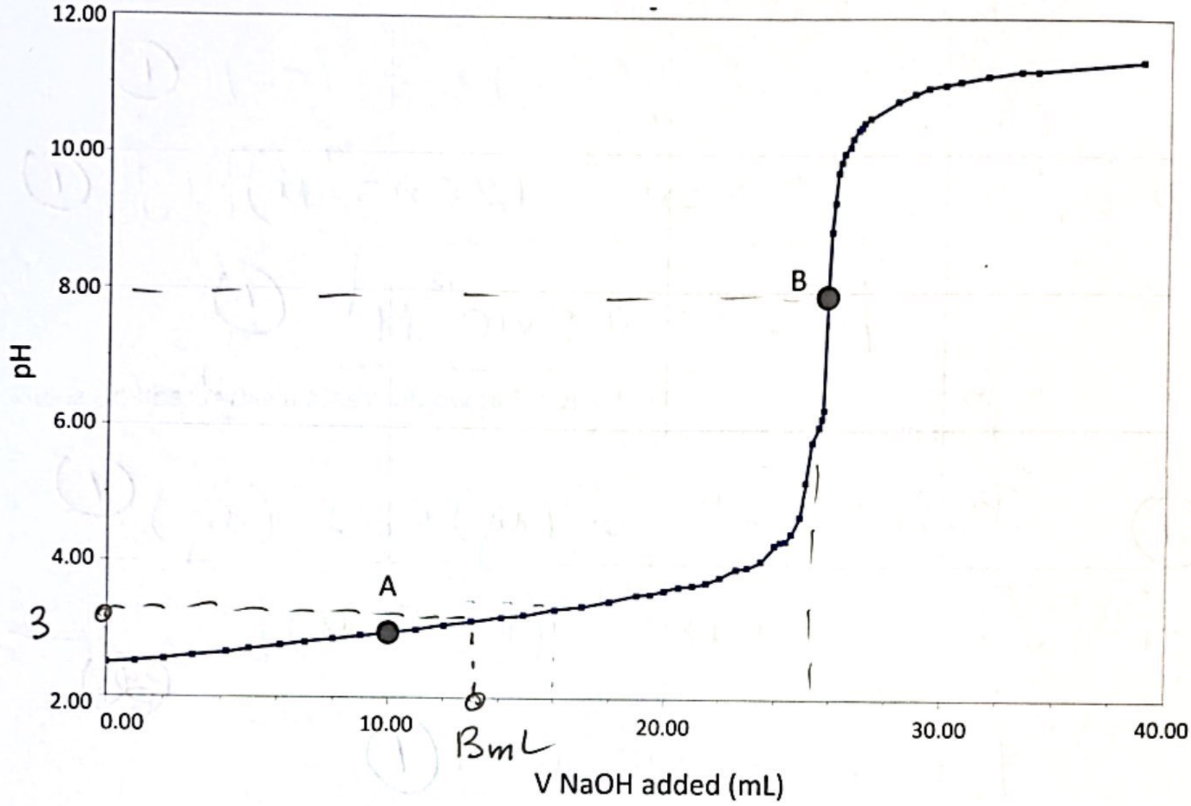
When PbI_2 begins precipitating, solution is saturated in $PbI_2(aq)$. So $[I^-] = 2.3\times10^{-3}$ M. (1)

for AgI: $K_{sp} = [Ag^+][I^-] \Rightarrow$ (1)

$$8.3\times10^{-17} = [Ag^+](2.3\times10^{-3}\,M)$$

$$\boxed{[Ag^+] = 3.6\times10^{-14}\,M} \quad (1)$$

10. Below is the titration curve of a salicylic acid ($C_6H_4OHCOOH$) solution with 0.100 M NaOH (aq).



a. Identify the major species in the solution at points A and B by circling them. For each point, make sure to indicate (by circling) whether H_3O^+ or OH^- is present at higher concentration. (4 points)

0.5 0.5 1

A	$C_6H_4OHCOOH$	$C_6H_4OHCOO^-$	H_3O^+	OH^-
B	$C_6H_4OHCOOH$	$C_6H_4OHCOO^-$ (1)	H_3O^+	OH^- (1)

b. Estimate to one significant figure the pK_a value of salicylic acid. (3 points)

At half equivalence point, pH = pKa (1)
Equivalence point occurs at ~26 mL ⇒
HEP occurs at ~13 mL (1)

At 13 mL pH = pKa ≃ 3 (1)

c. Which indicator would you pick if you wanted to observe a color change near the equivalence point? Briefly explain your answer. (3 points)

Indicator	pK_a	Color change (from low to high pH)	Indicator	pK_a	Color change (from low to high pH)
Cresol red	1.0	red to yellow	Methyl red	4.95	red to yellow
Methyl yellow	3.3	red to yellow	p-nitrophenol	7.2	clear to yellow
Methyl orange	3.4	red to orange	Phenol red	7.9	yellow to red
Bromophenol blue	3.85	yellow to blue	Phenolphthalein	9.4	clear to pink
Bromocresol green	4.7	yellow to blue	Alizarin yellow R	11.2	yellow to red

(1) need to observe color change @ pH ~ 8
need indicator that changes color at that
(1) pH - so indicator with pKa ~ 8

(1) Phenol red and p-nitrophenol would work well. Phenolphthalein could also work.
(Methyl red could be used in a pinch)