UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVELII) SEMESTER (I) EXAMINATIONS. December 2020

SUBJECT: Chemistry

COURSE UNIT: CHE4333 (Solid State and Surface Chemistry) Time :Three (03) hours

Answer **All** questions.

Velocity of light, c	=	2.997×10^{8} m s^{-1}
Avogadro number, N_A	=	6.022×10^{23} mol^{-1}
Universal gas constant, R	=	8.314 J K^{-1} mol^{-1}
	=	0.0821 dm^3 atm K^{-1} mol^{-1}
Boltzmann constant, k_B	=	1.381×10^{-23} J K^{-1}
Faraday constant, F	=	9.6485×10^{4} C mol^{-1}
Electron charge, e	=	1.602×10^{-19} C
Planck's constant, h	=	6.626×10^{-34} J s
Proton mass, m_p	=	1.673×10^{-27} kg
Electron mass, m_e	=	9.10×10^{-31} kg
Atomic mass unit, *amu*	=	1.6606×10^{-27} kg
Vacuum permittivity, ε_0	=	8.854×10^{-12} J^{-1} C^2 m^{-1}
1 eV	=	1.6022×10^{-19} J

Q1. Answer **all** parts.

a) *Discuss briefly the following statements pertaining to surface phenomena.*

i. Accumulation of amphiphiles at an interface is a spontaneous process and results in a decrease of the interfacial (surface) tension.

ii. Steric and electrostatic stabilizations are two main mechanisms for maintaining stability of colloids.

(20 marks)

b) Sketch the potential energy profiles for an H_2 molecule that undergoes precursor mediated activated chemisorption. Mark on the diagram,

i Activation energy for adsorption, E_a^{ads}.

ii Activation energy for desorption, E_a^{des}.

iii Dissociation energy of the molecule in the gas phase, D(H-H).

iv Enthalpy change for adsorption and desorption, ΔE (ads) and, ΔE (des) respectively.

v Equilibrium bond distance, r_e of the adsorbed molecule on the surface.

(05 x5 marks)

c) In an experiment carried out on Fishcher -Tropsch synthesis using single -crystal Ni(110) plane as the catalyst, a series of saturated hydrocarbons and a small yield of unsaturated hydrocarbons were produced as the main and the minor products of the reaction respectively.

i. If the number of atoms per square centimeter exposed on a surface formed by Ni(110) plane is, 1.14×10^{15}, calculate the surface density of sites.

(05 marks)

ii. Calculate the time for 20% of the sites on a Ni(110) surface to be covered, with linearly adsorbed CO under typical reaction conditions if the sticking probability is 0.62.
If you assume that CO dissociates readily on the surface of the catalyst, what is the time required for the dissociative chemisorption of CO for a same coverage?

Note: Collision frequency of CO on the same surface under the given conditions is $7.3 \times 10^{18} m^{-2} s^{-1}$.

(20 marks)

iii. Comment on the time required for monolayer coverage of the surface.

(10 marks)

iv. Write a short account on chemisorption of ethylene on a Ni surface that can be found among the products of the experiment mentioned above.

(20 marks)

02. Answer **all** parts.

a) Explain the difference between hexagonal and cubic close packed arrangements in a crystal lattice.

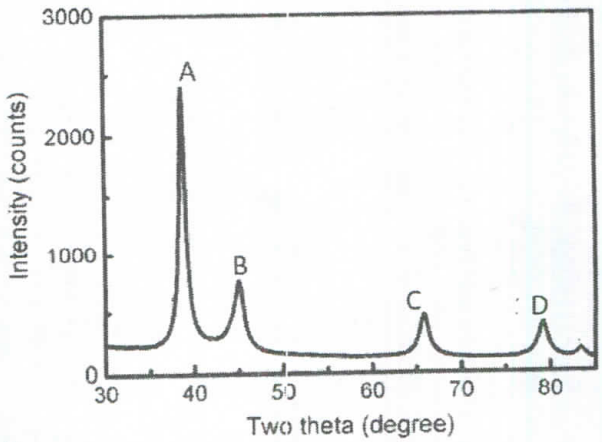
(10 marks)

b) In ionic crystals positive ions are packed in holes between the closest packed planes of negative ions.

i. Name the three types of holes found in ionic crystals. Explain using diagrams.
ii. Which property of ions dictates the type of holes forms in different ionic crystals?

(25 marks)

c) X-ray diffraction pattern of colloidal gold particles (FCC lattice) are shown in the Figure below.



