PILLAI COLLEGE OF ENGINEERING, NEW PANVEL
(Autonomous) (Accredited 'A+' by NAAC)
END SEMESTER EXAMINATION
SECOND HALF 2021

BRANCH: FE (MECH/AUTO)

Subject: Engineering Chemistry – I Solution **Time: 02.00 Hours**
Max. Marks: 45 **Date: 08-04-2022**

Q.1. Attempt all

a) Give the theory of EDTA titration with relevant equations.

The hard water whose hardness is to be determined is first buffered and few drops of EBT is added. The solution becomes wine red coloured due to the formation of M-EBT complex.

M^{2+} + EBT → M-EBT

In the course of the titration, EDTA which is added from the burette first combines with free Ca^{2+} or Mg^{2+} ions to form a stable colourless M-EDTA complex. After all the free metal ions are consumed, the next drop of the EDTA added displaces the indicator from the M-EBT complex giving the blue colour.

M-EBT + EDTA → M-EDTA + EBT

Thus at the equivalence point there is a colour change from wine red to blue.

Expalnation - 2 M
Equations – 1 M

b) Compare LPG and CNG.

LPG	CNG
composition is Propane = 24.5%, Butane = 38.5 % and iso butane = 37%. To identify the gas leakage some amount of mercaptons are added.	composition of Natural Gas is CH_4 = 70 - 90 %, C_2H_6, C_3H_8, C_4H_{10} = 5- 10 %.
Calorific value is 25,000 kcal/m^3	Calorific value is 12500 kcal/m^3
Less dense than air	More dense than air.
Gas is compressed in the liquid state	Natural Gas is put under high pressure of 1200-1400 atm.

Any three points – 3 M

c) Why does a part of the nail inside the wood undergo corrosion?

When a part of the nail is inside the wood, it develops a condition of differential aeration corrosion. The part of the nail inside the wood is poorly oxygenated and acts as anode, whereas the part of the nail outside will have more access to oxygen and act as cathode.

At anode: : Fe $Fe^{++} + 2e^-$

At cathode $O_2 + H_2O + 2e^{\ominus} \longrightarrow 2OH^{\ominus}$ (reduction)

$Fe + O_2 + H_2O \longrightarrow Fe^{++} + 2OH^-$ or $Fe(OH)_2$

Differential aeration corrosion – 1 M
Anode, cathode – 1 M
Equations – 1 M

d) Define degrees of Freedom. Calculate the degrees of freedom for the following system (i) two partially miscible liquids in the absence of vapour (ii) saturated NaCl solution.

Degrees of Freedom - It is defined as the smallest number of independent variables such as pressure,

	temperature and concentration that must be specified in order to define completely the state of a system. (i)C = 2, P = 2, F = 2 (ii)C=2, P=2, F=2 **Definition – 1 M** **Calculating F - 2 M**
e)	**Give the composition, properties and uses of Wood's metal.** *Composition:* 50% Bi + 25% Pb + 12.5% Sn + 12.5% Cd *Properties:* (i) Melts at 71^0C *Uses:* It is used for fire-alarms, automatic sprinklers, making safety plug for pressure cookers, for making boilers and electric fuses, for soldering, casting for dental works. **Composition – 1 M** **Properties – 1 M** **Uses – 1M**
Q.2.	**Attempt all**
a)	**What is meant by knocking in IC Engines. How is it related to chemical constitution. How knocking can be reduced.** Knocking is also defined as a sharp metallic noise produced in an internal combustion engine and results in a loss of energy. In an I.C.Engine (spark ignition) a mixture of fuel and air is compressed and ignited by an electric spark and the essential chemical reaction is oxidation of hydrocarbon molecules. After the initiation of the combustion reaction by the spark, the flame should spread rapidly and smoothly through the gas mixture and the expanding gas drives the piston down the cylinder. In some cases the rate of oxidation becomes so great so that the mixture gets ignited spontaneously producing a sound called knocking. The rate of oxidation depends on the number of carbon atoms in the molecule, on the structure of hydrocarbon and on the temperature. The temperature in turn depends on the compression ratio i.e., the ratio of the gaseous volume at the end of the suction stroke to that at the end of the compression stroke. Theoretically the power output and the efficiency should increase continuously with increase in C.R. The compression ratio corresponding to the maximum output is called the Highest Useful Compression Ratio. When the C.R is increased beyond this value the fuel gets ignited even before the regular spark. This pre ignition of the fuel ahead of the flame is called Knocking. The knocking tendency depends on the fuel constituents. The tendency to knock decreases in the order: Straight chain hydrocarbons > branched chain hydrocarbons > olefins > cycloalkanes > aromatics Knocking can be reduced by adding antiknocking agents **Explanation – 2 M** **Chemical constitution – 1 M** **Knocking can be reduced – 1 M**
b)	**20 ml of standard hard water (containing 15 g $CaCO_3$ per litre) required 25 ml of EDTA solution for the end point. 100 ml of water sample required 18 ml EDTA solution, while the same water after boiling required 12 ml EDTA solution. Calculate the carbonate and non carbonate hardness. What is the buffer used in this titration and what is its pH?**

