Chemistry 2710 Spring 2004 Test 2

Total marks: 44

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 booklets provided.

Clarity may be considered in evaluating your answers. Make sure to explain your reasoning (in a few words) for any mathematical derivation or calculation presented.

1. The simplest mechanism to which the SSA can be applied is

   $$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}.$$

   The following is a sensible scaling for the variables in this mechanism:

   $$\begin{aligned} a &= [\mathrm{A}]/[\mathrm{A}]_0 \\ b &= \frac{k_2[\mathrm{B}]}{k_1[\mathrm{A}]_0} \\ \tau &= k_1 t \end{aligned}$$

   Assuming this scaling, derive conditions for the validity of the steady-state approximation. [10 marks]

   Hint: You really only have to work with the rate equation for [B] since I've given you the scaling.

2. The following is part of the mechanism by which the enzyme rubisco (E) converts ribulose 1,5-bisphosphate (R) and carbon dioxide to 3-phosphoglycerate (P):

   $$\mathrm{E} + \mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C_1} \qquad\qquad \mathrm{C_2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{C_3} + \mathrm{P}$$

   $$\mathrm{C_1} + \mathrm{CO_2} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C_2} \qquad\qquad \mathrm{C_3} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{E} + \mathrm{P}$$

   (a) Determine the overall reaction. [3 marks]

   (b) Obtain an expression for the equilibrium constant in terms of the rate constants. [7 marks]

   (c) The rate constants for these steps have been estimated from experimental data and are given in table 1. The equilibrium constant has also been measured. Its value is 2.979×10^5. Are the rate constant estimates consistent with the equilibrium constant? [4 marks]

Constant	Value		Constant	Value	
k_1	1×10^5	$\mathrm{L\,mol^{-1}s^{-1}}$	k_3	7.5	$\mathrm{s^{-1}}$
k_{-1}	0.5	$\mathrm{s^{-1}}$	k_{-3}	5×10^3	$\mathrm{L\,mol^{-1}s^{-1}}$
k_2	5×10^5	$\mathrm{L\,mol^{-1}s^{-1}}$	k_4	7.5	$\mathrm{s^{-1}}$
k_{-2}	0.15	$\mathrm{s^{-1}}$	k_{-4}	5×10^3	$\mathrm{L\,mol^{-1}s^{-1}}$

Table 1: Rate constants for the reaction catalyzed by rubisco. From A. Laisk, H. Eichelmann, V. Oja, A. Eatherall and D. A. Walker, Proc. R. Soc. London, Ser. B **237**, 389 (1989).

3. Many reactions have steps which occur exclusively on the surface of the container in which they are carried out. In these cases, the rate of reaction can depend on the surface area of the vessel. Data from these reactions can be very hard to reproduce, at least until you realize what the problem is and start taking the surface area of the container into account. For example, the following scheme has been proposed for the reaction of nitrogen dioxide with water:[1]

$$\mathrm{2NO_{2(g)}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_{4(g)}}$$

$$\mathrm{N_2O_{4(g)}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{N_2O_{4(surface)}}$$

$$\mathrm{N_2O_{4(surface)}} \xrightarrow{k_3} \mathrm{ONONO_{2(surface)}}$$

$$\mathrm{ONONO_{2(surface)}} + \mathrm{NO_{2(g)}} \xrightarrow{k_4} \mathrm{N_2O_{4(surface)}} + \mathrm{NO_{2(g)}}$$

$$\mathrm{ONONO_{2(surface)}} + \mathrm{H_2O_{(surface)}} \xrightarrow{k_5} \mathrm{HONO_{(g)}} + \mathrm{HNO_{3(g)}}$$

The law of mass action applies to species adsorbed onto surfaces, except that the "concentration" for such a species is in fact the amount per unit area (sometimes called the surface coverage and measured in, e.g., $\mathrm{mol/m^2}$) rather than an amount per unit volume. The rate constants k_2 and k_4, which both involve a gaseous species reaching the surface, are both proportional to the area of the container because the rate of collisions between gas-phase molecules and the surface is proportional to the area.

Assume that reactions 1 and 2 rapidly reach equilibrium and that the intermediate $\mathrm{ONONO_2}$ reaches a steady state on the surface. Derive a rate law for this mechanism. Discuss how the overall rate of reaction would behave in containers of different areas, holding all other experimental conditions constant. [20 marks]

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[1] B. J. Finlayson-Pitts, L. M. Wingen, A. L. Sumner, D. Syomin and K. A. Ramazan, Phys. Chem. Chem. Phys. **5**, 223 (2003).