CHEMISTRY 104 – Summer 2023
Hour Exam I Answers

Multiple Choice (3 points each)

1.	A	11.	D
2.	E	12.	E
3.	D	13.	E
4.	B	14.	B
5.	D	15.	C
6.	C	16.	A
7.	D	17.	C
8.	B	18.	C
9.	B	19.	B
10.	A	20.	A

WRITTEN OUT PROBLEMS – Show all work for partial credit.

21. Consider the following reaction at 25°C:

(6 pts.) $\qquad$ $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

The standard free energy of formations (ΔG_f°) for $N_2O_4(g)$ and $NO_2(g)$ are 98 kJ/mol and 52 kJ/mol, respectively. If at equilibrium, $P_{N_2O_4} = 0.50$ atm, calculate the equilibrium partial pressure of NO_2.

$$\Delta G^\circ = \sum \Delta G_{f,\,prod}^\circ - \sum \Delta G_{f,\,react}^\circ = 2(52\,kJ) - \left[1(98\,kJ)\right]$$

$$\Delta G^\circ = 6\,kJ = 6000\,J$$

$$\Delta G^\circ = -RT \ln K, \quad \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-6000\,J}{\frac{8.3145\,J}{K\cdot mol}(298K)}$$

$$\ln K = -2.422, \quad K = e^{-2.422} \doteq 0.0888$$

$$K = 0.0888 = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{P_{NO_2}^2}{0.50\,atm}$$

$$\boxed{P_{NO_2} = 0.21\,atm}$$

22. White phosphorous exists in two crystalline forms, the α form and the β form. At 1 atmosphere, the β form is stable at temperatures below −76.9°C. Above −76.9°C, the α form is stable. Which statement (a-c) is/are **true** concerning the $P_\beta \rightarrow P_\alpha$ transition?
(6 pts.)

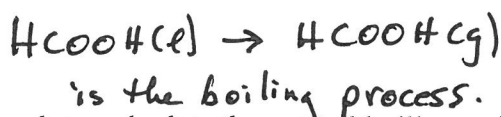a. Is the $P_\beta \rightarrow P_\alpha$ transition endothermic or exothermic? Explain.

$P_\beta \rightarrow P_\alpha$; this transition is spontaneous at temps above −76.9°C.

$$\Delta G = \overset{+}{\Delta H} - T\overset{+}{\Delta S}$$

For a process that is spontaneous $\overset{above}{\vee}$ some temperature, the signs of ΔH and ΔS must both be positive. Since ΔH is positive, this transition is endothermic.

b. Which is the more disordered crystalline form of phosphorus, the α or the β form? Explain.

Since ΔS is positive for the $P_\beta \rightarrow P_\alpha$ transition, the alpha (α) form is more disordered.

$HCOOH(l) \rightarrow HCOOH(g)$
is the boiling process.

23. Given the following data, calculate the normal boiling point for formic acid (HCOOH).

(7 pts.)

	ΔH_f° (kJ/mol)	S° (J/K·mol)
HCOOH(l)	−410.	130.
HCOOH(g)	−363	251

$\Delta H^\circ = \Sigma \Delta H_{f,prod}^\circ - \Sigma \Delta H_{f,react}^\circ = -363 \, kJ - (-410. \, kJ) = 47 \, kJ$

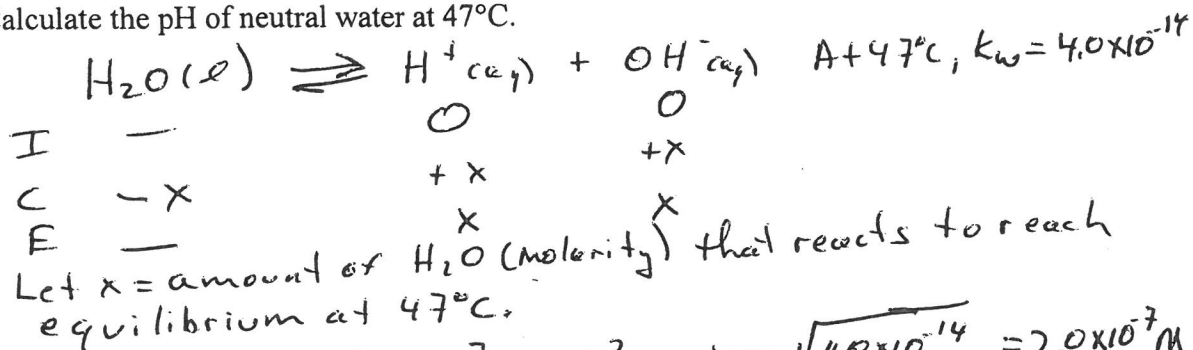$\Delta S^\circ = \Sigma S_{prod}^\circ - \Sigma S_{react}^\circ = 251 - 130. = 121 \, J/K$

At normal boiling point, $\Delta G^\circ = 0$ and $\Delta H^\circ = T\Delta S^\circ$.