	Buffer used is Ammonium chloride – ammonia buffer pH – 9-10 **Problem solution – 4 M** **Buffer & pH – 1 M**

c)	**Explain the rusting of iron with the help of electrochemical theory of corrosion.** According to this theory, there is the formation of a galvanic cell on the surface of metals. Some parts of the metal surface act as anode and rest act as cathode. Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode. The corrosion product is formed on the surface of the metal between anode and cathode. To understand the wet corrosion, let us take the example of corrosion of iron. Oxidation of metal takes place at anode while the reduction process takes place at cathode. By taking rusting of iron as an example, the reaction can be explained as that it may occur in two ways: (i) evolution of hydrogen (acidic medium) and (ii) absorption of oxygen (Neutral or alkaline medium). **At anode:** oxidation occurs. $Fe \longrightarrow Fe^{++} + 2e^-$ **<u>In acidic medium</u>** **At cathode:** ***Case I: Evolution of H_2*** The hydrogen ions (H^+) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (reduction) The overall reaction is $Fe + 2H^+ \longrightarrow Fe^{+2} + H_2$ **In this case, metals react in the** acidic environment and are dissolved (undergo corrosion) to release H_2 gas. All metals above hydrogen in electrochemical series can show this type of corrosion. **<u>In neutral and aerated medium</u>** ***Case II: Absorption of O_2*** This type of corrosion takes place in neutral or basic medium in the presence of oxygen. The following chemical reactions occur at anode and cathode. At anode $Fe \longrightarrow Fe^{++}$ **+ $2e^-$ (oxidation)** At cathode $O_2 + H_2O + 2e^{\ominus} \longrightarrow 2OH^{\ominus}$ (reduction) $Fe + O_2 + H_2O \longrightarrow Fe^{++} + 2OH^-$ or $Fe(OH)_2$ **Equations – 3 M** **Explanation – 3 M**

Q.3.	**Attempt all**
a)	**Explain caustic embrittlement in boilers and how it can be avoided?** Is a form of corrosion due to the high concentration of NaOH in boiler water. It is a fast type of corrosion. The water containing NaOH flows into the inter granular spaces or minor cracks which may be present in the inner side of the boiler. Here water evaporates and caustic soda concentration increases. This soda

attacks the boiler material and dissolves the boiler material as sodium ferrite.

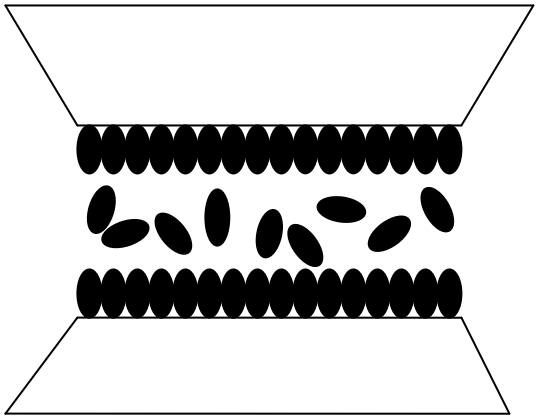
Explanation – 2 M
Equation – 1 M
Prevention – 1 M

b) What type of lubrication is applied in delicate instruments? Explain its mechanism with a neat diagram.

