Part I

From Tinoco, Sauer, Wang and Puglisi: Chapter 7, Problems 4, 5, 15, 18, 21

Part II

Problem A
The dissociation of the double helix d(AACAA)-d(TTGTT) has an activation energy of 35 kcal·mol⁻¹ and a rate constant of $10^4$ sec⁻¹ at 35°C. Calculate the entropy of activation. How might you explain the positive sign of $\Delta S^*$?

Problem B
Given that $\text{H}_3\text{O}^+$ reacts with an amine, whose pK is 9.25, with a diffusion–limited rate constant of $4.3 \times 10^{10}$ M⁻¹·sec⁻¹, calculate the rate of reaction of $\text{H}_2\text{O}$ with $\text{R-NH}_3^+$.

Problem C
Calculate the half-time of the reaction of lac repressor with operator, both present at an initial concentration of $10^{-11}$ M. Assume that the rate constant is $5 \times 10^9$ M⁻¹·sec⁻¹, and that the reverse reaction can be neglected.

Problem D
Derive an expression for the relaxation time of the third-order reaction

$$
\text{A} + \text{B} + \text{C} \xrightleftharpoons[k_-]{k_1} \text{D}
$$

Problem E
A proposed mechanism for decomposition of ozone ($\text{O}_3$) to oxygen is

$$
\text{O}_3 \xrightarrow{k_1} \text{O}_2 + \text{O}^- \\
\text{O}^- + \text{O}_3 \xrightarrow{k_2} 2\text{O}_2
$$

Use the steady-state approximation on the concentration of $\text{O}^-$ atoms to derive the rate law for the process, assuming that the second step is rate limiting and that both steps are irreversible.