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Q.P. Code 00064491

Physical Chemistry II (model answers)

1. **Attempt all questions.**
2. **All questions carry equal marks.**
3. **Draw neat labelled diagram wherever necessary.**
4. **Use of log table & non programmable calculator is allowed.**
5. **For Q.2,Q.3 & Q.4 attempt A&B OR C&D**

Do as directed. **15M**

Define the following terms

1. **System**-part of the universe which is under thermodynamic study.

2.**Adiabatic wall-** the boundary/wall which is non-conductor of heat and thus prevents the exchange of heat between system and surrounding.

3. **Exothermic reaction**- a reaction in which heat is evolved when reactants are converted into products.

4.**Unimolecular reaction** :One molecule breaks up into smaller parts the reaction is called Unimolecular reaction .

5. **Chemical kinetics** : Chemical kinetics deals with the rate at which chemical reactions take place & mechanism by which reaction takes place.

6. **Redox reaction** The reaction in which oxidation and reduction occurs simultaneously are called redox reaction.

7.**Reduction** It is a process which involves the addition of hydrogen or other electropositive element, or removal of oxygen or any other electronegative element.

Fill in the blanks

8.Enthalpy of the system is represented by symbol-**H**

9.If work is done by the system, w is **Negative.**

10.S.I. unit of internal energy is **Joules.**

11.In Second order reaction, the rate of the reaction is proportional to the product of **two** concentration .

12.The minus sign indicating that concentration of the reactant **decreases** with time.

Name the following-

13.A process in which volume of the system remains constant- **Isochoric process.**

State true or false

14.Decomposition of hydrogen peroxide is an example of first order reaction. **True**

15.The half time require to complete reaction is same for first & second order reaction. **False**

16.An element that loses an electron to another chemical species in a redox chemical reaction is known as reductant. **True**

Balance the following reaction.

17. $Fe_3O_4 + C \longrightarrow Fe + CO$

$Fe_3O_4 + 4C \longrightarrow 3Fe + 4CO$

18. $S + HNO_3 \longrightarrow SO_2 + NO_2 + H_2O$

$S + 4\,HNO_3 \longrightarrow SO_2 + 4\,NO_2 + 2H_2O$

Give one word for the following

19.A chemical reaction in which reactant involve more than one phase is called as **Heterogeneous reaction.**

20..A molecule that gain electrons. **Oxidant or oxidizing agent.**

Q2. A. i) Depending on the nature of the boundary, the systems are classified as 4M

a) Isolated system- system can neither exchange matter nor energy with the surrounding is called isolated system. The boundary prevents any interaction with the surrounding. E.g. boiling water kept in thermos tightly closed from top.
b) Open system- if matter and energy both can pass across the boundary, the system is called open system. E.g. hot water kept in a beaker placed on a table.
c) Closed system- if only energy can be exchanged across the boundary with its surrounding and not the matter, the system is called closed system. E.g. hot water in equilibrium with its vapour kept in a sealed metallic container.

Q2. A ii) a) q=0 since process is adiabatic

b) gas expands against external pressure, 4M

$w = -P(\Delta V)$

$= -1\ (8-2) = -6.0\ dm^3.atm$

As 1 atm= 101.325 Pa, w= -6x 101.325= - 607.95 J

$\Delta E = q + w = 0 + (-607.95) = -607.95\ J$

Q2. B. The major driving force for spontaneous processes is the change in randomness or disorder of a system which is known as entropy. Entropy is defined as a measure of disorderness of a system. The tendency of every spontaneous process is to attain the state of 7M equilibrium where entropy of the system becomes maximum. The entropy of solid is less than that of liquid and entropy of liquid is less than that of gas.

Characteristics –

i) Entropy is a thermodynamic state function. Its value depends upon pressure, volume and temperature of the system.
ii) It is denoted by symbol S.
iii) Δ S is positive if heat is absorbed and is negative if heat is lost by the system.
iv) In a reversible adiabatic process dq rev=0 therefore Δ S =0. The process is called isoentropic process.
v) Entropy is an extensive property and its value depends on quantity of the system.
vi) Units of entropy are Joules per Kelvin.
vii) Units of molar entropy are Joules per Kelvin per mole.

OR

Q2. C. Carnot proposed a hypothetical heat engine to demonstrate the maximum 8M

convertibility of heat into work. The heat engine consists of i) a cylinder fitted with weight frictionless piston.

