

Biophysical Chemistry

Week 9 Problems

To be handed in by Thursday 15th May 2014, 17:00

(either at my office 01/05 under the door or at the secretary's office 3rd floor or in exceptional circumstances as a single pdf file via e-mail)

1. A novel extracellular RNase from the mutant *Aspergillus niger* SA-13-20 was purified to homogeneity; the following data were obtained:

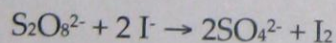
k_{cat} (s ⁻¹)	15.5	34.7	68.2	109.6	118.1	101.2	34.8	9.7
T (°C)	30	40	50	60	65	70	75	80

a) Calculate the E_a , as well as for 30 °C, the ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger for the reaction, considering: $\Delta G^\ddagger = RT [\ln(k_B T/h) - \ln k_{cat}] = \Delta H^\ddagger - T \Delta S^\ddagger$ and $\Delta H^\ddagger = E_a - RT$ where k_B = Boltzmann constant and h = Planck constant.

NB: k_{cat} in this example is considered to be like k_2 . Also, think carefully about which range to take for the calculation; data from a denatured enzyme is probably not very relevant!

b) What does the ΔS^\ddagger value tell you about the transition state?

2. The effect of the addition of sodium chloride on the rate of reaction between persulphate and iodide ions



at 25 °C was studied. When the initial concentration of potassium persulphate was 0.00015 M and that of potassium iodide was 0.0005 M, the rate constants k obtained for varying concentrations of sodium chloride were

$10^5 \times k$ (dm ³ mol ⁻¹ s ⁻¹)	1.733	1.862	2.000	2.147	2.300	2.417
[NaCl] (mM)	1.8	3.6	6.0	9.0	12.0	14.4

Show (by comparing with the theoretical equation) that the Brönsted-Bjerrum relationship ($\log_{10} k = \log_{10} k_0 + 2\alpha z_1 z_2 \sqrt{I}$) is obeyed when the activity coefficients are unity (i.e., = 1). Hint: plot a graph and calculate its slope.