

## EASTERN UNIVERSITY, SRI LANKA FIRST YEAR FIRST SEMESTER EXAMINATION IN SCIENCE 2016/2017 (AUGUST/ SEPTEMBER 2018) CH 1013 PRINCIPLES OF CHEMISTRY -I

Answer all questions

Time: 03 hours

Gas constant (R) = 8.314  $Jmol^{-1}K^{-1}$  2.303  $\frac{RT}{F}$  = 0.0591 V Faraday constant (F) = 96500 Cmol<sup>-1</sup> Plank's constant (h) =6.63x10<sup>-34</sup> Js, Velocity of light(C) = 3x10<sup>8</sup> ms<sup>-1</sup>, Mass of electron=9.1 x10<sup>-31</sup> kg,  $\varepsilon_0$  = 8.854 x 10<sup>-12</sup> C<sup>2</sup>N<sup>2</sup>m<sup>-2</sup>,  $e = 1.602 \times 10^{-19}$  C,  $1eV = 1.6 \times 10^{-19}$  J

1) a) *Define* the following terms.

i) Extensive properties ii) Adiabatic process

(10 marks)

- b) i) Write the mathematical expression for the first and second laws of thermodynamics.
  - ii) 2 moles of an ideal gas ( $C_{\nu} = 2.5 \text{ R}$ ) is maintained in a volume of 11.2 dm<sup>3</sup> at 273 K. The temperature of the gas is raised to 373 K. *Calculate w*,  $\Delta U$ , q, and  $\Delta H$  at constant volume
  - iii) Calculate the work done for an isothermal reversible expansion of 3 moles of Hydrogen gas from volume 2 dm<sup>3</sup> to 100 dm<sup>3</sup> at 273 K, which obeys to the equation of state  $P(v - \beta) = nRT$  where  $\beta$  is a constant and its value is 0.015 dm<sup>3</sup>.

(50 marks)

Contd.

c) i) Using the first and second laws of thermodynamics *show that* the entropy change (a on heating of 'n' moles of substance reversibly from temperature T<sub>1</sub> to T<sub>2</sub> at construction volume is,

$$\Delta S = C_{v} \ln\left(\frac{T_{2}}{T_{1}}\right)$$

Assume that  $C_{v}$  is independent of temperature.

ii) Calculate the entropy change ( $\Delta$ S) of 2 moles of an ideal gas ( $C_v = 2.5$  R) at 27<sup>°</sup> heated to 127<sup>°</sup> C

(20 mar

(20 mar)

d) Show that the following auxiliary relations for a reversible process.

i) 
$$dA = -SdT - PdV$$

- ii) dH = TdS + VdP
- 2) a) i) By using A = A(V,T), derive the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

iii) Using the above Maxwell relation, derive the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_{T} = T \left(\frac{\partial P}{\partial T}\right)_{V} - P \qquad (Hint: dU = TdS - PdV)$$

iii) Show that for an ideal gas  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ 

(30 mar

b) The following redox reaction occurs in a cell:

$$Mg(s) + Sn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Sn(s)$$

- i) Write the half-cell reactions.
- iii) Represent the electrochemical cell
- iv) Calculate the standard electrode potential  $E_{cell}^{\sigma}$  for this cell at 298 K.
- v) Calculate the change in standard Gibb's free energy ( $\Delta G^{\circ}$ ) at 298 K.

$$(E_{Mg^{2+}, Mg}^{\theta} = -2.37 \text{ V}, E_{Sn^{2+}, Sn}^{\theta} = -0.14 \text{ V})$$

Contd.

(40 mar

e) *Predict* the product(s) obtained from addition of singlet dichlorocarbene (Cl<sub>2</sub>C:) to each of the following compounds



5 a) The photo-electric effect has many practical applications. A photocell, such as the one below used in burglar alarm systems.



Ultraviolet light of wavelength 100 nm is used to illuminate the photocell. When a person interrupts the ultraviolet beam, the sudden drop in current activates a switch, which sets off the alarm.

- i) Define the terms 'threshold frequency', 'work function' and 'photoelectric effect'.
- ii) The work function of the metal used as a cathode in the photocell is  $8.7 \ge 10^{-19}$  J. *Calculate* the velocity at which the electrons are emitted.
- iii) What conclusion about the nature of light is drawn from the photoelectric effect?

(30 marks)

b) Briefly describe the following,

- i) Fajan's rules for chemical bonding
- ii) Non-valence cohesive forces
- iii) Dalton's atomic theory

(30 marks)

c) Briefly explain the postulates of Bohr Theory?

(20 marks) Contd.

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- d) What does Heisenberg's uncertainty principle say about an electron in an atom?
- 6 a) *Write* the four quantum numbers for each of seven electrons in nitrogen atom in the ground state.

(20 marks)

(20 marks)

b) *Describe* the bonding in  $CH_3^+$  using the valence-bond theory.

(20 marks)

- c) Explain the reasons for the following,
  - (i) Covalent bonds are directional bonds while ionic bonds are non-directional.
  - (ii) Water molecule has bent structure whereas carbon dioxide molecule is linear.

(30 marks)

d) The following questions pertain to the nitric oxide (NO) molecule,

i) *Draw* the molecular orbital energy diagram for this molecule. *Label* all of the orbitals specifically.

- ii) Write the molecular electron configuration for the molecule
- iii) Indicate whether the species is paramagnetic or diamagnetic
- iv) Determine the bond order for the molecule

v) Compare the relative stability of this molecule to NO<sup>+</sup> and NO<sup>-</sup>

(30 marks)

## End of paper