Homework #2 - Solutions

Due: April 21, 2016 (Tue), in class

1. Determine the pH of a buffer prepared by dissolving 5×10^{-4} M NaAc and 5×10^{-4} M HAc in pure water using i) numerical calculation method and ii) graphical method (pH-pC diagram).

(25 points)

Answer)

Equilibrium constants:

$$K_w = [H^+][OH^-] = 10^{-14} \quad (1)$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = 10^{-4.75} \quad (2)$$

Mass balance:

$$C_T = 10^{-4}\,M = 2[Na^+] = [HAc] + [Ac^-] \quad (3)$$

Charge balance:

$$[Na^+] + [H^+] = [Ac^-] + [OH^-] \quad (4)$$

i) numerical calculation

Assume $[Na^+] = \frac{1}{2}C_T \gg [H^+],\ [Ac^-] \gg [OH^-]$

Then, from (4): $[Ac^-] = \frac{1}{2}C_T$

From (3): $[HAc] = \frac{1}{2}C_T$

From (2): $[H^+] = 10^{-4.75}\,M = 1.8\times10^{-5}\,M$

From (1): $[OH^-]=10^{-9.25}=5.6\times10^{-10}\,M$

check the assumption:

$\frac{1}{2}C_T=5\times10^{-4}\,M\gg[H^+]=1.8\times10^{-5}\,M$*, if we accept <5% error.*

$[Ac^-]=5\times10^{-4}\,M\gg[OH^-]=5.6\times10^{-10}\,M$

$\therefore pH=4.75$ *or* $pH=4.8$

(It is better representing the data by rounding to one decimal place (pH=4.8) because we accepted <5% error. It is expected that the exact solution is slightly greater than 4.75, but the result should not exceed 4.8. 5% error generates 0.02 log unit difference.)

*** Exact solution, not accepting the error:*

From (3): $[HAc]=C_T-[Ac^-]$

Substituting into (2): $\frac{[H^+][Ac^-]}{C_T-[Ac^-]}=K_a$

$$[Ac^-]=\frac{C_TK_a}{[H^+]+K_a}$$

Substituting into (4):

$$\frac{1}{2}C_T+[H^+]=\frac{C_TK_a}{[H^+]+K_a}+\frac{K_w}{[H^+]}$$

Rearranging the equation:

$$[H^+]^3+\left(\frac{1}{2}C_T+K_a\right)[H^+]^2-\left(\frac{1}{2}C_TK_a+K_w\right)[H^+]-K_wK_a=0$$

Solving this third-order equation gives

$[H^+]=1.68\times10^{-5}$*,* $pH=4.77$

So, the exact solution gives only 0.02 difference in the pH value.

ii) graphical method

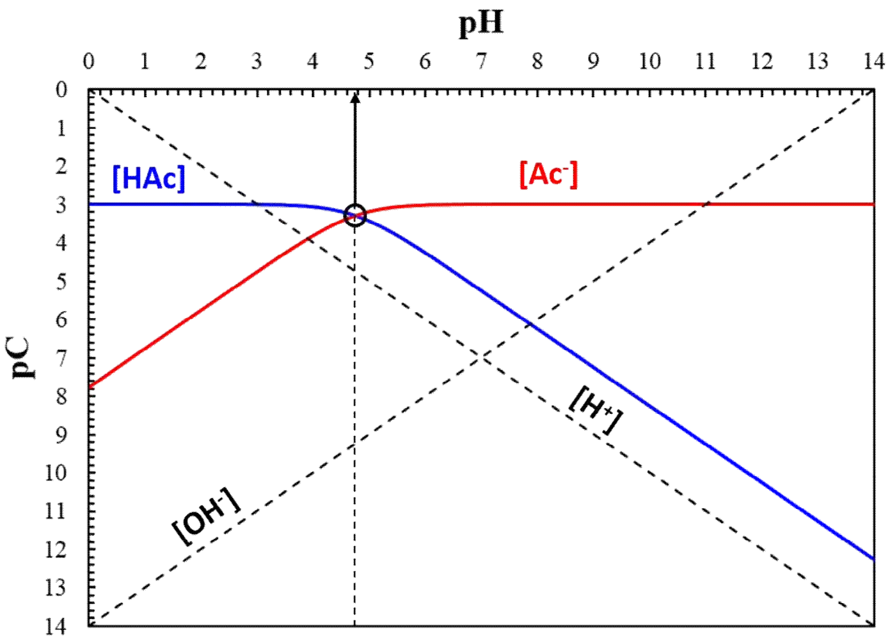
From (3) and (4):

$$\frac{1}{2}[HAc]+\frac{1}{2}[Ac^-]+[H^+]=[Ac^-]+[OH^-]$$

$$\frac{1}{2}[HAc]+[H^+]=\frac{1}{2}[Ac^-]+[OH^-]$$

or $[HAc]+2[H^+]=[Ac^-]+2[OH^-]$

Drawing the pC-pH diagram for HAc with $C_T=10^{-3}$ *M:*



From the diagram, when $[HAc]=[Ac^-]$, $[OH^-]$ *is sufficiently small, and the difference between* $[HAc]$ *and* $[H^+]$ *is approximately 1.6 log unit, so* $2[H^+]$ *is approximately 1.3 log unit smaller than* $[HAc]$ *(~5% of* $[HAc]$*). Accepting this error, we can select the point satisfying* $[HAc]=[Ac^-]$.

