

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 : **16-MAY-03**

TIME : **10.00**

TIME ALLOWED : **3 Hours**

*Answer FIVE QUESTIONS. Answer at least ONE from EACH PART.
Only the first FIVE answers given will be marked.
ALL questions carry a total of 20 marks each, distributed as shown []*

Universal gas constant: $R = 8.314 \text{ Jmol}^{-1} \cdot \text{K}^{-1}$

PART A

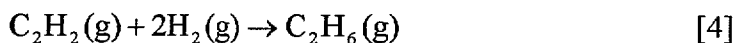
1.

i) Describe the criteria for spontaneity of a reaction, in terms of enthalpy, entropy and Gibbs free energy. [4]

ii) From the expression of the total entropy change of a system, derive the relationship:

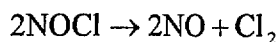
$$dG = dH - TdS \quad [5]$$

iii) Using the tables provided, calculate the standard reaction enthalpy and entropy at 25 °C for the following reaction, assuming that they do not vary with temperature. Comment on the values you obtain.



iv) Using the tables provided, find the temperature at which the reaction shown in (iii) is at equilibrium. [3]

v) On heating, nitrosyl chloride, NOCl, decomposes into nitric oxide and chlorine:



The reaction is endothermic, with $\Delta H_r^\circ = 77.07 \text{ kJ/mol Cl}_2$. Using the tables provided and assuming that standard enthalpies and entropies are unaffected by temperature, calculate the equilibrium constant for the reaction at 650K. [4]

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2.

i) Explain, using the Bohr frequency condition, the origin of the lines in the atomic spectrum of an element. [4]

ii) What is the highest frequency photon that can be emitted from the hydrogen atom and what is its wavelength? [4]

$$[h = 6.63 \times 10^{-34} \text{ Js, } c = 3 \times 10^8 \text{ m/s, Rydberg constant} = 3.29 \times 10^{15} \text{ Hz}]$$

iii) Name and explain, briefly, the relationship of each of the four quantum numbers to the properties of electrons in orbitals. For a given energy level, state the type and number of orbitals and the number of electrons that can be accommodated in those orbitals. [4]

iv) Explain, briefly, why molecular spectra are made up of bands, rather than the sharp lines of atomic spectra. [4]

v) The rotational energy of two different energy levels of a diatomic molecule can be written as:

$$E_1 = hBcJ(J + 1)$$

$$E_2 = hBc(J + 1)(J + 2)$$

$$\text{where: } B = \frac{h}{8\pi^2 \mu r^2 c}$$

and μ is the reduced mass.

Find the frequency of the $J = 3 \leftarrow 2$ transition in the rotational spectrum of $^{12}\text{C}^{16}\text{O}$ if the equilibrium bond length is 112.81 pm. [4]

[molar mass of C = 12.001 g mol⁻¹ and of O = 16.000 g mol⁻¹]

Avogadro's number, $N_{\text{AV}} = 6.023 \times 10^{23}$ particles/mol

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PART B.

- 3 For Anthracene, the following table of vapour and sublimation pressures is available:

T, °C	P, Torr
145.0	1
173.5	5
187.2	10
201.9	20
217.5	40
231.8	60
250.0	100
279.0	200
310.2	400
342.0	760

Knowing that the melting point of Anthracene is 217.5 °C, and starting from the Clausius-Clapeyron equation

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

clearly stating all your assumptions, determine:

- a) the average heat of vaporization [6]
- b) the average heat of sublimation [6]
- c) the heat of fusion [2]
- d) the temperature at which Anthracene will start separating out of a binary gas mixture containing 98% N₂ at 1 atm. [3]
- e) the gas phase composition of a binary mixture N₂/Anthracene at equilibrium at 145.0°C and 1 atm [3]

4.

A binary system of species 1 and 2 is at a fixed temperature T. At this temperature the pure component vapour pressures are $P_1^{\text{vap}} = 0.75$ bar and $P_2^{\text{vap}} = 0.32$ bar. This system exhibits an azeotrope at $x_1 = 0.29$. The liquid phase non-ideality can be represented by a simple activity coefficient equation:

$$\ln \gamma_1 = A(1 - x_1)^2 \quad \ln \gamma_2 = Ax_1^2$$

where x_1 is the liquid phase mole fraction of component 1.

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Clearly stating all your assumptions, determine:

- a) The value of A [10]
- b) The total pressure at the azeotrope [4]
- c) The total pressure and vapour phase composition at $x_1 = 0.6$ [6]

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PART C.

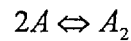
5.

- a) What is the effect of pressure on the equilibrium conversion of :
 - i) an isomerisation gas phase reaction
 - ii) a dehydrogenation gas phase reaction
 - iii) a polymerisation gas phase reaction.

