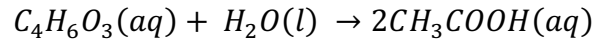


## INDIV.

### Problem #1: (26 points)

Streams of acetic anhydride ( $C_4H_6O_3$ ) and water are fed to a continuous stirred-tank reactor (CSTR) to carry out the following exothermic hydrolysis reaction to form acetic acid ( $CH_3COOH$ ).



The reaction is second-order with respect to acetic anhydride concentration with a rate constant which has a pre-exponential factor of  $2.4267 \cdot 10^9$  L/(min·mol) and an activation energy of 50,242 J/mol. Water is fed to the reactor at a rate of 400 g/min, and acetic anhydride is fed at a rate of 4.0 g/min. The reactor is operated to contain 0.85 L of liquid at all times. The densities of all reactants and product streams are sufficiently close to 1 g/cm<sup>3</sup> that the total volumetric flow rates into and out of the reactor are both 0.41 L/min. A key assumption that goes into CSTR systems is that the fluid inside of the reactor is perfectly mixed, meaning the concentration of all species leaving the reactor are identical to the concentration of all species within the reactor. MW of acetic anhydride is 102.1 g/mol.

- a) Determine the **acetic anhydride conversion** assuming isothermal steady-state operation of the CSTR at 40°C. (Hint): Perform a mass balance on acetic anhydride for the system and ensure the units of all terms are equal. **Circle final answer with proper units!** (8 points)

$$\frac{dm}{dt} = m_{IN} - m_{OUT} + m_{Gen} = 0 \text{ due to SS}$$

$$-r_{Cons} = kC_{Acetic\ Anhydride}^2$$

(1 point correct setup of Arrhenius equation)

$$k = A_0 \exp\left\{-\frac{Ea}{RT}\right\} = 2.4267 \cdot 10^9 \frac{L}{min \cdot mol} \exp\left\{-\frac{\frac{50,242 J}{mol}}{\frac{8.314 J}{mol \cdot K} \cdot 313.15 K}\right\}$$

$$C_{Acetic\ Anhydride} = \frac{m_{OUT}}{V_{OUT}} \text{ from hint!}$$

(1 point correctly solving for the reaction constant k)

$$\therefore k = 10.0959 \frac{L}{min \cdot mol} \therefore -r_{Cons} = 10.0959 \frac{L}{min \cdot mol} \left(\frac{m_{OUT}}{V_{OUT}}\right)^2$$

$$\text{Unit analysis of } r_{Cons}: \frac{L}{min \cdot mol} \left(\frac{g/min}{L/min}\right)^2 = \frac{g^2}{min \cdot mol \cdot L}$$

## INDIV.

We need to make it =  $\frac{g}{min}$   $\therefore$  divide by MW and multiply by volume

(3 points for determining the mass balance equation below)

$$0 = m_{IN} - m_{OUT} - k \left( \frac{m_{OUT}}{V_{OUT}} \right)^2 \cdot \frac{V_{Reactor}}{MW}$$

$$m_{IN} = m_{OUT} + m_{OUT}^2 \left( \frac{10.0959}{(0.41)^2} \right) \frac{(0.85)}{(102.1)} \left[ \frac{L}{min \cdot mol} \frac{min^2 mol}{L^2} \frac{g}{L} \right]$$

$$m_{IN} = m_{OUT} + \left( 0.50000 \frac{min}{g} \right) m_{OUT}^2 \therefore m_{IN} = 4.0 g/min$$

(1 points for correct quadratic equation below)

$$-4.0 + m_{OUT} + 0.5m_{OUT}^2 = 0$$

Factor or complete square or quad formula:

$$0.5(m_{OUT} + 1)^2 - 4.5 = 0$$
$$m_{OUT} = 2 g/mol$$

(2 points for correct final answer)

$$X = \frac{m_{OUT}}{m_{IN}} = 0.5$$

$X = 0.5$  or 50%

**Part a)**  
**ANSWER BOX**

## INDIV.

- b) Indicate whether the following changes (while keeping all other factors listed above the same) will increase, decrease or not change the extent of acetic anhydride conversion.

**Write answer on given lines below! (6 points)**

- i. Increasing the temperature of the reactor to 50°C: INCREASE
- ii. Doubling the volume of liquid within the CSTR: INCREASE
- iii. Double both the feed rates of both water and acetic anhydride: DECREASE
- iv. Doubling the pressure of the reaction vessel: NO CHANGE
- v. Decrease the velocity of fluid leaving the reactor: INCREASE

Note: This problem is graded very particularly to ensure that students do not earn points through guessing

(+1 point) for correctly labeling part i) as INCREASES

(+1 point) for correctly labeling part ii) as INCREASES

(+1 point) for correctly labeling part iii) as DECREASES

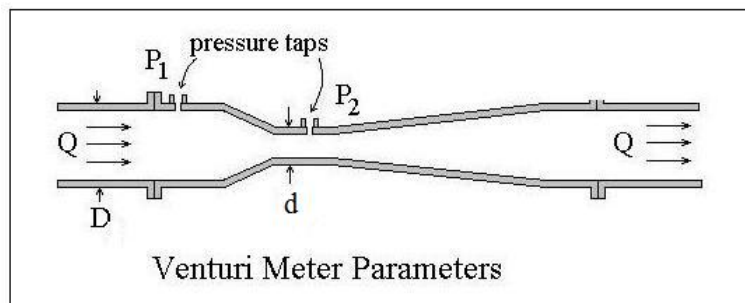
(+1 point) for correctly labeling part iv) as NO CHANGE

(+1 point) for correctly labeling part v) as NO CHANGE

(+1 points) if parts i), ii), iii), iv), and v), are **all correct**. If they even miss one part this points are not to be awarded.

