MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER–18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

Important Instructions to examiners:

1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills).
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

Q No.	Answer	Marking scheme
1a	**Attempt any six**	**12**
1.a-i	**Extensive property** An extensive property is a property that changes when the size of the sample changes. Examples are mass, volume, length, and total charge **Intensive property** An intensive property doesn't change when you take away some of the sample. Examples are temperature, color, hardness, melting point, boiling point, pressure, molecular weight, and density. Because intensive properties are sometimes characteristic of a particular material, they can be helpful as clues in identifying unknown substances.	1 1
1.a-ii	**Degrees of freedom** The Degrees of Freedom [F] is the number of independent intensive variables (i.e. those that are independent of the quantity of material present) that need to be specified in value to fully determine the state of the system. Typical such variables might be temperature, pressure, or concentration	2
1.a-iii	**Zeroth law of thermodynamics:** If two systems are in thermal equilibrium independently with a third system, they must be in thermal equilibrium with each other. This law helps define the notion of temperature.	2
1.a-iv	**Colloidal solution:** Whose size of particles ranges from 10 A^0 to 2000 A^0. Particles do not diffuse through parchment membrane. Particles pass through filter paper.	2

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **3** of **35**

	Particles scatter light. Particles are invisible even under a powerful microscope but its scattering effect can be observed under ultramicroscope.	
1.a-v	Aluminium alloys are alloys in which aluminium (Al) is the predominant metal. The typical alloying elements are **copper, magnesium, manganese, silicon, tin and zinc.** **Ex. duralumunium,**	2
1.a-vi	**Caustic embrittlement**: it is the phenomenon in which the material of a boiler becomes brittle due to local accumulation/ decomposition of sodium hydroxide at high temperature (200-250^{0}C). It occurs at the stressed parts of the boiler such as cracks,bends,rivets and joints. The accumulated sodium hydroxide attack the material of the boiler and dissolves iron as sodium ferrite. Sodium carbonate is used for the softening water by lime soda process. residual sodium carbonate left behind in the water undergoes hydrolysis to produce sodium hydroxide at high temperatures and pressures.	2
1a-vii	**Electrochemical(Wet corrosion):** It is the corrosion of the metal that occurs in the presence of liquid medium/aqueous environment, through electrochemical reactions. one part behaves as anode and undergoes oxidation and the other part act as a cathode and undergoes reduction.	2
1.b	**Answer any two**	**8**
1.b-i	**Properties of Teflon{any four)** Plastic light in weight. It is excellent resistance to corrosion. It resistant to weather. It is ease in fabrication. Easily and cheaply made in complicated shapes.	½ mark each

	It has good strength and good wear and impact resistance			
	Properties of PVC : (any four)			½ mark
	1. It is a white brittle solid material.			each
	2. It is fire retardant and extinguishable.			
	3. It has good resistance to weather.			
	4. It has good resistance to acids and alkalies and inorganic chemicals.			
	5. It is non-flammable and low cost material.			
	6. It has greater stiffness and rigidity than polyethylene.			
1.b-ii	**Differentiate between hydrophillic and hydrophobic colloids**			1 mark each for any 4
	Definition	Hydrophillic colloids are liquid loving colloids (Lyo means solvent and philic means loving).	Hydrophobic colloids are liquid hating colloids (Lyo means solvent and phobic means hating).	
	Nature of Sub	These sols are usually formed by the organic substances like starch, gum, proteins etc.	These sols are usually formed by the inorganic materials like metals, their sulphides etc.	
	Viscosity	The hydrophillic colloids are highly viscous in nature and have higher viscosity than that of the medium.	The Hydrophobic colloids have almost same viscosity as that of medium	
	Stability	Hydrophillic sols are relatively stable as strong forces of interaction exist between colloidal particles and liquid.	Hydrophobic sols are less stable as weak forces of interaction exist between colloidal particles and liquid	
	Hydration	They are highly	They are not much	

		hydrated.	hydrated.
	Ease of preparation	Prepared easily by directly mixing with the liquid dispersion medium.	Cannot be prepared directly. Prepared by special methods only.
	Visibility	Their particles are neither visible nor detected easily by the ultra microscope.	Their particles though not visible, can be detected easily by the ultra microscope.

1.b-iii	**Protection from corrosion (any one method)**	4 marks for any one method
	Various treatments are used to slow corrosion damage to metallic objects which are exposed to the weather, salt water, acids, or other hostile environments. Some unprotected metallic alloys are extremely vulnerable to corrosion, such as those used in neodymium magnets, which can spall or crumble into powder even in dry, temperature-stable indoor environments unless properly treated to discourage corrosion.	
	1)Surface treatments	
	When surface treatments are used to retard corrosion, great care must be taken to ensure complete coverage, without gaps, cracks, or pinhole defects. Small defects can act as an allowing corrosion to penetrate the interior and causing extensive damage even while the outer protective layer remains apparently intact for a period of time.	
	a)Applied coatings	
	Galvanization	
	Galvanized surface	
	Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the structural material. Aside from	

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **6** of **35**

cosmetic and manufacturing issues, there may be tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, but if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with active metal such as zinc or cadmium.

b)Reactive coatings

If the environment is controlled (especially in recirculating systems), corrosion inhibitors can often be added to it. These chemicals form an electrically insulating or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts

c)Anodization]

Anodizing is very resilient to weathering and corrosion, so it is commonly used for building facades and other areas where the surface will come into regular contact with the elements. While being resilient, it must be cleaned frequently. If left without cleaning, panel edge stainingwill naturally occur. Anodization is the process of converting an anode into cathode by bringing a more active anode in contact with it.

