

**KARPAGAM ACADEMY OF HIGHER EDUCATION****(Deemed to be University)****(Established Under Section 3 of UGC Act 1956)****Coimbatore - 641021.****DEPARTMENT OF CHEMISTRY****SUBJECT : NOVEL INORGANIC SOLIDS****SEMESTER : V****SUBJECT CODE: 17CHU503B****CLASS: III - B. Sc – Chemistry****Scope**

This course involves Synthesis and modification of novel inorganic solids of technological importance, nanomaterials, Engineering materials, composite materials and speciality polymers.

Objectives

The course enables the students to

1. Understand the Synthesis and modification of inorganic solids of technological importance
2. Understand the Synthesis and properties of nanomaterials
3. Understand the Synthesis of engineering materials used for mechanical construction
4. Understand the Synthesis and properties of composite materials
5. Understand the Synthesis and properties of speciality polymers

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

UNIT I**Synthesis and modification of inorganic solids:**

Conventional heat and beat methods, Co-precipitation method, Sol-gel methods, Hydrothermal method, Ion-exchange and Intercalation methods.

Inorganic solids of technological importance:

Solid electrolytes – Cationic, anionic, mixed Inorganic pigments – coloured solids, white and black pigments.

Molecular material and fullerenes, molecular materials & chemistry – one-dimensional metals, molecular magnets, inorganic liquid crystals.

UNIT II**Nanomaterials:**

Overview of nanostructures and nanomaterials: classification.

Preparation of gold and silver metallic nanoparticles, self-assembled nanostructures-control of nanoarchitecture-one dimensional control. Carbon nanotubes and inorganic nanowires.

Bio-inorganic nanomaterials, DNA and nanomaterials, natural and artificial nanomaterials, bionano composites.

UNIT III

Introduction to engineering materials for mechanical construction:

Composition, mechanical and fabricating characteristics and applications of various types of cast irons, plain carbon and alloy steels, copper, aluminium and their alloys like duralumin, brasses and bronzes cutting tool materials, super alloys thermoplastics, thermosets and composite materials.

UNIT IV

Composite materials:

Introduction, limitations of conventional engineering materials, role of matrix in composites, classification, matrix materials, reinforcements, metal-matrix composites, polymer-matrix composites, fibre-reinforced composites, environmental effects on composites, applications of composites.

UNIT V

Speciality polymers:

Conducting polymers - Introduction, conduction mechanism, polyacetylene, polyparaphenylene and polypyrrole, applications of conducting polymers, Ion-exchange resins and their applications. Ceramic & Refractory: Introduction, classification, properties, raw materials, manufacturing and applications.

Suggested Readings

Text Books:

1. Shriver & Atkins. *Inorganic Chemistry*, Peter Atkins, Tina Overton, Jonathan Rourke, Mark Weller and Fraser Armstrong. (2011-2012). 5th Edition. Oxford University Press.
2. Adam, D.M. (1974) *Inorganic Solids: An introduction to concepts in solid-state structural chemistry*. John Wiley & Sons.

Reference Books

1. Poole, C.P. & Owens, F.J. (2003). *Introduction to Nanotechnology*. John Wiley & Sons.
2. Rodger, G.E. (2002). *Inorganic and Solid State Chemistry*. Cengage Learning India Edition.
3. Gupta, M.C, Gupta, A. P, (2005), *Polymer Composite*, New Age International, Pvt Ltd, Publishers, New Delhi.
4. Madan. R.D, (2014), *Modern inorganic chemistry*, S. Chand & Company, Pvt Ltd., New Delhi.

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DEPARTMENT OF CHEMISTRY**SUBJECT NAME: NOVEL INORGANIC SOLIDS****SUB.CODE:17CHU503B****SEMESTER: V****CLASS: III -B. Sc Chemistry**

LECTURE PLAN
DEPARTMENT OF CHEMISTRY

S. No	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-I	
1	1	Synthesis and modification of inorganic solids: Conventional heat and beat methods,	T ₁ -601
2	1	Co-precipitation method, Sol-gel methods. Hydrothermal method.	T ₁ -624, 603
3	1	Ion-exchange and Intercalation methods.	T ₁ -634,295, 629,680,355
4	1	Inorganic solids of technological importance: Solid electrolytes – Cationic, Solid electrolytes - anionic, mixed	T ₁ -607, 609, 610
5	1	Inorganic pigments – coloured solids, white and black pigments.	T ₁ -642, R ₁ -130 T ₁ -643,644
6	1	Molecular material and fullerenes, molecular materials & chemistry	R ₁ - 429-431; T ₁ -647
7	1	one-dimensional metals, molecular magnets, inorganic liquid crystals	T ₁ - 648, 649,650
8	1	Recapitulation and Discussion of Important Questions	
		Total No of Hours Planned for Unit I =08	
		UNIT-II	
1	1	Nanomaterials: Overview of nanostructures and nanomaterials: classification.	T ₁ -653,654
2	1	Preparation of gold metallic nanoparticles,	T ₁ -659
3	1	Preparation of silver metallic nanoparticles,	T ₁ -659

4	1	Self-assembled nanostructures-control of nanoarchitecture-one dimensional control.	T ₁ -653, 666,669-672
5	1	Carbon nanotubes	T ₁ -356,671
6	1	Inorganic nanowires.	T ₁ -672
7	1	Bio-inorganic nanomaterials, DNA and nanomaterials,	T ₁ -681,681
8	1	Natural and artificial nanomaterials	T ₁ -682
9	1	Bio Nano composites.	T ₁ -682-683
10	1	Recapitulation and Discussion of Important Questions	
Total No of Hours Planned for Unit II=10			
		UNIT-III	
1	1	Introduction to engineering materials for mechanical construction: Composition, mechanical and fabricating characteristics and applications of various types of cast irons.	T ₁ -73, 79
2	1	Composition, mechanical and fabricating characteristics and applications of various types of plain carbon.	T ₁ -75, 328
3	1	Composition, mechanical and fabricating characteristics and applications of various types of alloy steels.	T ₁ -75,328
4	1	Composition, mechanical and fabricating characteristics and applications of various types of copper.	T ₁ -
5	1	Composition, mechanical and fabricating characteristics and applications of various types of aluminium.	T ₁ -325
6	1	Composition, mechanical and fabricating characteristics and applications of various types of alloys like duralumin.	T ₁ -323
7	1	Composition, mechanical and fabricating characteristics and applications of various types of brasses.	T ₁ -75
8	1	Composition, mechanical and fabricating characteristics and applications of various types of bronzes cutting tool materials.	T ₁ -75
9	1	Composition, mechanical and fabricating characteristics and applications of various types of super alloys thermoplastics, and thermosets.	R ₃ -87,88 R ₄ -27, 94

10	1	Composition, mechanical and fabricating characteristics and applications of various types of composite materials.	R ₃ -90
11	1	Recapitulation and Discussion of Important Questions.	
Total No of Hours Planned for Unit III=11			
		UNIT-IV	
1	1	Composite materials: Introduction	R ₃ -01
2	1	limitations of conventional engineering materials	R ₃ -02
3	1	role of matrix in composites	R ₃ -03
4	1	classification, and matrix materials	R ₃ -08, 05
5	1	reinforcements	R ₃ -39
6	1	metal-matrix composites, polymer-matrix composites	R ₃ -49
7	1	fiber-reinforced composites	R ₃ - 06
8	1	Environmental effects on composites, Applications of composites	R ₃ -46, 89
9	1	Recapitulation and Discussion of Important Questions	
Total No of Hours Planned for Unit IV=09			
		UNIT-V	
1	1	Speciality polymers: Conducting polymers - Introduction, conduction mechanism	R ₁ -281,283
2	1	Conducting polymers - polyacetylene	T ₁ -289
3	1	Conducting polymers - polyparaphenylene polypyrrole	R ₁ -285, R ₃ -412
4	1	applications of conducting polymers, Ion-exchange Resins and their applications.	R ₁ -292
5	1	Ceramic & Refractory: Introduction, classification	R ₄ -945
6	1	Ceramic & Refractory: properties, raw materials	R ₄ -946
7	1	Ceramic & Refractory: manufacturing and applications	R ₄ -947
8	1	Recapitulation and Discussion of important Questions	
9	1	Discussion of Previous ESE Question Papers.	
10	1	Discussion of Previous ESE Question Papers.	

	Total No of Hours Planned for unit V=10	
Total Planned Hours = 48		

Text Books:

1. Shriver & Atkins. *Inorganic Chemistry*, Peter Atkins, Tina Overton, Jonathan Rourke, Mark Weller and Fraser Armstrong. (2011-2012). 5th Edition. Oxford University Press.
2. Adam, D.M. (1974) *Inorganic Solids: An introduction to concepts in solid-state structural chemistry*. John Wiley & Sons.

Reference Books

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Batch – (2017-2020)

Unit-I-Multiple choice Questions

Unit-I-Multiple choice Questions

S. No	Question	Option- I	Option- II	Option- III	Option- IV	Answer
1.	Giant ionic structures are also name given to	ionic lattice	crystal lattice	metallic lattice	covalent lattice	ionic lattice
2.	The silicon (IV) oxide which is found in mineral quartz is very similar to	graphite	diamond	iron	Copper	diamond
3.	The metal which can be melted even by the warmth of human palm is	gallium	indium	aluminium	tungsten	gallium
4.	Metals can be hammered into different shapes and drawn into wires hence they are	soft	malleable	strong	weaker	malleable
5.	In sol-gel process the starting material is processed to form a dispersible oxide and forms a sol in contact with?	Water	Dilute acid	Water or dilute acid	Acid or alkali	Water or dilute acid
6.	Calcination of the gel produces?	Calcium	Carbon	Sulphur-di-oxide	Oxide	Oxide
7.	In sol-gel process removal of the liquid from the sol yields the gel, and the sol/gel transition controls	Process	Particle size and shape	Partical size	Partical shape	Particle size and shape

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Unit-I-Multiple choice Questions

	the?					
8.	Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as?	M(OR) _z	MOH	SiO ₂	Si(OEt) ₄	Si(OEt) ₄
9.	MOR + H ₂ O → MOH + ROH it is?	Hydrolysis	Condensation	Deposition	Decomposition	Hydrolysis
10.	Gelation resulting from the formation of an oxide- or alcohol-bridged network by which reaction?	Polycondensation	Substitution	Addition	Decomposition	Polycondensation
11.	The aging process of gels can exceed about?	6 days	5 days	7 days	8 days	7 days
12.	Ostwald ripening is also referred to as?	Polycondensation	Coarsening	Sol-gel	Decomposition	Coarsening
13.	Drying of gel is a complicated process due to fundamental changes in the structure of?	Sol	Product size	Gel	Product shape	Gel
14.	Monolith is termed as?	Xerogel	Gel	Sol	Syneresis	Xerogel
15.	If the solvent (such as water) is extracted under supercritical or	Xerogel	Gel	Sol	Aerogel	Aerogel