## INDIV.

- c) Prior to the fluid entering the reactor there is a Venturi meter (pictured below) which involves measuring a differential pressure of the fluid in the pipe ( $P_1$ ) and the fluid through a throat ( $P_2$ ). The flow meter is installed on a horizontal piece of pipe. Assuming there are no frictional losses and a constant volumetric flow rate in this process, determine if  $P_2$  is greater than, less than, or equal to  $P_1$ . Circle one option below and **explain (1-3 sentences). (3 points)**



$$P_2 > P_1$$

$$P_2 = P_1$$

$$P_2 < P_1$$

In this case intuition is wrong as  $P_2 < P_1$  because of **conservation of energy**. Since volumetric flow rate is conserved, the velocity of the fluid has to increase as it passes through the throat of the pipe, meaning that the kinetic energy is increased. This energy has to come from somewhere and with the pipe being horizontal the potential energy cannot change, meaning the pressure energy is forced to decrease.

(+1 point) for correctly identifying that  $P_2 < P_1$

(+2 points) for a correct explanation that explains why this is true.

Students who answer with any of the other two options will receive **0 points** on this problem no matter what.

- d) In industry, irreversible, exothermic reactions are known to be extremely dangerous. Why? **Explain (1-3 sentences). (3 points)**

This situation would be a runaway reaction because the process is exothermic, meaning as the reaction continues, heat is produced and thus the reaction mixture temperature increases. As the reaction mixture heats, the rate constant increases thus creating a positive feedback loop until the temperature builds to dangerous conditions.

(+1 point) for mentioning how exothermic reactions release/produce heat.

(+1 point) for mentioning how at higher temperatures the rate constant increases

(+1 point) for mentioning how the higher temperatures generate dangerous conditions.

## INDIV.

- e) A new catalyst is discovered which better facilitates the acetic anhydride hydrolysis is found and makes its rate of consumption half order with respect to acetic anhydride. If the process is tested in a beaker and has a conversion of 75% in 10 minutes, determine what conversion will be achieved at 28 minutes. The following system can be modeled by the differential equation and its solution form for this reaction system are given below:

$$\frac{-r_{Cons}V}{N_{AO}} = \frac{dX}{dt} \rightarrow \frac{k_{new}}{C_{AO}^{0.5}} \cdot t = 2 - 2(1 - X)^{0.5}$$

Where  $t$  is time,  $X$  is conversion of acetic anhydride, and  $C_{AO}$  is the initial concentration of acetic anhydride

**Circle final answer with proper units! (6 points)**

This problem is quite tricky as the information given has no mention of the initial concentration of acetic anhydride or what the new rate constant would be, but we do know that these are constant (independent of time) and through algebra we can rearrange the equation.

$$\frac{k_{new}}{C_{AO}^{0.5}} = \frac{2 - 2(1 - X_1)^{0.5}}{t_1} = \frac{2 - 2(1 - X_2)^{0.5}}{t_2}$$

By plugging in  $X_1 = 0.75$ , and  $t_1 = 10$  min, will cause the LHS = 0.1. From this the student will see that if they plug in 28 minutes to  $t_2$ , that the numerator would need to have a value of 3 which is **impossible!** Student should then identify that something is fishy and try to test if where the model is valid such as when the reaction would be complete i.e.  $X_2 = 1$ . We can quickly see that the reaction is 100% complete at  $t_2 = 20$  minutes.

$$X_2 = 1 \text{ at } 28 \text{ minutes}$$

Aside: If students were to try and “plug and chug”, they could calculate a “false numeric solution” by isolating  $X_2$  and getting  $X_2 = 0.84$ , seen below. The reason that this results is that we squaring a negative number which results in a parabolic shape as opposed to the true form of the model.

$$X_2 = 1 - \left( \frac{0.1t_2 - 2}{-2} \right)^2$$

**For grading:**

**(+3 points)** if students get the above relationship for the model at two different times.

**(+3 points)** for the correct answer with reasonable work/an explanation that shows they simply did not guess.

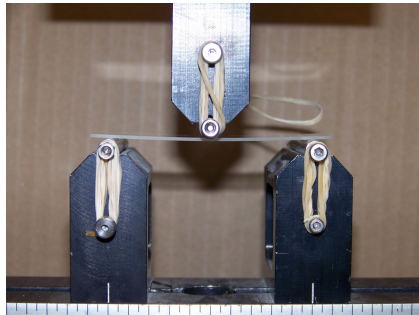
**$X_2 = 1$  at 28 minutes**

**Part e)  
ANSWER BOX**

# INDIV.

## **Problem #2: (17 points)**

A series of bend tests to failure were conducted on 20 soda-line glass slides. The slides all had the same nominal dimensions of 3" x 1" x 1mm. The surfaces of 10 slides were modified by glass-bead blasting. The remaining 10 slides were tested in the as-received condition. The beams were then loaded to failure in a 3-point bend configuration. Load, actuator, displacement, and time data were collected during those experiments, and it was observed that each specimen exhibited linear elasticity until failure. The failure loads for the two series of 10 specimens are summarized below.