OR

2)Cathodic protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel, and pipelines and tanks; steel pier piles, ships, and offshore oil platforms.

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

	a)Sacrificial anode protection Sacrificial anode attached to the hull of a ship For effective CP, the potential of the steel surface is polarized (pushed) more negative until the metal surface has a uniform potential. With a uniform potential, the driving force for the corrosion reaction is halted. For galvanic CP systems, the anode material corrodes under the influence of the steel, and eventually it must be replaced. The polarization is caused by the current flow from the anode to the cathode, driven by the difference in electrode potential between the anode and the cathode. b)Impressed current cathodic protection For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed current cathodic protection (ICCP) systems use anodes connected to a DC power source (such as a cathodic protection rectifier). Anodes for ICCP systems are tubular and solid rod shapes of various specialized materials. These include high silicon cast iron, graphite, mixed metal oxide or platinum coated titanium or niobium coated rod and wires. OR **3)Anodic protection** Anodic protection impresses anodic current on the structure to be protected (opposite to the cathodic protection). It is appropriate for metals that exhibit passivity (e.g. stainless steel) and suitably small passive current over a wide range of potentials. It is used in aggressive environments, such as solutions of sulfuric acid.	
2	**Attempt any four**	**16**
2-a	**Expression for Work done in Reversible Isothermal Expansion of Ideal gas** Consider a gas enclosed in a cylinder fitted with a weightless & frictionless piston, undergoing a reversible expansion process. The cylinder is in thermal equilibrium	4

SUMMER-18 EXAMINATION
Model Answer

with the surroundings so that the temperature of the gas remains constants while its expansion.

The total work done by the gas in the expansion process as the piston moves from position 1to position 2 during which volume is changing from V_1 to V_2(and its pressure is reduced from P_1 to P_2) is given by

$$W = W_{1-2} = \int_{1}^{2} PdV = \int_{v1}^{v2} PdV$$

The work done in reversible isotherm expansion of a gas is given by

$$W = P\,dV \int_{v1}^{v2} PdV \qquad (1)$$

The ideal gas equation is

PV = nRT

$$P = nRT/V \qquad (2)$$

Substituting for P from eq (2) eq (1 becomes)

$$W = \int_{V1}^{V2} (nRT/V)dV = nRT \int_{v1}^{v2} dV/V$$

Integrating gives

$$W = nRT \ln V_2 /V_1 \qquad (3)$$

We have $P_1 V_1 = nRT_1$ and $P_2 V_2 = nRT_2$

But $T_1 = T_2$---------------------- For Isothermal Process

$P_1 V_1 = P_2 V_2$

$V_2/ V_1 = P_1/P_2$

With this, equation (3) becomes

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

|		
	$W = nRT \ln P_1 / P_2$ $W = nRT \ln V_2 / V_1 = nRT \ln P_1 / P_2$ Since for an isothermal process , $\triangle U = 0$ and $\triangle T = 0$, Hence $\triangle H = 0$ We have $\triangle U = Q - W$ For an Isothermal Process $\triangle U = 0$. Therefore, the first law becomes $0 = Q - W$ $Q = W$ Thus, In an isothermal process ,Heat absorbed by a system gets completely converted into work or the work is done at the expense of heat absorbed and the temperature remains constant. Work done in isothermal reversible expansion of an ideal gas is given by $W = nRT \ln V_2 / V_1 = nRT \ln P_1 / P_2$	
2-b	**Properties of mild steel(any 4)** 1) It is cheap. 2) it has good tensile strength and ductility 3) It is malleable. 4) it can be easily rolled, forged ,bent and drawn 5) It is durable. 6) it is easily machined and weld able 7) It is relatively hard and easily annealed. 8) It easily rusts. 9) Its corrosion resistance is limited.	4
2-c	**Derivations of the Langmuir Adsorption Equation** Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.	4

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

$$A(g) + B(S) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} AB$$
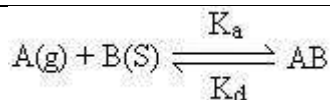
Where K_a represents equilibrium constant for forward reaction and K_d represents

equilibrium constant for backward direction.

According to Kinetic theory,

Rate of forward reaction = K_a [A] [B]

Rate of backward reaction = K_d [AB]

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

K_a [A] [B] = K_d [AB]

Or, $\dfrac{K_a}{K_d} = \dfrac{[AB]}{[A][B]}$

$K = \dfrac{K_a}{K_d} = \dfrac{[AB]}{[A][B]}$

The above equation represents the equilibrium constant for distribution of

adsorbate between the surface and the gas phase.

Derivation

Langmuir Equation which depicts a relationship between the number of active sites

of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.

To derive Langmuir Equation and new parameter ' θ ' is introduced. Let θ the

number of sites of the surface which are covered with gaseous molecules.

Therefore, the fraction of surface which are unoccupied by gaseous molecules will

be $(1 - \theta)$.

Now, Rate of forward direction depends upon two factors: Number of sited

available on the surface of adsorbent, $(1 - \theta)$ and Pressure, P. Therefore rate of

forward reaction is directly proportional to both mentioned factors.

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **11** of **35**

Rate of forward reaction $\propto$ P (1 - θ)

Rate of adsorption $\propto$ P (1 - θ)

Or, Rate of adsorption = K_a P (1 - θ)

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

Rate of desorption $\propto$ θ

Or, Rate of desorption = K_d θ

At equilibrium, rate of adsorption is equal to rate of desorption.