$\therefore pH=4.75$ *(when* $[HAc]=[Ac^-]$ *then* $pK_a=pH$*, so you don't have to read the graph), or*

$pH=4.8$*, considering error.*

2. The current atmospheric partial pressure of CO_2 is around $10^{-3.5}$ atm, and you have seen that the rainwater pH at this condition is approximately 5.6 assuming equilibrium. According to the Intergovernmental Panel on Climate Change (IPCC), the 2100 atmospheric CO_2 concentration is predicted to be 1000 ppm ($=10^{-3.0}$ atm) applying the worst case scenario. Estimate the rainwater pH in equilibrium with 1000 ppm CO_2 in the atmosphere. Use the graphical method (pH-pC diagram) for estimation.
(K_H for CO_2 = $10^{-1.5}$ M/atm)

(15 points)

Answer)

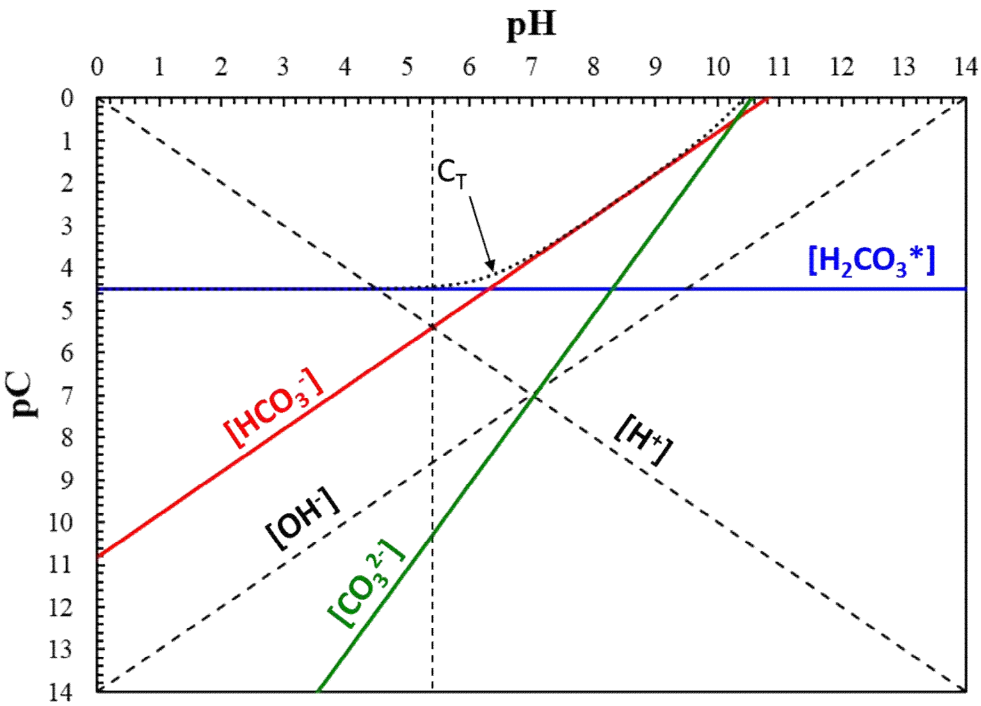
$$P_{CO_2} = 10^{-3.0}\, atm$$

$$p[H_2CO_3*] = p(K_H P_{CO_2}) = p(10^{-1.5}\, M/atm \cdot 10^{-3.0}\, atm) = 4.5$$

$$p[HCO_3^-] = p(K_H P_{CO_2}) + pK_{a1} - pH = 4.5 + 6.3 - pH = 10.8 - pH$$

$$p[CO_3^{2-}] = p(K_H P_{CO_2}) + pK_{a1} + pK_{a2} - 2pH = 4.5 + 6.3 + 10.3 - 2pH = 21.1 - 2pH$$

The pH-pC diagram is drawn as below:



Charge balance: $[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

When $[H^+] = [HCO_3^-]$, $[CO_3^{2-}]$ *and* $[OH^-]$ *are sufficiently small, so taking that point:*

pH = 5.4

* *Increase in atmospheric* CO_2 *results in acidification of waters. Ocean acidification is one of the side effect we are concerned with by* CO_2 *emission.*

3. Describe the difference in the cell wall of the Gram positive [G(+)] and Gram negative [G(-)] bacteria.

(10 points)

Answer)

G(-) bacteria have a thin peptidoglycan cell wall sandwiched between an inner cell membrane and an outer membrane containing lipopolysaccharide (LPS).

G(+) bacteria have a thick peptidoglycan layer and do not have an outer membrane.

4. Classify the following bacterium species by carbon sources, energy sources, and growth in the presence/absence of O_2.