3-point bend configuration

As-received slides		Treated slides	
Specimen #	Max Failure Load (N/mm <sup>2</sup> )	Specimen #	Max Failure Load (N/mm <sup>2</sup> )
1	87	1	44.2
2	129	2	49
3	96.3	3	53
4	104	4	47.6
5	139.6	5	47.5
6	104	6	44.7
7	122	7	55.2
8	99	8	48.1
9	121	9	50
10	110	10	49.9

- a) Using the data above, what is the advantage of glass-bead blasting of the soda-lime slides. **Explain (2-3 sentences).** (3 points)

From the data above we can see that the treated slides have a much lower average max failure load, however, a much lower standard deviation. This means that the treated slides have a very predictable failure stress which is desirable.

**1 point** for mentioning the lower average values of the treated slides.

**1 point** for mentioning the lower standard deviation or lower “spread of data”

**1 point** for a mentioning the better predictability of the treated slides load failure

## INDIV.

- b) A key idea in analysis of material failure is determining the probability of failure which can be done through the following formula below: **(14 points)**

$$P(\sigma) = \frac{\# \text{ of specimens in series that failed at or below stress } \sigma}{\text{Total \# of specimens in series} + 1}$$

Once calculated, the two-parameter Weibull failure probability relationship relates this probability of failure to the applied stress:

$$P(\sigma) = 1 - \exp\left\{-\left(\frac{\sigma}{\sigma_o}\right)^m\right\}$$

where  $\sigma_o$  is a scaling parameter and  $m$  is the Weibull modulus. The Weibull modulus is important because it indicates the variability in measured material strength of brittle materials. Assuming that you have properly calculated the probability of failure for the treated slides at each applied stress, explain how you would **graphically** determine  $\sigma_o$  and  $m$ . **Note:** You do not have to do any numeric calculations using the data; however, you do need to determine the proper ways to scale the axis. **Hint:** Convert the two-parameter Weibull failure relationship above into a slope-intercept form using the natural log rules below:

### Natural Log Rules:

$$\ln(\exp\{x\}) = x, \quad \ln(x^{-a}) = -a \cdot \ln(x) \text{ (where } a \text{ is any real number)}, \quad \ln(x/y) = \ln(x) - \ln(y)$$

When trying to graphically solve for model parameters we need to try and create a linear data line through axis manipulations.

$$P(\sigma) = 1 - \exp\left\{-\left(\frac{\sigma}{\sigma_o}\right)^m\right\} \rightarrow 1 - P(\sigma) = \exp\left\{-\left(\frac{\sigma}{\sigma_o}\right)^m\right\}$$

Take the natural log of both sides: **(1 point for this step)**

$$\ln(1 - P(\sigma)) = -\left(\frac{\sigma}{\sigma_o}\right)^m$$

Move the negative sign over and apply the classic natural log rule: **(1 point for this step)**

$$\ln\left(\frac{1}{1 - P(\sigma)}\right) = \left(\frac{\sigma}{\sigma_o}\right)^m$$

Take the natural log of both sides again: **(1 point for this step)**

$$\ln\left(\ln\left(\frac{1}{1 - P(\sigma)}\right)\right) = \ln\left(\frac{\sigma}{\sigma_o}\right)^m$$

Remove the power from the RHS: **(1 point for this step)**

$$\ln\left(\ln\left(\frac{1}{1 - P(\sigma)}\right)\right) = m \ln\left(\frac{\sigma}{\sigma_o}\right)$$

## INDIV.

Remove the division on the RHS: (1 points for this step)

$$\ln\left(\ln\left(\frac{1}{1-P(\sigma)}\right)\right) = m \ln(\sigma) - m \ln(\sigma_0)$$

The equation while it looks convoluted is now in slope intercept form:

$$y = mx + b$$
$$y = \ln\left(\ln\left(\frac{1}{1-P(\sigma)}\right)\right)$$

$$x = \ln(\sigma)$$

$$m = m$$

$$b = -m \ln(\sigma_0)$$

At this point we can see that we need to scale the y-axis to by the following:

$$y = \ln\left(\ln\left(\frac{1}{1-P(\sigma)}\right)\right)$$

(2 points for this proper y-axis scaling)

The x-axis can be scaled by:

$$x = \ln(\sigma)$$

(2 points for this proper x-axis scaling)

(2 point for full explanation of how to determine the Weibull modulus)

(3 points for full explanation of how to determine  $\sigma_0$  modulus)

Now we can easily find the fitting parameters as the slope of the linearized data is the Weibull modulus  $m$ .  $\sigma_0$  is a little trickier as we can solve for this by the following method:

$$\sigma_0 = \exp\left\{-\frac{b}{m}\right\}$$

Where  $b$  is the y-intercept.

Note: If the students create a final y scaling as the following but does everything else correctly:

$$y = \ln(-\ln(1 - P(\sigma)))$$

The student will be penalized only **1 point** as while this would be a valid expression for a computer, it is bad convection to have a negative sign in a natural logarithm.