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Unit-I-Multiple choice Questions

	near super critical conditions, the product is an?					
16.	Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against?	Decomposition	Rehydration	Dehydration	Condensation	Rehydration
17.	Densification and decomposition of the gels at high temperatures about?	<800°C	>700°C	>800°C	>900°C	>800°C
18.	Sol-gel method is _____ approach	Bottom up	Up bottom	Top down	Down top	Bottom up
19.	Sol-gel method is known since	1970	1980	1990	1985	1980
20.	The gel is a _____ mass.	Heavy molecular	Semi rigid	Light molecular	Rigid	Semi rigid
21.	The sol-gel is a _____ of solid particle	Sublimation	Melting	Cool down	Colloidal suspension	Colloidal suspension
22.	_____ undergo hydrolysis and poly condensation reactions.	Metal ions	Metal oxides	Metal carbonates	Metal nitrates	Metal oxides
23.	Sol-gel method is _____ chemical process	Wet	Dry	Semi Solid	Semi liquid	Wet
24.	The solvent evolves towards the formation of an inorganic continuous network containing a	Gel	Solid Phase	Semi solid phase	Gaseous phase	Gel
25.	Formation of an inorganic	Oxo	Nitro	Hydro	Azo	Oxo

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Unit-I-Multiple choice Questions

	continuous network containing the metal centres with _____					
26.	After drying process, the liquid phase is removed from the gel and _____ is performed.	Calcination	De-oxygenation	Oxygenation	Hydrogenation	Calcination
27.	One of the advantages of sol-gel method is able to get uniform and _____ powder	Micro size	Nano size	Large size	Small size	Large size
28.	Sol-gel method can produce _____ systems.	Uniform multi component	Non-uniform multi component	Multi component	Non-uniform multi component	Uniform multi component
29.	Metal nano particles particularly _____ nano particles are prepared by the chemical reduction method	Silver	Gold	Platinum	Tungsten	Sliver
30.	The _____ and citrate solution are used as reducing agents in chemical reduction method.	Hydrazine hydrate	Hydrazine	Hydrazone	Semi carbazene	Hydrazine hydrate
31.	To remove the excess silver ions the solution is washed with _____ under nitrogen stream	Heavy water	Mineral water	Deioniser water	Impure water	Deioniser water
32.	The transparent colourless solution is changed into	Pale red	pale blue	Purple	Dark brown	Pale red

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Unit-I-Multiple choice Questions

	pale yellow from _____ in chemical reduction method					
33.	Relative amounts of phases in a region can be deduced using	Phase rule	Lever rule	Either	Selection rule	Lever rule
34.	An invariant reaction that produces a solid up on cooling two liquids	Eutectic	Peritectic	Monotectic	Syntectic	Syntectic
35.	A solid + a liquid result in a liquid up on heating during _____ reaction	Eutectic	Peritectic	Monotectic	Syntectic	Monotectic
36.	A solid + a liquid result in a solid up on cooling during _____ reaction	Eutectic	Peritectic	Monotectic	Syntectic	Peritectic
37.	On heating, one solid phase results in another solid phase plus on liquid phase during _____ reaction	Eutectic	Peritectic	Monotectic	Syntectic	Peritectic
38.	A solid phase results in a solid plus another solid phase up on cooling during _____ reaction.	Eutectic	Peritectic	Eutectoid	Peritectoid	Eutectoid
39.	A solid phase results in a solid plus another solid phase up on heating during _____	Eutectic	Peritectic	Eutectoid	Peritectoid	Peritectoid

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Unit-I-Multiple choice Questions

	reaction					
40.	A liquid phase produces two solid phases during _____ reaction up on cooling.	Eutectic	Peritectic	Eutectoid	Peritectoid	Eutectic
41.	Liquid phase is involved in the following reaction	Monotectoid	Peritectic	Eutectoid	Peritectoid	Monotectoid
42.	Phases that exist on left side of an invariant reaction line are called	Hyper-phase	Pro-phase	Hypo-phase	solid phase	Hyper-phase
43.	The boundary line between (liquid) and (liquid+solid) regions must be part of _____	Solvus	Solidus	Liquidus	Tie-line	Liquidus
44.	The boundary line between (liquid+solid) and (solid) regions must be part of _____	Solvus	Solidus	Liquidus	Tie-line	Solidus
45.	The boundary line between (alpha) and (alpha+beta) regions must be part of _____	Solvus	Solidus	Liquidus	Tie-line	Solvus
46.	The word 'ceramic' meant for	soft material	hard material	burnt material	dry material	burnt material
47.	In which ceramic product is mostly used as pigment in paints	TiO ₂	SiO ₂	UO ₂	ZrO ₂	TiO ₂
48.	The ionic solids show brittleness because they are arranged in	Linear layers	Parallel layers	Combined laye	Closely packed	Closely packed
49.	Hydrothermal fluids are	Corrosive and	Corrosive	Abrasive	Corrosive	Corrosive and

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Unit-I-Multiple choice Questions

		Abrasive			resistant	Abrasive
50.	The efficiency of geothermal plant is about	5%	15%	25%	35%	15%
51.	Ion exchange resins are made of	Polystyrene	Lutein	Teflon	Sulphonated Bakelite	Sulphonated Bakelite
52.	Major ingredients of traditional ceramics	SiC	SiO ₂	Si ₃ N ₄	Al ₂ O ₃	SiO ₂
53.	In sol-gel process the starting material is processed to form a dispersible oxide and forms a sol in contact with?	Water	Dilute acid	Acid or alkali	Water or dilute acid	Water or dilute acid
54.	Which one is not a characteristic property of ceramic material?	high temperature stability	high mechanical strength	low hardness	low elongation	low hardness
55.	During sintering densification is not due to	Atomic diffusion	surface diffusion	bulk diffusion	grain growth	surface diffusion
56.	Calcination of the gel produces?	Calcium oxide	sulphur	oxygen	oxide	Oxide
57.	Colloidal suspension is known as?	Gel	Gel and sol	Sol	Electrical	Sol
58.	Which of the following pairs of compounds are examples of strong electrolytes?	sugar and calcium hydroxide	calcium hydroxide and hydrochloric acid	Hydrochloric acid and vinegar	vinegar and sugar	calcium hydroxide and hydrochloric acid

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Unit-I-Multiple choice Questions

59.	Since the ions are held in fixed positions by strong forces, electricity is not conducted by	electrodes	electrolytes	insulators	metals	insulators
60.	Electrolyte liquid may include	True solutions	molten solids	gases	solids	molten solids

UNIT I

Synthesis and modification of inorganic solids:

Conventional heat and beat methods, Co-precipitation method, Sol-gel methods, Hydrothermal method, Ion-exchange and Intercalation methods.

Inorganic solids of technological importance:

Solid electrolytes – Cationic, anionic, mixed Inorganic pigments – coloured solids, white and black pigments.

Molecular material and fullerides, molecular materials & chemistry – one-dimensional metals, molecular magnets, inorganic liquid crystals.

Synthesis and modification of inorganic solids

The solid samples can be synthesized in variety of shapes and sizes depending upon their necessities, such as, single crystals, amorphous solids, thin films, thick films, polycrystalline powder, etc. Several methods available to synthesize high quality samples in bulk and thin film forms are, Solid State Reaction (SSR), Vapor Phase Transport (VPT), Co-precipitation, Sol - Gel, Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Pulsed Laser Deposition (PLD), Chemical Solution Deposition (CSD), Metal-Organic Chemical Vapor Deposition (MOCVD), Sputtering, Flux Growth Technique, Electrochemical Methods etc.

Conventional heat and beat methods

Solid State Reaction (SSR) this is the most widely used method for the synthesis of polycrystalline bulk manganite. Solid State Reaction (SSR) method provides large range of selection of starting materials like, oxides, carbonates, etc. Since, solids do not react with each other at room temperature (RT), it is necessary to heat them at elevated temperatures as high as

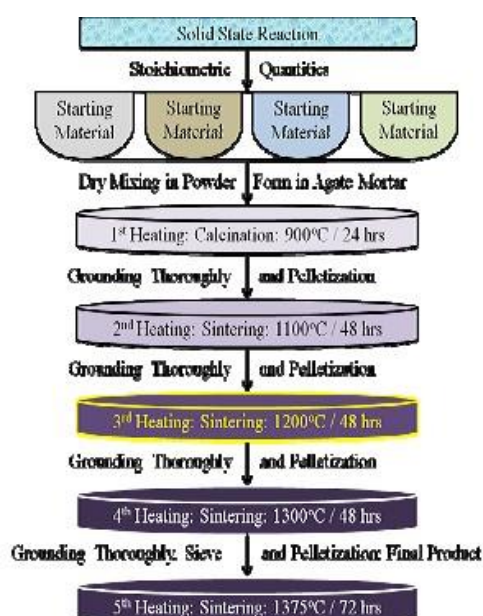
up to 1500oC for the proper reaction to take place at appreciable rate. Thus, both, thermodynamic and kinetic factors are important in SSR. In SSR method, the solid reactants react chemically without the presence of any solvent at high temperatures yielding a product which is stable. The major advantage of SSR method is, the final product in solid form is structurally pure with the desired properties depending on the final sintering temperatures. This method is environment friendly and no toxic or unwanted waste is produced after the SSR is complete. Fig. 2.1 shows various steps involved in conventional SSR route. The final product of SSR is usually in the form of a powder or a sintered, polycrystalline piece.

Large single crystals are not usually obtained by this method.

Steps Involved -

1. Take appropriate high purity starting materials, fine grain powders, in stoichiometric proportions
2. Weigh all of them, as per the calculations performed
3. Mix them together, thoroughly using agate mortar and pestle or ball milling (for large quantity sample)

4. Heat the solid powder mixture (calcination) at elevated temperatures in air using muffle furnace.
5. Repeat the calcination process twice with intermittent grinding
6. The black powder is pelletized to form uniform and compact pellets which are sintered at more elevated temperatures (~ 1375oC) for prolonged duration



Schematic illustration of sample preparation by conventional solid state reaction route

The final solid pellet sample possesses all the required properties of manganite. The final temperature and duration of sintering may vary depending on the nature and properties of the sample under preparation.

