

# Final Exam Logistics

The final exam for CHM1311B will be written on Saturday Dec. 6th, 9:30 - 12:30 in the Sports Complex (SCS) on King Edward. There are 3 ice rink areas prepared for exams that are assigned to this course (SCS 1, SCS 2 and SCS 3), and seats are assigned according to last name.

If your last name begins with:	Exam Location
A – Kon	SCS 1
Kos – Willia	SCS 2
Willou – Z	SCS 3

Seat assignments will be posted in the room where the exam is to be written.

## The exam is cumulative:

20% from midterm 1 material (Chapters 1 – 4, 12.4, 19.1)

40% midterm 2 (Chapters 5, 8.4, 14, 15, 16)

40% new material (Chapters 17, 6, 7.1, 7.2, 8.1, 8.6)

# Some Points of Clarification from Chapter 17

When do we use Henderson-Hasselbalch?

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Use it for buffers:

- Remember, any weak acid or weak base is essentially a buffer!
- Use it for titrations of weak acid or weak base.
- If we are below equivalence point, such that both HA and A<sup>-</sup> are present then H-H equation can be used to find pH of the titrated solution

How do we find out if we are below equivalence point in a titration?

CALCULATE  $n_{\text{HA}}$  (OR  $n_{\text{A}^-}$ ) BEING TITRATED

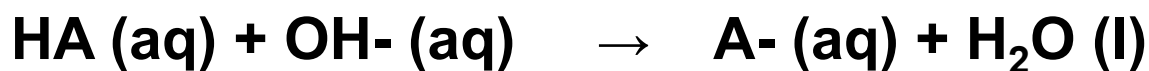
CALCULATE  $n_{\text{H}_3\text{O}^+}$  (OR  $n_{\text{OH}^-}$ ) BEING ADDED

# Key Points on Calculations with Buffered Solutions

After addition of a strong acid or base to a buffer, deal with neutralization first, then equilibrium.

## 1) Neutralization reaction after addition of:

**A strong base**



**A strong acid**



THIS IS ALL WE NEED TO CONSIDER IF WE ARE FAR PAST EQUIV. POINT

IF WE ARE BELOW EQUIVALENCE POINT USE THIS TO

FIND  $[\text{A}^-]$  &  $[\text{HA}]$  FOR HENDESEN-HASSELBALCH

## 2) Equilibrium reaction for: (AT OR CLOSE TO EQUIVALENCE PT.)

**Base ionization**



**Acid dissociation**





$$pK_a (\text{ACETIC ACID}) = 1.8 \times 10^{-5}$$

$$pK_c = 4.7447$$

17.31 A buffer is prepared by mixing 204 mL of 0.452 mol/L HCl and 0.500 L of 0.400 mol/L sodium acetate. (See [Appendix C](#).)

a. What is the pH?

$$pH = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

b. What mass of KOH must be added to 0.500 L of the buffer to change the pH by 0.15 units?



$$n_{\text{A}^-} = c_{\text{A}^-} \cdot V_{\text{A}^-}$$

$$\text{INITIAL} = (0.400 \text{ M})(0.500 \text{ L})$$

$$= 0.2 \text{ mol}$$

$$n_{\text{HA}} = n_{\text{H}_3\text{O}^+} = (0.204 \text{ L})(0.452 \text{ M})$$

$$= 0.0922$$

$$[\text{A}^-] = \frac{n_{\text{A}^-, \text{AFTER RX}}}{V_T} = \frac{n_{\text{A}^-, \text{INITIAL}} - n_{\text{H}_3\text{O}^+}}{V_{\text{A}^-} + V_{\text{H}_3\text{O}^+}} = \frac{0.2 \text{ mol} - 0.0922}{0.704 \text{ L}} = 0.153 \frac{\text{mol}}{\text{L}}$$

$$[\text{HA}] = \frac{n_{\text{HA}}}{V_T} = 0.131 \frac{\text{mol}}{\text{L}} \Rightarrow \text{H-H } pH = 4.81$$

$$\text{b) } pH = 4.96$$

$$\log \frac{[\text{A}^-]}{[\text{HA}]} = pH - pK_a \quad \frac{[\text{A}^-]}{[\text{HA}]} = 1.64$$

$$\text{LET } x = [\text{OH}^-] \text{ ADDED}$$

$$\frac{[\text{A}^-]_0 + x}{[\text{HA}]_0 - x} = 1.64$$

SOLVE FOR  $x = [\text{OH}^-] = 0.0235 \text{ M}$

$$n = cV$$

$$\frac{m}{M} = n$$

$$m = cVM$$

$$= (0.0235 \text{ M})(0.500 \text{ L})(56.11 \text{ g/mol})$$

$$= 0.66 \text{ g}$$

## Equilibrium Questions:

There are really only 2 types of equilibrium questions that we see, either;

- 1) Find K
- 2) Find the concentration of a reactant or product. This is mainly what we see in Chapter 17.

