UNIVERSITY COLLEGE LONDON

University of London

EXAMINATION FOR INTERNAL STUDENTS

For The Following Qualifications:-

B.Eng.   *M.Eng.*

Chemical Eng E857: Chemistry II

COURSE CODE   :   **CENGE857**

UNIT VALUE   :   **0.50**

DATE   :   **15-MAY-06**

TIME   :   **10.00**

TIME ALLOWED   :   **3 Hours**

*Answer **FOUR QUESTIONS**, one from each section A, B, C and D.*
Only the first four answers will be marked.
Maximum: 80 marks.

Graph Paper is provided. Universal Gas Constant R=8.314 J mol⁻¹K⁻¹

PART A

1.

i) Starting from the definition of the differential molar Gibbs energy, $dg = -sdT + vdp$, derive the Clausius-Clapeyron equation and discuss under which assumptions the following simplified equation holds: [10]

$$ln\frac{P_{vp}}{P_0} = -\frac{\Delta h}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

ii) Estimate the vapour pressure of ethylbenzene at 347.2 and 460 K using both the Clausius-Clapeyron and the Lee-Kesler relations given below. [10]

The normal boiling point of ethylbenzene is 409.3 K, and the critical point is $T_C = 617.1$ K and $P_C = 36.0$ bar.

$$ln\frac{P_{vp}}{P_C} = f^{(0)}(T_r) + \omega f^{(1)}(T_r)$$

$$\omega = -log\frac{P_{vp}}{P_C} - 1 \quad at \quad T_r = 0.7$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862\ln T_r + 0.169347 T_r^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721\ln T_r + 0.43577 T_r^6$$

(T_r: reduced temperature = T/T_C)

2.

i) The Ambrose method is given below.

$$T_C = T_b\left[1 + \frac{1}{1.242 + \sum \Delta T_A - 0.023\Delta Platt}\right] \quad (T_C \ in \ K)$$

$$P_C = \frac{M}{(0.339 + \sum \Delta P_A - 0.026\Delta Platt)^2} \quad (P_C \ in \ bar)$$

CONTINUED

a) Give the definition of the ΔPlatt number and explain for which molecules it is useful. [4]

b) For aromatic molecules the ΔPlatt number can be calculated by substituting a carbon group for the aromatic ring. Show that for 1,2,3-Trimethylbenzene the ΔPlatt number is zero. [4]

ii) The normal boiling point for 1,2,3-Trimethylbenzene is 449.3 K and the molecular weight M = 120.20.

Values for the group contributions (ΔT_A, ΔP_A) for the Ambrose method are given in the table below.

Group	ΔT_A	ΔP_A
Benzene	0.448	0.924
—CH_3	0.138	0.226
Correction for first substitution	0.010	0
Correction for each subsequent	0.030	0.020
Correction for ortho pairs	−0.040	−0.050

An ortho-pair is a pair of contiguous substitutions on the aromatic ring.

Determine:

c) The critical temperature [6]

b) The critical pressure [6]

PLEASE TURN OVER

PART B

3.

i) Describe, with the aid of diagrams and pointing out the important features, the differences between:

    a)   the approximation of the potential energy curve for a vibrating diatomic molecule using Hooke's law for simple harmonic motion

    b)   the actual potential energy curve as a result of anharmonicity

                                                            [10]

ii) What are overtone bands and how do they modify the selection rule for a vibrating diatomic molecule?   [3]

iii) A molecule has a strong vibrational fundamental band indicating C-H bending at 730 cm^{-1}. Stating any assumptions that you make, what are the wavenumbers for the first and second overtone bands for this bond?   [3]

iv) Analysis of the fundamental, first overtone and second overtone bands of HCl in the electronic ground state gave:

$$\frac{E_{vib}}{hc} = 2990.9\left(\upsilon + \frac{1}{2}\right) - 52.82\left(\upsilon + \frac{1}{2}\right)^2 cm^{-1}$$

On absorption of the first infrared photon:

    a)   Calculate the wave number of the fundamental band.

    b)   Show that u = 28 at the dissociation limit.

    c)   Estimate the dissociation energy in Joules.