Precipitation and co-precipitation

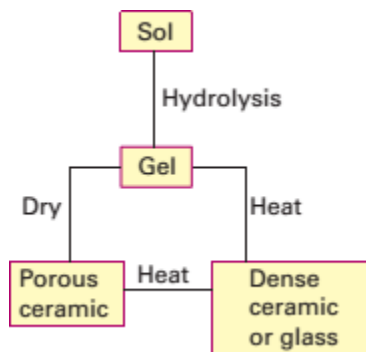
In this process the desired component is precipitated from the solution. Co precipitation is used for simultaneous precipitation of more than one component. Catalysts based on more than one component can be prepared easily by co-precipitation. The precipitation process is used for preparation of bulk catalysts and support material such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 etc.

Process

In general, the metal hydroxides are precipitated from their precursor salt solution because of their low solubility. The precipitation of hydroxides can be performed either by starting from an alkaline solution which is acidified or from acidic solution by raising the pH. However, most hydroxides for technical application are precipitated from an acidic solution by the addition of an alkaline precipitating agent. Usually, ammonia or sodium bicarbonate is used as the precipitating agent. Highly soluble inorganic salts such as nitrates, carbonates or chlorides are generally used as metal precursors. For example, preparation of alumina is done by precipitating aluminium hydroxide from aluminium nitrate solution by addition of ammonium hydroxide.

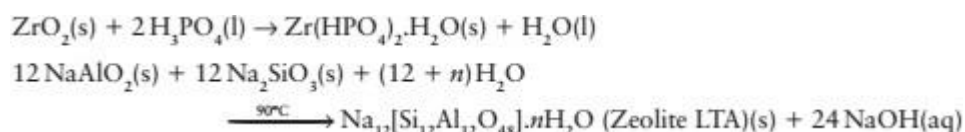
Sol Gel

Sol - Gel is a chemical solution based process of synthesizing wide range of materials especially mixed oxides which is used due to its advantages of flexible nature, low temperature synthesis etc. The control over the stoichiometry of the resultant product is a benefit of this method. Sol - Gel method has been widely used in synthesizing not only glasses and ceramics but also organics and biomaterials. Sol - Gel process provide variety of precursors to select as starting materials, covers the wide range of systems including conventional superconductors, high temperature superconductors, ferrites, manganites, multiferroics, Dilute Magnetic Semiconductors (DMS) etc. It also provides better results for inorganic as well as organic compositions. It offers homogeneous particle growth having small size (at nanoscale), uniform size distribution and mono dispersive nature of the particles. Sol-gel is very easy to handle and set-up, cost effective and yields predefined stoichiometric compounds. Fig. 2.3 depicts various steps involved in the synthesis of crystalline oxides using Sol - Gel.



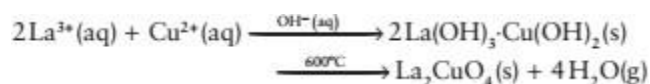
b) Solution methods

Frameworks formed from polyhedral species can often be obtained by condensation reactions in solution. Many inorganic materials, especially framework structures, can be synthesized by crystallization from solution. Although the methods used are very diverse, the following are typical reactions that occur in water:



Solution methods are extended by using **hydrothermal techniques**, in which the reacting solution is heated above its normal boiling point in a sealed vessel. Such reactions are important for the synthesis of open-structure alumina silicates (zeolites), analogous porous structures based on linked oxo-polyhedra (Section 24.13a), and related **metal-organic frameworks** (MOF) in which metal ions are linked by coordinating organic species, such as carboxylates (Section 24.13b). These porous structures are often thermodynamically metastable with respect as conversion to denser structure types so they cannot be made by direct high-temperature reactions. For example, the sodium alumina silicate zeolite $\text{Na}_{12}[\text{Si}_{12}\text{Al}_{12}\text{O}_{48}] \cdot n\text{H}_2\text{O}$ formed in solution converts on heating above 800°C to the dense alumina silicate NaSiAlO

4. More recently, other solvents such as liquid ammonia, supercritical CO₂, and organic amines have been used in so-called **solvothermal reactions**. A reaction in solution can also be used as an initial stage in the synthesis of many materials, particularly oxides, normally obtained through direct high-temperature reaction. The advantages of starting with solutions is that the reactants are mixed at the atomic level, so overcoming the problems associated with the direct reaction of two or more solid phases consisting of micrometre-sized particles. In the simplest reaction of this type, a solution of metal ions (for example, solutions of metal nitrates) is converted to a solid through a variety of methods such as evaporation of the solvent, precipitation as a simple mixed metal salt, or formation of a gel. This solid is then heated to produce the target material. Examples are



As well as the advantages of reduced reaction times, a result of the intimate mixing of the reactants, the final decomposition temperature is somewhat lower than that needed for the direct reaction of the oxides. The use of a lower temperature can also have the effect of reducing the size of the particles formed in the reaction. Further discussion of routes involving gel formation, or so-called ‘sol–gel processes’, are included in Sections

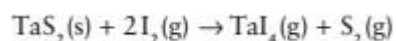
24.8 and 25.4. Although high-temperature direct-combination methods and solvothermal techniques

are the most commonly used methods in materials chemistry, some reactions involving solids can occur at low temperatures if there is no major change in structure. These so-called ‘intercalation reactions’

Intercalation

The layered metal sulfides and their intercalation compounds were introduced in Section 19.9. Here we develop a broader picture of their structures and properties. (a) Synthesis and crystal growth Key point: d-Metal disulfides are synthesized by the direct reaction of the elements in a sealed tube and purified by using chemical vapour transport with iodine. Compounds of the chalcogens with d metals are prepared by heating mixtures in a sealed tube (to prevent the loss of the volatile elements). The products obtained in this manner can have a variety of compositions. The preparation of crystalline dichalcogenides suitable for chemical and structural studies is often performed by chemical vapour transport (CVT), as described below. It is possible in some cases simply to sublime a compound, but the CVT technique can also be applied to a wide variety of nonvolatile compounds in solid-state chemistry.

In a typical procedure, the crude material is loaded into one end of a borosilicate or fused quartz tube. After evacuation, a small amount of a CVT agent is introduced and the tube is sealed and placed in a furnace with a temperature gradient. The polycrystalline and possibly impure metal chalcogenide is vaporized at one end and redeposited as pure crystals at the other (Fig. 24.37). The technique is called chemical vapour transport rather than sublimation because the CVT agent, which is often a halogen, produces an intermediate volatile species, such as a metal halide. Generally, only a small amount of transport agent is needed because on crystal formation it is released and diffuses back to pick up more reactant. For example, TaS₂ can be transported with I₂ in a temperature gradient. The reaction with I₂ to produce gaseous products



is endothermic, so the equilibrium lies further to the right at 850°C than at 750°C. Consequently, although TaI₄ is formed at 850°C, at 750°C the mixture deposits TaS₂. If, as occasionally is the case, the transport reaction is exothermic, the solid is carried from the cooler to the hotter end of the tube.

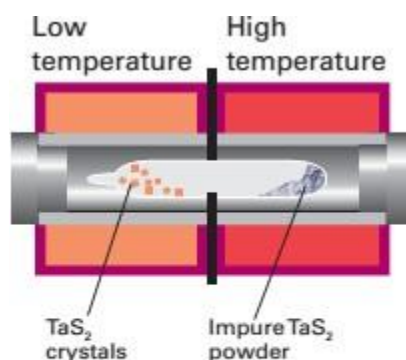


Figure 24.37 Vapour transport crystal growth and purification of TaS_2 . A small quantity of I_2 is present to serve as a transport agent.

Intercalation and insertion

We have already introduced the idea that alkali metal ions may insert between graphite sheets (Section 14.5), metal disulfide slabs (Section 19.9), and metal oxide layers (as in Li_xCoO_2 , Section 24.7h) to form intercalation compounds. For a reaction to qualify as an intercalation, or as an insertion reaction, the basic structure of the host should not be altered when it occurs. Reactions in which the structure of one of the solid starting materials is not radically altered are called topotactic reactions. They are not limited to the type of insertion chemistry we are discussing here. For example, hydration, dehydration, and ion exchange reactions may also be topotactic. The π conduction and valence bands of graphite are contiguous in energy (we have seen in fact that graphite is formally a semimetal, Section 3.19) and the favourable Gibbs energy for intercalation arises from the transfer of an electron from the alkali metal atom to the graphite conduction band. The insertion of an alkali metal atom into a dichalcogenide involves a similar process: the electron is accepted into the d band and the charge-compensating alkali metal ion diffuses to positions between the slabs. Some representative alkali metal insertion compounds are listed in Table 24.5. The insertion of alkali metal ions into host structures can be achieved by direct combination of the alkali metal and the

disulfide: Key points: Insertion compounds can be formed from the d-metal disulfides either by direct reaction or electrochemically; insertion compounds can also be formed with molecular guests. We have already introduced the idea that alkali metal ions may insert between graphite sheets (Section 14.5), metal disulfide slabs (Section 19.9), and metal oxide layers (as in Li_xCoO_2 , Section 24.7h) to form intercalation compounds. For a reaction to qualify as an intercalation, or as an insertion reaction, the basic structure of the host should not be altered when it occurs. Reactions in which the structure of one of the solid starting materials is not radically altered are called topotactic reactions. They are not limited to the type of insertion chemistry we are discussing here. For example, hydration, dehydration, and ion exchange reactions may also be topotactic. The π conduction and valence bands of graphite are contiguous in energy (we have seen in fact that graphite is formally a semimetal, Section 3.19) and the favourable Gibbs energy for intercalation arises from the transfer of an electron from the alkali metal atom to the graphite conduction band. The insertion of an alkali metal atom into a dichalcogenide involves a similar process: the electron is accepted into the d band and the charge-compensating alkali metal ion diffuses to positions between the slabs. Some representative alkali metal insertion compounds are listed in Table 24.5. The insertion of alkali metal ions into host structures can be achieved by direct combination of the alkali metal and the disulfide:



Insertion may also be achieved by using a highly reducing alkali metal compound, such as butyllithium, or the electrochemical technique of electro intercalation (Fig. 24.41). One advantage of electro intercalation is that it is possible to measure the amount of alkali metal incorporated by monitoring the current (I) passed during the synthesis (using $ne\text{ It/F}$). It is also possible to distinguish solid-solution formation from discrete-phase formation. As illustrated in Fig. 24.42, the formation of a solid solution is characterized by a gradual change in potential as intercalation proceeds. In contrast, the formation of a new discrete phase yields a steady potential over the range in which one solid phase is being converted into the other, followed by an abrupt

change in potential ΔE when that reaction is complete. Insertion compounds are examples of mixed ionic and electronic conductors. In general, the insertion process can be reversed either chemically or electrochemically. This reversibility makes it possible to recharge a lithium cell by removal of Li from the compound. In a clever synthetic application of these concepts, the previously unknown layered disulfide VS_2 can be prepared by first making the known layered compound LiVS_2 in a high-temperature process. The Li is then removed by reaction with I_2 to produce the metastable layered VS_2 , which has the TiS_2 structure:



We can imagine the insertion of ions into one-dimensional channels, between two-dimensional planes of the type we have been discussing, or into channels that intersect to form three-dimensional networks (Fig. 24.43). Aside from the availability of a site for a guest to enter, the host must provide a conduction band of suitable energy to take up electrons reversibly (or, in some cases, be able to donate electrons to the host). Table 24.6 illustrates that a wide variety of hosts are possible, including metal oxides and various ternary and quaternary compounds. We see that intercalation chemistry is by no means limited to graphite and layered disulfides.

