Marks Scored:

KATHMANDU UNIVERSITY
End Semester Examination
February/March, 2019

Level: B.E./B.Sc./B. Pharm./B. Tech. Course : CHEM 101
Year : I Semester: I

Exam Roll No. : Time: 30 mins. F. M. : 20

Registration No.: Date 17 FEB 2019

SECTION "A"
[20 Q × 1 = 20 marks]

Select the most appropriate answer.

1. For a reaction: $CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$; $\Delta H^\circ_{298} = -67.64$ kcal. where Cp (CO) = 6.97 ca/mole.deg, Cp (O_2) = 7.05 ca/mole.deg and Cp (CO_2) = 8.96 ca/mole.deg. Then, ΔH° at 398 K is given by:
[ ] - 60.64 kcal [ ] - 64.80 kcal [ ] - 65.78 kcal [ ] - 67.79 kcal

2. If the equilibrium constants of the following equilibria, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ and $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2} O_2(g)$ are K_1 and K_2 respectively. Which of the following relation is correct?
[ ] $K_2 = [1/K_1]$ [ ] $K_2 = [K_1]^2$ [ ] $K_2 = [1/K_1]^2$ [ ] $K_1 = [1/K_2]^3$

3. The evaporation of liquid water to form water vapor at 1 atm pressure above the temperature of boiling is....., if enthalpy change is 9710 cal and entropy change is 26 eu.
[ ] a spontaneous condensation process [ ] an irreversible process
[ ] an exothermic process [ ] a reversible process

4. Which one of the following is an example of chain branching reaction?
[ ] $O_2 + M \longrightarrow 2O^\cdot$ [ ] $OH^\cdot + H_2 \longrightarrow H_2O + H^\cdot$
[ ] $O_2 + H^\cdot \longrightarrow OH^\cdot + O^\cdot$ [ ] $2HO_2 \longrightarrow H_2O_2 + O_2$

5. If the reaction is: $2MnO_4^- + 5C_2O_4^{--} + 16\,H^+ \rightleftharpoons 2Mn^{++} + 10CO_2 + 8H_2O$ then milliliters of 0.10M $KMnO_4$ required to react completely with 0.05 mole of oxalate ion is:
[ ] 100 ml [ ] 150 ml [ ] 200 ml [ ] 250 ml

6. Which one of the following is correct if 150 mL of 0.10 M $Pb(NO_3)_2$ is mixed with 100 mL of 0.20 M NaCl ? (**Given**, $PbCl_2(s) \longrightarrow Pb^{2+}(aq) + 2\,Cl^-(aq)$; Ksp = 1.2×10^{-5})
[ ] $PbCl_2$ will be in soluble form in solution [ ] $PbCl_2$ will precipitate from solution
[ ] $PbCl_2$ will not precipitate from solution [ ] $PbCl_2$ will precipitate and be soluble

7. Which one of the following salt has higher solubility in water?
[ ] BaF_2 (Ksp= 1.7×10^{-6}) [ ] CaF_2 (Ksp = 1.7×10^{-10})
[ ] $ZnCO_3$ (Ksp = 2×10^{-10}) [ ] $AgBrO_3$ (Ksp = 5.2×10^{-5})

8. If the solubility of Ag_2CrO_4 in pure water is 0.78×10^{-4} M then its solubility in 0.05 M $AgNO_3$ is:
[ ] 7.9×10^{-8} M [ ] 2.8×10^{-9} M [ ] 7.2×10^{-7} M [ ] 7.6×10^{-10} M

9. What is the significance of the Third Law of Thermodynamics?
   [ ] The absolute entropy of a substance decreases with increasing temperature
   [ ] The change in entropy of the universe must be positive for a spontaneous process
   [ ] The absolute value of entropy can be measured for some very pure substances
   [ ] The change in entropy of the universe equals the sum of the change in entropy of the system plus the change in entropy of the surroundings

10. In galvanic cell, which statement is true?
   [ ] Electrical energy produces the chemical reaction
   [ ] Oxidation occurs at cathode
   [ ] Chemical reaction produces the electrical energy
   [ ] Reduction occurs at anode

Fill in the blanks with most appropriate value or word.

11. For a reaction, A + B $\rightarrow$ C, the rate law is; $\frac{d[C]}{dt} = K[A]^2[B]^2$ On doubling the concentration of A and B, the rate of reaction increases by a factor of.....

