PROBLEM SET I

a. The Boltzmann distribution describes the effect of temperature on the distribution of energies of the solvent molecules. This distribution shows that the average kinetic energy of the solvent is higher than the most likely arrangement of molecules in solution. Explain why this is true and how this observation is related the effect of temperature on the rate of a reaction (5 sentences).

b. Discuss the difference between a velocity and a rate constant (3 sentences).

c. Why are enzymes more effective catalysts than are simple chemical catalysts (3 sentences)

d. Given that the half-life for decay of radioactive ^{32}P is 14 days, what is the rate constant for its decay (show your work, include units)?

e. A simple reaction converts reactant A to product B with a 1:1 stoichiometry

$$A \rightarrow B$$

The rate constant for this reaction, k, is measured to be 0.0027 s^{-1}. If the reaction begins with an initial concentration of 22 μmoles L^{-1}, what is the concentration of the product B that would be produced after 5 minutes? Calculate the velocity of the reaction after 5 minutes.

f. The enzyme urease catalyses the hydrolysis of urea to ammonia and carbon dioxide. At 21°C the uncatalysed reaction has an activation energy (E_A) of 125 kcal mol^{-1}, whereas in the presence of urease this is lowered to 46 kcal mol^{-1}. By what factor does urease increase the speed of the reaction?

g. The uncatalyzed breakdown of the dipeptide Ala-Gly

$$\text{Ala-Gly} \rightarrow \text{Ala} + \text{Gly}$$

was measured as a function of temperature. Table 6 presents the amount of dipeptide remaining at various times after initiating the reaction.

Table 1

Time (Hrs)	Temperature (°C) 8°	12°	16°	20°	25°	30°
0	0.045	0.045	0.045	0.045	0.045	0.045
2	0.040	0.039	0.038	0.036	0.034	0.030
4	0.037	0.035	0.032	0.029	0.025	0.020
6	0.033	0.031	0.027	0.024	0.019	0.014
8	0.030	0.027	0.023	0.019	0.015	0.009
10	0.027	0.024	0.020	0.016	0.011	0.006
12	0.025	0.021	0.017	0.013	0.008	0.004
14	0.023	0.019	0.014	0.010	0.006	0.003
16	0.021	0.017	0.012	0.008	0.005	0.002
18	0.019	0.015	0.010	0.007	0.004	0.001
20	0.017	0.013	0.009	0.005	0.003	0.001

a. Calculate the rate constant for degradation of this peptide at each temperature. Be sure to show your work and the equations you used.

b. Calculate the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction. Be sure to show your work and the equations you used.

c. Calculate the the $\Delta G^{\ddagger}$ for the reaction at 40°C