Contemporary zeolite chemistry and ion exchange

Key points: New zeolite framework structures are synthesized by using complex template molecules;

important applications of zeolites include gas absorption and ion exchange. The role of structure-directing agents in the synthesis of zeolitic materials was described in Section 14.15. Following the discovery of a large number of new microporous structures from the 1950s onwards, many of which were prepared in the laboratory using organic templates, more recent work on zeolites has been directed towards the systematic study of template–framework relationships. These studies can be divided into two major categories. One is to understand the interaction between the framework and template through computer modelling and experiment (Section 26.14). The other is to design templates with specific geometries to direct the formation of zeolites with particular

pore sizes and connectivity. One particular area that has become the focus of much attention is the use of bulky organic and organometallic molecules as templates in the quest for new, very large pore structures. This approach has been used to make the first zeolitic materials containing 14-ring channels.⁵ Thus, the microporous silica UTD-1 (Fig. 24.47a) has been prepared by using a permethylated bis-cyclopentadienyl cobalt metallocene and the siliceous CIT-5 (CFI structure type) was prepared by using a polycyclic amine and lithium (Fig. 24.47b). Other more complex amines have been synthesized with the aim of using them as templates in zeolite synthesis and to obtain desirable pore geometries. The addition of fluorides into the zeolite precursor gel improves reaction rates and acts as a template for some of the smaller cage units, for example where linked TO₄ (T = Si, Al, P, etc.) tetrahedra arranged at the corners of a cube surround a central F ion. As part of the overall growth in the number of known synthetic zeolites, there has been a significant increase in the proportion that can be made in (essentially) pure silica form so that over 20 structural types of zeolitic silica polymorphs are now known. The use of low H₂O/SiO₂ ratios is a key factor for producing these materials and the new 'silica' phases so produced are of unusually low density, for example a purely siliceous framework with the same topology as the naturally occurring mineral chabazite, Ca_{1.85}(Al_{3.7}Si_{8.3}O₂₄), is the least dense silica polymorph known, with—according to the normal atomic radii—only 46 percent of the unit cell volume occupied. These pure silica zeolites have no overall framework charge and no extra-framework cations; as a result they are hydrophobic, leading to specific applications in molecular absorption of low polarity molecules and catalysis (Section 26.14). The experimental determination of the location of template molecules by X-ray and neutron diffraction has proved important for establishing template–framework relationships. Examples of such work include establishing the location of the templating ions in fluoride–silicalite at the channel intersections (Fig. 24.48). These approaches to the determination of structure are often used in association with computer modelling (Chapter 8). Much of the attention directed at new zeolites focuses on obtaining ever larger pore sizes or a particular pore geometry, with the eventual aim of improving their catalytic properties (Section 26.14). For example, larger pore sizes would allow larger, more complex organic molecules to undergo transformations inside the zeolite cavity. However, we

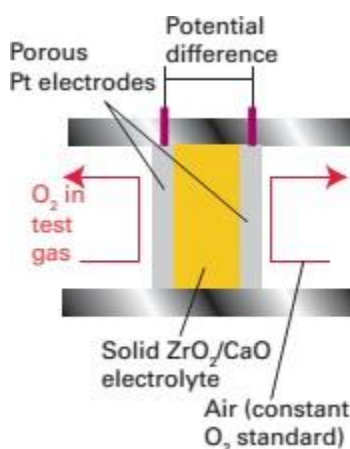
should also consider the other main applications of zeolites, which are as absorbents for small molecules and as ion exchangers. Zeolites are excellent absorbents for most small molecules such as H_2O , NH_3 , H_2S , NO_2 , SO_2 , and CO_2 , linear and branched hydrocarbons, aromatic hydrocarbons, alcohols, and ketones in the gas or liquid phase. Zeolites with different sized pores may be used to separate mixtures of molecules based on size, and this application has led to their description as molecular sieves. Through the correct selection of zeolite pore, it is possible to control the rates of diffusion of various molecules with different effective diameters, leading to separation and purification. Figure 24.49 illustrates this application schematically. Another important area where the ion-exchange properties of zeolites are exploited is in the trapping and removal of radionuclides from nuclear waste. Several zeolites, including the widely used clinoptilolite, have high selectivities for the larger alkali metal and alkaline earth metal cations, which in nuclear waste include ^{137}Cs and ^{90}Sr (Fig. 24.50). These zeolites may be vitrified by further reaction with glass-forming oxides, as discussed in Section 24.8.

Solid electrolytes

Any electrochemical cell, such as a battery, fuel cell, electrochromic display, or electrochemical sensor, requires an electrolyte. In many applications, an ionic solution (for example, dilute sulfuric acid in a lead–acid battery) is an acceptable electrolyte, but because it is often desirable to avoid a liquid phase due to possible spillage, there is considerable interest in the development of solid electrolytes. Two important and thoroughly studied solid electrolytes with mobile cations are silver tetraiodomercurate(II), Ag_2HgI_4 , and sodium alumina with the composition $\text{Na}_x\text{Al}_{11}\text{O}_{17}$. Other recently developed fast-cationic conductors include NASICON (a name formed from the letters in sodium, Na, Superionic Conductor)

of composition $\text{Na}_x\text{Zr}_2\text{P}_3\text{Si}_x\text{O}_{12}$ and a number of proton conductors that operate at or a little above room temperature, such as CsHSO_4 above 160°C . Solids exhibiting high anion mobility are rarer than cationic conductors and generally show high conductivity only at elevated temperatures: anions are typically larger than cations and so the energy barrier for diffusion through the solid is high. As a consequence, fast anion conduction in solids is limited to F and

O₂ (with ionic radii 133 pm and 140 pm, respectively). Despite these limitations, anionic conductors play an important role in sensors and fuel cells, where a typical material is ‘yttrium-stabilized zirconia’ (YSZ), of composition Y_xZr_{1-x}O_{2x2}). Table 24.1 summarizes some typical ionic conductivity values of solid electrolytes and other ionically conducting media.



Solid cationic electrolytes

Key points: Solid inorganic electrolytes often have a low-temperature form in which the ions are ordered on a subset of sites in the structure; at higher temperatures the ions become disordered over the sites and the ionic conductivity increases. Below 50°C, Ag₂HgI₄ has an ordered crystal structure in which Ag and Hg ions are tetrahedrally coordinated by I ions and there are unoccupied tetrahedral holes (Fig. 24.5a). At this temperature its ionic conductivity is low. Above 50°C, however, the Ag and Hg²⁺ ions are randomly distributed over the tetrahedral sites (Fig. 24.5b) and as a result there are many more sites that Ag ions can occupy within the structure than there are Ag ions present. At this temperature the material is a good ionic conductor, largely on account of the mobility of the Ag ions between the different sites available for it. The close-packed array of polarizable I ions is easily deformed and results in a low activation energy for

the migration of an Ag ion from one ion site to the next. There are many related solid electrolytes having similar structures containing soft anions, such as AgI and RbAg₄I₅, both of which have highly mobile Ag ions so that the conductivity of RbAg₄I₅ at room temperature is greater than that of aqueous sodium chloride. Below 50°C, Ag₂HgI₄ has an ordered crystal structure in which Ag and Hg ions are tetrahedrally coordinated by I ions and there are unoccupied tetrahedral holes (Fig. 24.5a). At this temperature its ionic conductivity is low. Above 50°C, however, the Ag and Hg²⁺ ions are randomly distributed over the tetrahedral sites (Fig. 24.5b) and as a result there are many more sites that Ag ions can occupy within the structure than there are Ag ions present. At this temperature the material is a good ionic conductor, largely on account of the mobility of the Ag ions between the different sites available for it. The close-packed array of polarizable I ions is easily deformed and results in a low activation energy for the migration of an Ag ion from one ion site to the next. There are many related solid electrolytes having similar structures containing soft anions, such as AgI and RbAg₄I₅, both of which have highly mobile Ag ions so that the conductivity of RbAg₄I₅ at room temperature is greater than that of aqueous sodium chloride.

Solid anionic electrolytes

Key point: Anion mobility can occur at high temperatures in certain structures that contain high levels of anion vacancies. Michael Faraday reported in 1834 that red-hot solid PbF₂ is a good conductor of electricity. Much later it was recognized that the conductivity arises from the mobility of F ions through the solid. The property of anion conductivity is shared by other crystals having the fluorite structure. Ion transport in these solids is thought to be by an interstitial mechanism in which an F ion first migrates from its normal position into an interstitial site (a Frenkel-type defect, Section 3.16) and then moves to a vacant F site.

Structures that have large numbers of vacant sites generally show the highest ionic conductivities because they provide a path for ion motion (although at very high levels of defects, clustering of the defects or the vacancies can lower the conductivity). These vacancies, which are equivalent to extrinsic defects, can be introduced in fairly high numbers into many simple oxides and

fluorides by doping with appropriately chosen metal ions in different oxidation states. Zirconia, ZrO_2 , at high temperature has a fluorite structure, but on cooling the pure material to room temperature it distorts to a monoclinic polymorph. The cubic fluorite structure may be stabilized at room temperature by replacing some Zr^{4+} with other ions, such as the similarly sized Ca^{2+} and Y^{3+} ions. Doping with these ions of lower oxidation number results in the introduction of vacancies on the anion sites to preserve the charge neutrality of the material and produces, for example, $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2x/2}$, the material mentioned previously as ‘yttrium stabilized zirconia’ (YSZ). This material has completely occupied cation sites in the fluorite structure but high levels of anion vacancies, with $0 < x < 0.15$. These vacant sites provide a path for oxide-ion diffusion through the structure so that a typical electrical conductivity, in, for example, $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ is 5 S cm^{-1} at 1000°C ; note that this conductivity is much lower than typical solid-state cation conductivities—even at these very high temperatures—due to the large anion size. The high oxide-ion conductivity of calcium-oxide doped zirconia is exploited in a solidstate electrochemical sensor for measuring the partial pressure of oxygen in automobile exhaust systems (Fig. 24.9).² The platinum electrodes in this cell adsorb O atoms and, if the partial pressures of oxygen are different between the sample and reference side, there is a thermodynamic tendency for oxygen to migrate through the electrolyte as the O_2 ion. The thermodynamically favoured processes are:

Mixed ionic-electronic conductors

Key point: Solid materials can exhibit both ionic and electronic conductivity.