Hydrodynamic or fluid film or thick film lubrication

In this type of lubrication, the lubricant is forming a thick film having about 1000 A^{o} thickness between the moving surfaces so that the direct surface-to-surface contact and welding of junction rarely occurs. The lubricant covers the irregularities of the sliding surfaces and forms a thick layer in between. The coefficient of friction is very low i.e. 0.001 to 0.03 under hydrodynamic lubrication.

When oil is introduced between the moving surfaces, some of the oil molecules are held up tightly at the surface due to adsorption. The remaining oil molecules are loosely arranged away from metal surfaces. The frictional resistance is only due to the internal resistance between the particles of lubricants moving over each other. So the lubricant chosen should have the minimum viscosity and should remain in place and separate the surfaces.



Thick film lubrication

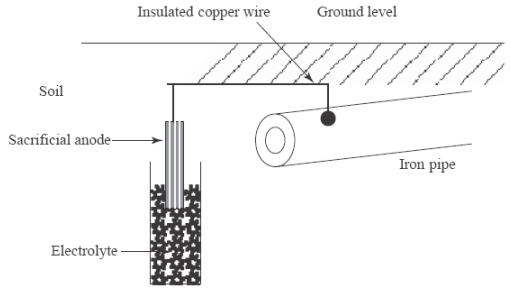
Type of lubrication – 1 M
Mechanism – 3 M
Diagram -1 M

c) Explain the two cathodic protection methods for corrosion prevention.

The principle involved in the process is to force the metal to be protected to behave like cathode and thereby corrosion does not occur. They are of two types:

Sacrificial anode protection method. (galvanic protection method)

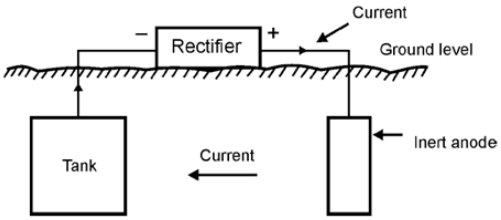
In this method, a more active metal like Zn, Mg is connected to the structure to be protected. The corrosion is concentrated at the more active metal and thus saving the metal structure from corrosion. The more active metal employed is called sacrificial anode. The corroded block can be replaced.



This method is used normally to protect pipelines carrying water or industrial wastes and which are normally embedded under the soil thereby facing the conditions of soil corrosion as well as microbiological corrosion. This is the method of choice where there is no source of electricity and when a completely underground system is desirable .This is most economical method for short term protection because the capital investment is low.

Impressed current cathodic protection

In impressed current method, a current applied in the opposite direction that of corrosion current, thereby nullifying the effect of the latter one on the base metal i.e. converting the base metal to cathode from an anode. Such an impressed current can be obtained by using d.c. source such as battery or dry cell along with an insoluble anode such as platinum, stainless steel, graphite etc.



In this method the insoluble anodic metal used (i.e. platinum, steel, scrap iron etc.)is normally embedded underground. To this, with the help of d.c. current source, the impressed current is applied and whole of this assembly is connected to the metallic structure to be protected. The connections are done by using wires. The insoluble anode is kept inside back-fill made up of gypsum or any such material, which can help in increasing the electrical contact with the soil. Such an anode can be single, if the area of the metallic structure to be protected is small or there can be many such anodes, connected in series if the area of the metallic structure to be protected is wider i.e. long pipeline etc.

Diagram – 2 M

Explanation – 2 M each

Q.4. **Attempt all**

a) **Explain the structure of Graphite. Based on this explain why it can be used as a lubricant.**

Graphite is the most widely used of all solid lubricants. It consists of a layered lattice structure. A layer of hexagonally arranged sp^2 hybridized carbon atoms in the planar graphite molecules bonded covalently. The two neighboring parallel layers are 3.7 A^o apart and are held together by weak vander Waals forces. Therefore the force required to shear layers is very low and the molecules can slip over each other easily by mechanical force. Hence, graphite powder is very soapy to touch or very soft and can act as lubricant.