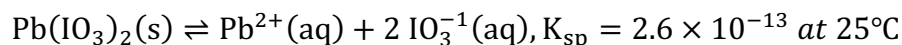
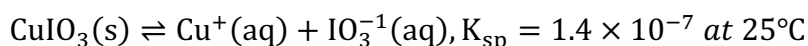


## INDIV.

### **Problem #3: (9 points)**

500 mL of a 0.25 M  $\text{Cu}^+$  aqueous solution is mixed with 250 mL of a 0.3 M  $\text{Pb}^{2+}$  aqueous solution at 25°C. Into this mixed solution, an aqueous solution of  $\text{IO}_3^-$  is added dropwise. Assume no volume change of the mixed solution upon addition of  $\text{IO}_3^-$  solution.

Given:  $\text{CuIO}_3$  and  $\text{Pb}(\text{IO}_3)_2$  are sparingly soluble salts in water.



- a) Determine which sparingly soluble salt will precipitate first. Show all work and **circle your final answer.** (6 points)

After mixing, the concentration of the metal ions are:

$$[\text{Cu}^+] = \frac{(0.25 \text{ M})(500 \text{ mL})}{(500 \text{ mL} + 250 \text{ mL})} = 0.167 \text{ M}$$

$$[\text{Pb}^{2+}] = \frac{(0.3 \text{ M})(250 \text{ mL})}{(500 \text{ mL} + 250 \text{ mL})} = 0.100 \text{ M}$$

For  $\text{CuIO}_3(\text{s})$ ,  $K_{\text{sp}}(\text{CuIO}_3(\text{s})) = [\text{Cu}^+][\text{IO}_3^-] = 1.4 \times 10^{-7}$ . This means that:

$$[\text{IO}_3^-] = \frac{K_{\text{sp}}}{[\text{Cu}^+]} = \frac{1.4 \times 10^{-7}}{0.167 \text{ M}} = 8.38 \times 10^{-7} \text{ M}$$

For  $\text{Pb}(\text{IO}_3)_2$ ,  $K_{\text{sp}}(\text{Pb}(\text{IO}_3)_2) = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = 2.6 \times 10^{-13}$ . This means that:

$$[\text{IO}_3^-] = \sqrt{\frac{K_{\text{sp}}}{[\text{Pb}^{2+}]}} = \sqrt{\frac{2.6 \times 10^{-13}}{0.100 \text{ M}}} = 1.61 \times 10^{-6} \text{ M} > 8.38 \times 10^{-7} \text{ M}$$

This means that the  $\text{CuIO}_3(\text{s})$  will precipitate first.

Alternative:

At  $[\text{IO}_3^-] = 8.38 \times 10^{-7} \text{ M}$ ,

$$Q(\text{Pb}(\text{IO}_3)_2) = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = (0.100 \text{ M})(8.38 \times 10^{-7} \text{ M})^2 = 7.02 \times 10^{-14}$$

This means that:

## INDIV.



As a result, the  $\text{Pb}(\text{IO}_3)_2$  will not precipitate.

+1 pt for correct substitution to solve for new concentration of  $[\text{Pb}^{2+}]$  and  $[\text{Cu}^+]$  after mixing.

+1 pt for both correct equilibrium expressions

+1 pt for correct substitution to solve for  $[\text{IO}_3^-]$  required to precipitate  $\text{CuIO}_3(\text{s})$

+1 pt for correct substitution to solve for  $[\text{IO}_3^-]$  required to precipitate  $\text{Pb}(\text{IO}_3)_2$

+1 pt for correct  $[\text{IO}_3^-]$  values required to precipitate both  $\text{Pb}(\text{IO}_3)_2$  &  $\text{CuIO}_3(\text{s})$

+1 pt for correct **circled** final answer (BASED ON CALCULATIONS)

- b) When the second precipitate begins to form, calculate the percentage of the first metal ion remaining in solution. Show all work and **circle your final answer.** (3 points)

When  $\text{Pb}(\text{IO}_3)_2$  begins to precipitate,

$$[\text{IO}_3^-] = 1.61 \times 10^{-6} \text{ M}$$

This means that:

$$[\text{Cu}^+] = \frac{K_{sp}(\text{CuIO}_3(\text{s}))}{[\text{IO}_3^-]} = \frac{1.4 \times 10^{-7}}{1.61 \times 10^{-6} \text{ M}} = 0.0870 \text{ M}$$

$$\% \text{ of Cu}^+ \text{ remaining} = \frac{0.0870 \text{ M}}{0.167 \text{ M}} = 52.1\%$$

+1 pt for correct substitution to solve for cation remaining when second precipitate begins to form (Based on part a)

+1 pt for correct substitution to solve for percent remaining

+1 pt for correct final answer.

