

Tutor Marked Assignment

Make sure you know how to complete and send in your TMA and PT3 form: detailed instructions are given in *Completing TMA and CMA forms* in your *Student Handbook*.

Covering: **Blocks 1 and 2**

Cut-off date:

Friday 4 April 2003

Question 1

This question carries 35% of the marks for this assignment, and tests Objectives 1–5 of Block 1.

Any thermodynamic data you need to answer this question should be taken from the *S342 Data Book*.

Suppose that you wanted to produce vinyl chloride (chloroethene, $\text{CH}_2=\text{CHCl}$) from methane (CH_4) and chloroform (trichloromethane, CHCl_3) by way of the following gas-phase reaction:



(a) (12 marks) (i) Using the analysis developed in Section 5 of Block 1, derive an expression for the equilibrium constant, K_p , for reaction 1 in terms of the equilibrium yield of vinyl chloride, y , and the total pressure, p_{tot} . You should assume that the reactants are mixed initially in stoichiometric proportions. Include the intermediate steps in your derivation, and state any further assumptions that you make.

(ii) State, giving your reasons, the maximum equilibrium yield of vinyl chloride that is theoretically possible.

(b) (7 marks) Assuming an overall pressure of one bar, determine the temperature at which the equilibrium yield of vinyl chloride from reaction 1 will be 33% (that is, $y = 0.33$). State, and comment on, any assumptions or approximations that you make.

(c) (8 marks) A possible competing reaction leads to the formation of 1,1-dichloroethane (CHCl_2CH_3), as follows:



Construct a hand-drawn graph showing plots of $\ln K^{\ominus}$ against $1/T$ for reactions 1 and 2 in the temperature range 300–1000 K. Include in your answer a table of your calculated values.

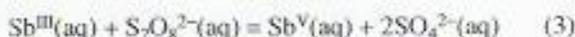
(d) (8 marks) Suppose now that reaction 1 takes place unacceptably slowly at the temperature calculated in part (b). With reference to your plots from part (c), and other relevant information, what do you conclude about the reaction conditions that would be likely to maximize the actual yield of the desired product (vinyl chloride), while keeping the unwanted byproduct (1,1-dichloroethane) to a minimum? Support your clearly stated conclusions by discussing the influence on the yield of both thermodynamic and kinetic factors. (About 200 words)

Question 2

This question carries 25% of the marks for this assignment, and tests Objectives 1, 2, 3, 5, 6–9, 12 and 13 of Block 2.

Note that you may find the *Kinetics Toolkit* from S205 *The Molecular World* (included in the first mailing) helpful when tackling this question.

The oxidation of an antimony(III) complex ion by the peroxydisulfate ion, $\text{S}_2\text{O}_8^{2-}$, under certain conditions in aqueous solution can be represented by the following time-independent stoichiometry:



(a) (4 marks) Define the term 'reaction variable', x . Use the reaction variable to show how monitoring the formation of the sulfate ion, SO_4^{2-} , in reaction 3 would allow kinetic reaction profiles for the reactants, Sb^{III} and $\text{S}_2\text{O}_8^{2-}$, to be determined.

(b) (16 marks) In practice, reaction 3 can be followed by monitoring the disappearance of Sb^{III} as a function of time. The results of an experiment carried out at 308 K are given in Table 1; the initial concentration of peroxydisulfate ion was $[\text{S}_2\text{O}_8^{2-}]_0 = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$.

Table 1 Values of the concentration of the antimony(III) complex ion, $[\text{Sb}^{\text{III}}]$, as a function of time for reaction 3 at 308 K.

time s	$[\text{Sb}^{\text{III}}]$ $10^{-4} \text{ mol dm}^{-3}$
0	2.50
600	1.96
1200	1.49
1800	1.08
2400	0.74
3000	0.46
3600	0.25

Handwritten notes: "Draw [Sb^{III}] vs t" with a graph showing a decreasing curve. Signature: JAF

Suggest a plausible rate equation for reaction 3. Then use the information provided to determine the partial order of reaction with respect to Sb^{III} . Indicate clearly your reasons for choosing the method of data analysis that you use, include your reasoning and calculations, and show all necessary data in tabular form.

Handwritten equation: $\frac{dI}{dt} = k \text{ Slope}$