What is the effect of the temperature on the equilibrium constant and equilibrium conversion of a chemical reaction.

[5]

- b) The equilibrium constant – expressed in terms of partial pressures – of the dimerisation reaction:



is $K_p = 5 \text{ bar}^{-1}$

If there is only A initially, what is the equilibrium conversion at

- i) 1 bar
- ii) 10 bar

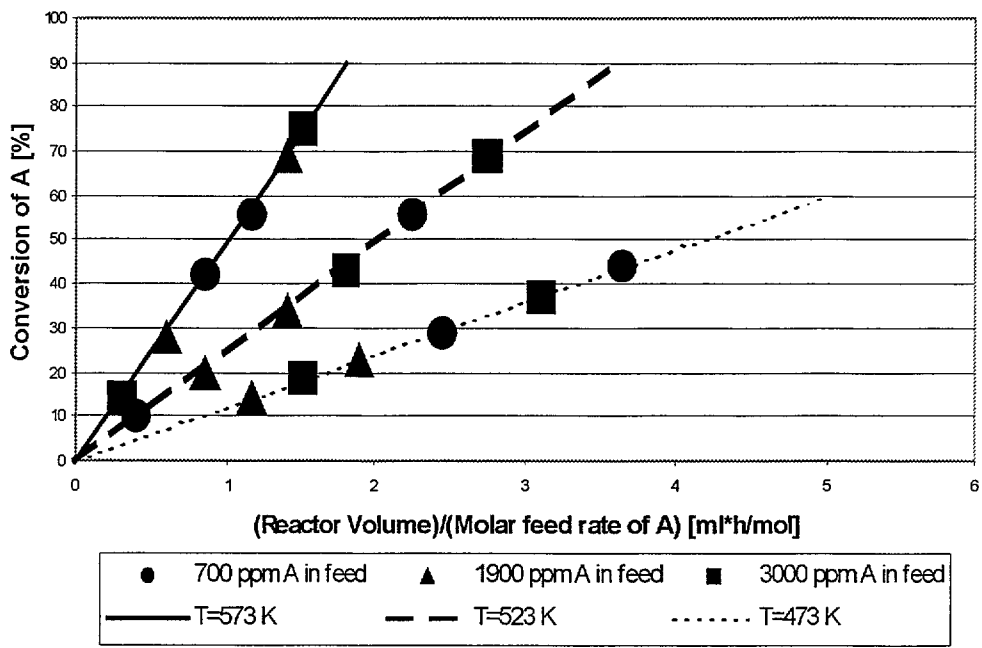
[15]

6.

In a series of experiments of decomposition of a compound A the kinetic data shown in the figure overleaf 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 cm^3) to the molar feed rate of A (F_{A0} , in mol/h) at different feed concentrations of A (in ppm by mass). What can you deduce about the apparent reaction order of the reaction over the temperature range studied? [6]

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

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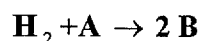


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PART D

7.

The hydrogenolysis of a component A to B was studied over a commercial solid catalyst in a recycle catalytic reactor with internal recycle containing 40 g of catalyst:



Only H_2 and A are fed into the reactor at 573 K. The following experimental data are available:

Total molar feed rate [mol/h]	Partial pressure of A in feed [atm]	Partial pressure of hydrogen in feed [atm]	Mole fraction of B in exit stream
1.70	0.5	0.5	0.05
0.60	0.5	0.5	0.16
0.75	0.6	0.6	0.10
0.30	0.4	0.6	0.16
2.75	0.6	0.4	0.06

Calculate the reaction rate for each experiment, in $\text{mol}/(\text{kg}_{\text{cat}} \cdot \text{h})$, as well as the corresponding partial pressures of the reactants for these reaction rates. [8]

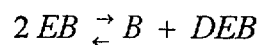
Assuming the validity of a power kinetic law for the reaction rate, as a function of the partial pressures of the reactants, calculate using data from the three first experiments, the total order and the specific reaction rate (kinetic constant). [8]

Using the value of the specific rate calculated above and data from the last two experiments, calculate the individual orders of reaction for each reactant. [4]

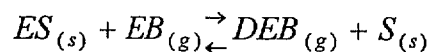
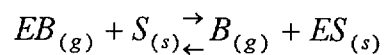
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8.

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



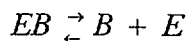
the following reaction mechanism is suggested:



where $ES_{(s)}$ is an adsorbed ethene species, $S_{(s)}$ catalytic active site.

From these steps the adsorption of ethylbenzene (step 1) has found to be much faster than the reaction of adsorbed ethene with a gaseous ethylbenzene molecule (step 2). Derive a kinetic expression for the reaction rate of disproportionation. [14]

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



Extend the above mechanism to include the dealkylation reaction and derive a kinetic expression for its reaction rate. [6]

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