Most ionic conductors, such as sodium alumina and YSZ, have low electronic conductivity (that is, conduction by electron rather than ion motion). Their application as solid electrolytes, in sensors for instance, requires this feature to avoid shorting-out the cell. In some cases a combination of electronic and ionic conductivity is desirable, and this type of behaviour can be found in some d-metal compounds where defects allow O_2 conduction and the metal d orbitals provide an electronic conduction band. Many such materials are perovskite-based structures with mixed oxidation states at the B cation sites (Section 3.9). Two examples are La

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$. These oxide systems are good electronic conductors with partially filled bands as a result of the nonintegral d-metal oxidation number and can conduct by O_2 migration through the perovskite O_2 ion sites. This type of material is of use in solid oxide fuel cells (SOFC, Box 24.1), one type of fuel cell mentioned in Box 5.1, in which one electrode has to allow diffusion of ions through a conducting electrode.

Inorganic pigments

Many inorganic solids are intensely coloured and are used as pigments in colouring inks, plastics, glasses, and glazes. Whereas many insoluble organic compounds (for example the C.I. Pigment Red 48, which is calcium 4-((5-chloro-4-methyl-2-sulfophenyl) azo)-3-hydroxy-2-naphthalenecarboxylic acid) are also used as pigments, inorganic materials often have advantages in terms of applications associated with their chemical, light, and thermal stability. Pigments were originally developed from naturally occurring compounds such as hydrated iron oxides, manganese oxides, lead carbonate, vermilion (HgS), orpiment (As_2S_3), and copper carbonates. These compounds were even used in prehistoric cave paintings. Synthetic pigments, which are often analogues of naturally occurring compounds, were developed by some of the earliest chemists and alchemists, and the first synthetic chemists were probably those involved in making pigments. Thus, the pigment Egyptian blue ($\text{CaCuSi}_4\text{O}_{10}$) was made from sand, calcium carbonate, and copper ores as long as 3000 years ago. This compound and a structural analogue, Chinese blue ($\text{BaCuSi}_4\text{O}_{10}$), which was first made about 2500 years ago, have a structure containing square-planar copper(II) ions surrounded by Si_4O_{10} groups (Fig. 24.63). Inorganic pigments continue to be important commercial materials and this section summarizes some of the recent advances in this field. As well as producing the colours of inorganic pigments as a result of the absorption and reflection of visible light, some solids are able to absorb energy of other wavelengths (or types, for example electron beams) and emit light in the visible region. This luminescence is responsible for the properties of inorganic phosphors.

Coloured solids

Key point: Intense colour in inorganic solids can arise through dd transitions, charge transfer (and the analogous interband electron transfer), or intervalence charge transfer. The blue colour of CoAl_2O_4 and $\text{CaCuSi}_4\text{O}_{10}$ stems from the presence of dd transitions in the visible region of the electromagnetic spectrum. The characteristic intense colour of cobalt aluminate is a result of having a noncentrosymmetric tetrahedral site for the metal ion, which removes the constraint of the Laporte selection rule of octahedral environments (Section 20.6). The chemical and thermal stabilities are due to the location of the Co^{2+} ion in the close-packed oxide arrangement. Other inorganic pigments with colours based on dd transitions include Ni-doped TiO_2 (yellow) and $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (green).

White and black pigments

Some of the most important compounds used to modify the visual characteristics of polymers and paints have visible-region absorption spectra that result in them appearing either white (ideally no absorption in the visible region) or black (complete absorption between 380 and 800 nm).

(a) White pigments

Key point: Titanium dioxide is used almost universally as a white pigment. White inorganic materials can also be classified as pigments and vast quantities of these compounds are synthesized for applications such as the production of white plastics and paints. Important commercial compounds of this class that have been used extensively historically are TiO_2 , ZnO , and ZnS , lead(II) carbonate, and lithopone (a mixture of ZnO and BaSO_4); note that none of the metals in these materials has an incomplete d-electron shell that might otherwise induce colour through dd transitions. Titanium dioxide, TiO_2 , in either its rutile or anatase forms (Fig. 24.66), is produced from titanium ores, often ilmenite, FeTiO_3 , by the sulfate process (which involves dissolution in concentrated H_2SO_4 and subsequent precipitation through hydrolysis) or the chloride process (which is based on the reaction of mixed complex titanium oxides with chlorine to produce TiCl_4 , which is then combusted with oxygen at over 1000°C). These routes produce

very high quality TiO_2 free from impurities (which is essential for a bright white pigment) of controlled particle size. The desirable qualities of TiO_2 as a white pigment derive from its excellent light scattering power, which in turn is a result of its high refractive index ($n_r = 2.70$), the ability to produce very pure materials of a desired particle size, and its good light-fastness and weather resistance. Uses of titanium dioxide, which nowadays dominates the white pigment market, include paints, coatings, and printing ink (where it is often used in combination with coloured pigments to increase their brightness and hiding power), plastics, fibres, paper, white cements, and even foodstuffs (where it can be added to icing sugar, sweets, and flour to improve their brightness).

Black, absorbing, and specialist pigments

Key points: Special colour, light absorbing, and interference effects can be induced in inorganic materials used as pigments. The most important black pigment is carbon black, which is a better defined, industrially manufactured form of soot. Carbon black is obtained by partial combustion or pyrolysis (heating in the absence of air) of hydrocarbons. The material has excellent absorption properties right across the visible region of the spectrum and applications include printing inks, paints, plastics, and rubber. Copper(II) chromite, CuCr_2O_4 , with the spinel structure (Fig. 24.18), is used less frequently as a black pigment. These black pigments also absorb light outside the visible region, including the infrared, which means that they heat up readily on exposure to sunlight. Because this heating can have drawbacks in a number of applications, there is interest in the development of new materials that absorb in the visible region but reflect infrared wavelengths; $\text{Bi}_2\text{Mn}_4\text{O}_{10}$ is one compound that exhibits these properties.

Examples of more specialist inorganic pigments are magnetic pigments based on coloured ferromagnetic compounds such as Fe_3O_4 and CrO_2 , and anticorrosive pigments such as zinc phosphates. The deposition of inorganic pigments as thin layers on to surfaces can produce additional optical effects beyond light absorption. Thus deposition of TiO_2 or Fe_3O_4 , as thin

layers a few hundred nanometres thick, on flakes of mica produces lustrous or pearlescent pigments where interference effects between light scattered from the various surfaces and layers produces shimmering and iridescent colours.

Molecular materials and fullerides

The majority of compounds discussed so far in this chapter have been materials with extended structures in which ionic or covalent interactions link all the atoms and ions together into a three-dimensional structure. Examples include infinite structures based on ionic, as in NaCl, or covalent interactions, as in SiO₂. These materials are widely used in applications such as heterogeneous catalysis, rechargeable batteries, and electronic devices due to the chemical and thermal stability that derives from their linked structures. It is often possible to tune the properties of many solids exactly, for example by doping, introducing defects, or forming solid solutions. However, control of the arrangement of atoms into a particular structure cannot be achieved to the same degree for solids as for molecular systems. Thus a coordination or organometallic chemist can modify a molecule by introducing a wide range of ligands, often through simple substitution reactions. The desire to combine the synthetic and chemical flexibility of molecular chemistry with the properties of classical solid-state materials has led to the rapid emergence of the area of molecular materials chemistry, where functional solids are produced from linked and interacting molecules or molecular ions.

Fullerides

Key points: Solid C₆₀ can be considered as a close-packed array of fullerene molecules interacting only weakly through van der Waals forces; holes in arrays of C₆₀ molecules may be filled by simple and solvated cations and small inorganic molecules. The chemical properties of C₆₀ span many of the conventional borders of chemistry and include the chemistry of C₆₀ as a ligand (Section 14.6). In this section we describe the solid-state chemistry of solid fullerene, C₆₀(s), and the MnC₆₀ fulleride derivatives that contain discrete C₆₀ⁿ⁻ molecular anions. The synthesis and chemistry of the more complex carbon nanotubes are discussed in Section 25.7.

Crystals of C₆₀ grown from solution may contain included solvent molecules, but with the correct crystallization and purification methods—for example, using sublimation to eliminate the solvent molecules—pure C₆₀ crystals may be grown. The solid structure has a face-centred cubic array of the C₆₀ molecules as shown in Fig. 24.67, as would be expected on the basis of efficient packing of these almost spherical molecules. At room temperature the molecules can rotate freely on their lattice positions and powder X-ray diffraction data collected from crystalline C₆₀ are typical of an fcc lattice with a lattice parameter of 1417 pm. The molecules are separated by a distance of 296 pm, which is similar to the value found for the interlayer separation in graphite (335 pm). On cooling the solid, the rotation halts and adjacent molecules align relative to each other such that an electron-rich region of one C₆₀ molecule is close to an electron-poor region in its neighbor.

Molecular materials chemistry

The ability to modify the shapes, and thus the packing and arrangements of inorganic molecules in the solid state, is one valuable aspect of molecular materials chemistry. This capability, when associated with some of the specific properties of inorganic compounds such as the unpaired d electrons of d metals, can allow control of magnetic and electronic properties. This section considers a number of such inorganic molecular materials being developed at the frontiers of the subject.