Peaks depicted in the spectrum are due to the reflection from (111), (200), (220), (311), and (222) miller planes. X-ray wavelength used in this experiment was 0.154 nm. Side length of this FCC lattice is 0.408 nm. By performing appropriate calculations assign miller planes for the peaks denoted by A, B, and C. (You must show your calculations to obtain full credits and no marks will be awarded for guesses)

Interplanner distance is given by $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$

Assume first-order diffraction, n = 1 and atomic mass unit (amu) is 1.66×10^{-27} kg

(25 marks)

d) Indicate whether the following statements are true or false. If it is <u>true</u> briefly explain the reasons and if it is <u>false</u> correct the statement and give an explanation. (You can include diagrams in your explanations.)

i. Schottky defects enhance the density of related solids but remain electrically neutral.
ii. Frenkel defects are occurred in ionic crystals due to the presence of extra cations in interstitial sites.
iii. Conductivity of silicon increases on doping it with phosphorus.
iv. Energy gap between valence band and conduction band is larger in semiconductors than in insulators.
v. NaCl (Rock salt) forms octahedral lattice structure while CsCl forms cubic lattice structure.

(40 marks)

03. Answer **all** Parts.

a) The polarizability volume of carbon tetrachloride is 10.5×10^{-30} m^3 and its density at 20 °C is 1.59 g cm^{-3}. Calculate the dielectric constant of liquid CCl_4 at 20 °C. The molar mass of CCl_4 is 153.8 g mol^{-1}.

(20 marks)

b) The intermolecular pair potential (V) between two hydrogen molecules at a distance r is approximated by

$$V(r) = \frac{A}{r^{13}} - \frac{B}{r^6}$$

where, A and B are constants. The first and second terms describe the repulsive and attractive interactions between the two molecules, respectively.

i. Write down three types of attractive intermolecular interactions that contribute to the total van der Waals interactions.

(15 marks)

ii. Using the above pair potential $V(r)$, show that,

(I) $r_e = \left(\frac{13A}{6B}\right)^{1/7}$, where r_e is the equilibrium distance between the two molecules.

(10 marks)

(II) $r_0 = \left(\frac{A}{B}\right)^{1/7}$, where r_0 is the separation at which the pair potential is zero.

(05 marks)

(III) $V_{VDW} = -\frac{13}{6}V_R$, where V_{VDW} is the van der Waals energy contribution while V_R is the repulsive energy contribution to the **minimum** potential energy.

(10 marks)

(IV) $F_{max} = -\frac{9B}{13A}$, where F_{max} is the **greatest** net attractive force between two molecules.

(20 marks)

iii. The two constants A and B for the interaction between two H_2 molecules are 2.1×10^{-14} J $Å^{13}$ and 1.9×10^{-17} J $Å^6$. Calculate the minimum potential energy in kJ mol^{-1}, and compare your values with the bond energy (432 kJ mol^{-1}) and bond length (0.74 Å) of H_2.

(20 marks)

04. Answer **all** parts.

a) Materials in the nanometer scale may exhibit properties distinctively different from that of bulk. This opens door for many nanotechnology applications.

i. Explain what makes nanoparticles different from their bulk counterparts.

(05 marks)

ii. Compare properties of bulk gold with nanogold.

(05 marks)

iii. List **five (05)** key application areas of nanotechnology and briefly explain its societal impact using suitable examples.

(15 marks)

b) "Surfactants play very important role in metallic nanoparticle synthesis"

i. Discuss the above statement.

(10 marks)

ii. Give **two (02)** examples of surfactants used in nanoparticle synthesis.

(05 marks)

iii. Describe briefly **two (02)** wet chemical methods available to synthesize metallic nanoparticles.

(20 marks)

c) Write an account on each of the following topics.

(40 marks)

i. Quantum dots
ii. LSPR
iii. Buckminsterfullerene
iv. Carbon nanotubes

05. Answer **all** parts.

a) Most chemical industries depend upon reactions involving catalysts.

i. Distinguish between homogeneous and heterogeneous catalytic processes and give potential advantages and disadvantages of both types of catalysis.

(20 marks)

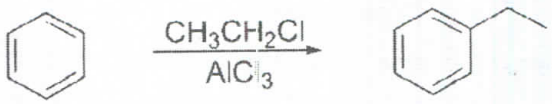
ii. Write down the sequential steps occurs in heterogeneously catalyzed reaction.

(14 marks)

iii. Name the important methods used for characterization of a heterogeneous catalyst.

(20 marks)

b) The traditional synthesis of ethylbenzene is a Friedel-Crafts alkylation, such as that shown below: The modern industrial synthesis involves mixing ethylene and benzene in the presence of a zeolite (ZSM-5). In what ways would you consider this method to be greener than the Friedel-Crafts reaction?



(16 marks)

c) Catalytic Dehydrogenation of 2-methyl propane was carried out using Pt-Cu bimetallic catalyst in a fixed bed continuous flow reactor to which 6.346×10^{-6} moles of 2-methyl propane per unit time were continuously introduced. Using a gas chromatograph, products and unreacted 2-methyl propane per unit time were analyzed after 20 min. of time on stream. Total amount of unsaturated C_4 products, total amount of C_3 products and unreacted 2-methyl propane were calculated and they were 1.343×10^{-6}, 2.32×10^{-7} and 8.98×10^{-7} moles respectively. Estimate the conversion of 2-methyl propane, selectivity for unsaturated C_4 products and the yield of C_3 products of the reaction at 20 min of time on stream.

(30 marks)

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