

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 : **02-MAY-02**

TIME : **10.00**

TIME ALLOWED : **3 hours**

02-C0187-3-60

© 2002 *University of London*

TURN OVER

Answer **FIVE QUESTIONS**, at least **ONE** from each **SECTION A, B, C and D**.
ALL questions carry a total of **20 MARKS** each, distributed as shown []

$R=8.312 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ Graph paper is needed

SECTION A

1. A humid air stream at 40 °C and 90% relative humidity is to be processed.

Determine:

The vapour pressure of water at 40 °C. [8]

The partial pressure of water in the air stream. [4]

The condensation temperature of the humid air. [8]

For water you can assume:

Normal boiling point: 100 °C

Heat of vaporisation at nbp: 40.66 kJ/mol

Use the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta h}{T\Delta v}$$

Clearly state your simplifying assumptions.

TURN OVER

2. For the system Methanol (1) – Water (2) at 100 °C the following experimental data have been reported (Griswold J. and Wong S.Y., Chem. Eng. Progr. Symp. Ser., 1952, 3,48)

Table cannot be reproduced – copyright permission not obtained.
Please refer to the article cited above, for table of P,Torr; x_1 ; and y_1

Using the Equal Area consistency criterion, i.e. $\int_0^1 \ln \frac{y_1}{\gamma_2} dx_1 = 0$, verify the thermodynamic consistency of this data set. You can assume the vapour phase to be ideal and neglect the Poynting correction for the liquid phase. In order for the data set to be of acceptable quality the difference between the areas should be less than 10% the sum of the areas.

[20]

TURNOVER

SECTION B

3. Nitrogen in the upper atmosphere absorbs thermal neutrons to form radioactive ^{14}C which decays by β -emission via a first-order process with a rate coefficient of $k\text{ s}^{-1}$. Derive an expression for the half-life of ^{14}C in terms of k [8]

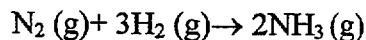
A religious relic made of cotton has a ^{14}C activity of $13.2\text{ counts min}^{-1}\text{ g}^{-1}$ compared to a fresh sample of cotton of $15.0\text{ counts min}^{-1}\text{ g}^{-1}$. Given the half-life of ^{14}C is 5700 years calculate the age of the relic. [12]

4. Draw and label a diagram to show the variation of temperature and pressure with increasing altitude of the Earth's atmosphere. [4]

By what mechanisms is ozone (a) formed (b) destroyed in the stratosphere and why is it important to maintain the level of ozone in that region. [8]

List the main processes that can occur following the absorption by gas molecules of light quanta and show the difference in terms of electronic energy levels between fluorescence and phosphorescence. [8]

5. The Haber-Bosch process for the synthesis of ammonia follows the reaction:



Derive an expression for the equilibrium constant, K_p , of the reaction in terms of the partial pressures of reactants and products. [10]

Calculate the value of K_p at 298K given that the standard free energy of formation of ammonia is -16.45 kJ/mol . [10]

(Hint. The standard free energy change in a reaction is related to the equilibrium constant by: $\Delta G^\ominus = -RT \ln K_p$)

TURN OVER

SECTION C

6. a) The reaction between A and B was investigated by measuring the initial rate (r_0) of the reaction when the initial concentration of one of the reactants (C_{A0} or C_{B0}) was kept constant. Two sets of data at 25°C are given below:

i) $C_{A0} = 1.00 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$					
$C_{B0}/10^{-6} \text{ mol} \cdot \text{cm}^{-3}$	10.00	7.00	4.00	2.00	1.00
$r_0/10^{-7} \text{ mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$	3.16	2.65	2.05	1.42	1.00
ii) $C_{B0} = 1.00 \times 10^{-5} \text{ mol} \cdot \text{cm}^{-3}$					
$C_{A0}/10^{-6} \text{ mol} \cdot \text{cm}^{-3}$	10.00	7.00	4.00	2.00	1.00
$r_0/10^{-7} \text{ mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$	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.

Keeping both initial concentrations the same ($C_{A0} = 1.00 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$, $C_{B0} = 1.00 \times 10^{-5}$) the initial rate (r_0) was measured at different temperatures:

T/K	303	308	313
$r_0/10^{-7} \text{ mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$	4.41	6.08	8.31

Determine the activation energy of the reaction. [15]

- b) $10^{-3} \text{ m}^3 \cdot \text{min}^{-1}$ of liquid containing A and B ($C_{A0} = 0.10 \text{ kmol} \cdot \text{m}^{-3}$, $C_{B0} = 0.03 \text{ kmol} \cdot \text{m}^{-3}$) 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 $C_{Af} = 0.02 \text{ kmol} \cdot \text{m}^{-3}$, $C_{Bf} = 0.01 \text{ kmol} \cdot \text{m}^{-3}$, $C_{Df} = 0.04 \text{ kmol} \cdot \text{m}^{-3}$.

Calculate the rate of reaction for A, B, D and find the stoichiometry of the reaction. Assume that the density of the reaction solution does not change as the reaction proceeds. [5]

7. A CSTR of 160 cm^3 is used for the liquid phase reversible reaction:

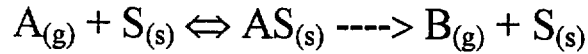


The total flow is $1 \text{ cm}^3 \cdot \text{s}^{-1}$ and the inlet contains no B. The measured conversion is 80% of the equilibrium conversion. Thermodynamic calculations on the other side resulted in a value of the reaction equilibrium constant equal to 4. Estimate the reaction kinetic constants of the forward and backward reactions. [20]

TURN OVER

SECTION D

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



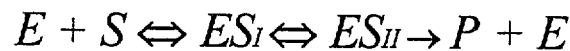
where S is the catalytic active site. Experimental runs have revealed that the first reaction step (adsorption of A) is very fast and can be considered at equilibrium. Derive the kinetic expression for this reaction, using partial pressures of A and B. For the estimation of the kinetic parameters, experimental runs were carried out in a recycle reactor with 60 cm³/min overall inlet flow and 1g of catalyst. The reaction temperature was 200°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]

9. In a continuous flow experiment, substrate (S) (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:



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

[20]

END OF PAPER