CML522 2015–16 **Minor 1** Feb. 12, 2016 Time: 1 hr.

Information for questions 1– 3.

In a recent paper (Int. J. Chem. Kinet. **47**, 773 (2015)) it is claimed that if the reaction A $\xrightarrow{k_a}$ B $\xrightarrow{k_b}$ P is monitored by absorbance measurements, the absorbance signal is given by

$$\text{Abs} = \frac{\epsilon_\text{A}(k_\text{a} - k_\text{b}) - \epsilon_\text{B}k_\text{a} + \epsilon_\text{P}k_\text{b}}{k_\text{a} - k_\text{b}} c_0 \text{e}^{-k_\text{a}t} + \frac{(\epsilon_\text{B} - \epsilon_\text{P})k_\text{a}}{k_\text{a} - k_\text{b}} c_0 \text{e}^{-k_\text{b}t} + \epsilon_\text{P} c_0.$$

Here ϵ_A, ϵ_B, and ϵ_P are the molar absorptivities of A, B, and P at the detection wavelength and c_0 is the initial concentration of A. The concentrations of B and P are zero initially.

1. Verify that the expression for the absorbance is correct. [10]
2. What happens to the absorbance expression when $\epsilon_\text{B} = \epsilon_\text{P}$? Is there any condition under which a similar simplification is achieved? [5]
3. If the conditions given in 2 is satisfied in an experimental system, how would it affect your results or conclusions? [5]

Sketch the fraction present of each species versus the time elapsed for the following two cases:

4. A in equilibrium with B and C simultaneously with first-order rate constants k_1, k_{-1} and k_2, k_{-2}, respectively, and $k_1 = 1.0 \times 10^{-2}$, $k_{-1} = 1.0 \times 10^{-4}$, $k_2 = 1.0 \times 10^{-3}$, and $k_{-2} = 1.0 \times 10^{-6}$ (with appropriate units). [5]
5. A decaying to B and B decaying to C with first-order rate constants of k_1 and k_2, respectively, and $k_2/k_1 = 20$ ($[\text{A}]_0 \neq 0$, $[\text{B}]_0$ and $[\text{C}]_0 = 0$). [5]

Information for questions 6– 9.

The mechanism for the binding of ethidium (a drug) to DNA was reported by Meyer-Almes and Porschke in Biochemistry **32**, 4246 (1993). Amongst the techniques employed by them were T-jump experiments. They claim that the reciprocal of the relaxation time constant measured over a range of DNA concentrations in the T-jump experiments showed a linear variation with the concentration when the model employed was

$$\text{ethidium} + \text{DNA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex}$$

6. Derive an expression for the relaxation time in a T-jump experiment for their model. [10]
7. Under what condition is their claim (linear variation of relaxation time with DNA concentration) valid? [5]
8. How could you obtain the relevant rate constants from this linear variation of relaxation time with DNA concentration? [5]