

## Biophysical Chemistry

### Week 9 Problems

To be handed in by Wednesday 29<sup>th</sup> May 2013, 12:00

(either at my office 01/05 under the door or at the secretary's office 3<sup>rd</sup> floor)

1. The enzyme ER  $\alpha$ -mannosidase I catalyses the removal of a single mannose residue from the Man<sub>9</sub>GlcNAc<sub>2</sub> structure. In a recent paper, the following data were obtained:

$\ln k_{\text{cat}} \text{ (s}^{-1}\text{)}$	0	0.3	0.8	1.1	1.6	2.0	2.2	2.5
$T \text{ (}^{\circ}\text{C)}$	5	10	15	20	25	30	35	40

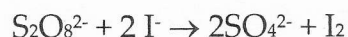
Calculate the  $E_a$ , as well as for 25  $^{\circ}\text{C}$ , the  $\Delta G^{\ddagger}$ ,  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  for the reaction in **kilocalories** (kcal; 1 calorie is 4.1819 J), considering:

$$\Delta G^{\ddagger} = RT [\ln(k_B T/h) - \ln k_{\text{cat}}] = \Delta H^{\ddagger} - T \Delta S^{\ddagger} \text{ and } \Delta H^{\ddagger} = E_a - RT$$

where  $k_B$  = Boltzmann constant and  $h$  = Planck constant.

NB:  $k_{\text{cat}}$  in this example is considered to be like  $k_2$ .

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



at 25  $^{\circ}\text{C}$  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

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

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