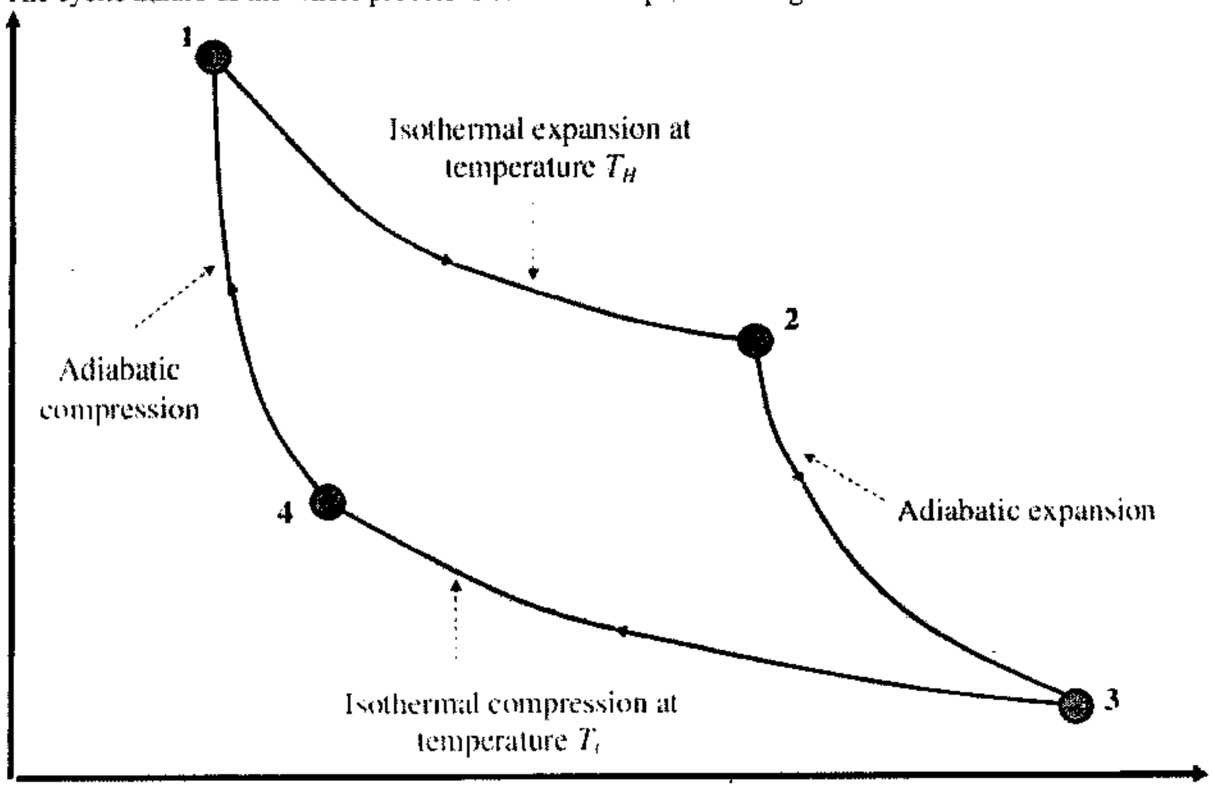
ii) one mole of ideal gas placed in the cylinder. Iii) Hot reservoir (source of heat) at temperature $Ø_2$

Iv) cold reservoir (sink of heat) at temperature $Ø_1$ v) Insulator.

The gas in the cylinder is subjected to four successive steps as follows-

i) Isothermal expansion
ii) Adiabatic expansion.
iii) Isothermal compression.
iv) Adiabatic compression.

The cyclic nature of the whole process is seen with help of P-V diagram



Step 1-

The container is paced on hot reservoir at T2 K and one mole of gas in the cylinder is allowed to expand isothermally reversibly from volume V1 to V2. On account of sudden expansion, the gas cools. In order to maintain the isothermal conditions, q2 quantity of heat is taken from the source. Since it is isothermal process, $\Delta E = 0$ if q2 is the heat absorbed by the gas and w is the work done by it. according to first law, $\Delta E_1 = q_2 - w_1$

The isothermal expansion is shown by curve AB

Step 2-

The cylinder is then removed from the hot reservoir and insulated perfectly. The gas is now allowed to expand reversibly and adiabatically from volume V2 to V3. since no heat is transferred, q= 0.

The gas uses its internal energy for expansion. As a result temperature of gas falls to T1 K. the work done w2 is given by $\Delta E = q - w$,q=0

$\Delta E_2 = -w_2$

Step 3-

Insulation is removed and cylinder is placed on cold reservoir. The gas is compressed isothermally reversibly at temp T1 , from volume V3 to V4. During compression the temperature of the gas increases. In order to maintain isothermal conditions ,q1 quantity of heat is transferred to the sink and w3 is the work done on the gas.

