Chemistry 24b (Spring term 2004)
Problem Set #2
Due: 4/19/04, 11AM, in class

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 $\Delta S^{\neq}$?

Problem B

Given that H_3O^+ reacts with an amine, whose pK is 9.25, with a diffusion–limited rate constant of 4.3 x 10^{10} M^{-1}·sec^{-1}, calculate the rate of reaction of H_2O with R-NH3$^+$.

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 x 10^9M^{-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

$$A + B + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D$$

Problem E

A proposed mechanism for decomposition of ozone (O_3) to oxygen is

$$O_3 \xrightarrow{k_1} O_2 + O\cdot$$

$$O\cdot + O3 \xrightarrow{k_2} 2\,O_2$$

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