12. In the given reaction, $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$, ... is favored by increasing the pressure.

13. One of the most outstanding example of .....catalysis is hydrogenation of unsaturated organic compounds.

14. The pH of a 0.2 M aqueous solution of NaCN is..... (Given, K_a for HCN = 4.0 $x10^{-10}$ and $K_h = 2.5\ x10^{-5}$).

15. The cell which can be used once but cannot be restored to nearly new condition by reversing the current flow is called..... .....

16. A certain sulfide of iron contains 46.5% iron by weight. Then, the empirical formula of the compound is .....

17. Molarity of 5.0 m ethanol solution (Density of solution = 0. 95 g/mL) is .....

18. The enthalpy change is numerically equal to the heat absorbed (q_p) when the reaction is carried out at..... .....

19. The entropy change (ΔS) at constant molar heat capacity (C_p) for 'n' moles of any material from T_1 to T_2 is given by.....

20. For the reaction, NOBr (g) $\rightleftharpoons$ NO (g) + ½ Br_2 (g); Kp = 0.15 at 350 K. If the mixture consists of 0.50 atm. of NOBr, 0.40 atm of NO and 0.20 atm. of Br_2 at the same temperature, then net reaction will be .....

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SECTION "B"

Attempt *ANY FIVE* questions. (**Q. N. 1 is compulsory**)

1. a. Consider the galvanic cell constructed by connecting two half cells at 25^0C

$Fe^{+++} + e^- \longrightarrow Fe^{++}$, $\varepsilon^0 = 0.771$

$I_3^- + 2e^- \longrightarrow 3I^-$, $\varepsilon^0 = 0.536$

Answer the following questions. [4 × 1= 4]

i. Write down the spontaneous cell reaction for the combination of two electrodes.
ii. Calculate the standard cell potential.
iii. Which electrodes become negatively and positively charged? Give the reason.
iv. What would be the effect on cell voltage if concentrations of reactant and product vary?

b. Ammonia generates hydroxyl ion in the aqueous solution according to the reaction;

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$; $Ka = 1.8 \times 10^{-5}$

Calculate the concentration of NH_3, NH_4^+, H_3O^+ and OH^- in a solution prepared from 0.01 moles of ammonia and one litre of water. [3]

2. a. Consider the following reaction.

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2$; Equilibrium constant (Kp) = 2.4

Answer the following questions. [4 × 1 = 4]

i. Predict the effect of introduction of inert gas in the equilibrium of the reaction.
ii. Calculate the equilibrium pressure of SO_2Cl_2, SO_2 and Cl_2.
iii. Calculate the fraction dissociated if 1.53 atm. of un-dissociated SO_2Cl_2 is present in 1L vessel initially.
iv. What will be the fraction dissociated if 1 atm. of Cl_2 is added in (iii) externally?

b. Derive the relation, Cp = Cv + R, where symbols have their usual meanings. [2]

3. a. Complete and balance the following redox reactions by ion-electron method. [2 × 1.5=3]

i. $H_2O_2 + I^- \longrightarrow I_2 + H_2O$ (Acidic solution)

ii. $ClO^- + CrO_2^- \longrightarrow CrO_4^{--} + Cl^-$ (Basic solution)

b. Define 'equilibrium state'. Explain liquid vapour equilibrium with their major features. [1+2=3]

4. a. Show different conditions of spontaneity in terms of free energy change. Calculate the value of equilibrium constant (K) for the reaction, $NO + O_3 \rightleftharpoons NO_2 + O_2$ and correlate the value of K with product formation. (Given, $\Delta G^0 = -47.3$ kcal.) [3]

b. Ethanol and methanol form a solution that is very nearly ideal. The vapor pressure of ethanol is 44.5 mm and that of methanol is 88.7 at 20°C. (a) Calculate the mole fractions of methanol and ethanol in a solution obtained by mixing 60 gm of ethanol with 40 gm of methanol. (b) Calculate the partial pressures and the total vapor pressure of this solution and the mole fraction of ethanol in the vapor. [3]

5. a. Consider that a solution of hydrogen sulfide has been added slowly to a mixture of solution containing both Zn^{++} and Fe^{++} at 0.1M concentration in order to carry the selective precipitation. [4 × 1= 4]