What is the most important step in setting up your solution to these problems?

WRITING CORRECT BALANCED EQUATION

In some questions (especially acid/base/buffer questions) it is not always obvious what equation we should be starting with.

How to identify the correct equation?

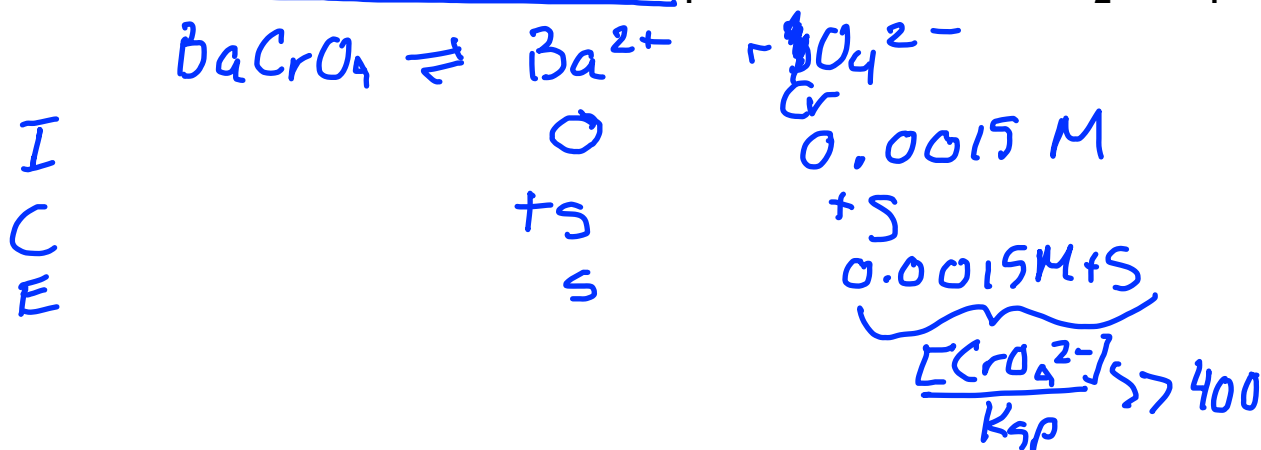
Ask these questions:

- 1) What is the question asking for?
- 2) What K do you have to work with?

Some examples...

$$K_{sp} = 2.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}]$$

Find the molar solubility of BaCrO<sub>4</sub> in  $1.5 \times 10^{-3} \text{ M Na}_2\text{CrO}_4$ .



$$K_{sp} = s(0.0015 \text{ M})$$

$$s = 1.4 \times 10^{-7} \text{ M}$$

Find the pH at the equivalence point and the volume of  $0.0372 \text{ M NaOH}$  needed to reach the equivalence point in a titration of  $28.9 \text{ mL}$  of  $0.0850 \text{ M H}_2\text{SO}_3$ .



We can think of this process as two separate steps:

1) Add enough acid so that we turn all  $\text{H}_2\text{SO}_3$  into  $\text{HSO}_4^-$ . Do we need an ice table to figure this out?