# INDIV.

## **Problem #4: (8 points)**

Ulaanbaatar, the capital city of Mongolia, has many neighborhoods with *gers* (see photo) and small homes that use coal stoves for heating throughout the long, cold winters. Some of these neighborhoods are in relatively low and narrow valleys, and with the mixing layer height being only 50.0 m in wintertime (because it is so cold), the stove emissions cannot flow over the hilltops and thus are transported up or down the valley with the mean wind. Wind speed are very low, typically 1.0 m/s. The most densely populated valley is about 1.0 km (from hill to hill, across the valley)  $\times$  2.0 km (along the valley floor) and has a residential dwelling density of 2500 stoves/km<sup>2</sup>. Traditional stoves emit 6.0 grams of particulate matter (PM) per kg coal burned, while improved stoves emit 3.0 g PM/kg coal. Household coal consumption is 20.0 kg coal per day for both traditional and improved stoves. The PM concentration upwind of the neighborhood is 65  $\mu\text{g}/\text{m}^3$ . Assuming the neighborhood initially has only traditional stoves, what percentage of traditional stoves should be replaced with improved stoves to reduce the outdoor PM concentration to 150  $\mu\text{g}/\text{m}^3$  for the above condition? Assume the neighborhood air is well mixed.



First, let's start with a mass balance:

$$\frac{\partial m}{\partial t} = \dot{m}_{IN} - \dot{m}_{OUT} + \dot{m}_{gen} + \dot{m}_{dep}$$

Since we are given many things in terms of concentrations we can convert the mass equation above to be in the following form to make life easier:

$$V \frac{\partial C}{\partial t} = u_{wind} C_{IN} - u_{wind} C_{Local} + \dot{m}_{gen} + \dot{m}_{dep}$$

We can assume that none of the PM is depleted and we can assume steady state resulting in the equation below where:

$$\begin{aligned} u &= \text{wind speed (m/s)} \\ C_{IN} &= \text{uphill PM concentration } (\mu\text{g}/\text{m}^3) \\ C_{Local} &= \text{local PM concentration } (\mu\text{g}/\text{m}^3) \\ H &= \text{mixing height of valley (m)} \\ \hat{E} &= \text{PM emission rate per unit area } \left( \frac{\mu\text{g}}{\text{m}^2\text{s}} \right) \end{aligned}$$

$$\frac{u}{\Delta x} (C_{IN} - C_{Local}) + \frac{\hat{E}}{H} = 0$$

From here we can solve for the emission rate per unit area:

## INDIV.

$$\hat{E} = \frac{uH}{\Delta x} (C_{Local} - C_{IN}) = \frac{(1 \text{ m/s})(50 \text{ m})}{2000 \text{ m}} \left( 150 \frac{\mu\text{g}}{\text{m}^3} - 65 \frac{\mu\text{g}}{\text{m}^3} \right) = 2.125 \frac{\mu\text{g}}{\text{m}^2 \cdot \text{s}}$$

Now we can find the total emission of the neighborhood per day:

$$E = \hat{E} \Delta x \Delta y = \left( 2.125 \frac{\mu\text{g}}{\text{m}^2 \cdot \text{s}} \right) (1 \text{ km} \cdot 2 \text{ km}) \left( 10^6 \frac{\text{m}^2}{\text{km}^2} \right) = 4.25 \cdot 10^6 \frac{\mu\text{g}}{\text{s}}$$

$$E = 4.25 \frac{\text{g}}{\text{s}} = 3.67 \cdot 10^5 \frac{\text{g}}{\text{day}}$$

Now that we have the total particulate matter every day, we need to determine the total number of stoves present:

$$\text{Total Stoves} = 2500 \frac{\text{stoves}}{\text{km}^2} (1 \text{ km} \cdot 2 \text{ km}) = 5000 \text{ stoves}$$

$$3.67 \cdot 10^5 \frac{\text{g}}{\text{day}} = \left( \frac{20 \text{ kg coal}}{\text{day}} \right) \left( \frac{6 \text{ g PM}}{\text{kg coal}} \right) (X \text{ traditional stoves}) \\ + \left( \frac{20 \text{ kg coal}}{\text{day}} \right) \left( \frac{3 \text{ g PM}}{\text{kg coal}} \right) (5000 - X \text{ traditional stoves})$$

This results in the equation:

$$18,360 \frac{\text{g PM}}{\text{kg coal}} = 6X + 3(5000 - X) \therefore X = 1120$$

This means that to get the desired neighborhood PM concentration, only 1120 traditional stoves can remain. As a result:

$$\% = \frac{3880 \text{ improved}}{5000 \text{ total}}$$

**78% of traditional stoves need to be replaced.**

- (+1 point) attempting to create a mass balance
- (+1 point) for correct mass balance above
- (+1 point) for correct emission rate per day
- (+1 point) for correct number of total stoves
- (+1 point) for correct expression to solve for the number of traditional stoves that remain.
- (+3 points) for correct final answer.

