# Chemistry 2710 Spring 2002 Test 3

**Name:** _____

**Student number:** _____

**Aids allowed:** Calculator. One $8\frac{1}{2} \times 11$-inch piece of paper containing any information you need. No other printed materials (e.g. periodic tables, calculator manuals) are allowed.

**Instructions:** Answer all questions in the spaces provided. If you run out of space for a particular question, you can use the backs of the pages but make sure to clearly label any continued work.

Graphs should be drawn on the graph paper attached and clearly labeled with the corresponding question number. You can use a graphing calculator instead of hand-drawn graphs, but you should in these cases provide a clearly labeled and reasonably accurate sketch of the graph.

Clarity may be considered in evaluating your answers. Make sure to explain in detail the procedures used to obtain the answers you present.

**Useful data:**

$$h = 6.626\,068\,8 \times 10^{-34}\,\mathrm{J/Hz}$$
$$k_B = 1.380\,65 \times 10^{-23}\,\mathrm{J/K}$$
$$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$$
$$1\,\mathrm{bar} = 100\,000\,\mathrm{Pa}$$
$$1\,\mathrm{m}^3 = 1000\,\mathrm{L}$$

| Question | 1 | 2 | 3 |
|---|---|---|---|
| Mark | | | |

DO NOT OPEN THIS PAPER UNTIL INSTRUCTED TO DO SO.

1. Enzyme catalysis is not the only biochemical process which obeys the Michaelis-Menten rate law. Transport of nutrients and other chemicals across cell membranes also frequently obeys the Michaelis-Menten equation. In the simplest case, the transport mechanism can be represented by

$$\mathrm{T} + \mathrm{N}_{(\mathrm{out})} \rightleftharpoons \mathrm{C} \rightarrow \mathrm{T} + \mathrm{N}_{(\mathrm{in})},$$

where N is a nutrient and T is a transporter (a protein whose role is to facilitate the movement of N across the membrane). Note that, give or take a change in notation, this is just the Michaelis-Menten mechanism except that the "reactant" and "product" are chemically identical but located on opposite sides of cell membrane. The following data have been obtained for the rate transport of sucrose into a strain of *Bacillus*:[1]

| [sucrose] ($\mu$mol/L) | 6.3 | 17.1 | 23.3 | 34.7 | 48.3 |
|---|---|---|---|---|---|
| $v$ ($\mu$mol min$^{-1}$g$^{-1}$) | 0.151 | 0.296 | 0.389 | 0.488 | 0.540 |

(a) Do these data obey Michaelis-Menten kinetics? Discuss briefly. [6 marks]

(b) Regardless of your answer to part a, determine the best-fit values of $v_{\max}$ and $K_M$. [6 marks]

[1] C.J. Peddie et al., *Extremophiles* **4**, 291 (2000). The rates are given in units of micromoles of sucrose transported per minute per gram of cellular protein. The division by the amount of protein is meant to normalize the results to the amount of transporter present in the cells studied. The assumption is that the amount of transporter is a constant fraction of the total amount of protein in the cells.

2. Fluorinated organic compounds are currently replacing chlorofluorocarbons as refrigerants and anaesthetics. Little is known of their atmospheric chemistry and, in particular, of their reactivity toward common stratospheric species such as hydroxide radicals. Consider the elementary reaction[2]

$$\mathrm{OH_{(g)}} + \mathrm{CF_3CH_2OCHF_{2(g)}} \rightarrow \text{products}.$$

(a) The following data have been obtained for this reaction:[3]

| $T$ (K) | 292 | 298 | 347 | 402 |
|---|---|---|---|---|
| $10^{-7}k$ ($\mathrm{L\,mol^{-1}s^{-1}}$) | 1.3 | 1.0 | 2.5 | 6.6 |

Calculate the activation energy and preexponential factor. [10 marks]

Note: No graph is necessary.

[2]The products are unspecified because the reaction can produce a number of different products depending on where the OH radical attacks, the energies of reactant and product, and so on. In other words, this reaction really stands for a whole family of elementary reactions. However, for the purposes of the calculations performed in this question, this can be treated as a simple elementary reaction.

[3]S.D. Beach et al., *Phys. Chem. Chem. Phys.* **3**, 3064 (2001).

(b) Calculate the entropy of activation at 298 K. Discuss briefly what the value calculated tells you about the transition state of this reaction. [10 marks]

3. Show that the following mechanism is kinetically indistinguishable from (leads to the same rate law as) the ordinary Michaelis-Menten mechanism:

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C}_1 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}_2 \overset{k_3}{\rightarrow} \mathrm{E} + \mathrm{P}.$$

Provide equations for $K_M$ and $v_{\max}$ appropriate to this mechanism. [10 marks]