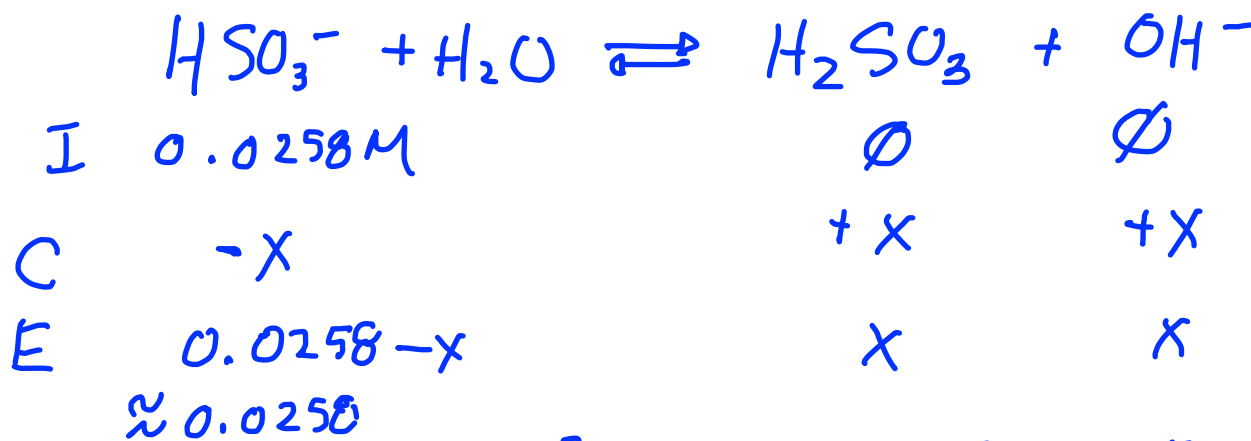
① CALCULATE  $n_{\text{H}_2\text{SO}_3} = c_{\text{H}_2\text{SO}_3} V_{\text{H}_2\text{SO}_3} = 0.002456 \text{ mol} = n_{\text{OH}^-}$

② CALCULATE  $V_{\text{OH}} = cV \quad V_{\text{OH}} = \frac{n_{\text{OH}^-}}{c_{\text{OH}}} = 66.03 \text{ mL}$

$$\textcircled{3} \text{ CALCULATE } [\text{HSO}_3^-] = \frac{n_{\text{HSO}_3^-}}{(0.06603 + 0.0289) \text{ L}} = 0.0258 \text{ M}$$

**Step 2:**

Let the  $\text{HSO}_3^-$  react with  $\text{H}_2\text{O}$  to reach the equilibrium. What is the equation and equilibrium constant we need for this part?



$$K_b = \frac{x^2}{0.0258}$$

$$x = 1.35 \times 10^{-7}$$

$$= [\text{OH}^-]$$

$$\text{pH} = 7.13$$

$$K_{a,1} = 1.4 \times 10^{-2}$$

$$K_b = \frac{K_w}{K_a} = 10^{-14}$$

$$= 7.14 \times 10^{-13}$$

$$\frac{[\text{HSO}_3^-]}{K_b} \gg 400$$



How do we handle the next equivalence point?

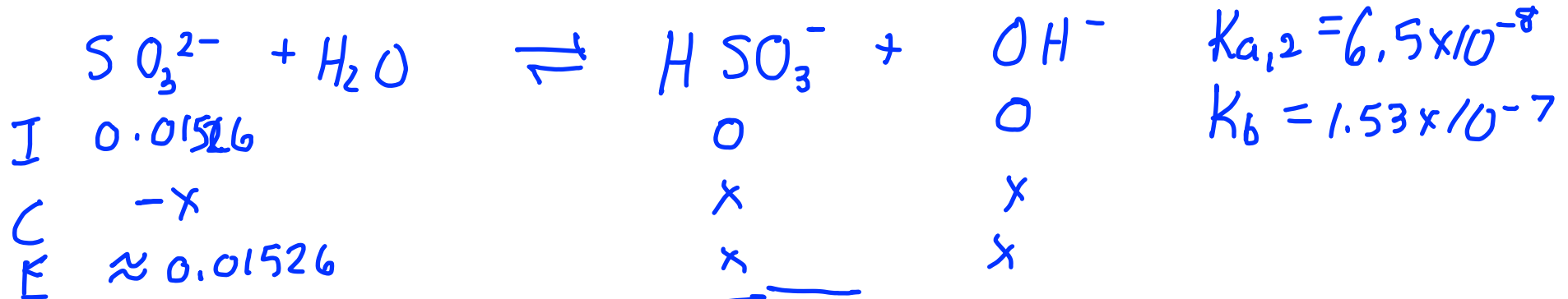
1) Neutralization reaction  $n_{\text{OH}^-} = 2 n_{\text{H}_2\text{SO}_3}$

FOR 1 EQUIVALENCE WE NEED 66.03 mL

∴ FOR 2<sup>nd</sup> EQUIVALENCE POINT WE NEED 2 × 66.03 mL

$$[\text{SO}_3^{2-}] = \frac{n_{\text{HSO}_3^-}}{V_T} = \frac{0.024565 \text{ mol}}{(0.06603 \times 2) + 0.0289 \text{ L}} = 0.01526 \text{ M}$$