# INDIV.

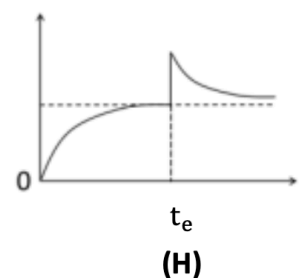
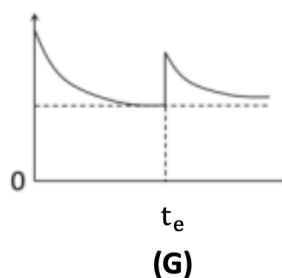
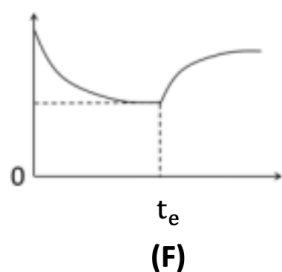
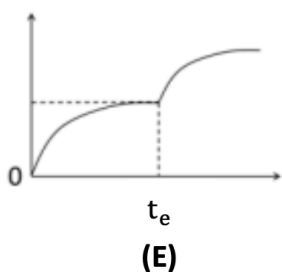
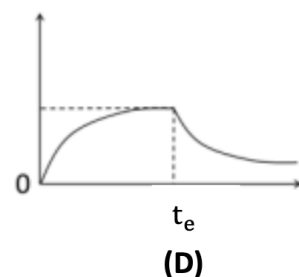
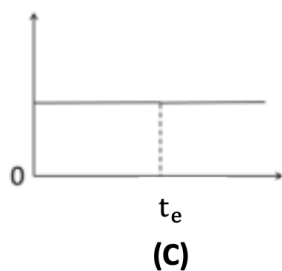
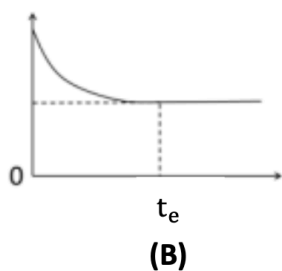
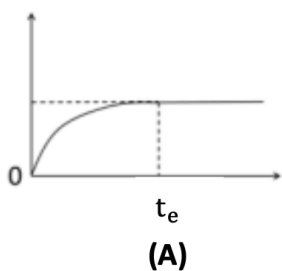
## Problem #5: (6 points)

The reaction of  $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$  is performed in a sealed vessel with a fixed volume. Initially, at  $t = 0$ , only  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are present. The system is then allowed to reach equilibrium, and then a “stress” is applied to the system at  $t = t_e$ .

Please select the plot from the choices below (A-H) that best represents the plot of the partial pressure of  $\text{CO}_2$  and the plot of the concentration of  $\text{H}_2\text{CO}_3$  with respect to time. **Write the correct corresponding letter on the lines provided.**

Note: each plot may be chosen more than once.

You may assume that each stress is applied separately and that all other conditions remain the same.



a) Stress:  $\text{CO}_2$  is added:

$P_{\text{CO}_2}$  vs time:           **G**          

$[\text{H}_2\text{CO}_3]$  vs time:           **E**          

b) Stress:  $\text{H}_2\text{O}$  is added (assume no volume change).

$P_{\text{CO}_2}$  vs time:           **B**          

$[\text{H}_2\text{CO}_3]$  vs time:           **A**

## INDIV.

c) Stress:  $N_2$  is added and the total pressure is increase

$P_{CO_2}$  vs time:     **B**    

$[H_2CO_3]$  vs time:     **A**    

d) Stress:  $H_2CO_3$  is added (assume no volume change).

$P_{CO_2}$  vs time:     **F**    

$[H_2CO_3]$  vs time:     **H**    

Note: This problem is graded very particularly to ensure that students do not earn points through guessing

(+1 point) for correctly labeling both plots in part a)

(+1 point) for correctly labeling both plots in part b)

(+1 point) for correctly labeling both plots in part c)

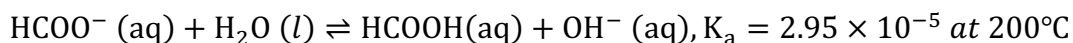
(+1 point) for correctly labeling both plots in part d)

(+2 points) if parts a), b), c), and d) are all correct. If they even miss one plot these points are not to be awarded.

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### **Problem #6: (20 points)**

The formate ion ( $\text{HCOO}^-$ ) is the conjugate base of formic acid ( $\text{HCOOH}$ ).  $K_a(\text{HCOOH}) = 2.95 \times 10^{-5}$  at  $200^\circ\text{C}$ . A  $0.50\text{ M}$  aqueous solution of  $\text{HCOO}^-$  is allowed to equilibrate at  $200^\circ\text{C}$  resulting in the following equilibrium concentrations:



$$\begin{aligned} [\text{HCOO}^-]_{eq} &= 0.4997\text{ M} & [\text{H}_2\text{O}]_{eq} &= \text{excess} & [\text{HCOOH}]_{eq} &= 2.88 \times 10^{-4}\text{ M} \\ & & [\text{OH}^-]_{eq} &= 2.88 \times 10^{-4}\text{ M} & & \end{aligned}$$

- a) Use the data above to determine the autoionization constant  $K_w$  for pure water at  $200^\circ\text{C}$ . Circle your final answer while showing all supporting work. (3 points).

$$\begin{aligned} K_w &= K_a K_b \therefore K_b = \frac{[\text{OH}^-][\text{HCOOH}]}{[\text{HCOO}^-]} = \frac{[2.88 \times 10^{-4}\text{ M}][2.88 \times 10^{-4}\text{ M}]}{[0.4997]} \\ &= 1.66 \times 10^{-7} \end{aligned}$$

$$K_w(200^\circ\text{C}) = (2.95 \times 10^{-5})(1.66 \times 10^{-7})$$

$$\mathbf{K_w(200^\circ\text{C}) = 4.9 \times 10^{-12}}$$

(+2 points) for correct  $K_b$  calculation.