$T_{bp} = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{47,000 \, J}{121 \, J/K} = \boxed{388 \, K} = 115°C$

24. K_w is the equilibrium constant for the autoionization of water reaction. The value of K_w depends on temperature. For example, at 25°C, $K_w = 1.0 \times 10^{-14}$ and at 47°C, $K_w = 4.0 \times 10^{-14}$.

(7 pts.)

a. Calculate the pH of neutral water at 47°C.

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ At 47°C, $k_w = 4.0 \times 10^{-14}$

	H^+	OH^-
I	—	0	0
C	−x	+x	+x
E	—	x	x

Let x = amount of H_2O (molarity) that reacts to reach equilibrium at 47°C.

$k_w = 4.0 \times 10^{-14} = [H^+][OH^-] = x^2$, $x = \sqrt{4.0 \times 10^{-14}} = 2.0 \times 10^{-7} M$

$pH = -\log[H^+] = -\log x$, $pH = -\log(2.0 \times 10^{-7}) = \boxed{6.70}$

b. Calculate the pOH of a 0.10 M $HClO_4$ solution at 47°C.

$[OH^-] = \dfrac{k_w}{[H^+]} = \dfrac{4.0 \times 10^{-14}}{0.10} = 4.0 \times 10^{-13}$

Note: $HClO_4$ is a strong acid. Assume it completely dissociates in water, so $[H^+] = 0.10 M$.

$pOH = -\log[OH^-] = -\log(4.0 \times 10^{-13}) = \boxed{12.40}$

25. Consider 0.10 M solutions of the following nine substances:
(9 pts.)

$$KF, \ H_2SO_4, \ HONH_2, \ HF, \ HCl, \ RbOH, \ HONH_3NO_3, \ Sr(OH)_2, \ CaBr_2$$

Rank these nine solutions from lowest pH to highest pH. K_a for HF = 7.2×10^{-4} and K_b for $HONH_2$ = 1.1×10^{-8}. Under each substance in your final ranking, label each as either a strong acid (SA), weak acid (WA), strong base (SB), weak base (WB), or neutral (N) species.

H_2SO_4 and HCl are strong acids. The H_2SO_4 solution will be more acidic than the HCl solution (lower pH) because H_2SO_4 is both a strong acid and a weak acid (HSO_4^-)

RbOH and $Sr(OH)_2$ are strong bases. The $Sr(OH)_2$ solution will be more basic (higher pH) than the RbOH solution since $Sr(OH)_2$ breaks up into $2OH^-$ ions when it dissolves.
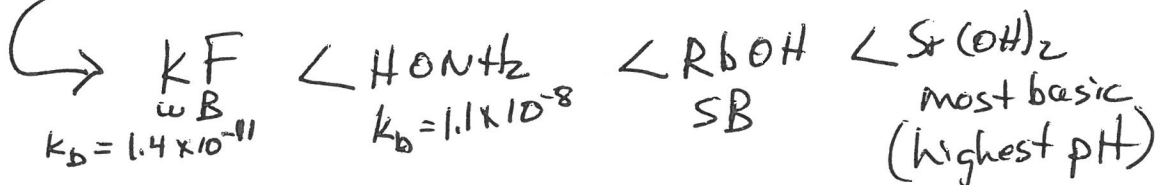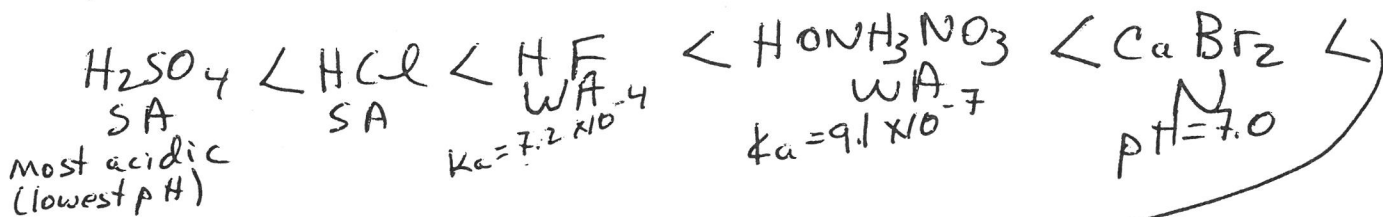
$CaBr_2 \rightarrow Ca^{2+} + 2Br^-$; both Ca^{2+} and Br^- ions are garbage ions (conjugates of something strong). $CaBr_2$ solution will have pH = 7.0

$HONH_2$ is a weak base ($K_b = 1.1 \times 10^{-8}$). HF is a weak acid ($k_a = 7.2 \times 10^{-4}$).