K_a P (1 − θ) = K_d θ

We can solve the above equation to write it in terms of θ.

K_aP – K_aP θ = K_d θ

K_aP = K_aP θ + K_d θ

K_aP = (K_d + K_aP) θ

$$\theta = \frac{K_a P}{K_d + K_a P}$$

Divide numerator and denominator on RHS by K_d, we get

$$\theta = \frac{\dfrac{K_a}{K_d} P}{\dfrac{K_d}{K_d} + \dfrac{K_a}{K_d} P}$$

Now put

$$K = \frac{K_a}{K_d}$$

in above equation we get

$$\theta = \frac{KP}{1 + KP}$$

Langmuir Adsorption Equation

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **12** of **35**

	This is known as Langmuir Adsorption Equation.	
2-d	**Features of electrochemical series:**	4
	• Metals having higher negative electrode potential show more corrosion.	
	• Metals having higher positive potential show less or no corrosion.	
	• Metals at top of the series called anodic (active),where as the metals at bottom of the series are called cathodic or noble.	
	• When two metals coupled ,then the metal with less potential becomes anode with respect to the other and gets corroded.	
	• Higher corrosion rate is obsereved with metals that are farther apart from each other in the series, when used in couple.	
	• The metal with less electrode potential displaces the metal having more electrode potential.	
	Electrode potential series of Dissimilar Metals.	
	Largest, corrosive part, positive.	
	Magnesium	
	Ninc	
	Cadmlum	
	Aluminum	
	Steel	
	Iron	
	Stainless-Steel	
	Solder	
	Lead	
	Tin	
	Nickel	
	Brass	

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
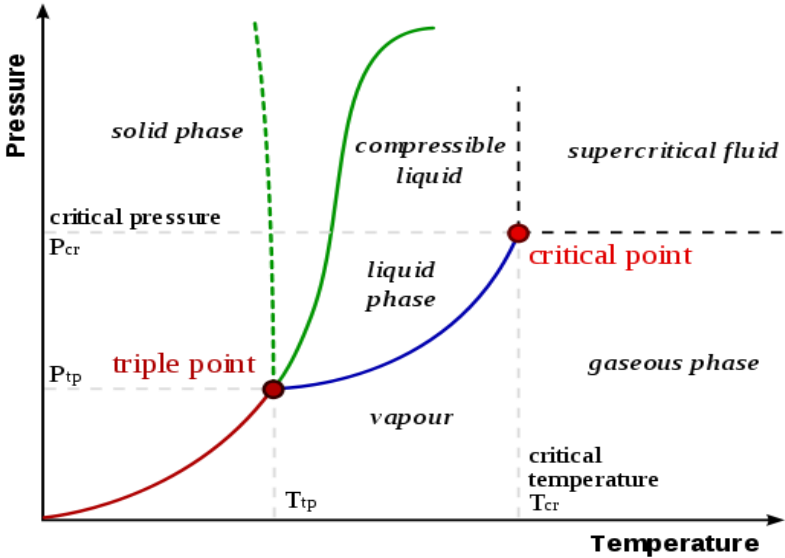**(ISO/IEC - 27001 - 2005 Certified)**

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **13** of **35**

	Copper Bronze Silver Solder Silver Titanium Graphite Gold Platinum Smallest, protected part, negative	
2-e	**Water system:** **Triple point** – the point on a phase diagram at which the three states of matter: gas, liquid, and solid coexist **Critical point** – the point on a phase diagram at which the substance is indistinguishable between liquid and gaseous states F**usion(melting) (or freezing) curve** – the curve on a phase diagram which represents the transition between liquid and solid states	4

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

	Vaporization (or condensation) curve – the curve on a phase diagram which represents the transition between gaseous and liquid states **Sublimation** (or deposition) curve – the curve on a phase diagram which represents the transition between gaseous and solid states Phase diagrams plot pressure (typically in atmospheres) versus temperature (typically in degrees Celsius or Kelvin). The labels on the graph represent the stable states of a system in equilibrium. The lines represent the combinations of pressures and temperatures at which two phases can exist in equilibrium.	
2-f	**DRY CORROSION Mechanism**: When a metal is exposed to air it gets oxidized by loosing its valence electrons & reduction of oxygen take place $M+n/4 (o^2) =>$ $M^{n+} + O^{2-}$ At point of contact of m^{n+} & o^{2-} metallic oxide will form & that metallic oxide scale forms a barrier to restrict further oxidation of inside metal . Since size of cation (M^{n+}) is smaller than anion . Hence cation will diffuse much faster than anion through the scale for continuation of oxidation , it can be possible if the metallic oxide barrier is sufficiently porous . The nature of oxide film plays very important role in oxidation corrosion. a. When oxide film is stable and tightly adhering , it will act as protective coating and corrosion is prevented. b. When oxide film is unstable and has tendency to decompose back to metal and oxygen , it does not go into oxidation corrosion. When film is volatile then metal surface again come into contact with air and oxidation take place d. If film is sufficiently porous then continuous oxidation take place. 2. Liquid metal corrosion - When a liquid metal is allowed to flow over solid metal at high temperature is called liquid metal corrosion. Due to this solid metal gets weak. Example- In nuclear reactor sodium metal is used as coolant & it leads to corrosion of cadmium.	4
3	**Attempt any four**	**16**
3-a	**Lead Lining:**	4