(+1 point) for correct  $K_w$  calculation.

- b) Determine the **pH** and the **pOH** of a  $0.10\text{ M}$  aqueous solution of  $\text{HCOOH}$  at  $200^\circ\text{C}$ . **Use the method of successive approximations and show all supporting work. Circle your final answers. (10 points)**

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I	0.1 M	excess	0	0
C	-x	excess	+x	+x
E	0.1 M -x	excess	x	x

$$K_a = 2.95 \times 10^{-5} = x^2 / (1 \times 10^{-1} - x) \text{ where } x = [\text{H}_3\text{O}^+]$$

Using method of successive approximations:

$$x_1 = \sqrt{(2.95 \times 10^{-5} \times 0.1)} = 1.72 \times 10^{-3}$$

$$x_2 = \sqrt{(2.95 \times 10^{-5} \times (0.1 - 1.72 \times 10^{-3}))} = 1.70 \times 10^{-3}$$

$$x_3 = \sqrt{(2.95 \times 10^{-5} \times (0.1 - 1.70 \times 10^{-3}))} = 1.70 \times 10^{-3}$$

$$[\text{H}_3\text{O}^+] = 1.70 \times 10^{-3}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(1.70 \times 10^{-3}) = 2.77$$

$$\text{pOH} = \text{p}K_w - \text{pH} = -\log_{10}(4.9 \times 10^{-12}) - 2.77 = 8.54$$

(+3 points) for correct ICE table.

(+1 point) for correct  $K_a$  expression.

(+3 points) for using the method of successive approximations to determine the equilibrium hydronium concentration.

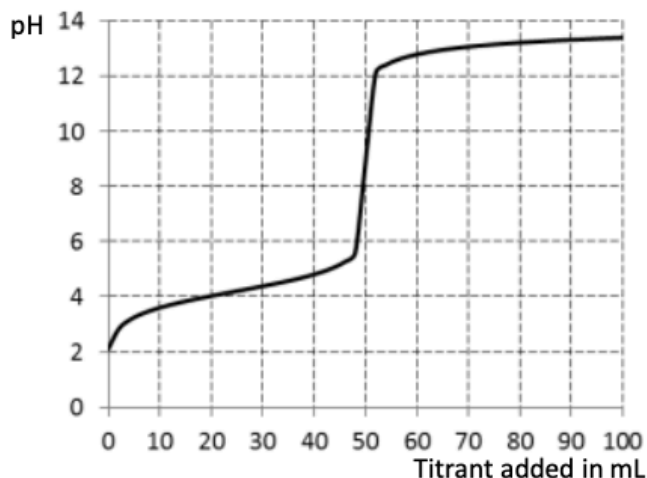
(+1 points) for calculating the correct pH of the solution.

(+2 points) for calculating the correct pOH of the solution using the autoionization of water calculated in part a) (Note this number does not have to be correct, it just needs to be consistent with part a)).



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- c) In the same lab, you find a graph of a titration curve for one of the analyte/titrant pairs (A-D) in the table below. The initial volume of monoprotic acid analyte (an aqueous solution) is 50 ml. The titrant is NaOH (aq). Using the information given below, circle the correct answer to each of the following questions. (7 points)



Pair	Analyte	[Analyte]	$K_a(\text{Analyte})$	[NaOH]
A	$\text{C}_6\text{H}_5\text{COOH}$	1 M	$6.50 \times 10^{-5}$	1 M
B	$(\text{CH}_3\text{CO})_3\text{CH}$	1 M	$1.26 \times 10^{-6}$	0.1 M
C	HCl	0.01 M	N/A	0.01 M
D	HCl	0.01 M	N/A	0.1 M

- i) **TRUE** **FALSE** The volume of titrant required to reach the equivalence point is the same for pair A and pair C.
- ii) **TRUE** **FALSE** Continual addition of titrant for pair C will ultimately lead to a pH > 13.
- iii) **TRUE** **FALSE** For the given curve, addition of titrant to the half equivalence point gives a pH equal to the  $pK_a$  of  $(\text{CH}_3\text{CO})_3\text{CH}$ .
- iv) **TRUE** **FALSE** The pH at the equivalence point for mixtures C and D is the same.
- v) **TRUE** **FALSE** The pH at the half equivalence point for mixtures C and D is the same.
- vi) The Analyte-Titrant Pair corresponding to the graph is....(circle one) **A** B C D.

**Note:** This problem is graded very particularly to ensure that students do not earn points through guessing.

For **each correctly answered** part, a student will be awarded **+1 point**. However, for each **incorrectly answer** part, a student will be deducted **-1 point**. If a student left it blank, no points will be deducted. Note that the lowest a student can earn on this question is **0 points**. No student should ever be awarded negative points overall. If student gets **all 6 parts** correct, and extra **+1 point** will be awarded resulting in a total of **7 points**. If a student get even one incorrect or leaves even one blank, then this extra point will not be awarded.