$KF \rightarrow K^+ + F^-$ (F⁻ is a weak base with $k_b = \frac{1 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$)
      garbage   wk base

$HONH_3NO_3 \rightarrow HONH_3^+ + NO_3^-$
                wk acid   garbage

$HONH_3^+$ is a weak acid with $k_a = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.1 \times 10^{-7}$.

The order is:

$$H_2SO_4 < HCl < HF < HONH_3NO_3 < CaBr_2$$
   SA   SA   WA   WA   N

Most acidic $k_a = 7.2 \times 10^{-4}$ $k_a = 9.1 \times 10^{-7}$ pH = 7.0
(lowest pH)

$$\rightarrow KF < HONH_2 < RbOH < Sr(OH)_2$$
   wB   SB   most basic

$k_b = 1.4 \times 10^{-11}$ $k_b = 1.1 \times 10^{-8}$ (highest pH)

26.   Consider the titration of 50.0 mL of 0.10 M Sr(OH)$_2$ by 0.10 M HNO$_3$. Sketch a titration
        curve for this titration and label the axes. On your sketch, indicate the pH at the equiva-
        lence point and the volume of Sr(OH)$_2$ required to reach the equivalence point. What are
        the major species present at the equivalence point after all of the strong base has reacted?
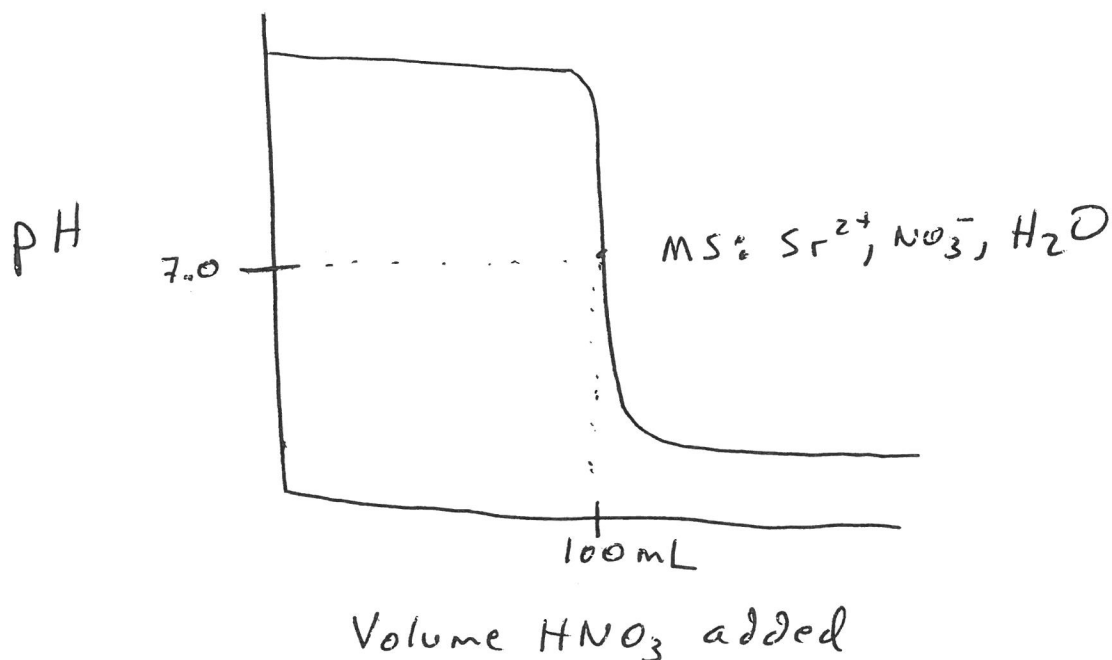**(5 pts.)**

This is a strong base titrated by a strong acid.