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **15** of **35**

	Lead lining is the process of applying lead to sheet metal, plastics or castings. Vulcan GMS uses a variety of contact cements and epoxies based on the application.	
	Lead can be saw cut, router cut or die cut to produce the lead blank needed for the application. We can use other processes like spinning or forming to generate the needed profiles.	
	Vulcan can apply the sheets or shapes with pressure if needed to ensure a solid bond or expansion. We can also use a variety of techniques to ensure that there are no joints (overlap joints, stop joints, lead burned joints or corner extrusions) which could cause radiation leaks.	
	We also can lead line nearly any application for products such as X-Ray tube housing, X-Ray tunnels, X-Ray tanks and collimators, which are all typically used in the medical X-ray and security markets.	
3-b	**Material of construction for**: 1. Ethanol: Tanks should be double-walled and must be either steel, fiberglass jacketed steel, or UL-listed fiberglass 2. Conc. Sulphuric Acid: Store in a metallic or coated fiberboard drum using a strong polyethylene inner package 3. Toulene: Polytetrafluorethylen (PTFE) 4. Conc.Nitric Acid: Aluminium and its alloy	1 mark each
3-c	**Application of Adsorption:** • **In preserving vacuum:** In Dewar flasks activated charcoal is placed between the walls of the flask so that any gas which enters into the annular space either due to glass imperfection or diffusion though glass is adsorbed. • **In glass masks:**	1 mark each for any 4

SUMMER-18 EXAMINATION
Model Answer

All gas masks are devices containing suitable adsorbent so that the poisonous gases present in the atmosphere are preferentially adsorbed and the air for breathing is purified.

- **In clarification of sugar:**

  Sugar is decolorized by treating sugar solution with charcoal powder. The latter adsorbs the undesirable colors present.

- **In paint industry:**

  The paint should not contain dissolved gases as otherwise the paint does not adhere well to the surface to be painted and thus will have a poor covering power. The dissolved gases are therefore, removed by suitable adsorbents during manufacture. Further, all surfaces are covered with layers of gaseous, liquid or solid films. These have to be removed before the paint is applied. This is done by suitable liquids which adsorbs these films. Such liquids are called wetting agents. The use of spirit as wetting agent in furniture painting is well known.

- **In chromatographic analysis:**

  The selective adsorbent of certain substances from a solution by a particular solid adsorbent has helped to develop technique for the separation of the components of the mixture. This technique is called chromatographic analysis. For example: in column chromatography a long and wide vertical tube is filled with a suitable adsorbent and the solution of the mixture poured from the top and then collected one by one from the bottom.

- **In catalysis:**

  The action of certain solids as catalysts is best explained in terms of adsorption. The theory is called adsorption theory. According to this theory, the gaseous reactants are adsorbed on the surface of the solid catalyst. As a result, the

	concentration of the reactants increases on the surface and hence the rate of reaction increases. The theory is also able to explain the greater efficiency of the catalyst in the finely divided state, the action of catalyst promoters and poisons. • **In adsorption indicators:** Various dyes which owe their use to adsorption have been introduced as indicators particularly in precipitation titrations. For example: KBr is easily titrated with $AgNO_3$ using eosin as an indicator. • **In softening of hard water:** The use of ion exchangers for softening of hard water is based upon the principle of competing adsorption just as in chromatography. In removing moisture from air in the storage of delicate instruments: Such instruments which may be harmed by contact with the moist air are kept out of contact with moisture using silica gel.	
3-d	**Sulphur System** The phase diagram of sulphur is somewhat more complicated than that of water although both are one component systems. Sulphur can exist in four different phases: (i) Two well-defined crystalline allotropic forms in the solid state, e.g., Monoclinic sulphur, S_m Rhombic sulphur, S_r At room temperature rhombic sulphur is more stable and on heating it passes on to monoclinic sulphur which exists within a range of temperature and pressure hounded by PQR (Figure). The temperature at which rhombic sulphur passes on to the monoclinic form is 95.5^0 C. This is known as the transition temperature for	2 marks for diagram and 2 marks for description

rhombic sulphur to get converted into monoclinic sulphur.

(ii) Liquid Sulphur, S_l.

(iii) Sulphur Vapour, S_v

In all these phases we are dealing with the same chemical entity, sulphur. So, it is a one component system. The system can be easily understood if the water system has been carefully studied. The important features of this system will be clear if reference is made to Figure, which is a pressure – temperature (P – t) diagram.
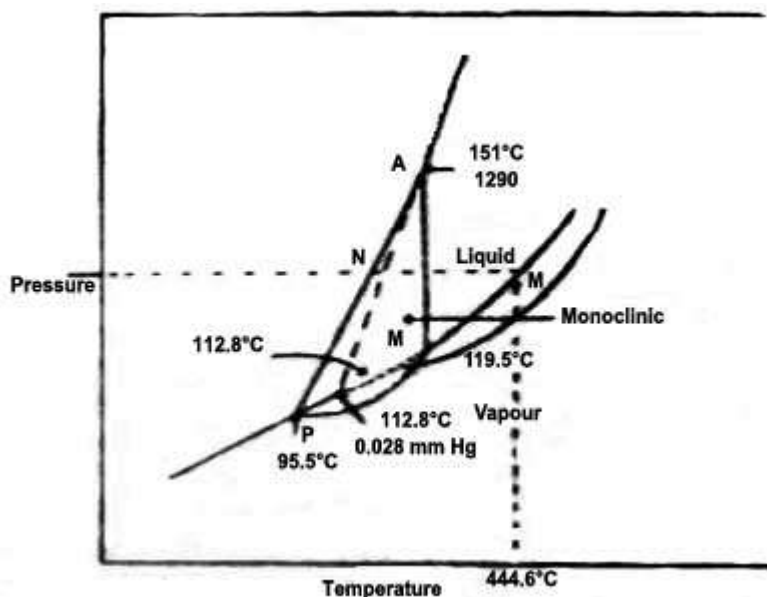

Fig: Phase diagram (P – t) of sulphur (schematic)

In the Figure the following can be identified:

(a) The solid curves AP, PR, PQ, QB, QR and RT and the dotted curves PS, QS and RS. Alone these curves the system is univariant, i.e., any one of the two variables temperature and pressure will define the system.

