

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. $k_{ET} = 3.3 \times 10^{11} \text{ s}^{-1}$, $k_{NR} = 3.3 \times 10^9 \text{ s}^{-1}$

Solution:

$$\Phi_{ET} = \frac{k_{ET}}{k_{ET} + k_{NR}} = \frac{3.3 \times 10^{11}}{3.3 \times 10^{11} + 3.3 \times 10^9} = 0.99$$

$$\Phi_{ET} = \underline{0.99}$$

What is the time constant for the ET process? $\tau_{ET} = 1/k_{ET} = 1/3.3 \times 10^{11} \text{ s}^{-1}$

$$\tau_{ET} = \underline{3 \times 10^{-11} \text{ seconds or 3 picoseconds}}$$

- 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.

Solution:

$$k_{ET} = 1/\tau_{ET} = 1/30 \times 10^{-12} \text{ s} = 3.3 \times 10^{10} \text{ s}^{-1}.$$

$$\Phi_{ET} = \frac{k_{ET}}{k_{ET} + k_{NR}}, k_{NR} = k_{ET} \left(\frac{1}{\Phi_{ET}} - 1 \right) = k_{ET} \left(\frac{1}{0.5} - 1 \right) = k_{ET}$$

$$k_{ET} = \underline{3.3 \times 10^{10}} \text{ s}^{-1}, k_{NR} = \underline{3.3 \times 10^{10}} \text{ s}^{-1}$$

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 $k_{\text{hybrid}} = 10^6 \text{ M}^{-1}\text{s}^{-1}$ calculate the half-time for hybridization.

Solution:

$$\tau_{1/2} = 1/k_{\text{hybrid}} [\text{ssDNA}] = 1/(10^6 \text{ M}^{-1}\text{s}^{-1})(10^{-6} \text{ M}) = 1 \text{ second}$$

$$\tau_{1/2} = \underline{1 \text{ second}}$$

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

$$\tau_{1/2} = 1/k_{\text{hybrid}} [\text{ssDNA}] = 1/(10^6 \text{ M}^{-1}\text{s}^{-1})(10^{-8} \text{ M}) = 100 \text{ seconds}$$

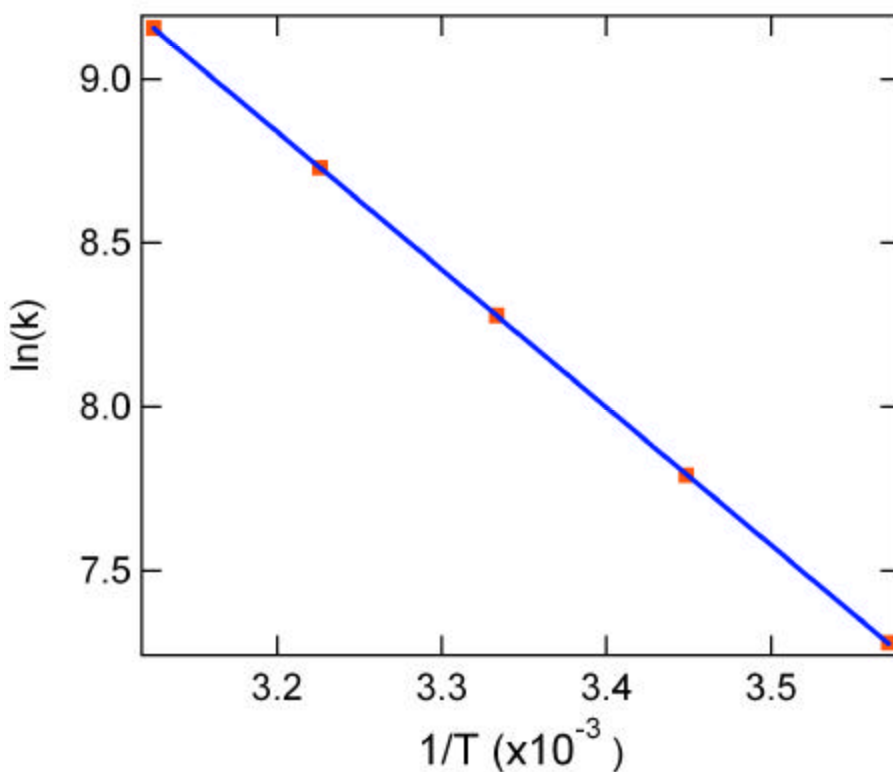
$$\tau_{1/2} = \underline{100 \text{ seconds}}$$

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 determine 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

Solution:

- a. We determine the activation energy and prefactor of the Arrhenius rate constant ($k = Ae^{-E_a/RT}$) by plotting $\ln(k)$ vs $1/T$. On such a plot the data should be approximately linear with slope $-E_a/R$ and intercept $\ln(A)$.



The slope is 4205.0 and the intercept is 22.3.
 These values give $E_a = 34.8$ kJ/mol and $A = 4.8 \times 10^9$.