(a) One-dimensional metals

Key points: A stack of molecules that interact with each other along one dimension, as occurs in a number of crystalline platinum complexes, can show conductivity in that direction; a Peierls distortion ensures that no one-dimensional solid is a metallic conductor below a critical temperature. A one-dimensional metal is a material that exhibits metallic properties along one direction in the crystal and nonmetallic properties orthogonal to that direction. Such properties arise when the orbital overlap occurs along a single direction in the crystal (as in VO₂). Several classes of one-dimensional metals are known and include (SN)_x and organic polymers, such as

doped polyacetylenes $[(CH)I_{0.25}]_n$, but this section is concerned specifically with chains of interacting d metals, particularly Pt. In such materials, the structural requirements for a one-dimensional metal are satisfied by the presence of square-planar complexes that stack one above another (Fig. 24.70). The ligands surrounding the metal atom ensure large inter chain separations, of at least 900 pm, while the average intra chain metal-metal distance is less than 300 pm. Square-planar complexes are commonly found for metal ions with d8 configurations, and the overlap of orbitals between d8 species is greatest for the heavy d metals of Period 6 (which use 5d orbitals). Hence the compounds of interest are mainly associated with Pt(II) and Ir(I), where a band is formed from overlapping d z^2 and pz orbitals. The dz^2 band is full for Pt(II), and a partially full level is achieved by oxidation of the platinum. Many d8 integral oxidation number tetracyanoplatinate(II) complexes are semiconductors with dPtPt 310 pm, and the partial oxidation of these salts results in PtPt distances of less than 290 pm and metallic behaviour. Typical means of oxidizing the chain are the incorporation of extra anions into the structure or the removal of cations. The first one-dimensional metal Pt complex was made in 1846 by oxidation of a solution of $K_2Pt(CN)_4 \cdot 3H_2O$ with bromine, which on evaporation gave crystals of $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$, known as KCP (as in Fig. 24.70). The electronic properties of one-dimensional solids are not quite as simple as has been implied by the discussion so far, as a theorem due to Rudolph Peierls states that, at $T = 0$, no one-dimensional solid is a metal! The origin of Peierls' theorem can be traced to a hidden assumption in the discussion so far: we have supposed that the atoms lie in a line with a regular separation. However, the actual spacing in a one-dimensional solid (and any solid) is determined by the distribution of the electrons, not vice versa, and there is no guarantee that the state of lowest energy is a solid with a regular lattice spacing. In fact, in a one-dimensional solid at $T = 0$, there always exists a distortion, a Peierls distortion, which leads to a lower energy than in the perfectly regular solid. An idea of the origin and effect of a Peierls distortion can be obtained by considering a one-dimensional solid of N atoms and N valence electrons (Fig. 24.71). Such a line of atoms distorts to one that has long and short alternating bonds. Although the longer bond is energetically unfavourable, the strength of the short bond more than compensates for the weakness of the long bond and the net effect is a

lowering of energy below that of the regular solid. Now, instead of the electrons near the Fermi surface being free to move through the solid, they are trapped between the longer-bonded atoms (these electrons have antibonding character, and so are found outside the internuclear region between strongly bonded atoms). The Peierls distortion introduces a band gap in the centre of the original conduction band, and the filled orbitals are separated from the empty orbitals. Hence, the distortion results in a semiconductor or insulator, not a metallic conductor.

(b) Molecular magnets

Molecular solids containing individual molecules, clusters, or linked chains of molecules can show bulk magnetic effects such as ferromagnetism.

Molecular inorganic magnetic materials, in which individual molecules, or units constructed from such molecules, contain d-metal atoms with unpaired electrons, is a class of compounds of growing interest. Generally the phenomena associated with long-range interaction of electron spins, such as ferromagnetism and antiferromagnetism, are much weaker as the short, superexchange-type pathways that are found in metal oxides do not exist. However, as with all molecular systems the opportunity exists to tune interactions between metal centres by tailoring the ligand properties.

(c) Inorganic liquid crystals

Inorganic metal complexes with disc- or rod-like geometries can show liquid crystalline properties.

Liquid crystalline, or mesogenic, compounds possess properties that lie between those of solids and liquids and include both. For instance, they are fluid, but with positional order in at least one dimension. Such materials have become widely used in displays. The molecules that form liquid crystalline materials are generally calamitic (rod-like) or discotic (disc-like), and these shapes lead to the ordered liquid-type structures in which the molecules align in a particular direction (Fig. 24.73). Although most liquid crystalline materials are totally organic

there is a growing number of inorganic liquid crystals based on the coordination compounds of metals and on organometallic compounds. These metalcontaining liquid crystals show similar properties to the purely organic systems but offer additional properties associated with a d-metal centre, such as redox and magnetic effects.

POSSIBLE QUESTIONS

UNIT-I

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. Give some examples of cationic and anionic electrolytes
2. Write a note coloured solids
3. Give examples of white and black pigments.
4. Define molecular magnets
5. Write a note on inorganic liquid crystals
6. What is meant by fullerides?

PART-C (6 MARKS)

1. How prepare inorganic solids by using Conventional heat and beat methods
2. Write detail about Co-precipitation method, Sol-gel methods
3. Explain the following methods
 - a) Hydrothermal method
 - b) Ion-exchange
 - c) Intercalation methods
4. Write detail about Solid electrolytes and colour solids
5. Give the technological importance Inorganic solids
6. Detail in Molecular material and fullerides

KARPAGAM ACADEMY OF HIGHER EDUCATION

SUBJECT : NOVEL INORGANIC SOLIDS

SEMESTER : V

Class : III-B. Sc Chemistry

SUBJECT CODE: 17CHU503B

Batch – (2017-2020)

Unit-II-Multiple choice Questions

Unit-II-Multiple choice Questions

S. No	Question	Option-I	Option-II	Option-III	Option-IV	Answer
1.	Which of the following is used in electro optic modulators?	Lithium tantalite	Barium sodium niobate	Lithium niobate	Lithium sodium niobate	Lithium niobate
2.	Carbon has _____ valence electrons?	3	2	1	4	4
3.	Carbon forms _____ bonds.	physical	metallic	ionic	covalent	covalent
4.	Which of the following is not a way to represent chemical bonds?	chemical formula	electron dot diagram	ball and stick model	structural diagram	chemical formula
5.	Which of the following is not a form of carbon?	diamond	fullerene	microtubules	graphite	microtubules
6.	Which form of carbon has the highest melting point?	graphite	fullerene	diamond	microtubules	diamond
7.	Which form of carbon is used as the lead in lead pencils?	microtubules	fullerene	diamond	graphite	graphite
8.	Which form of carbon is man-made?	diamond	fullerene	graphite	microtubules	fullerene
9.	In a nanotube, carbon atoms are arranged in the shape of	a crystal	flat layers	a geodesic dome	a hollow cylinder	a hollow cylinder
10.	In diamond, carbon atoms are arranged in the shape of	a crystal	flat layers	a geodesic dome	a hollow cylinder	a crystal

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Unit-II-Multiple choice Questions

11.	Buckyballs are a type of _____ shaped like _____	fullerene; a hollow cylinder	graphite; flat layers	graphite; a crystal	fullerene; a geodesic dome	fullerene; a geodesic dome
12.	Carbon nanotube is made of?	Circular tube made of graphite	Nanotubes are hollow cylinders made up of carbon atoms	Nanotubes are made of carbon sheet	Circular tube made of Carbon	Circular tube made of Carbon
13.	What is a nanofluid?	Nanofluids are fluids in nanosize device	Nanofluids are mixture of different fluids	Nanofluids are fluids with suspensions of solid nano particles	Nanofluids are fluids in nanosize scale	Nanofluids are fluids with suspensions of solid nano particles
14.	Carbon nanotubes are stronger than steel.	Carbon nanotubes are 100 times stronger than steel at one	Carbon nanotubes are 10 times stronger than steel at one	Carbon nanotubes are 1000 times stronger than steel at one sixth of the weight	Carbon nanotubes are 10 times stronger than steel at one	Carbon nanotubes are 100 times stronger than steel at one
15.	Carbon nanotubes have the ability to sustain temperature as high as:	800 C	2800 C	3000 C	1000 C	2800 C
16.	Single Walled Carbon Nano tubes are	excellent conductors	Poor conductor	Poor conductor than MWCNT	semi-conductor	excellent conductors

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17.	Nanofluid thermal conductivity is increase by a factor of 20-30% by adding	10-15% of nano particles	20-30% of nano particles	3-4% of nano particles	5-7% nano particles	20-30% of nano particles
18.	Tensile youngs modulus of SWCNT	A greater than c-fiber P100 by 1.6 times	Lower than c-fiber P100 by 1.6 times	A greater than c-fiber P100 by 2.8 times	Lower than c-fiber P100 by 2.8 times	A greater than c-fiber P100 by 1.6 times
19.	carbon nanotubes are	Large molecules	small molecules	long chain molecule	small chain molecule	Large molecules
20.	CNT has Howmany nanometers	1-3	1-8	1-6	1-4	1-3
21.	CNT are already being used in polymers to control	enhance conductivity	Poor conductivity	medium conductivity	no conductance	enhance conductivity
22.	he discovery of carbon nanotubes (CNT) in	1992	1991	1988	1987	1991
23.	A carbon nanotube is	Tube shaped material	plain shape material	square shape material	no shape	Tube shaped material
24.	A single-walled carbon nanotube is	One layer	two layers	three layers	six layers	One layer
25.	The atomic number of carbon is	6	8	15	18	6
26.	Carbon has _____protons	2	6	4	8	2
27.	Carbon has _____neutrons	6,7,8	8,6,7	7,8,6	8,7,6	6,7,8
28.	Carbon has _____electrons.	4	8	2	6	6

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29.	How many chemical bonds does each carbon atom form to create a sheet of graphene?	3	5	7	9	3
30.	How many nanotubes are in the sample shown by Dr. Baughman?	two	three	five	many	many
31.	Which property of nanotubes is especially unique and useful?	Tensile strength	elastic modulus	mechanical property	conductivity	Tensile strength
32.	What two properties of carbon nanotubes make them an ideal material for muscles?	Tensile and mechanical	tensile and electrical	physical and thermal	laser and tensile	Tensile and mechanical
33.	CNT improves	electrical conductivity	thermal conductivity	electrical and thermal conductivity	no conductivity	electrical and thermal conductivity
34.	Carbon nanotubes are	Less toxicity	High toxicity	no toxicity	medium toxicity	Less toxic
35.	Scientists have created a new structure by encapsulating a single layer of fullerene molecules between	two graphene sheets	three graphene sheets	four graphene sheets	one graphene sheets	two graphene sheets
36.	Carbon Nanotube Solar Cells: Twice as Efficient as Current Models	Lighter	Heavier	Harder	Smaller	Lighter

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Unit-II-Multiple choice Questions

37.	Engineers Now Understand How Complex Carbon Nanostructures Form	microscopic tubular	macroscopic tubular	universal tubular	large tubular	microscopic tubular
38.	Reusable Carbon Nanotubes Could Be the Water Filter of the Future, Says Study	Improved SWCNT	Enhanced SWCNT	suppressed SWCNT	worsed SWCNT	Enhanced SWCNT
39.	Plant Inspiration Could Lead to Flexible Electronics	Versatile and light-weight	Versatile and small-weight	Limited and small-weight	Limited and light-weight	Versatile and light-weight
40.	Find the odd one out.	Frequency mixing	Second-harmonic generation	Optical mixing	Raman and Rayleigh scattering	Frequency mixing
41.	Which of the following is used in electro optic modulators?	Lithium tantalite	Barium sodium niobate	Lithium niobate	Lithium sodium niobate	Lithium niobate
42.	Carbon has _____ valence electrons?	3	2	1	4	4
43.	Carbon forms _____ bonds	physical	metallic	ionic	covalent	covalent
44.	Which of the following is not a way to represent chemical bonds?	chemical formula	electron dot diagram	ball and stick model	structural diagram	chemical formula
45.	Which of the following is not a form of carbon?	diamond	fullerene	microtubules	graphite	microtubules
46.	Which form of carbon has the highest melting point?	graphite	fullerene	diamond	microtubules	diamond
47.	Which form of carbon is used as the lead in lead pencils?	microtubules	fullerene	diamond	graphite	graphite
48.	Which form of carbon is man-made?	diamond	fullerene	graphite	microtubules	fullerene