$\Delta E_3 = -q_1 - w_3$

Step 4-

The cylinder is removed from cold reservoir and insulated again. The gas is then compressed adiabatically reversibly from V4 to V1so that the system returns to its initial state. This being an adiabatic process , q=0 and the work done w4 is given by

$\Delta E4 = -w_4$

The total change in internal energy is

$\Delta E = \Delta E1 + \Delta E2 + \Delta E3 + \Delta E4$

$= (q2-w1) + (-w2) + (-q1-w3) + (-w4)$

$= q2-w1-w2-q1-w3-w4$

$= (q2-q1) - (w1+w2+w3+w4)$

$= (q2-q1) - w_m$

For cyclic process, $\Delta E=0$

i.e. $w_m = q2-q1$

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Q2.D. Objectives 7M

i) It helps to predict the feasibility of chemical processes under given set of conditions of temperature , pressure and volume.
ii) It tells us the extent to which a chemical reaction can occur after its feasibility is =
iii) It helps to formulate the conditions for a chemical process to provide better yields of the product.
iv) To deduce some important generalization of physical chemistry.

Limitations-

i) It is applicable to macroscopic systems only.
ii) It fails to predict rate of reaction.
iii) It can not explain mechanism of reaction.
iv) It can predict possibility of a process not its success as it does not take into account a obstacles in the path.

Q.3 A)Derive integrated rate equation for first order reaction. 8M

In a first order reaction the rate of reaction is directly proportional to the concentration of the reacting substance . It may be represent as

A --------------> Products

If a is the initial Molar concentration of the substance &x is the amount reacting in time t is . then amount remaining after time t is (a-x)

$dx/dt \propto (a-x)$

$dx/dt = k(a-x)$

by taking integration

$\int dx / a - x = k \int dt$

$-\ln(a-x) = kt + k'$

When t =0, x = 0 then ,

$-\ln a = k'$

Hence, $K = 2.303/t \times \log_{10}(a/a-x)$

This is equation for first order reaction

Q.3 B) Discuss the kinetic characteristics of second order reaction . 7M

There are three kinetic characteristics of second order reaction

(i) Unit of rate constant k

(ii) Time to complete definite fraction of reaction.

(iii)Graphical interpretation.

Describe each characteristics.

OR

Q.3 C) Show that for first order reaction time to complete first order reaction is independent of initial concentration. 8M

According to first order reaction ,

K = 2.303 /t X $\log_{10}$(a /a-x)

Rearranging the equation

t = 2.303 /k X $\log_{10}$(a /a-x)

when x = a/2 & t = $t_{1/2}$

$t_{1/2}$ = 2.303 /k x $\log_{10}$ a/(a-a/2)

$t_{1/2}$ = 0.693 /k

Thus , the half time for a first order reaction is a constant & independent of initial concentration

Q.3 D)A second order reaction with equal initial concentration is 66.67% complete in 2 hours Calculate specific reaction rate. 7M

According to second order reaction ,

K = 1/at . x/(a-x)

Solution :

a = 100 , x = 66.67 , a-x = 33.33 , t = 2 hrs = 120 min

K = 1/(100x120) x (66.67/33.33)

K = 8.33 x 10^{-5} x 2.00

K = 16.66 min^{-1}

Q.4A) Justify oxidation and reduction reaction proceed side by side. 8M

Oxidation and reduction reactions always proceed side bv side and are always complementary in nature. Whenever a substance undergoes oxidation, another substance undergoes reduction. This is also true vice versa.

Example

1. $HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$

In this reaction $SnCl_2$ is oxidized to $SnCl_4$ and $HgCl_4$ is reduced to $HgCl_2$.

2. $Br_2 + H_2S \longrightarrow HBr + S$

In this reaction H_2S is oxidized to S and Br is reduced to HBr.

3. $Cl_2 + H_2S \longrightarrow 2HCl + S$

In this reaction H_2S is oxidized to S and Cl_2 is reduced to HCl_2.

Q.4B) Write the balanced chemical equation of following reaction. 7M

$$Cr_2O_7^{-2} + Fe^{+2}(aq) \longrightarrow Cr^{+3}(aq) + Fe^{+3}(aq)$$

Step 1 to 6 all reaction with equation

Overall balanced reaction

$$Cr_2O_7^{-2} + 6\,Fe^{+2} + 14\,H^+ \longrightarrow 2\,Cr^{+3} + 6\,Fe^{+3} + 7\,H_2O$$

OR

Q.4C)Explain the ion electron method of balancing equations. 8M

[illegible] ion electron method [illegible] called the half reaction method [illegible] two half equations [illegible] oxidation [illegible] reduction [illegible] balanced separately and then combined [illegible] the balanced redox equation.