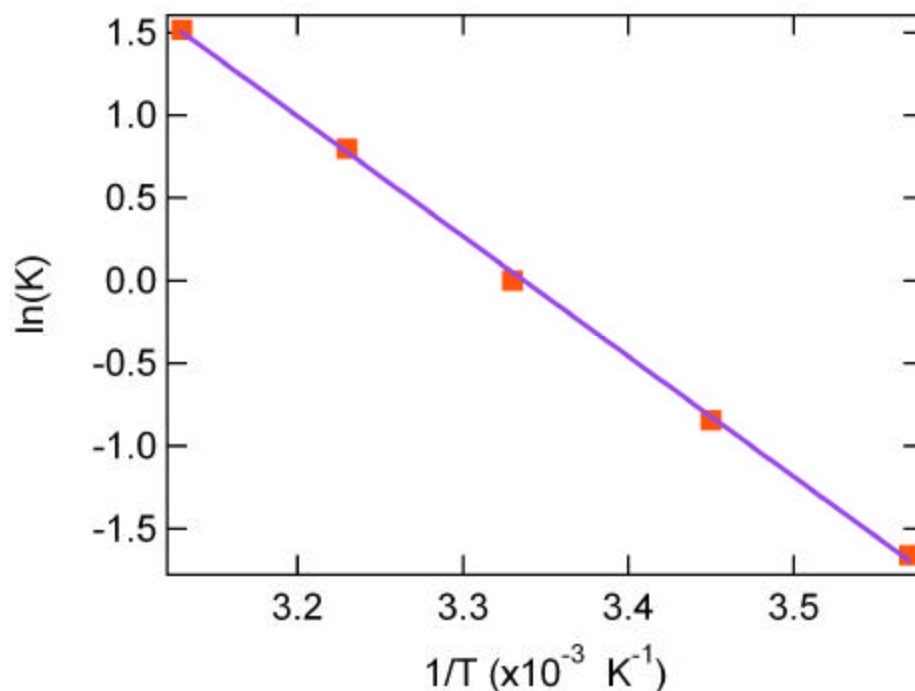
- b. The equilibrium constant for the unfolding process $f \leftrightarrow u$ is $K_u = [u]/[f] = 1 - ff/ff$ where ff is the fraction folded. Once we have determined K_u we can determine the folding rate constant from microscopic reversibility ($K_u = k_u/k_f$ or $k_f = k_u/K_u$).

T (K)	k_{obs} (unfolding)	Fraction folded	K_u	k_f
280	1450	0.84	0.19	7630
290	2420	0.70	0.43	5630
300	3936	0.50	1.00	3936
310	6180	0.31	2.22	2780
320	9470	0.18	4.56	2076

c. To determine the thermodynamic parameters we first use a van't Hoff plot to determine the enthalpy.

K_u	T (K)	$\ln(K_u)$	$1/T$ (K^{-1})
0.19	280	-1.661	0.00357
0.43	290	-0.843	0.00345
1.00	300	0.000	0.00333
2.22	310	0.797	0.00323
4.56	320	1.517	0.00313

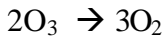
The plot looks like this:



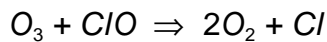
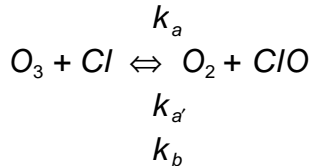
The enthalpy is obtained from the slope; Slope = -7261.1 K , $\Delta H^\circ = (\text{Slope in K})R = (7261.1)8.31 \text{ J/mol-K} = 60,339.0 \text{ J/mol}$ or approximately 60 kJ/mol .

To obtain the entropy use the fact that $\Delta G^\circ = 0$ at 300 K (because the equilibrium constant is $K = 1$ at that temperature). Using the fact that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ we can further state that $\Delta S^\circ = \Delta H^\circ/300 \text{ K} = 60,000 \text{ J/mol}/ 300 \text{ K} = 200 \text{ J/mol-K}$.

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 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 simply this expression.

Solution:

Using the steady state approximation for the intermediate chlorine oxide we find:

$$\begin{aligned} \frac{d[\text{ClO}]}{dt} &= k_a[\text{O}_3][\text{Cl}] - k_{a'}[\text{O}_2][\text{ClO}] - k_b[\text{O}_3][\text{ClO}] \\ 0 &= k_a[\text{O}_3][\text{Cl}] - k_{a'}[\text{O}_2][\text{ClO}] - k_b[\text{O}_3][\text{ClO}] \\ [\text{ClO}] &= \frac{k_a[\text{O}_3][\text{Cl}]}{k_{a'}[\text{O}_2] + k_b[\text{O}_3]} \end{aligned}$$

Substituting the expression into the rate law we have:
for the second process.

In the limit that $k_b[\text{O}_3] \gg k_{a'}[\text{O}_2]$ we find that:

$$v = k_a[\text{Cl}][\text{O}_3] + k_a[\text{Cl}][\text{O}_3]$$

Substituting into the original expression we have that:

$$\frac{d[\text{O}_3]}{dt} = -2k_a[\text{Cl}][\text{O}_3]$$