(b) Well-defined areas to the right of lines AP, PQ and QB, area above RQB, area

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **19** of **35**

to the left of APRT, area enclosed by PQR. Within any of these areas the system is bivariant, i.e., the values of both temperature and pressure have to be stated tit define a point.

(c) The points P, Q, R and S. All four of these are triple points as at each point three phases co-exist and the system becomes invariant. The three phases that co-exist are different at different temperatures and pressures.

As in the case of water each of the solid curves show equilibrium between two phases:

Along AP solid rhombic sulphur is in equilibrium with vapour and the curve shows, the variation of vapour pressure of rhombic sulphur with temperature. This is the sublimation curve of rhombic sulphur.

Along PR rhombic sulphur is in equilibrium with monoclinic sulphur and the curve shows the variation of the transition temperature for the conversion of rhombic sulphur to monoclinic sulphur at different pressures.

The curve PQ shows the variation of vapour pressure of monoclinic sulphur with temperature. Along PQ monoclinic sulphur is in equilibrium with vapour. It is the sublimation curve for monoclinic sulphur.

The curve QB shows the variation of vapour pressure of liquid sulphur with temperature. Along QB liquid sulphur and vapour are in equilibrium. The curve shows the effect of pressure on the boiling point at sulphur.

Along QR monoclinic sulphur ad liquid sulphur are in equilibrium and the curve shows the variation of the melting temperature of monoclinic sulphur with pressure.

	The dotted curves PS, QS and RS show temperature/pressure values for the metastable equilibria – PS between rhombic sulphur and vapour. QS between solid monoclinic sulphur and vapour and RS between solid rhombic sulphur and liquid. The curve RT represents equilibrium between solid rhombic sulphur and liquid sulphur and shows the effect of pressure on the melting point of rhombic sulphur. Similarly, it can be pointed out that to the left of the curve APR the system consists of only rhombic, sulphur, in the area to the right of APQB sulphur exists only in the vapour phase, the area bounded by PQR defines the region of temperature and pressure where monoclinic sulphur can exist and the region between the lines RQ and QB is where sulphur is in the liquid state.	

3-e	**Enthalpy** is a defined thermodynamic potential, designated by the letter "H", that consists of the internal energy of the system (U) plus the product of pressure (P) and volume (V) of the system
	
	$$H = U + PV$$
	
	Since enthalpy, H, consists of internal energy, U, plus the product of pressure (P) and the volume (V) of the system, which are all functions of the state of the thermodynamic system, enthalpy is a state function.
	
	The enthalpy of a homogeneous system is defined as
	
	$$H = U + pV$$
	
	where
	
	        H is the enthalpy of the system
	        U is the internal energy of the system
		1
		
		3

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **21** of **35**

p is the pressure of the system

V is the volume of the system.

The enthalpy is an extensive property. This means that, for homogeneous systems, the enthalpy is proportional to the size of the system. It is convenient to introduce the specific enthalpy $h = H/m$ where m is the mass of the system, or the molar enthalpy $H_m = H/n$, where n is the number of moles (h and H_m are intensive properties). For inhomogeneous systems the enthalpy is the sum of the enthalpies of the composing subsystems

$$H = \Sigma_k H_k$$

where the label k refers to the various subsystems. In case of continuously varying p, T, and/or composition the summation becomes an integral:

$$H = \int \rho h \, dV,$$

where ρ is the density.

The enthalpy H(S,p) of homogeneous systems can be derived as a characteristic function of the entropy S and the pressure p as follows: we start from the first law of thermodynamics for closed systems for an infinitesimal process

$$dU = \delta Q - \delta W.$$

Here, δQ is a small amount of heat added to the system and δW a small amount of work performed by the system. In a homogeneous system only reversible processes can take place so the second law of thermodynamics gives $\delta Q = TdS$ with T the

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

	absolute temperature of the system. Furthermore, if only pV work is done, $\delta W = pdV$. As a result $$dU = TdS - pdV.$$ Adding $d(pV)$ to both sides of this expression gives $$dU + d(pV) = TdS - pdV + d(pV)$$ or $$d(U + pV) = TdS + Vdp.$$ So $$dH(S,p) = TdS + Vdp.$$	
3-f	**First law of thermodynamics:** The first law of thermodynamics states that energy can't be created or destroyed, but it can be changed. This means that anything that uses energy is changing the energy from one kind of energy to another.	2
	Second law of thermodynamics : The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time. The total entropy can remain constant in ideal cases where the system is in a steady state (equilibrium), or is undergoing a reversible process. In all spontaneous processes the total entropy always increases and the process is irreversible.	2