[illegible] for balancing redox equations

Step 1 [illegible]

Step 2 Separate the redox reaction into half reactions

a) Assign oxidation numbers for each atom

b) Identify and write out all redox couples in reaction

c) Combine these redox couples into two half-reactions

Step 3 Balance the atoms in each half reaction

a) Balance all other atoms except H and O

b) Balance the oxygen atoms with H_2O

c) Balance the hydrogen atoms with H^+

d) In a basic medium, add [illegible] OH^- [illegible] H^+

Step 4 Balance the charge with e^-

Step 5 Make electron gain equivalent to electron loss in the half reactions

Step 6 Add the half-reactions together

Step 7 Simplify the equation

Finally, check that the elements and charges are balanced

Q.4D)What are addition reactions? Explain using suitable examples. 7M

An addition reaction, in [illegible] chemistry, is in its simplest terms an organic reaction where two [illegible] molecules combine to form a larger one (the adduct).

Addition reactions are limited to chemical compounds that have multiple bonds, such as molecules with carbon-carbon double bonds (alkenes), or with triple bonds (alkynes). Molecules containing [illegible] double bonds like carbonyl (C=O) groups, or imine (C=N) groups, can undergo [illegible] have double bond character.

An addition reaction is the reverse of an elimination reaction. For instance the hydration of an alkene to an alcohol is reversed by dehydration.

There are two main types of polar addition reactions: electrophilic [illegible] and nucleophilic addition. Two non-polar addition reactions exist as well, called [illegible] addition and cycloadditions. Addition reactions are also encountered in polymerizations and called addition polymerization. *(any example)*

....

(6)

Q.5 Write a short note on (any three) 15M

a) **Zeroth law of thermodynamics**

Consider two closed systems A and B in which temperature of A is greater than temperature of B. if the two systems are brought together and physically joined but kept separate from each other , despite the connection, matter will not be exchanged between the two systems , but energy transfer will take place . the temperature will change until $T_A = T_B$. At this point the two systems are said to be in thermal equilibrium. The transfer of energy from one system to another due to temperature difference is called heat. If a third system C temperature T_C is in thermal equilibrium with system A, then system C must be in thermal equilibrium with system B also. This is zeroth law of thermodynamics.

Statement- if of the three systems A,B,C, A and B are separately in thermal equilibrium with C , then A and B are also in thermal equilibrium with one another.

b) **Graphical method for determining order of reaction.**

The expression for rate constant for first order reaction can be rearranged as ,

$\log_{10}(a-x) = -kt/2.303 + \log_{10} a$

this equation is a type of y =mx +c, for a given reaction , the value of a & a-x at different values of t are evaluated from the experimental observations . If plot of $\log_{10}(a-x)$ against t is a straight line with negative slope &intercept on y axis then order of reaction will be one

Give representation of graph

For second order reaction for equal initial concentration

$1/a-x = kt + 1/a$

This equation is of type y = mx+c according to which plot of 1/a-x against t is straight line with positive slope equal to k &intercept on y axis gives the value of 1/a.

Give representation of graph

c) **Order of reaction :**

The way in which the rate of reaction varies with concentration ns of reacting substances is generally indicated by the order of reaction .

The number of molecules (or atoms 0 whose concentration determine the rate of the reaction is called the order of reaction it is experimentally found that the rate of a chemical reaction is proportional to the n_A th power of reactant A n_B th power of reactant B & so on then ,

Rate of reaction = $k\, C_A^{nA} \times k\, C_B^{nB} \times$ ---------

Where k is proportionality constant & overall order of reaction

$n = n_A + n_B +$-------------

Give examples of first & second order reactions

d)Write a note on oxidizing agents.

Oxidising agent is any substance that supplies oxygen or any other electronegative element Or an Oxidising agent may remove hydrogen or any other electropositive element.

Oxidising agent is also called as Oxidant. Oxidising agent itself is reduced during the reaction.

Eg. Oxygen, Chlorine, fluorine, H_2O_2 , potassium permanganate, potassium dichromate and Ozone are oxidising agents.

$Mg + O_2 \rightarrow 2\ MgO$

$Mg + Cl_2 \rightarrow MgCl_2$

$2H_2S + O_2 \rightarrow 2S + 2H_2O$

e)Calculate oxidation number of C in CO_2 and S in H_2S

i) C in CO_2

Let the oxidation number of C in CO_2 be x.

The sum of oxidation number of various atoms in CO_2=x+2(-2)=x-4

But the sum of oxidation number of various atoms in CO_2(neutral) is Zero...(rule 7)

Therefore x-4=0 OR x=+4

Thus oxidation number of C in CO_2 is +4

ii) S in H_2S

Let the oxidation number of S in H_2S be x.

Sum of oxidation number of various atoms in H_2S =2(+1)+x=2+x

But the sum of oxidation number of various atoms in H_2S (neutral) is zero...(Rule 7)

Therefore 2+x=0 OR x=-2

Thus the oxidation number of S in H_2S is -2