- *Acidithiobacillus ferrooxidans*
- *Escherichia coli*
- *Nitrobacter vulgaris*

(15 points)

Answer)

Acidithiobacillus ferrooxidans: uses CO_2 *as carbon source, obtains energy using* Fe^{2+} *or inorganic sulfur (*S^{2-}*,* HS^-*,* S^0*, etc.) under aerobic conditions, but also found to be grown under anaerobic conditions obtaining energy using* H_2 *or inorganic sulfur, using* Fe^{3+} *as an electron acceptor.*

→ autotroph, chemotroph, facultative aerobe

Escherichia coli: uses organic compounds as carbon source, obtains energy using organic compound decomposition, grown anaerobically by fermentation but can switch into aerobic respiration

→ heterotroph, chemotroph, faculatative anaerobe

Nitrobacter vulgaris: uses inorganic carbon as carbon source, obtains energy by converting nitrite (NO_2^-) into nitrate (NO_3^-), uses O_2 as an only electron acceptor

→ autotroph, chemotroph, obligate aerobe

5. Mathematically derive the steady state solutions (in the form of $C = f(C_0, k, \tau)$) for PFR and CSTR when a substance is degraded in the reactors by a chemical reaction described by 2nd order reaction rate. For an influent concentration of 10 mg/L and a second order reaction rate constant of 3 L/mg/d, compare the effluent concentrations of the steady state PFR and CSTR at a hydraulic retention time (HRT) range of 0 to 1 day.

   Note: compare the effluent concentrations of PFR and CSTR by plotting the concentrations against HRT. In other words, x-axis: HRT, y-axis: effluent concentrations of PFR and CSTR.

(25 points)

Answer)

i) PFR, 2nd order reaction

Taking a thin plate with a thickness of Δx at a distance of x from the inlet as CV (same as the diagram drawn in the lecture note):

mass balance equation: $\Delta V \frac{\partial C}{\partial t} = QC - Q(C + \Delta C) - kC^2 \Delta V = 0$ *(steady state)*

$$0 = -v \cdot \frac{\Delta C}{\Delta x} - kC^2$$

$$\Delta x \rightarrow 0: \ 0 = -v \cdot \frac{dC}{dx} - kC^2$$

$$\int_{C_0}^{C_e} \frac{dC}{C^2} = -\frac{k}{v}\int_0^L dx$$

$$\frac{1}{C_0} - \frac{1}{C} = -\frac{k \cdot L}{v} = -k \cdot \tau$$

$$C = \frac{1}{1/C_0 + k\tau}$$

ii) CSTR, 2^{nd} order reaction

Taking the whole reactor as CV:

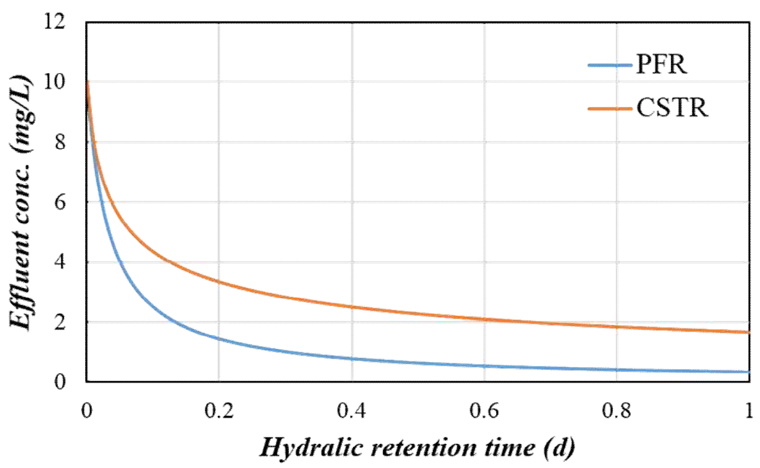
mass balance equation: $V\frac{dC}{dt} = QC_0 - QC - kC^2V = 0$ *(steady state)*

$$k\tau C^2 + C - C_0 = 0$$

$$C = \frac{-1 + \sqrt{1 + 4k\tau C_0}}{2k\tau}$$

iii) Comparing PFR and CSTR

Applying the solutions and the conditions given, following graph can be obtained.



PFR outperforms CSTR for 2nd order reaction, which is the same conclusion as what we saw in the class for 1st order reaction.

For 1st order reaction, we saw that the substance removal efficiency ($(1 - C_e/C_0) \times 100(\%)$ *is not a function of* C_0, *but for 2nd order reaction, the removal efficiency is different for different* C_0. *The greater the* C_0, *the greater the removal efficiency we will get for any reactor types.*

6. Read the following article discussing the ecology of *Vibrio cholerae* and briefly summarize the article. (in less than 0.5 page, strictly monitored for plagiarism).

   Cottingham, K.L.; Chiavelli, D.A.; Taylor R. K. Environmental microbe and human pathogen: the ecology and microbiology of *Vibrio cholerae*. *Frontiers in Ecology and the Environment*. Vol. 1, No. 2, 80-86, 2003.

   link:

   http://onlinelibrary.wiley.com/doi/10.1890/1540-9295(2003)001%5B0080:EMAHPT%5D2.0.CO;2/abstract

(10 points)