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

|		
	The increase in entropy accounts for the irreversibility of natural processes	
4	**Attempt any four**	**16**
4-a	i)$\Delta S = n\,C_v \ln (T_2 / T_1)$	1
	$= 2*1.5\ R \ln(320/90)\ldots..R=1.987$ cal/mol.k	
	$=7.55$ eu(cal/k)	
	ii))$\Delta S = n\,C_p \ln (T_2 / T_1)$	1
	$C_p - C_v = R$	
	$C_p = 4.9675$	1
	$\Delta S = 12.58$ eu	1
4-b	**Galvanic cell**:	4
	It is physically impossible to measure the potential difference between a piece of metal and the solution in which it is immersed. We can, however, measure the *difference* between the potentials of two electrodes that dip into the same solution, or more usefully, are in two different solutions. In the latter case, each electrode-solution pair constitutes an oxidation-reduction *half cell*, and we are measuring the sum of the two *half-cell potentials*.	
	This arrangement is called a **galvanic cell**. A typical cell might consist of two pieces of metal, one zinc and the other copper, each immersed each in a solution containing a dissolved salt of the corresponding metal. The two solutions are separated by a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through.	

SUMMER-18 EXAMINATION
Model Answer

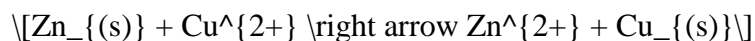Subject title: Physical Chemistry & Material of Construction   Subject code   17423
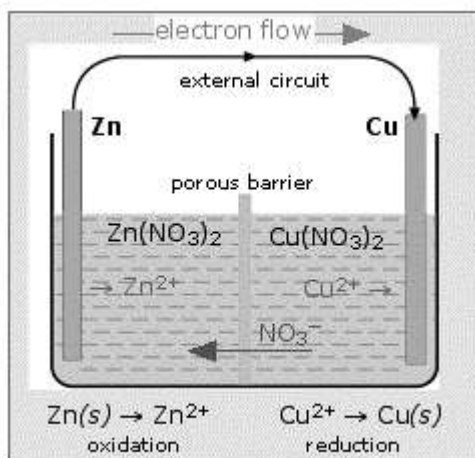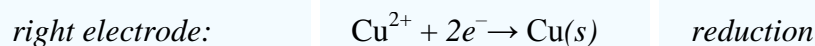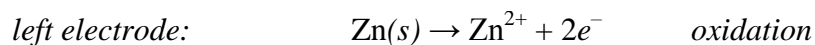

If we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain when Zn^{2+} ions emerge from the zinc in the left cell would be able to flow through the external circuit and into the right electrode, where they could be delivered to the Cu^{2+} ions which become "discharged", that is, converted into Cu atoms at the surface of the copper electrode. The net reaction is the oxidation of zinc by copper(II) ions:

$$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$$

but this time, the oxidation and reduction steps (half reactions) take place in separate locations:

left electrode:	$Zn(s) \rightarrow Zn^{2+} + 2e^-$	*oxidation*
right electrode:	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	*reduction*

SUMMER-18 EXAMINATION
Model Answer

4-c		4

Electroplating:

Electroplating is the process of plating one metal onto another by hydrolysis, most commonly for decorative purposes or to prevent corrosion of a metal. There are also specific types of electroplating such as copper plating, silver plating, and chromium plating. Electroplating allows manufacturers to use inexpensive metals such as steel or zinc for the majority of the product and then apply different metals on the outside to account for appearance, protection, and other properties desired for the product. The surface can be a metal or even plastic.

Sometimes finishes are solely decorative such as the products we use indoors or in a dry environment where they are unlikely to suffer from corrosion. These types of products normally have a thin layer of gold, or silver applied so that it has an attractive appeal to the consumer. Electroplating is widely used in industries such as automobile, airplanes, electronics, jewelry, and toys. The overall process of electroplating uses an electrolytic cell, which consists of putting a negative charge on the metal and dipping it into a solution that contains metal salt (electrolytes) which contain positively charged metal ions. Then, due to the negative and positive charges, the two metals are attracted to each other.

The Purposes of Electroplating:

1. Appearance

2. Protection

3. Special surface properties

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

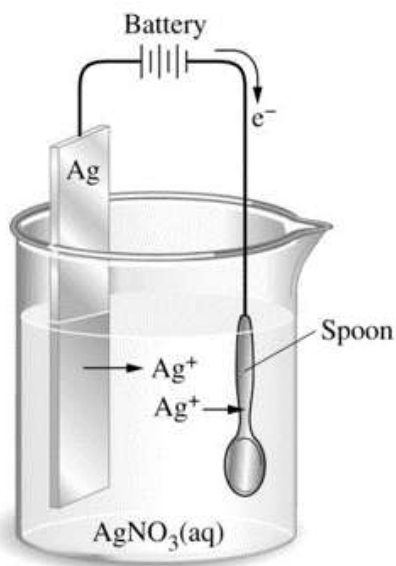Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **26** of **35**

4. Engineering or mechanical properties

The cathode would be the piece to be plated and the anode would be either a sacrificial anode or an inert anode, normally either platinum or carbon (graphite form). Sometimes plating occurs on racks or barrels for efficiency when plating many products. Please refer to electrolysis for more information. In the figure below, the Ag^+ ions are being drawn to the surface of the spoon and it eventually becomes plated. The process is undergone using silver as the anode, and a screw as the cathode. The electrons are transferred from the anode to the cathode and is underwent in a solution containing silver.

