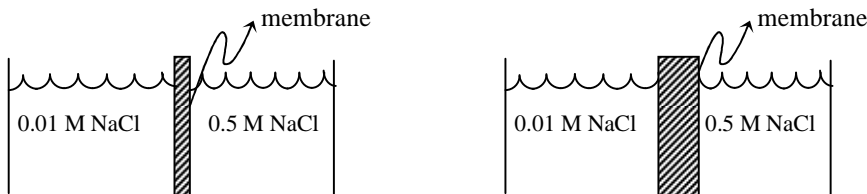


Constants: $R = 8.314$ or 0.08206 you know the units.

$1 \text{ atm} = 1.0135 \times 10^5 \text{ Pa}$

Part 1: Answer 4 of the following 5 questions. If you answer more than 4 cross out the one you wish not to be graded. Otherwise only the first 4 will be graded. 9 points each.

1. Two well-mixed solutions are separated by a membrane of thickness δ . The membrane is permeable to NaCl. Two separate experiments are conducted with membranes of different thicknesses, but with NaCl solutions at the same concentrations, as shown below. Assume the diffusion coefficient of NaCl in both membranes is the same. In which case is the diffusive flux larger and why? Relate your answer explicitly to terms in Fick's First Law of diffusion.



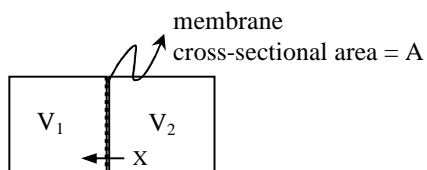
2. Organisms require iron for survival. Reduced iron in the form of Fe^{2+} is readily available for acquisition by living systems. However, Fe^{2+} is rapidly oxidized by oxygen in air. The oxidation of Fe^{2+} follows the rate law:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k_{\text{eff}} [\text{Fe}^{2+}]^2$$

where $k_{\text{eff}} = 7.30 \times 10^{-4} \text{ mol}^{-1} \text{ L hr}^{-1}$. Assume an initial concentration of 0.100 M Fe^{2+} . How long would it take for the concentration of Fe^{2+} to drop to 0.0100 M ?

CH341 Test 1

3. Assume two well-mixed compartments with volumes V_1 and V_2 are separated by a membrane. Substance X diffuses through the membrane, which has cross-sectional area A :



Prove for diffusion of substance X across a membrane that the rate of concentration change in compartment 1 is given by:

$$\frac{d[X]}{dt} = \frac{dc_X}{dt} = J_m (A/V_1)$$

4. From a thermodynamic perspective, are spontaneous processes always irreversible? Explain. (No credit for just a yes or no answer).

CH341 Test 1

5. What role do gradients play in flux-force relationships?

Part 2: Answer 4 of the following 6 questions. If you answer more than 4 cross out the ones you wish not to be graded. Otherwise only the first 4 will be graded. 16 points each.

6. For the reaction $O + NO + M \rightarrow NO_2 + M$, k at 300.0 K is $6.00 \times 10^9 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$, and k at 1000.0 K is $3.00 \times 10^{10} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. Calculate the activation energy.

7. The limiting molar conductivities of KCl, KNO_3 , and $AgNO_3$ are $14.99 \text{ mS m}^2 \text{ mol}^{-1}$, $14.50 \text{ mS m}^2 \text{ mol}^{-1}$, and $13.34 \text{ mS m}^2 \text{ mol}^{-1}$, respectively. What is the limiting molar conductivity of AgCl?

CH341 Test 1

8. A 2.32×10^{-5} M solution of a substance is placed outdoors in a 10.0 cm path length cell with an irradiated cross sectional area of 1.00×10^{-2} m². The molar absorption coefficient of the solution at 500 nm is $3410. \text{ M}^{-1} \text{ cm}^{-1}$. Assume that the solar flux at this wavelength is $4.96 \text{ mol m}^{-2} \text{ day}^{-1}$ (in other words, moles of photons per meter squared per day).¹ Calculate the number of moles of photons absorbed by the solution in one day.

9. Calculate the uncertainty in $\ln(k_2/k_1)$ if $k_2 = 4.65 \times 10^7 \pm 0.23 \times 10^7 \text{ s}^{-1}$ and $k_1 = 1.35 \times 10^7 \pm 0.08 \times 10^7 \text{ s}^{-1}$.

CH341 Test 1

10. Consider the following proposed mechanism for the decomposition of ozone. M is an unreactive gas molecule that collides with the ozone to break the ozone apart:

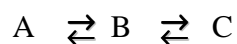


Assume $k'_2 \gg k_2$. Show that the rate law that corresponds to this mechanism is:

$$\frac{d[\text{O}_2]}{dt} = \frac{2 k'_2 k_2 [\text{O}_3]^2 [\text{M}]}{k_{-2} [\text{O}_2] [\text{M}] + k'_2 [\text{O}_3]}$$

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11. Consider the bidirectional reaction:



The initial rate law for the reaction, starting with A only, is experimentally determined to be:

$$\frac{d[A]}{dt} = -k_{\text{obs},f} [A]_0$$

If the reverse reaction is run starting with C only, the initial rate law is determined to be:

$$\frac{d[C]}{dt} = -k_{\text{obs},r} [C]_0$$

Why isn't the equilibrium constant for the overall reaction given by the ratio of the forward to the reverse rate constants, $k_{\text{obs},f}/k_{\text{obs},r}$?

Literature Cited:

1. This solar flux is the flux averaged over a day in summer at 40°N latitude in a 10 nm band centered on 500 nm:
A. Leifer, *The Kinetics of Environmental Aquatic Photochemistry*, American Chemical Society, Washington, D.C., 1988. p. 261