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	:	**18–MAY–05**
TIME	:	**10.00**
TIME ALLOWED	:	**3 Hours**

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Answer **FOUR QUESTIONS,** *one from each section A, B, C and D. Total maximum: 80 marks.*

Graph paper needed.

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

PART A

1.

For chlorine, the following table of vapour and sublimation pressures is available:

T, °C	P, Torr
−118.0	1
−106.7	5
−101.6	10
−93.3	20
−84.5	40
−79.0	60
−71.7	100

a) Starting from the definition of the differential molar Gibbs energy
$dg = -sdT + pdv$, derive the Clausius-Clapeyron equation and discuss under which assumptions the following simplified equation holds

$$\ln\frac{P}{P_0} = -\frac{\Delta h}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$ [5]

Appropriately plot the data from the table above and
b) estimate the average heat of vaporization   [5]
c) estimate the average heat of sublimation   [5]
d) estimate the heat of fusion   [3]
e) show that the triple point is at approximately −101 °C   [2]

2.

The normal boiling point of 2,4-dimethylpentane (C_7H_{16}) is 353.7 K and the molar mass M = 100.2. According to the Ambrose method:

$$T_C = T_b\left[1 + \frac{1}{1.242 + \Sigma\Delta T_A - 0.023\Delta\text{Platt}}\right] \quad T_C, \text{ K}$$

$$P_C = \frac{1.01325M}{(0.339 + \Sigma\Delta P_A - 0.026\Delta\text{Platt})^2} \quad P_C, \text{ bar}$$

ΔPlatt is the difference of the Platt number of the molecule and that of n-Heptane.

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The group contributions are

Group	ΔT_A	ΔP_A
—CH$_3$ ·	0.138	0.226
＞CH$_2$	0.138	0.226
—CH—	0.095	0.220
—C—	0.018	0.196

Determine

a)   The critical temperature   [6]

b)   The critical pressure   [6]

c)   The acentric factor from the Lee and Kesler equation   [8]

$$\ln P_R^{Vap} = f^0(T_R) + \omega f^1(T_R)$$

where

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

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

PART B

3.   The solution of the Schrödinger equation for a rotating diatomic molecule is:

$$E_r = \frac{h^2}{8\pi^2 \mu r^2} J(J+1)$$

i.   What is the selection rule for allowable rotational transitions?   [1]

ii.   Find the expression for the rotational energy between two adjacent energy
      levels and, from this, the corresponding wavenumber.   [4]

      Figure 1 shows the far-infrared spectrum of $^{12}C^{16}O$ between the rotational
      transitions of J = 3 and J = 9.

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iii. Explain why far-infrared radiation gives rise to molecular rotations. [5]

iv. What does '% Transmission' refer to? [3]

v. Using the graph in figure 1, estimate the CO bond length. [5]

vi. Show that the wavenumber of the $J = 4 \leftarrow 3$ transition is 19.29 cm^{-1}. [2]

Avogadro's number, $Av = 6.023 \times 10^{23} \text{ mol}^{-1}$

Planck's constant, $h = 6.626 \times 10^{-34} \text{ Js}$

speed of light, $c = 3 \times 10^8 \text{ m/s}$

$1\text{Å} = 10^{-10} \text{m}$
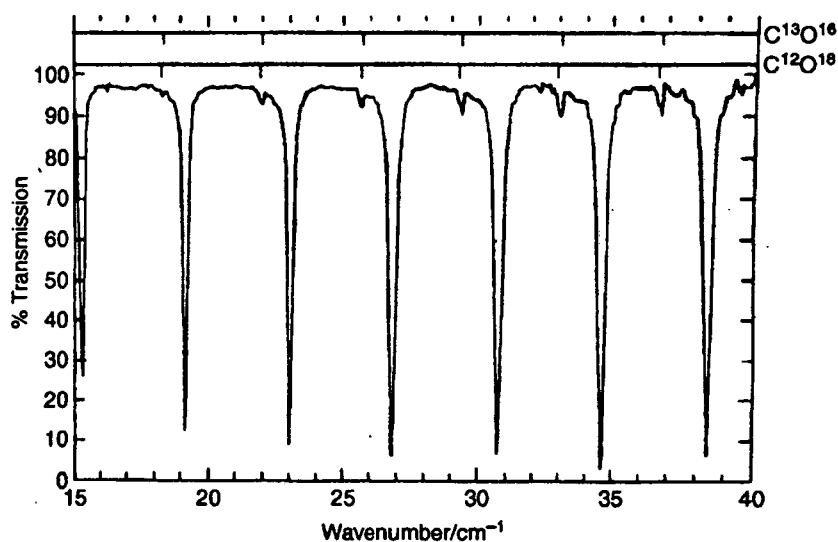
Figure1: Far-infrared spectrum of CO showing transitions from $J = 3$ to $J = 9$ (after Hollas, 2004).