   [4]

4.

i) Why are molecular spectra more complex than atomic spectra? What processes would you expect in the interaction of ultraviolet, infrared and microwave radiation with a molecule?   [4]

ii) The molecule hydrogen chloride (HCl) absorbs infrared radiation at 2881cm^{-1}. Calculate:

    a)   the wavelength of this radiation

    b)   the frequency of this radiation

    c)   the energy change associated with this absorption

[Planck's constant, h = 6.626 x 10^{-34} Js   speed of light, c = 3 x 10^8 m/s]

                                                                   [3]

CONTINUED

iii) Explain why exposure to sunlight can cause skin damage, sunburn and, in extreme cases, skin cancer. [7]

iv) The UV absorption spectra of some of the active components of sun-creams are shown in figure 1. With reference to your answer to (iii), why is TiO_2 considered to be a good sun block. Why is there some concern over its use? [2]

v) Describe, briefly, the design and operating principle of a UV-TiO_2 reactor for the disinfection of E. Coli contaminated water. What is the role of TiO_2 in this case? [4]
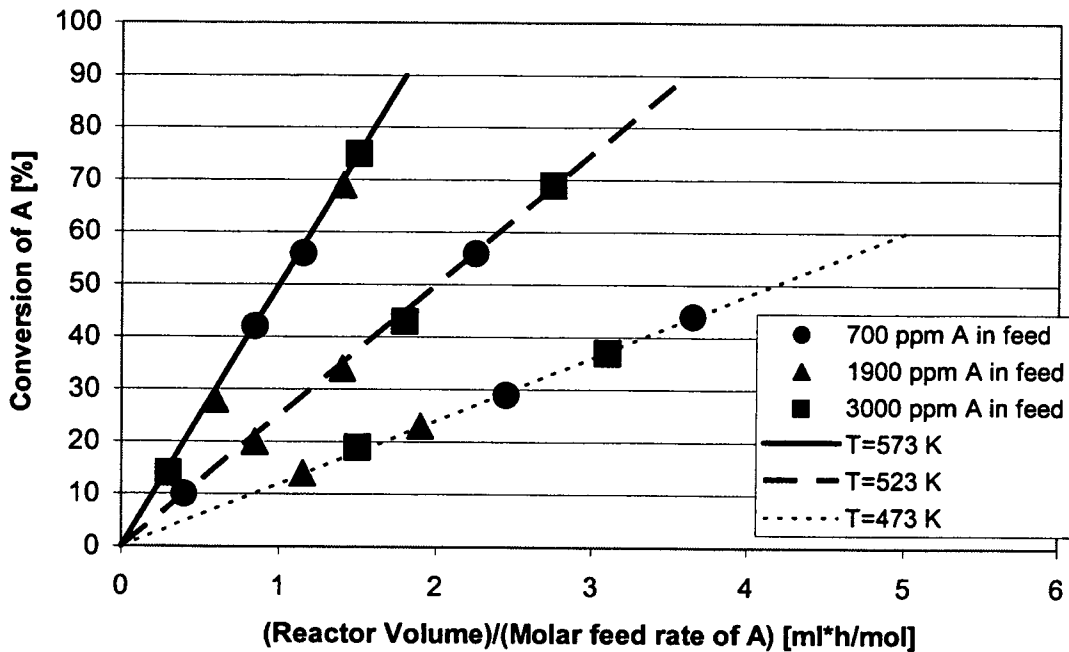
Figure 1
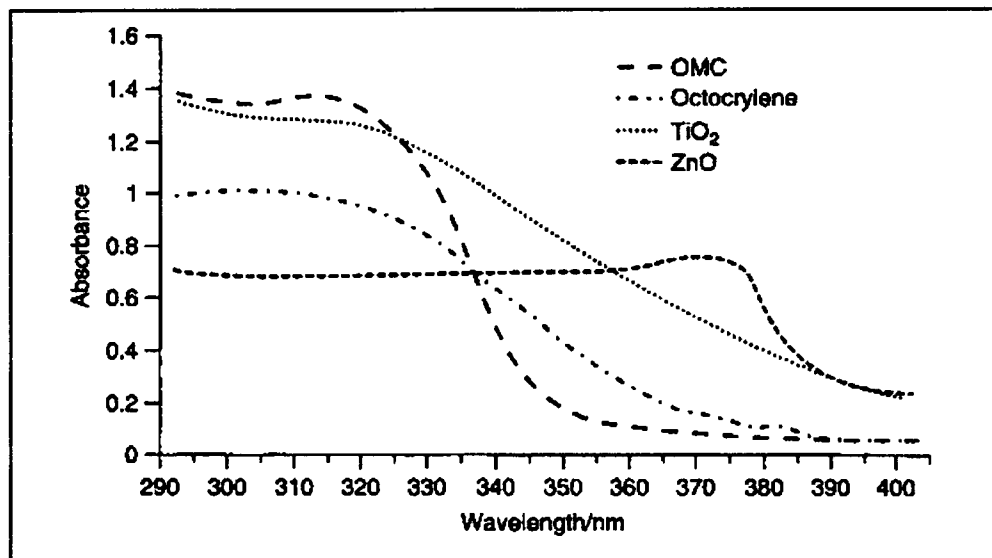
PART C