4 d	**Phase rule:**	
	$$F = C - P + 2$$ where *F* is the number of degrees of freedom, *C* is the number	4

SUMMER-18 EXAMINATION
Model Answer

	of components and *P* is the number of phases in thermodynamic equilibrium with each other. The number of degrees of freedom is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature or pressure that can be varied simultaneously and arbitrarily without determining one another.		
4-e	**Comparison of lyophilic and lyophobic solutions**:		1 mark each for any 4

Properties	**Lyophilic solutions**	**lyophobic solutions**
Ease of preparation	Prepared easily by directly mixing with the liquid dispersion medium.	Cannot be prepared directly. Prepared by special methods only.
Stability	They are quite stable and are not easily precipitated or coagulated.	They are easily precipitated by addition of a small amount of a suitable electrolyte.
Hydration	They are highly hydrated.	They are not much hydrated.
Reversible and irreversible nature	They are reversible in nature i.e. once precipitated can return the colloidal sol by simply remixing with the dispersion medium.	They are irreversible in nature i.e. once precipitated cannot return the colloidal sol by simply addition of the dispersion medium.
Nature of substance	These sols are usually formed by the organic substances like starch, gum, proteins etc.	These sols are usually formed by the inorganic materials like metals, their sulphides etc.
Viscosity	Their viscosity is much than that of the medium.	Their viscosity is almost the same as that of the medium.
Surface tension	Their surface tension is usually lower than that of the dispersion medium.	Their surface tension is nearly small than that of the dispersion medium.

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **28** of **35**

	Visibility	Their particles are neither visible nor detected easily by the ultra microscope.	Their particles though not visible, can be detected easily by the ultra microscope.	
	Migration in an electric field	Their particles may migrate in either direction.	Their particles migrate only in one direction of electric field.	
4-f	**Characteristics of corrosion protective coating (any 4)** Protective coatings are unique method of corrosion control. They are used to give long term protection under a broad range of corrosive conditions, extending from atmospheric exposures to frill immersion in strongly corrosive solution. 1. Protective solution provides little or no structural strength, yet they provide other material so that the strength and the integrity of a structure can be maintained. 2. The function of protective coatings is to prevent highly corrosive industrial fumes, liquids, solids, or gases from contacting the reactive underlying substrate of the structure. This physical separation of two highly reactive materials, the atmosphere and the substrate, is extremely important. 3. That coatings are, in general, a relatively thin film separating the two reactive materials indicates the vital importance of the coating and the concept of a corrosion free structure. 4. The coating must be, according to this concept a completely continuous film in order to fulfill its function. Any imperfection becomes a focal point for corrosion and the breakdown of the structure.	1 mark each
5	**Answer any 4**	**16**
5-a	**Effect of temperature on corrosion**: For most chemical reactions, the reaction rate increases with increasing temperature. 1. Temperature affects the corrosion rate of metals in electrolytes primarily through its effect on factors which control the diffusion rate of oxygen. 2. The corrosion of iron and steel is an example of this because temperature affects the corrosion rate by virtue of its effect on the oxygen	2

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **29** of **35**

	solubility and oxygen diffusion coefficient. 3. As temperature increases the diffusion coefficient of oxygen also increases which tends to increase the corrosion rate. 4. The net affect of mild steel, is that the corrosion rate approximately doubles for a temperature rise of 30°C up to a maximum temperature at about 80°C, the rate then falls off in an open system because the decrease in oxygen solubility becomes the most important factor. 5. In a closed system, where oxygen cannot escape the corrosion rate continues to increase indefinitely with temperature until all the oxygen is consumed. **Effect of pH on corrosion:** The pH of a solution is an important factor in the corrosion resistance of materials because hydrogen ions can interact and modify the surface and therefore alter the corrosion resistance of a material. Moreover, interactions between pH and dissolved species such as chloride ions can enhance the effect of hydrogen ions.	2
5-b	$P = 3$ - Water, Ice, Steam $C=1$ $F=C-P+2$ $F = 0$ - No degrees of freedom	1 1 1 1
5-c	**Adsorption**: Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent.	4

Mechanism of Adsorption:
It is mainly divided into three steps as follows::

Step 1 : Molecule diffusion process into the thin layer of fluid(Called as fluid film) which is attached on the adsorbent.

Step 2 : According to developing of diffusion, the surface diffusion process which attached the vapour or gas along the pores. It is called as mixed diffusion because there exist two diffusion of pore diffusion and surface diffusion.

Step 3 : Adsorption process in the pore adsorption sites

5-d	**Importance of lining**: a. to protect against corrosion b. to prevent the contamination of the materials being processed. c. minimize the effect of a abrasion. d. ease of cleaning. e. provide high mechanical strength.

Different types of linings are :

1. Lead lining: it is having high corrosion resistance but it is soft and has poor mechanical property. Because of this it is used for protection of mild steel.

2. Glass lining: glass has excellent resistance to all acids except hydrofluoric. Their general applications are for equipment such as reactors, columns, pipes etc.