4.

i. What is the word LASER an acronym of? [1]

ii. Explain the principle of laser radiation, including brief descriptions of:
the methods of pumping
how the laser beam is formed [14]

iii. In the N_2/CO_2 gas laser, what is the purpose of the nitrogen? Why is nitrogen a suitable gas for this purpose? [5]

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PART C

5.

a) The reaction between A and B was investigated by measuring the initial rate (r_o) of the reaction when the initial concentration of one of the reactants (C_{Ao} or C_{Bo}) was kept constant. Two sets of data at 25°C are given below:

i) $C_{Ao} = 1.00 \times 10^{-6}\,mol\,cm^{-3}$

$C_{Bo}/10^{-6}\,mol\,cm^{-3}$	10.00	7.00	4.00	2.00	1.00
$r_o/10^{-7}\,mol\,cm^{-3}.s^{-1}$	3.16	2.65	2.05	1.42	1.00

ii) $C_{Bo} = 1.00 \times 10^{-5}\,mol\,cm^{-3}$

$C_{Ao}/10^{-6}\,mol\,cm^{-3}$	10.00	7.00	4.00	2.00	1.00
$r_o/10^{-7}\,mol\,cm^{-3}.s^{-1}$	31.6	22.1	12.7	6.32	3.16

Determine the partial orders of reaction with respect to both A and B, and calculate the value of the rate constant.

The initial rate (r_o) was measured at different temperatures keeping the initial concentrations of reactants at $C_{Ao} = 1.00 \times 10^{-6}\,mol\,cm^{-3}$ and $C_{Bo} = 1.00 \times 10^{-5}\,mol\,cm^{-3}$ at all temperatures.

T/K	303	308	313
$r_o/10^{-7}\,mol\,cm^{-3}.s^{-1}$	4.41	6.08	8.31

Determine the activation energy of the reaction. [15]

b) $10^{-3}\,m^3.min^{-1}$ of liquid containing A and B ($C_{A0} = 0.10\,kmol\,m^{-3}$, $C_{B0} = 0.03\,kmol\,m^{-3}$) flow into a continuous stirred tank reactor of volume $10^{-3}\,m^3$ A and B react giving a product D, with an unknown stoichiometry. The concentrations of A, B and D in the outlet stream are $C_{Af} = 0.02\,kmol\,m^{-3}$, $C_{Bf} = 0.01\,kmol\,m^{-3}$, $C_{Df} = 0.04\,kmol\,m^{-3}$.

Calculate the rate of reaction for A, B and D and find the stoichiometry of the reaction.

Assume that the density of the reaction solution does not change as the reaction proceeds. [5]

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6.
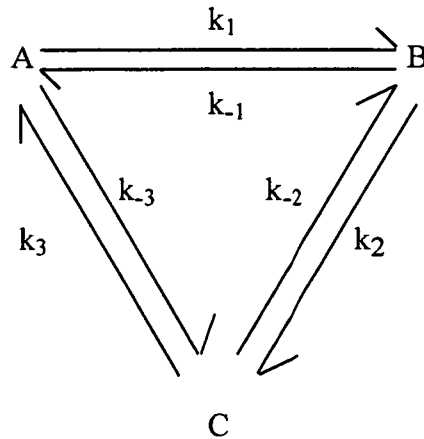
For the above network of isomerisation reactions the values of the equilibrium constants K_2 and K_3 for reactions 2 and 3 respectively are $K_2=2.028$ and $K_3=0.242$. Calculate the equilibrium constant K_1 and the composition of the reaction mixture at equilibrium, expressed as mole-fractions.   [4]

These reactions are carried out in an isothermal CSTR with feed containing no B or C. Formulate the mole balances for all three components, as a function of all six kinetic constants and the residence time.   [3]

In a series of kinetic measurements the concentrations of the three components at the outlet are measured. Explain why it is not possible to estimate the extension of all three reactions and consequently all kinetic constants through these experiments.   [4]
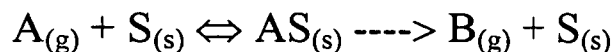
Estimate the composition (mole-fractions) of the reactor outlet for the following values of residence time: $\tau = 1$ s and $\tau = 10$ s, if $k_{-1} = 0.497$ s^{-1}, $k_{-2} = 4.990$ s^{-1} and $k_{-3} = 3.012$ s^{-1}.   [9]

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PART D

7.

The mechanism for the irreversible solid catalysed reaction $A_{(g)} \longrightarrow B_{(g)}$ is the following:

$$A_{(g)} + S_{(s)} \Leftrightarrow AS_{(s)} \longrightarrow B_{(g)} + S_{(s)}$$

where S is the catalytic active site. Experimental runs have revealed that the first reaction step (adsorption of A) is very fast and can be considered at equilibrium.

Derive the kinetic expression for this reaction, using partial pressures of A and B.

For the estimation of the kinetic parameters, experimental runs were carried out in a recycle reactor with 60 cm^3 /min overall inlet flow and 1g of catalyst. The reaction temperature was 200 $^\circ$C and the total pressure 1 bar. The inlet consisted in all runs of an inert gas and only A (no B) at various mole fractions (y_{Ao}).

The measured outlet mole fraction of A (y_A) in each run is given below:

Run	1	2	3	4	5	6
y_{Ao}	0.05	0.10	0.15	0.20	0.25	0.30
y_A	0.0270	0.0550	0.0840	0.1139	0.1448	0.1765

Calculate the reaction rate of each run and estimate the parameters of the kinetic model. [20]

8.

Consider the catalytic hydrogenation in series of a diene (D) (containing two double bonds) to the corresponding alkene (E) (hydrogenation of one double bond) and then to alkane (A) (hydrogenation of the second double bond). From mechanistic studies we know that the reaction takes place through adsorption of the reactant and surface reaction of the adsorbed diene with hydrogen from the gas phase. The hydrogenation of the second double bond takes place through a surface reaction of the adsorbed alkene with gaseous hydrogen. It was also found that the limiting reaction steps are the surface reaction steps.

Draw the reaction mechanism for the whole reaction system and derive kinetic expressions for the reaction rates of both reactions. [20]

END OF PAPER

Semilog Graph paper