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Unit-II-Multiple choice Questions

49.	In a nanotube, carbon atoms are arranged in the shape of	a crystal	flat layers	a geodesic dome	a hollow cylinder	a hollow cylinder
50.	In diamond, carbon atoms are arranged in the shape of	a crystal	flat layers	a geodesic dome	a hollow cylinder	a crystal
51.	Buckyballs are a type of _____ shaped like	fullerene; a hollow cylinder	graphite; flat layers	graphite; a crystal	fullerene; a geodesic dome	fullerene; a geodesic dome
52.	The size of nanoparticles is between	100 to 1000 nm	0.1 to 10 nm	1 to 100 nm	0.01 to 1 nm	1 to 100 nm
53.	Who coined the word Nanotechnology?	Eric Drexler	Michael Faraday	Granqvist	Buhrman	Eric Drexler
54.	Carbon nanotubes are stronger than steel.	Carbon nanotubes are 100 times stronger than steel at one	Carbon nanotubes are 10 times stronger than steel at one	Carbon nanotubes are 1000 times stronger than steel at one sixth of the weight	Carbon nanotubes are 10 times stronger than steel at one	Carbon nanotubes are 100 times stronger than steel at one
55.	Carbon nanotubes have the ability to sustain temperature as high as:	800 C	2800 C	3000 C	1000 C	2800 C
56.	Single Walled Carbon Nano tubes are	excellent conductors	Poor conductor	Poor conductor than MWCNT	semi-conductor	excellent conductors
57.	Nanofluid thermal conductivity is increase by a factor of 20-30% by adding	10-15% of nano particles	20-30% of nano particles	3-4% of nano particles	5-7% nano particles	20-30% of nano particles

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58.	carbon nanotubes are	Large molecules	small molecules	long chain molecule	small chain molecule	Large molecules
59.	Find the odd one out.	Frequency mixing	Second-harmonic generation	Optical mixing	Raman and Rayleigh scattering	Frequency mixing
60.	Tensile youngs modulus of SWCNT	A greater than c-fiber P100 by 1.6 times	Lower than c-fiber P100 by 1.6 times	A greater than c-fiber P100 by 2.8 times	Lower than c-fiber P100 by 2.8 times	A greater than c-fiber P100 by 1.6 times

UNIT II

Nanomaterials:

Overview of nanostructures and nanomaterials: classification.

Preparation of gold and silver metallic nanoparticles, self-assembled nanostructures-control of nanoarchitecture-one dimensional control. Carbon nanotubes and inorganic nanowires.

Bio-inorganic nanomaterials, DNA and nanomaterials, natural and antisical nanomaterials, bionano composites.

Top-down and bottom-up fabrication

Key points: Top-down fabrication methods carve out or add on nanoscale features to a bulk material by using physical methods; bottom-up fabrication methods assemble atoms or molecules in a controlled manner to build nanomaterials piece by piece. There are two basic techniques for the fabrication of nanoscale entities. The first is to take a macroscale (or microscale) object and carve out nanoscale patterns. Methods of this sort are called top-down approaches. In top-down approaches, patterns are first designed on a large scale, and their lateral dimensions are reduced and then used to transfer the nanoscaled features into or on to the bulk material. Physical interactions are used in top-down fabrication approaches, such as photolithography, e-beam lithography, and soft lithography. The most common and well-known approach is photolithography, the technique used to fabricate very large-scale integrated circuits having feature dimensions on the 100 nm scale (Fig. 25.4). The second technique is to build larger objects by controlling the arrangement of their component smaller-scale objects. Methods of this sort are called bottom-up approaches and start with control over the arrangements of atoms and molecules. This chapter emphasizes the bottom-up approach to nanoscale fabrication because of its focus on the interactions of atoms and molecules and their arrangement into larger functional structures. The two basic approaches most widely used to prepare nanomaterials, solution methods and vapour-phase methods, are bottom-up methods because control over the arrangement of individual atoms is exerted to achieve larger-scale structures.

(a) Solution-based synthesis of nanoparticles

Key points: Solution-based synthetic methods are the main techniques for nanoparticle synthesis because they have atomically mixed and highly mobile reagents, allow for the incorporation of stabilizing molecules, and have been widely successful in practice; the two stages of crystallization from solution are nucleation and growth. As discussed in Chapter 24, the two basic techniques used to generate inorganic solids are direct-combination methods and solution-based methods. The former does not lend itself well to the synthesis of nanoparticles because the

reactants tend to be larger than nanoparticles and therefore require long times to reach equilibrium. Moreover, the use of elevated temperatures leads to particle growth and coarsening during the reaction period, resulting in large crystallite sizes. There are, however, some examples of using mechanical ball-milling at low temperature to break macroscopic powders into nanoparticles. However, solution-based methods permit excellent control over the crystallization of inorganic materials and are widely used. The techniques used to make nanoparticles are similar to those described in Chapter 24 to make solid-state compounds. Special care must be taken to control the size and shape of the particles during nanoparticles synthesis, as well as their uniformity in size and shape. By fine-tuning the crystallization process from solution, highly monodisperse, uniformly shaped nanoparticles of a wide range of compositions can be prepared from combinations of elements from throughout the periodic table. Because the reactants in solution-based methods are mixed on an atomic scale and solvated in a liquid medium, diffusion is fast and diffusion distances are typically small. Therefore, reactions can be carried out at low temperature, which minimizes the thermally driven particle growth that is problematic in direct combination methods. Although the specifics of each reaction differ greatly, the basic stages in solution chemistry are:

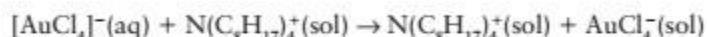
1. Solvate the reactant species and additives.
2. Form stable solid nuclei from solution.
3. Grow the solid particles by addition of material until the reactant species are consumed.

The basic aim in solution synthesis is to generate in a controlled manner the simultaneous formation of large numbers of stable nuclei that undergo little further growth. If growth is to occur, it should occur independently of the nucleation step because then all particles have a chance to grow to similar sizes. If performed successfully, the particles will be monodisperse and in the nanometre range. The drawback to the solution method is that the particles can undergo Ostwald ripening, in which smaller particles in the distribution redissolve and their solvated species reprecipitate on to larger particles, so increasing the size distribution and decreasing the

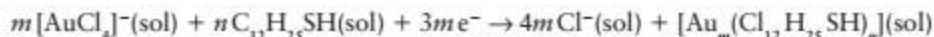
total particle count. To prevent this unwanted ripening, stabilizers, surfactant molecules that help to stabilize the particles against growth and dissolution, are added. As there are many methods to synthesize nanoparticles, we limit this discussion to a few well-known examples. The first example is metallic nanoparticles, such as gold. In 1857, Michael Faraday found that reduction of an aqueous solution of $[\text{AuCl}_4]^-$ with phosphorus in CS₂ produced a deep-red suspension that contained nanoparticles of gold. Because sulfur forms chemical bonds to gold, sulfur-containing species are good stabilizing agents and the most widely used stabilizer for gold nanoparticles contain a thiol group (SH). An approach has been developed in the same spirit as Faraday's to control the size and dispersity of gold nanoparticles by using $[\text{AuCl}_4]^-$ and thiol stabilizers. The reaction is relatively simple and the procedure produces air-stable gold nanoparticles with diameters between 1.5 and 5.2 nm. In the so-called Brust-Schiffrin method, $[\text{AuCl}_4]^-$ is first transferred from water to methylbenzene (toluene) by using tetraoctylammonium bromide as a phase-transfer agent.

The methylbenzene contains dodecanethiol as a stabilizer and, after transfer, NaBH_4 is used as a reducing agent to precipitate Au nanoparticles with dodecanethiol surface groups:

Transfer:



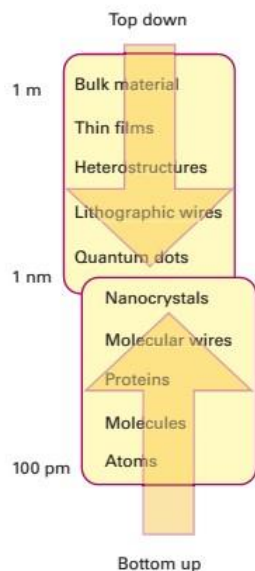
Precipitation (of the $[\text{Au}_m(\text{C}_{12}\text{H}_{25}\text{SH})_n]$ nanoparticle):



where sol is methylbenzene. The ratio of stabilizer ($\text{C}_{12}\text{H}_{25}\text{SH}$) to metal (Au) controls the particle size in the sense that higher stabilizer:metal ratios lead to the smaller metal core sizes. By adding the NaBH_4 reductant quickly and cooling the system as soon as possible after the reaction terminates, smaller and more monodisperse nanoparticles are formed.

The rapid addition of reductant improves the probability of simultaneous formation of all nuclei. By cooling the solution quickly, both post-nucleation growth and dissolution of particles

are minimized. Similar approaches can be used for other metal nanoparticles. Quantum dots of materials such as GaN, GaP, GaAs, InP, InAs, ZnO, ZnS, ZnSe, CdS, and CdSe have been investigated for their optical properties (Section 25.2) because their interband absorption and fluorescence occur in the visible spectrum. As an early example of their preparation, dimethylcadmium is dissolved in mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO), and the selenium source, which is often Se dissolved in TOP or TOPO, is added at room temperature. The solution is injected into a reactant vessel containing vigorously stirred, hot TOPO, which permits widespread nucleation of TOPO-stabilized CdSe QDs. The addition of the room-temperature liquid lowers the temperature of the solution and prevents further nucleation or growth (because the activation barriers are so high). The solution is then reheated to a temperature that allows for slow growth but no further nucleation. This step leads to nanoparticles with narrow size distributions and sizes in the range 2–12 nm. Alternative, less hazardous synthetic methods have been developed and are being pursued. Cadmium sulfide can be grown in pH-controlled aqueous solutions of Cd(II) salts with polyphosphate stabilizers by the addition of a sulfur source. For example, at pH 10.3 the addition of Na₂S causes the precipitation of CdS nanoparticles from aqueous solutions containing Cd(NO₃)₂ and sodium polyphosphate.