OH^- + H^+ → H_2O is the neutralization reaction
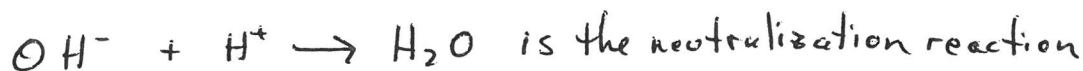
$$mmol\ OH^- = \frac{50.0\,mL\ |\ 0.10\,mmol\ Sr(OH)_2\ |\ 2\,mmol\ OH^-}{mL\ |\ 1\,mmol\ Sr(OH)_2} = 10.\,mmol\ OH^-$$

Volume HNO$_3$
required to $= \dfrac{10.\,mmol\ H^+\ |\ 1\,mL}{|\ 0.10\,mmol\ H^+} = 100.\,mL\ HNO_3$
reach equiv. pt

At 100. mL HNO$_3$ added, the added H^+ neutralizes
all of the OH^- present. The major species present at
the equivalence point are Sr^{2+}, NO_3^- and H_2O. These
are garbage ions, so pH = 7.00 at equivalence point.

pH

7.0

MS: Sr^{2+}, NO_3^-, H_2O

100 mL

Volume HNO$_3$ added

Titration rxn: $HOCl_{(aq)} + OH^-_{(aq)} \rightarrow OCl^-_{(aq)} + H_2O_{(l)}$

At equivalence point, moles $HOCl$ = moles OH^-

$M_A V_A = M_B V_B$, $25.0\,mL(0.400M) = V_B(0.200M)$, $V_B = 50.0\,mL$ to reach equiv. point.

27. The next four questions refer to the titration of 25.0 mL of 0.400 *M* hypochlorous acid (HOCl) by 0.200 *M* KOH. The K_a value for HOCl is 3.5×10^{-8}.

(13 pts.)

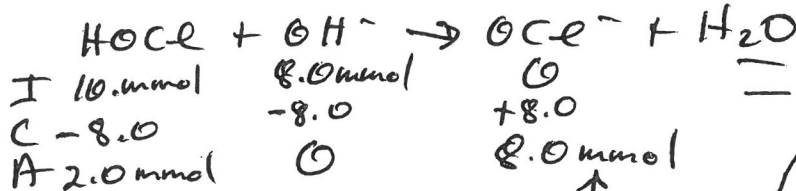A. At what volume of KOH added does $[H^+] = 3.5 \times 10^{-8}$ *M*?

$K_a = 3.5 \times 10^{-8}$ & $[H^+] = K_a$ at the halfway point to equivalence.

$Volume_{to\ \frac{1}{2}way\ point} = \dfrac{50.0\,mL}{2} = \boxed{25.0\,mL}$

B. Calculate the pH after 40.0 mL of KOH has been added.

mmol $HOCl = 25.0\,mL(0.400M) = 10.\,mmol$
mmol OH^- added $= 40.0\,mL(0.200M) = 8.0\,mmol$

$$HOCl + OH^- \rightarrow OCl^- + H_2O$$

I	10.mmol	8.0 mmol	0
C	-8.0	-8.0	+8.0
A	2.0 mmol	0	8.0 mmol

buffer solution results

$pH = pK_a + \log\dfrac{[base]}{[acid]}$

$pK_a = -\log(3.5 \times 10^{-8})$
$pK_a = 7.456$
$pH = 7.456 + \log\left(\dfrac{8}{2}\right)$
$pH = 7.456 + 0.602 = \boxed{8.06}$

C. Calculate the pH at the equivalence point. mmol OH^- added = 10.mmol = 50.0(0.200)

$$HOCl + OH^- \rightarrow OCl^- + H_2O$$

I	10.	10.	0
C	-10	-10	+10
A	0	0	10.mmol
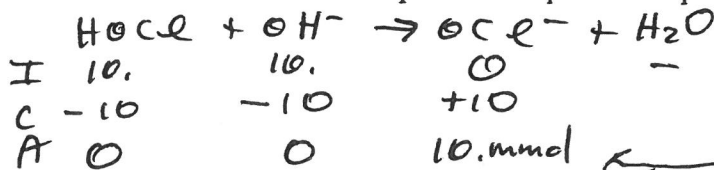
Only a weak base is present at equivalence point.

k_b for $OCl^- = \dfrac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.86 \times 10^{-7}$