Answer the following questions.

i. Define the terms, selective precipitation and solubility product.

ii. Which salt precipitates out first and why?

iii. Find the concentration of S^{--} ion when first and second salts just start to precipitate.

iv. Find the concentration of cation of first precipitate when the second salt just starts to precipitate. (Given, Ksp for $[Zn^{++}][S^{--}] = 4.5 \times 10^{-24}$ and Ksp for $[Fe^{++}][S^{--}] = 1.0 \times 10^{-19}$)

b. 'Entropy is a measure of the number of microscopic states associated with a particular macroscopic state'. Give the reasonable explanation. [2]

6. a. The proposed reaction mechanism for the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is

$$N_2O_5 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_3 + NO_2 \xrightarrow{K_2} NO + NO_2 + O_2$$

$$NO_3 + NO \xrightarrow{K_3} 2NO_2$$

Where, K_1, K_{-1}, K_2 and K_3 are rate constants respectively.

Answer the following questions.

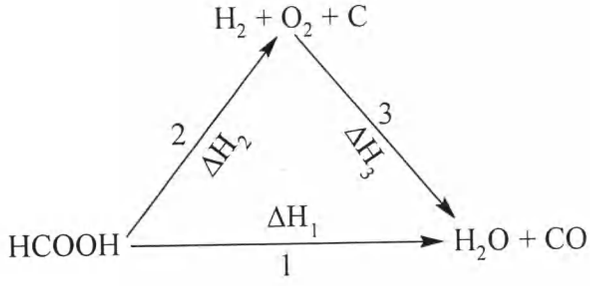
i. Derive the differential rate law for the above reaction with help of steady-state approximation. [2]

ii. What is the overall order and molecularity of the reaction? [1]

b. State the Avogadro's number. A sample of an unknown oxide of barium gave upon exhaustive heating 5gm of pure BaO and 366 cc of oxygen gas measured at 273.1 K and 1 atm-pressure. What is the empirical formula of the unknown oxide? What weight of oxide was present initially? (Given, atomic weight of Ba = 137.33) [0.5+2.5= 3]

7. a. Show that the logarithm of reactant concentration decreases linearly as time increases for a reaction following first order kinetics. Also correlate half-life period with the initial concentration of reacting species for this reaction. [2+1= 3]

b. Define the term 'standard enthalpy of formation'. Calculate the standard enthalpy change (ΔH^0) for the reaction; HCOOH *(l)* = CO *(g)* + H_2O *(l)*
(Where, ΔH^0_f (CO) = -26.41kcal/mole, ΔH^0_f (H_2O, l) = -68.32 kcal/mole and ΔH^0_f (HCOOH, l) = -97.8 kcal/mole) [3]



Alternative paths for conversion of reactant to product

SECTION "C"

[3Q × 8 = 24 mark]

Attempt *ANY THREE* questions.

8. a. Define the term 'buffer solution'. Derive a Henderson's equation for acidic buffer solution and also mention its significance. [1+3=4]
   b. What do you mean by 'Enzyme Catalysis'? Discuss the mechanism for enzyme catalysis given by Michaelis-Menten equation. Also predict the kinetics with respect to substrate and enzyme. [1+3=4]

9. a. Establish the relation, $K = 10^{\Delta So/2.3R} \times 10^{-\Delta Ho/2.3RT}$ where symbols have their usual meanings. Predict relation of 'K' with ΔS^0 and ΔH^0 in terms of molecular chaos and minimum energy. [3+1=4]
   b. What is a 'Galvanic cell'? 'The standard cell potential (ΔE^0) represents the driving force of a chemical reaction occurring in any electrochemical cell'. Describe clearly. [1+3=4]

10. a. Define the 'boiling point elevation'. Deduce a relation to show the dependence of the boiling point on concentration. [1+3=4]
    b. State and explain the second law of thermodynamics. Establish a relation for entropy change for any reversible isothermal expansion of an ideal gas. [2+2=4]

11. a. Deduce a relation between standard free energy change and standard cell potential for any operating system which is an electrochemical cell. [4]
    b. Define the term 'acid- base indicator'. How do you predict the end point in the different acid base titrations by using the appropriate acid-base indicators? [1+3=4]