2) Reaction of conjugate base with water

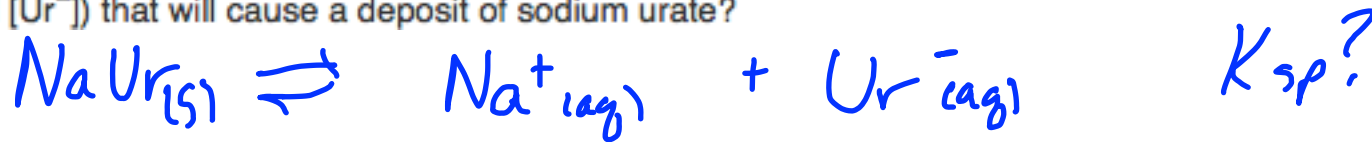


$$[\text{OH}^-] = \sqrt{K_b (0.01526)}$$

$$= 4.835 \times 10^{-5} \text{ M}$$

$$\text{pH} = 9.68$$

17.119 Gout is caused by an error in metabolism that leads to a buildup of uric acid in body fluids, which is deposited as slightly soluble sodium urate ( $C_5H_3N_4O_3Na$ ) in the joints. If the extracellular  $[Na^+]$  is 0.15 mol/L and the solubility of sodium urate is 0.085 g/100. mL, what is the minimum urate ion concentration (abbreviated  $[Ur^-]$ ) that will cause a deposit of sodium urate?



$$S = 0.085 \text{ g/100 mL}$$

$$= 0.85 \text{ g/L} = 4.47 \times 10^{-3} \text{ M}$$

MW = 190

$$K_{sp} = S^2$$

$$= (4.47 \times 10^{-3})^2$$

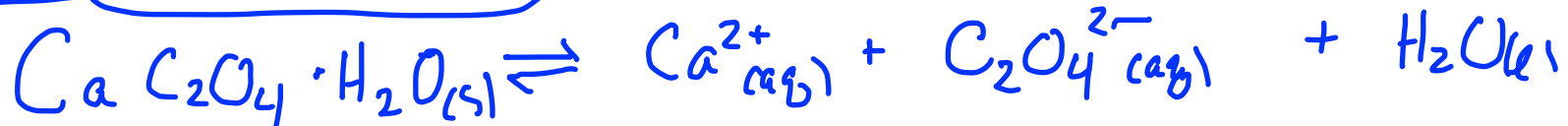
$$= 2.00 \times 10^{-5}$$

	$NaUr_{(s)}$	$Na^+$	$Ur^-$	
I		0.15 M	$\emptyset$	$K_{sp} = (0.15) S$
C		S	S	
E		0.15 + S	S	$S = \frac{K_{sp}}{0.15} = 1.33 \times 10^{-4} \text{ M}$
		$\approx 0.15$		



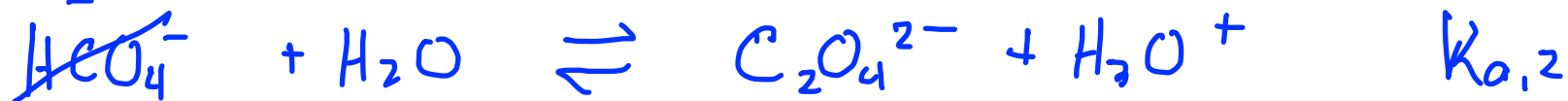
Some kidney stones form by the precipitation of calcium oxalate monohydrate ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ;  $K_{sp} = 2.3 \times 10^{-9}$ ). The pH of urine varies from 5.5 to 7.0, and the average  $[\text{Ca}^{2+}]$  in urine is  $2.6 \times 10^{-3} \text{ M}$ .

If the concentration of oxalic acid in the urine is  $3.0 \times 10^{-13} \text{ M}$ , will kidney stones form at pH = 5.5?



DOES RXN GO BACKWARD UNDER PHYSIOLOGICAL CONDITIONS  
NEED TO CALCULATE  $Q_{sp}$  & COMPARE TO  $K_{sp}$   
KIDNEY STONES WILL FORM IF  $Q_{sp} > K_{sp}$

$$Q = [\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}]$$



$$K = K_{a,1} \times K_{a,2}$$

$$\begin{aligned} &= (5.6 \times 10^{-2}) (5.4 \times 10^{-5}) \\ &= 3.024 \times 10^{-6} \end{aligned}$$

$$K = \frac{[H_3O^+]^2 [C_2O_4^{2-}]}{[H_2C_2O_4]}$$

$$\begin{aligned} [C_2O_4^{2-}] &= \frac{K [H_2C_2O_4]}{[H_3O^+]^2} \\ &= \frac{(3.024 \times 10^{-6}) (3.0 \times 10^{-13})}{(10^{-5.5})^2} \\ &= 9.07 \times 10^{-8} \text{ M} \end{aligned}$$