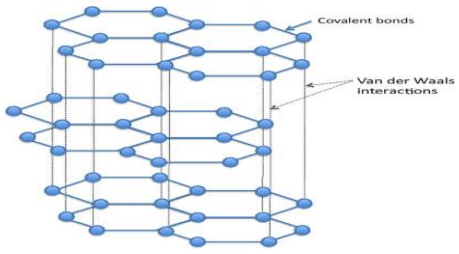


Diagram – 1 M, Explanation – 3 M

b) **Draw a neat labeled phase diagram of water system and explain.**

The diagram consists of,

1. Areas:- AOB, AOC, BOC represents the conditions for vapour, liquid and solid phase respectively. With in these single phase area, the system is bi variant. Therefore from phase rule,

$F = C - P + 2$ (C=1, P=1)

$F = 2$

Hence the system is bivariant.

2. **Curves:- OA, OB, OC, OA'**

The degrees of freedom for these systems where two phases exist in equilibrium, P = 2, C = 1,

F=1

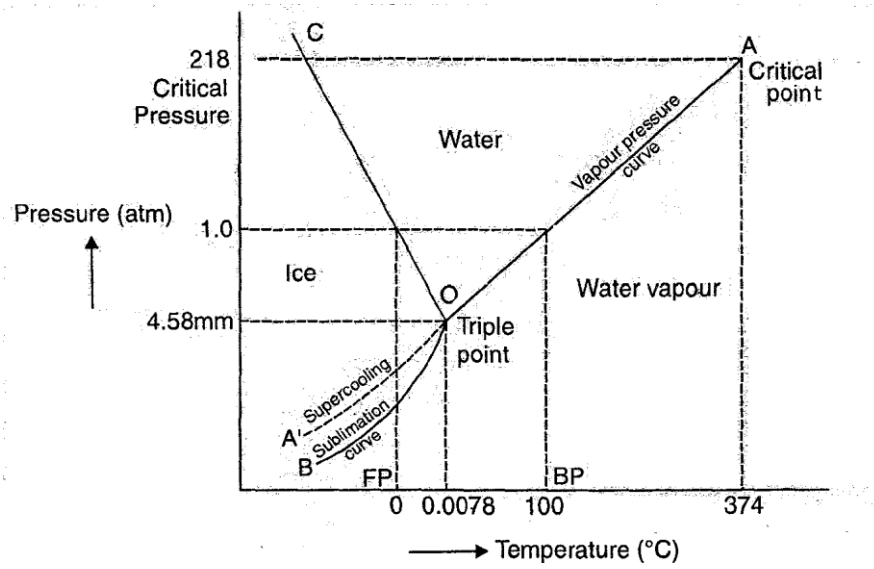
The system is univariant.

i) **Curve OA**: - Separates the liquid region from vapour region and is known as vapourisation curve of water. At any given temperature, there is only one value of pressure at which water vapour is in equilibrium with liquid water and vice versa. Just above the curve the liquid is the stable phase, while below this vapour is the stable phase. The curve OA has an upper limit at 374^{o}C and 218 atm which is the critical point beyond which the liquid phase merges in to vapour phase and are no longer distinguishable.

ii) **Curve OB**:- represents the variation of vapour pressure of solid with temperature. This is the sublimation curve where, solid and vapour are in equilibrium. The curve terminates at B, at -273^{o}C temperature (absolute zero), beyond which the two phases merge into each other.

iii) **Curve OC**:- called the melting (fusion) curve which divides the solid from liquid region. The curve indicates the influence of pressure on the melting point of ice. The curve starts from O and extend to very high values of pressure. The slope of the curve is negative implying that the melting point is lowered by the increase of pressure or ice melts with a decrease in volume.

3. **Triple Point, O** :- The three curves OA, OB and OC meet at O at which solid, liquid and vapour co exist in equilibrium. This point at 273.16K (0.0075^{0}C) and 4.58 mm of Hg pressure is called Triple point. At this point C =1, P = 3. Therefore F = 0. The system is invariant.



Explanation 3 M

Diagram 2 M

c) **A coal sample was found to have the following percentage composition: C = 75%, H = 5.2 %, O = 12 %, N = 3.2 %, and ash = 4.5%.**

(i)Calculate the volume of air required for the perfect combustion of 1 kg of fuel, assuming NTP conditions.

(ii) Also calculate the GCV and NCV of the coal sample.