5.

i)   In a series of experiments of the decomposition of a compound A, the kinetic data shown in the figure below were obtained. In these experiments a nitrogen stream containing various concentrations of A was fed to an isothermal laboratory CSTR. Each point in the figure represents one complete run and the plot gives the conversion of A (X_A) versus the ratio of reactor volume (V_R, in ml, i.e. cm³) to the A molar feed rate (F_{A_0}, in mol/h) at different feed concentrations of A (in ppm by mass). Prove that the apparent reaction order is zero over the temperature range studied.   [6]

ii)   Calculate the specific reaction rates (kinetic constants) at the various temperatures, the activation energy and the pre-exponential factor.   [14]


(Reactor Volume)/(Molar feed rate of A) [ml*h/mol]

Legend:
● 700 ppm A in feed
▲ 1900 ppm A in feed
■ 3000 ppm A in feed
—— T=573 K
— — T=523 K
······ T=473 K

6.

The first order gaseous decomposition of component A,

$$A \rightarrow B + C$$

was carried out in a constant volume and constant temperature vessel to allow the application of the "total pressure method" for estimating the kinetic constant. There is one complication however.

The reversible dimerisation reaction

$$2C \Leftrightarrow D$$
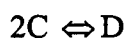
also occurs.

It may be assumed that this additional reaction immediately reaches equilibrium, the dimerisation equilibrium constant being $K_P=4.0$ bar^{-1}.

From the following data determine the first-order reaction rate constant of the decomposition reaction. At the start only A was present.

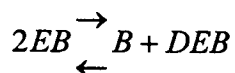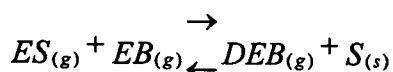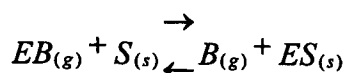| t [min]	0	30	60	90	120	150	180
P_{tot} [bar]	1.000	1.129	1.222	1.296	1.356	1.405	1.446

[20]

PART D

7.

i) For the solid catalysed disproportionation of ethylbenzene (EB) to benzene (B) and diethylbenzene (DEB)

$$2EB \underset{\leftarrow}{\overset{\rightarrow}{}} B + DEB$$

the following reaction mechanism is suggested:

$$EB_{(g)} + S_{(s)} \underset{\leftarrow}{\overset{\rightarrow}{}} B_{(g)} + ES_{(s)}$$

$$ES_{(g)} + EB_{(g)} \underset{\leftarrow}{\overset{\rightarrow}{}} DEB_{(g)} + S_{(s)}$$

where $S_{(s)}$ is the catalytic active site and $ES_{(s)}$ is an adsorbed ethene species. From these steps the adsorption of ethylbenzene has been found to be much faster than the reaction of adsorbed ethene with a gaseous ethylbenzene molecule.

Derive a kinetic expression for the reaction rate of disproportionation. [14]

ii) A side reaction of this system is the dealkylation of ethylbenzene to ethene (E) and benzene (B)

$$EB \underset{\leftarrow}{\overset{\rightarrow}{}} B + E$$
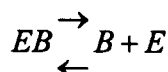
Extend the mechanism shown in (i) to include the dealkylation reaction and derive a kinetic expression for its reaction rate. [6]

8.

In a continuous flow experiment, substrate (S), i.e. reactant and enzyme (E) solutions are fed continuously through a light absorption cell. Measured absorption spectra reveal the presence of two enzyme-substrate complexes ES_I (green) and ES_{II} (red). For this system a suitable reaction scheme is

$$E + S \Leftrightarrow ES_I \Leftrightarrow ES_{II} \rightarrow P + E$$

where P is the reaction product.

Assuming the last reaction step to be the slowest, develop a suitable reaction rate expression. [20]

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