

1. It is often said the the primary charge separation step of photosynthesis is the most efficient electron transfer reaction known.
- a. Assuming that the dominant processes are electron transfer (ET) and non-radiative (NR) return to the ground state calculate the quantum yield for the primary charge separation step to three significant figures. $k_{ET} = 3.3 \times 10^{11} \text{ s}^{-1}$, $k_{NR} = 3.3 \times 10^9 \text{ s}^{-1}$

$$\Phi_{ET} = \underline{\hspace{2cm}}$$

What is the time constant for the ET process? $\tau_{ET} = \underline{\hspace{2cm}}$ seconds

- b. A mutant reaction center has a measured time constant of $\tau_{ET} = 30$ picoseconds and a quantum yield of $\Phi_{ET} = 0.5$. Calculate the ET and NR rate constants.

$$k_{ET} = \underline{\hspace{2cm}} \text{ s}^{-1}, k_{NR} = \underline{\hspace{2cm}} \text{ s}^{-1}$$

2. Consider DNA hybridization of the following palindromic sequence in solution:

ATATGGCCATAT'
TATACCGGTATA

Assuming the initial concentration is 10^{-6} M and the rate constant for hybridization is $k_{\text{hybrid}} = 10^6 \text{ s}^{-1}$ calculate the half-time for hybridization.

$$\tau_{1/2} = \underline{\hspace{2cm}}$$

How does the half-life change if the concentration is decreased to 10^{-8} M ?

$$\tau_{1/2} = \underline{\hspace{2cm}}$$

3. Calculate a.) the activation energy and prefactor for the Arrhenius rate constant for the unfolding of the protein "foldase" given the data in the table. b.) Using the fraction folded determine the folding rate constant at each temperature. c.) Finally, use the data to estimate ΔH° and ΔS° for the unfolding reaction.

T (K)	k_{obs} (unfolding)	Fraction folded
280	1450	0.84
290	2420	0.70
300	3936	0.50
310	6180	0.31
320	9470	0.18

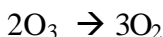
a. A (unfolding) = _____ E_a (unfolding) = _____

b.

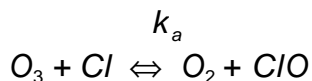
T (K)	k_{obs} (folding)
280	
290	
300	
310	
320	

c. ΔH° (unfolding) = _____ ΔS° (unfolding) = _____

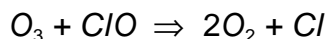
4. It is known that chlorine derived from chlorofluorocarbons (CFCs) used as refrigerants can make their way into the stratosphere and catalytically degrade ozone. As a consequence the rate law for the degradation of ozone



is first order in chlorine. Based on the scheme below, use the steady state approximation to explain the find the rate law for the above reaction in terms of the elementary rate



$$k_{a'}$$

$$k_b$$


constants, k_a , $k_{a'}$ and k_b using the assumption $k_b[\text{O}_3] \gg k_{a'}[\text{O}_2]$.

Given the above assumption the rate of disappearance of ozone is:

$$\begin{aligned} \frac{d[\text{O}_3]}{dt} &= -k_a[\text{O}_3][\text{Cl}] + k_{a'}[\text{O}_2][\text{ClO}] - k_b[\text{O}_3][\text{ClO}] \\ &\approx -k_a[\text{O}_3][\text{Cl}] - k_b[\text{O}_3][\text{ClO}] \end{aligned}$$

Use the steady state approximation to simplify this expression.