3. rubber lining: here lining is generally in the form of sheets or thin films applied

SUMMER-18 EXAMINATION
Model Answer

	by using specific adhesive. 4. plastic lining: the method of plastic lining preparation of the surface plays important part in subsequent adhesion of film to the metal surface.	
5-e	**Homogeneous systems**: a system consisting of a single phase is called a homogeneous system. eg: as one phase, for e.g (NaCl + H2O) though this are present Na+ and Cl- ions still it is a one phase system. Completely miscible liquids constitute a one phase system (H2O+C2H5OH). **Heterogeneous system:** a system consisting of more than one phase is called heterogeneous system. Ex:A mixture of diamond and graphite will constitute a two phase system as they have different crystal structure.	2 2
5-f	**Types of adsorption are:** **1.Physical Adsorption** **2.Chemical Adsorption** **Physical Adsorption**: When the force of attraction existing between adsorbate and adsorbent are weak Vanderwaal forces of attraction, the process is called Physical Adsorption or Physisorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. ΔHadsorption is 20-40KJ/mol. It takes place at low temperature below boiling point of adsorbate.As the temperature increases in, process of Physisorption decreases. Chemical Adsorption: When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called **Chemical Adsorption**. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption. i.e. $\Delta H_{adsorption}$ is 200-400KJ/mol . It can take place at all temperature. With the	1 1.5 1.5

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

	increases in temperature, Chemisorption first increases and then decreases.	
6	**Answer any 4**	**16**
6-a	**Pitting corrosion**: It is supposed by some that gravitation causes downward-oriented concentration gradient of the dissolved ions in the hole caused by the corrosion, as the concentrated solution is denser. This however is unlikely. The more conventional explanation is that the acidity inside the pit is maintained by the spatial separation of the cathodic and anodic half-reactions, which creates a potential gradient and electromigration of aggressive anions into the pit.This kind of corrosion is extremely insidious, as it causes little loss of material with small effect on its surface, while it damages the deep structures of the metal. The pits on the surface are often obscured by corrosion products.Pitting can be initiated by a small surface defect, being a scratch or a local change in composition, or a damage to protective coating. Polished surfaces display higher resistance to pitting. **Uniform corrosion**: it is corrosion of a metal either through chemical or electrochemical reaction that proceeds evenly or uniformly over the entire exposed surface or over very large area of the surface. thus, A uniform layer of rust formed on the metal surface and there is a more or less uniform wastage of material. This type of corrosion usually observed on the outer surface of a container exposed at atmosphere. It can be prevented by selecting proper materials, cathodic protection, use of inhibitors and protective coatings.	2 2
6-b	**Factors affecting rate of corrosion are**:	4

MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
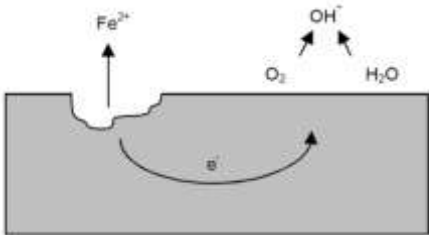**(ISO/IEC - 27001 - 2005 Certified)**

SUMMER-18 EXAMINATION
Model Answer

Subject title: Physical Chemistry & Material of Construction   Subject code   17423   Page **33** of **35**

	Nature of the metal Nature of environment. 1) **Nature of metal:** a. purity of metal b. surface area of metal c. relative area of cathodic or anodic parts d. position in the galvanic series e. nature of the oxide film f. solubility of the corrosion product g. physical state of the metal h. Volatility of the corrosion product. 2) **Nature of the environment**: a. temperature of the environment b. pH of the environment c. presence of impurities in the environment d. amount of oxygen present in the environment e. nature of anions and cations present in the environment f. Presence of suspended particles in the environment. g. humidity of environment	
6-c	**Isobaric process**: An isobaric process is a thermodynamic process in which the pressure stays constant: $\Delta P = 0$. **Isochoric process**: An isobaric process is a thermodynamic process in which the volume stays constant: $\Delta V = 0$. **Isothermal process:** An isothermal process is a change of a system, in which the temperature remains constant: $\Delta T = 0$.	4
6-d	**Methods of preparation of lyophobic solution**: 1) Dispersion methods: in this method colloiodal size particles are formed by	2

Subject title: Physical Chemistry & Material of Construction   Subject code   17423

	breaking down large macro-sized particles. Those are: • mechanical dispersion method • electrical dispersion method • peptization 2) Aggregation method: here colloidal size particles are formed by aggregation of single molecules. Those are: • double decomposition • reduction • Oxidation.	2
6-e	**Gibb's phase rule** states that the number of degrees of freedom in a physical system at equilibrium is equal to the number of components in the system minus the number of phase plus the constant2.mathematically ,it is stated as follows: F = C –P+2 i)Phase: A Phase is a component part of the system that is immiscible with the other parts (e.g. solid, liquid, or gas); a phase may of course contain several chemical constituents, which may or may not be shared with other phases. The number of phases is represented in the relation by P. ii) Component: The Chemical Constituents are simply the distinct compounds (or elements) involved in the equations of the system. (If some of the system constituents remain in equilibrium with each other whatever the state of the system, they should be counted as a single constituent.) The number of these is represented as C. iii) Degrees of freedom The Degrees of Freedom [F] is the number of independent intensive variables (i.e. those that are independent of the quantity of material present) that need to be specified in value to fully determine the state of the system. Typical such variables might be temperature, pressure, or concentration	1 1 1 1

SUMMER-18 EXAMINATION
Model Answer

6-f	**Lining** is a layer of material on the inner surface of something; usually for protection or decorative appearance Linings prevent corrosion in a wide range of difficult applications. Linings are commonly used in applications such as: Cylindrical lining, bushing - A cylindrical metal lining used to reduce friction Furnace lining, refractory - Lining consisting of material with a high melting point, used to line the inside walls of a furnace Protective covering - A covering that is intended to protect from damage or injury Strip lining - Thin sheet strips of corrosion-resistant alloy attached by spot welding in the field to protect an unclad vessel The most commonly used lining materials are polymers, refractories, cement and bricks. Which materials are used for lining depends on the materials and surroundings upon which lining is to be applied.	4