12. Write short notes on (*ANY TWO*) [4 × 2 = 8]
    a. Non-ideal solution showing negative deviation
    b. Corrosion and ways to prevent corrosion
    c. Molecularity and order of reaction
    d. Different concepts of 'Acids and Bases'

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SECTION "A"
[20 Q × 0.5 = 10 marks]

Choose the correct answer:

1. The Ice Age is colloquially reffered as:
   a) Neolithic b) Mesolithic c) Paleolithic d) Pleistocene

2. The prehistoric settlement where access from roof were used for the circulation between dwellings is:
   a) Catal Huyk b) Jericho c) Khirokitia d) Skara Brae

3. The stepped pyramid is tomb of Egyptian Pharaoh:
   a) Khufu b) Khafra c) Menkaura d) Zoser

4. The bent pyramid is typical pyramid with angle of inclination at lower part.... and upper part...:
   a) 54.4^{o} & 43.9^{o} b) 60.5^{o} & 50.5^{o} c) 65.8^{o} & 53.5^{o} d) 43.9^{o} & 54.4^{o}

5. A richly carved stone coffin placed inside Egyptian pyramid is:
   a) Hieroglyphs b) Mummy c) Cenotaph d) Sarcophagus

6. The rare vestibule of classical Greek temple is:
   a) Naos b) Pronaos c) Epinaos d) Narthex

7. In Acropolis of Athens, Parthenon is temple having :
   a) Hexastyle b) Octastyle c) Decastyle d) Heptastyle

8. The capital of Composite order is combination of :
   a) Doric and Ionic b) Tuscan and Ionic
   c) Corinthian and Ionic d) Corinthian and Tuscan

9. This front part of the Roman ancient theater upon which the actors performed is:
   a) Proscenium b) Skene c) Parados d) Parascenium

10. Pendentive Dome and dome on pendentive is contribution of:
    a) Roman period b) Byzantine period c) Greek period d) Egyptian period

11. The dome of Hagia Sophia is constructed over:
    a) Rectangular Plan b) Square plan c) Circular plan d) Hexagonal plan

12. Which of of the following was not the standard architectural feature of Gothic Architecture:
a) Pointed Arch b) Tall spires c) Hypostyle hall d) Flying buttress

13. What city served as the intellectual, financial, and artistic center of Renaissance Italy throughout most of the 1400s?
a) Milan b) Rome c) Venice c) Florence

14. Saint Mark's Bascillica, Venice is finest example of :
a) Gothic style b) Byzantine style
c) Early Christian Style d) Renaissance Style

15. High Renaissance is also known as:
a) Neoclassical b) Quattrocento c) Mannerism d) Baroque

Fill in the blanks.

16. The roofed open arcade often seen on the north side of ancient Egyptian house is .....

17. The room reserved for male to entertain male guests in ancient Greek house is .....

18. The name given to the structure of female figures used in Greek Temples Erectheion is .....

19. Any building with circular ground floor plan and sometime covered with dome is .....

20. The High Renaissance style in Rome began with the work of .....

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SECTION "B"
(Short answer questions)
[10Q × 2 = 20 marks]

Students are encouraged to support their answers with necessary figures, illustration and drawings. Attempt *ANY TEN* questions.

1. Neolithic settlement of Skara Brae
2. Gallery grave of Neolithic period
3. Tomb of Pharaoh Khufu
4. Mortuary temple of Queen Hatshepsut
5. Erechtheion
6. Roman Thermae
7. Pisa Cathedral
8. Norte Damn, Paris
9. Milan Cathedral
10. Saint Basil cathedral, Moscow
11. Tempietto, Rome
12. The Pantheon

SECTION "C"
(Long answer questions)
[4Q × 5 = 20 marks]

13. Describe the different types of Temple constructed in the history of Egypt. Explain them in details.
14. Explain how did the evolution of Temple Architecture evolved in the Greek History? Discuss its special features such as proportion and Optical Refinement

OR

What are the major differences between Greek and Roman Theater? Explain in detail all the parts of Greek theater.

15. Discuss the different types of dwelling structures constructed during the Roman period in terms of their technology and material.

OR

What are the social factors behind the development of entertainment / leisure structure during the Roman period? Discuss in brief any two types of entertainment structures.

16. What were the major architecture typologies that emerged during the Romanesque period? Explain in detail the general characteristics of Romanesque church with necessary figure and diagram.