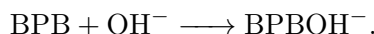


CYL565 2014-15 Homework # 1

January 16, 2015

Use a computer program wherever possible. Indicate which program you used.

1. The bleaching of bromophenol blue (BPB) by OH^- can be followed by measuring the absorbance at a particular wavelength. Note that $A = \epsilon lc$, where ϵ is the molar absorptivity; l is the length of the cell; c is the concentration of the absorbing species. The reaction is



The product does not absorb at the wavelength used.

- (a) Express the rate of reaction per unit volume in terms of the change of absorbance with time, dA/dt .
 - (b) If A_0 is the absorbance of the solution at $t = 0$, derive the relation between A and t . What quantity should be plotted against time to determine the rate constant? Assume that the reaction is first order with respect to each of the reactants and that they are mixed in the stoichiometric ratio.
2. The concentration of *t*-butyl bromide as a function of time during its conversion to *t*-butyl alcohol in 90% acetone and 10% water is given below.

t (min)	0	9	18	27	40	54	72	105
$(\text{CH}_3)_3\text{CBr}$ (mol/L)	0.1056	0.0961	0.0856	0.0767	0.0645	0.0536	0.0432	0.0270

- (a) What is the order of the reaction? Describe how you determined it.
 - (b) What is the rate constant of the reaction?
 - (c) What is the half-life of the reaction?
3. This problem concerns the results in the paper Time-Resolved Resonance Fluorescence Study of Electronically Excited Iodine Atoms by Donovan *et. al.*, which is available on the course webpage.
 - (a) Discuss how the results in Table 1 of the paper were obtained.
 - (b) From Table 1 of the paper, arrive at the results in Table 2.
 - (c) Comment on how your results in question 3b compare with that in the paper.
 4. The reaction of *cis*-2-butene to *trans*-2-butene is first order in both directions. At 25 °C, the equilibrium constant is 0.406 and the forward rate constant is $4.21 \times 10^{-4} \text{ s}^{-1}$. Starting with a sample of the pure *cis* isomer with $[\textit{cis}]_0 = 0.115 \text{ mol/dm}^3$, how long would it take for half the equilibrium amount of the *trans* isomer to form.