$$Q_{sp} = [Ca^{2+}] [C_2O_4^{2-}] = 2.36 \times 10^{-10}$$

$$K_{sp} = 2.3 \times 10^{-9} \quad \therefore \text{NO KIDNEY STONES}$$

## Chapter 6 Equations

$$c = \lambda \times \nu$$

ENERGY IS QUANTIZED

$$\Delta E = nh\nu$$

ENERGY OF 1 PHOTON

$$\lambda = \frac{h}{m\nu}$$

$$E_n = -\frac{R_H}{n^2}$$

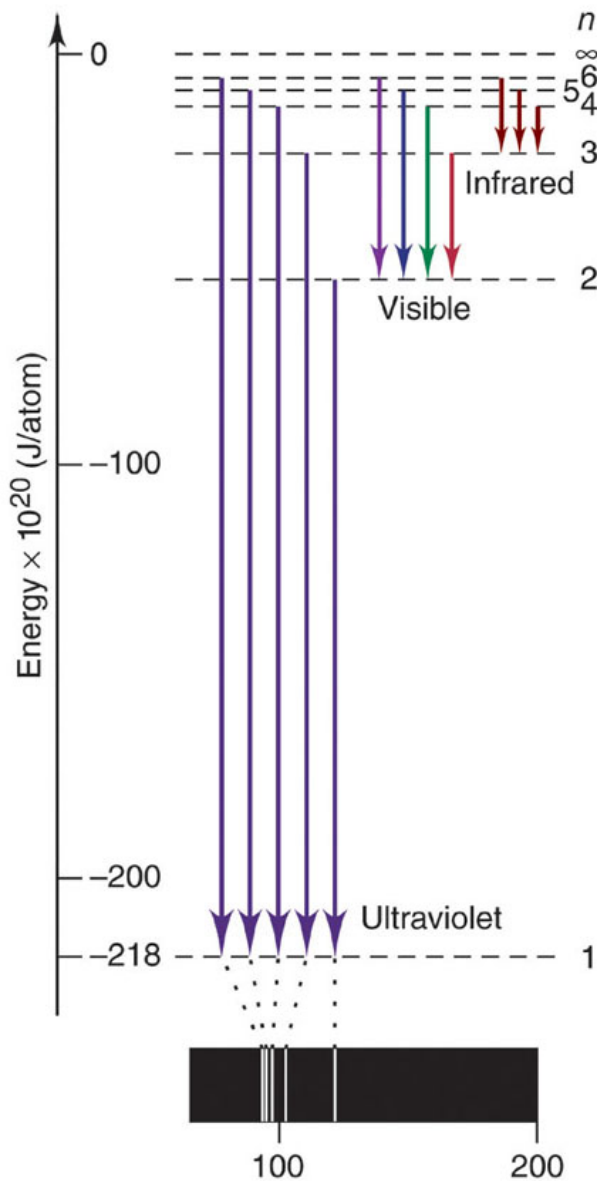
ENERGY OF AN  $e^-$  IN ENERGY LEVEL  $n$  IN A HYDROGEN ATOM

$$\Delta E > 0$$

COMES FROM ABSORBANCE OF PHOTON TO PROMOTE AN  $e^-$  FROM LOW ENERGY TO HIGH ENERGY

$$\Delta E < 0$$

$\therefore$  PHOTON IS EMITTED AS  $e^-$  RELAXES BACK TO LOWER ENERGY



Dec. 5th Review Wavelength (nm)

### Problem 6.25

What is the wavelength (nm) of the least energetic spectral line in the infrared series of the H atom?

$$n_f = 3$$

$$E = -\frac{R_H}{n^2}$$

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

$$\Delta E = -R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$= -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{3^2} - \frac{1}{4^2} \right)$$

$$= -1.0597 \times 10^{-19} \text{ J}$$

IF WE ARE ASKED FOR ENERGY EMITTED BY 1 mol H THEN

$$\Delta E_{\text{TOTAL}} = \Delta E_{\text{PHOTON}} \times N_A = 64 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta E = h\frac{c}{\lambda} \quad \lambda = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{1.0597 \times 10^{-19} \text{ J}}$$

$$= 1.870 \times 10^{-6} \text{ m}$$

$$= 1870 \text{ nm}$$