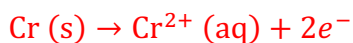
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### **Problem #7: (10 points)**

A student devises an electrochemical cell with the following cell notation:



- a) Write the half-cell reactions and the overall reaction for the galvanic cell. (2 points)



+1 point for **both** correct half reactions

+1 point for correct overall reaction

- b) Calculate  $\Delta\varepsilon$  for this galvanic cell. Show all work and **circle your final answer.** (4 points)

$$\Delta\varepsilon^{\circ} = \varepsilon_{red}^{\circ} + \varepsilon_{ox}^{\circ} = -0.28 \text{ V} + 0.91 \text{ V} = 0.63 \text{ V}$$

$$\Delta\varepsilon = \Delta\varepsilon^{\circ} - \frac{0.0257}{n} \ln \frac{[\text{Cr}^{2+}]}{[\text{Co}^{2+}]} = 0.63 \text{ V} - \frac{0.0257}{2} \ln \frac{[0.02]}{[0.9]}$$

$$\Delta\varepsilon = 0.68 \text{ V}$$

+1 point for correct standard cell voltage calculation

+1 point for mentioning/using the Nernst equation

+2 point for correct final answer

- c) The student monitored the  $[\text{Cr}^{2+}]$  vs time. The resulting data is shown in the table below. Determine the current (in amps) produced by this cell during the time period shown. Note: each half-cell has a total volume of 1 L. Show all work and **circle your final answer.** (4 points)

time (s)	$[\text{Cr}^{2+}]$
0	0.02
70	0.04
140	0.06

Hint: The Faraday constant is  $F = 96,485$  Coulombs per mol of electron.

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$$\text{Current} \left( \text{Amps} = \frac{\text{C}}{\text{s}} \right) = \frac{1}{\text{time (s)}} \left( \frac{96,485 \text{ C}}{1 \text{ mol e}^-} \right) \left( \frac{2 \text{ mol e}^-}{1 \text{ mol Cr}^{2+} \text{ produced}} \right) ([\text{Cr}^{2+}] - [\text{Cr}^{2+}]_0)(1L)$$

Next, we can plug in everything to solve for the current which no matter what combination of the data we plug in, results in:

$$\text{Current} \left( \text{Amps} = \frac{\text{C}}{\text{s}} \right) = 55 \text{ Amps}$$

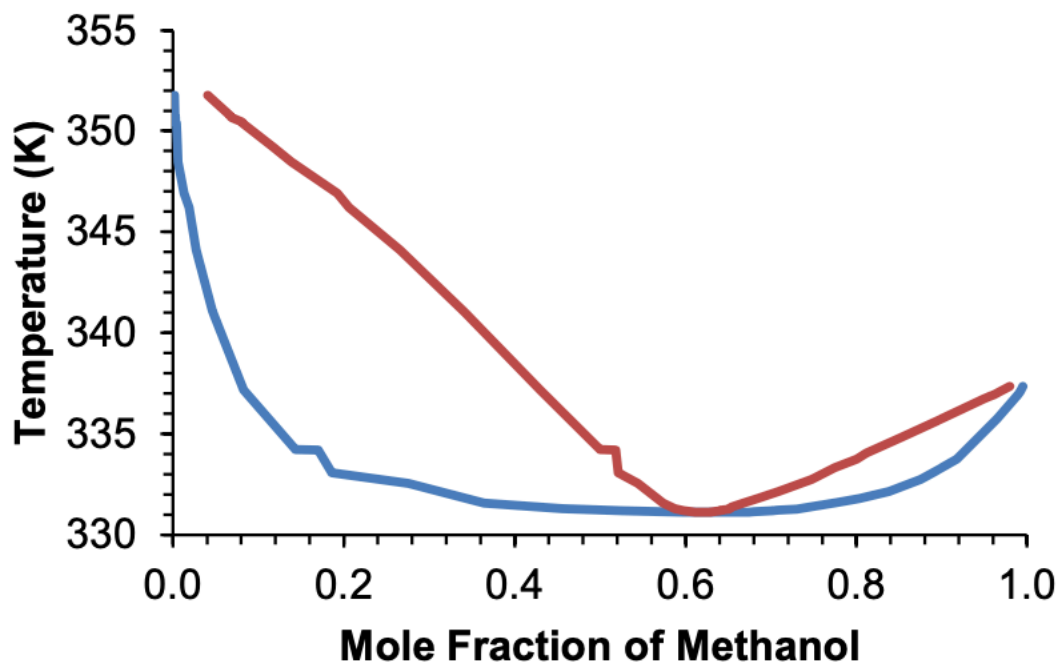
**+3 points** for correct setup of this problem

**+1 point** for correct final answer

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### **Problem #8: (4 points)**

The figure below provides information about the liquid-vapor equilibrium for a mixture of methanol and benzene.



- a) What is the name of the point at a mole fraction of about 0.6 where the vapor line (red) and liquid line (blue) overlap? (1 point)

**Azeotrope or Azeotropic point**  
**1 point all or nothing**

- b) A liquid at room temperature has a methanol fraction of 0.2. Will it be possible to produce pure benzene from this mixture by distillation? Briefly (1-2 sentences) explain your answer. (3 points)

Yes, pure benzene can be produced. By collecting liquids during a series of distillation steps, the methanol will be lost to the vapor and a liquid with 0 mole fraction of methanol i.e. pure benzene can be produced.

**+3 points if a correct answer with a satisfactory answer similar to the one above is presented.**

**No points are to be awarded if the student simply writes "yes"!**