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

I	10/75 uL		0	0
C	-x		+x	+x
E	0.133 -x		x	x
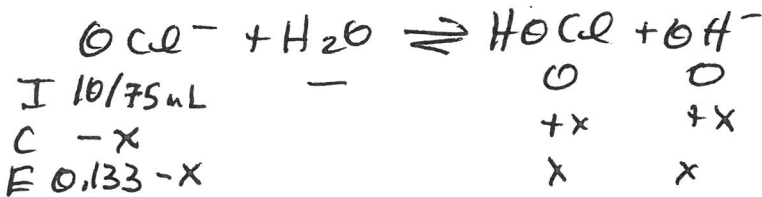
$k_b = 2.86 \times 10^{-7} = \dfrac{x^2}{0.133-x} \approx \dfrac{x^2}{0.133}$

$x = [OH^-] = 1.95 \times 10^{-4}\,M$
$pOH = -\log(1.95 \times 10^{-4}) = 3.71$
$pH = 14.00 - 3.71 = \boxed{10.29}$

D. Calculate the pH after 75.0 mL of KOH has been added.

mmol OH^- added $= 75.0\,mL(.200M) = 15\,mmol$

$$HOCl + OH^- \rightarrow OCl^- + H_2O$$

I	10.	15	0
C	-10	-10	+10
A	0	5	10
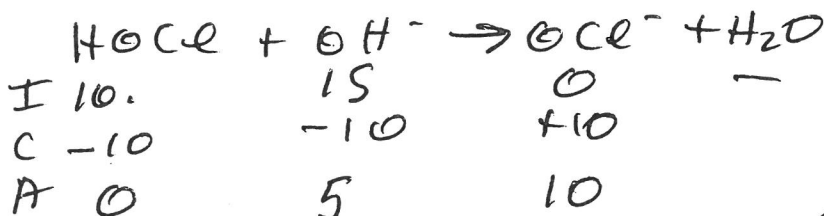
excess OH^- dominates

$[OH^-]_{excess} = \dfrac{5.0\,mmol}{100.0\,mL}$

$[OH^-] = 0.050\,m$
$pOH = -\log(0.050) = 1.30$
$pH = 14.00 - 1.30 = \boxed{12.70}$

28.   A.   Calculate the pH of a solution containing 0.35 M $HC_3H_5O_2$ and 0.65 M $KC_3H_5O_2$.
             K_a for $HC_3H_5O_2$ = 1.3 × 10^{-5}.

(7 pts.)

This is a buffer solution containing a weak acid ($HC_3H_5O_2$) and its conjugate base ($C_3H_5O_2^-$).

$$pH = pka + \log \frac{[C_3H_5O_2^-]}{[HC_3H_5O_2]} = -\log(1.3 \times 10^{-5}) + \log\left(\frac{0.65}{0.35}\right)$$

$$pH = 4.886 + 0.269 = \boxed{5.15}$$

B.   Calculate the pH after 0.30 mol of HCl is added to 2.0 L of a solution containing
0.35 M $HC_3H_5O_2$ and 0.65 M $KC_3H_5O_2$. Assume no volume change when the
HCl is added. K_a for $HC_3H_5O_2$ = 1.3 × 10^{-5}

Added H^+ reacts with best base to completion.

$$H^+ \quad + \quad C_3H_5O_2^- \quad \rightarrow \quad HC_3H_5O_2$$

I $\frac{0.30 mol}{2.0 L}$ 0.65 M   0.35 M

C   −0.15   −0.15   +0.15

A   0   0.50 M   0.50 M
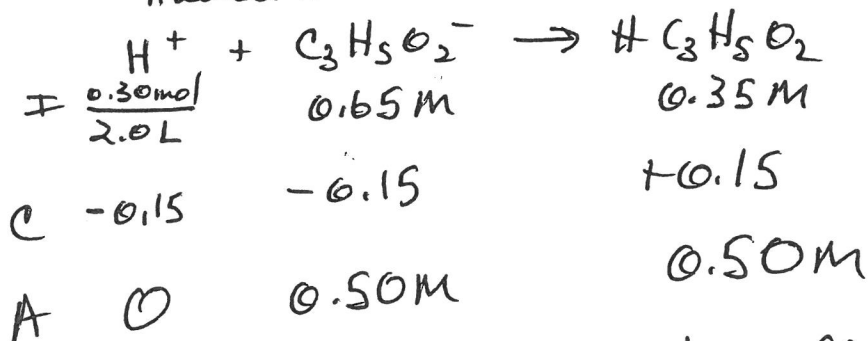
A buffer solution results after the H^+ reacts completely. Since $[C_3H_5O_2^-] = [HC_3H_5O_2]$,

$$pH = pka = \boxed{4.89}$$