These QDs range in size from 1 to 10 nm, and the size is controllable through the reactant concentrations and the rate of addition of the reactant. Oxide nanoparticles can also be grown by solution methods. Many applications use colloidal particles of oxides such as SiO₂ and TiO₂ for food, ink, paints, coatings, and so on. Many of the efforts to achieve controlled oxide nanoparticle growth stem from earlier work in traditional ceramic and colloidal applications, where particle sizes from 1 nm to 1 µm are used. Silica, SiO₂, and titania, TiO₂, are probably the best-known oxides grown from solution. Typical schemes involve the controlled hydrolysis of metal alkoxides. All successful hydrolysis reactions of metal alkoxides aim to follow the same basic rules as described above: the controlled nucleation stage and slow growth stage are performed independently. In all cases, strict monitoring of the pH, precursor chemistry, reactant concentration, rate of addition of reactant, and temperature is required to control the final size and shape of the particles. An important example of nanoparticle oxide use is in the photo electrochemical solar cell known as the Grätzel cell. This cell uses nanocrystalline TiO₂ as a medium to transfer electrons from an organoruthenium dye to a conductor. Nucleation occurs in the hydrolysis of titanium isopropoxide that is added dropwise into vigorously stirred 0.1 M HNO₃(aq). The filtered nanoparticles are then placed in an autoclave and allowed to grow by the hydrothermal addition of material. The size, shape, and state of agglomeration are controlled by adjusting the conditions of either the nucleation or the growth stage.

One-dimensional control: carbon nanotubes and inorganic nanowires

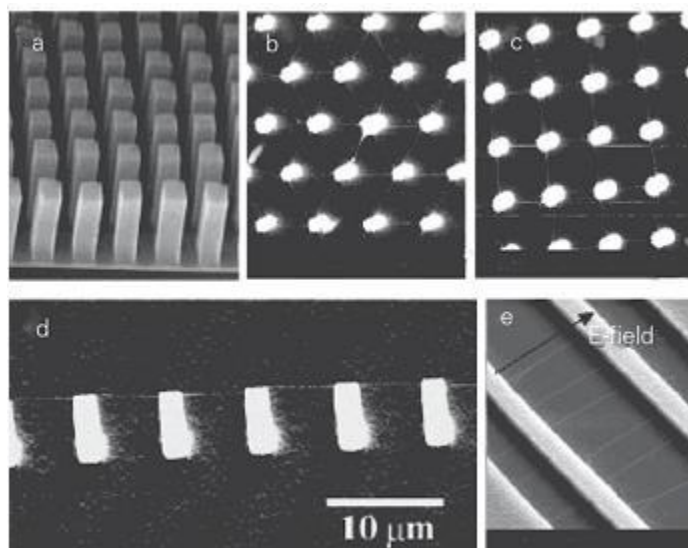
Key point: Dimensionality plays a crucial role in determining the properties of materials. The elongated one-dimensional morphology of nanorods, nanowires, nanofibres, nanowhiskers, nanobelts, and nanotubes has been studied extensively because one-dimensional systems are the lowest dimensional structures that can be used for efficient transport of electrons and optical excitation. They are therefore expected to be crucial to the function and integration of nanoscale devices. Not much is known, however, about the nature of localization that could preclude

transport through one-dimensional systems. Such systems should possess discrete molecular-like states extending over large distances and exhibit some exotic phenomena, such as the effective separation of the spin and charge of an electron. There are also many applications where one-dimensional nanostructures could be exploited, including nanoelectronics, very strong and tough composites, functional nanostructured materials, and novel probe microscopy tips. To address these fascinating fundamental scientific issues and potential applications, two important questions pose key challenges to the fields of condensed matter chemistry

and physics research. First, how can atoms or other building blocks be assembled rationally into structures with nanometre-sized diameters but much greater lengths? Second, what are the intrinsic properties of these quantum wires and how do these properties depend, for example, on their diameter and their structure? A key class of nanomaterials that offers potential answers to these questions is carbon nanotubes (CNTs). Carbon nanotubes are perhaps the best example of novel nanostructures fabricated through bottom-up chemical synthesis approaches. They have very simple chemical composition and atomic bonding configuration but exhibit remarkably diverse structures and unparalleled physical properties. These novel materials have found application as chemical sensors, fuel cells, field-effect transistors, electrical interconnects, and mechanical reinforcers. The structure and properties of buckminsterfullerene, C₆₀, and related species have produced much activity in the chemistry and materials sciences communities. The now familiar soccer-ball structure of C₆₀ itself was discussed in Chapter 14. Carbon nanotubes were discovered in the early 1990s by electron microscopy. The bonding, local coordination, and general structure of CNTs are similar to those of buckminsterfullerene, but CNTs can have a greatly extended length, leading to a tube rather than a ball structure (Fig. 25.16). Carbon nanotubes are cylindrical shells formed conceptually by rolling graphene (graphite-like) sheets into closed tubular nanostructures with diameters matching that of C₆₀ (0.5 nm) but lengths up to micrometres. A single-walled nanotube (SWNT) is formed by rolling a sheet of graphene into a cylinder along an (m,n) lattice vector in the graphene plane (Fig. 25.17). The (m,n) indices determine the diameter and chirality of the CNT, which in turn control its physical properties.

Most CNTs have closed ends where hemispherical units cap the hollow tubes. Carbon nanotubes self-assemble into two distinct classes, SWNTs and multiwalled carbon nanotubes (MWNTs). In MWNTs, the tube wall is composed of multiple grapheme sheets. Morphosynthetic control provides routes to tune the details of these self-assembled nanostructures. This self-assembly occurs during synthesis using several of the fabrication techniques we have already described, including pulsed laser ablation, laser-assisted catalytic growth, chemical vapour deposition (CVD) based on hydrocarbon gases, and carbon arc discharge. All these strategies rely on vaporizing carbon and condensing some fraction into extended nanostructures. Laser vaporization methods typically make relatively small amounts of nanocarbons; specialized CVD techniques have been developed to synthesize CNTs in quantities in excess of a few milligrams. In the CVD approach, a hydrocarbon gas such as methane is decomposed at elevated temperatures and C atoms are condensed on to a cooled substrate that may contain various catalysts, such as Fe. This CVD method is attractive because it produces open-ended tubes (which are not produced in the other methods), allows continuous fabrication, and can easily be scaled up to large-scale production. Because the tubes are open, the method also allows for the use of the nanotube as a templating agent.

In the arc discharge method, extremely high temperatures are obtained by shorting two carbon rods together, which causes a plasma discharge. Such plasmas easily achieve temperatures in excess of where carbon vaporizes (at about 4500 K). Low potential differences and moderately high currents are needed to produce this arc. The typical CNT formed by either the arc method or CVD is multiwalled. To encourage SWNT formation, it is necessary to add a metal catalyst such as Co, Fe, or Ni to the carbon source. These metal catalyst particles block the end-cap of each carbon hemisphere and thus promote SWNT growth. In addition, the growth directions of the nanotubes can be controlled by van der Waals forces, applied electric fields, and patterning of the metal catalyst onto different substrates. The patterned growth approach is feasible with discrete catalytic nanoparticles and scalable on large wafers to achieve large arrays of nanowires Figure.



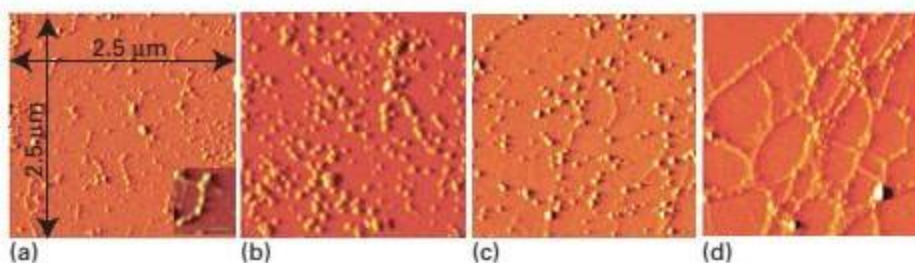
Bioinorganic nanomaterials Biological phenomena, such as DNA condensation, intercellular transport, tissue assembly, respiration, photosynthesis, and reproduction, originate and operate at the nanoscale.

Because biological processes use and manipulate materials at this length scale, it is not surprising that scientists and engineers are looking to natural systems for inspiration and to reach a better understanding of the design of robust and useful nanomaterials. This interest has spawned an extensive research effort termed biomimetics, the mimicking of biological systems. Of particular interest to us are materials that bridge solid-state inorganic materials and living cells, the so-called bioinorganic materials (Chapter 27). Their nano counterparts, the bioinorganic nanomaterials, promise to have a profound impact on the way we live; key applications include drug delivery, medical diagnostics, cancer therapy, and environmental pollution control, as well as chemical and biological sensing. Many biological structures (people, for instance) are produced from self-assembly of functional building blocks, which have

complex morphological architectures themselves. Despite success in understanding the basic principles of the biological assembly process, as well as in making inorganic materials through biological templating, it remains a key challenge to mimic natural pathways as efficient routes for fabricating artificial bionanomaterials. In this section we discuss some recent advances and offer a taste of the complexity, diversity, and architectures of exquisite bionanomaterials by using key examples of these types of materials.

DNA and nanomaterials Key point: Interactions between gold nanoparticles and DNA can cause the self-assembly of DNA into condensates and the ordering of nanoparticles into regular arrays that can be used for biosensors. DNA condensates are self-assembled nanostructures. The architecture of these condensates is driven by the components that become woven into the nano assembly. Electrostatic interactions drive the formation of DNA condensates. DNA is a negatively charged polyelectrolyte that interacts with positively charged ions, molecules, or modified nanoparticles to form ordered structures and convert from their random coils to a more compact form. This compact form, called a condensate, is essential for the organization of DNA into chromatin, a component of genes. Mimicking or controlling the DNA condensation process is the basis of the design of nonviral gene delivery vectors that have practical application in the treatment of cancer, drug delivery, and biosensing. Studies of DNA condensation in vitro have focused on the use of complex cations, including hexaamminecobalt (III) or polyamines as the positive charge centre in the condensate. Complex formation in these systems can be expected to mimic DNA wrapping around charged particles in living cells, such as positively charged histone proteins. Because the cationic particles can be fine-tuned with respect to size and charge density, the effect of those parameters on the complex formation patterns with DNA have begun to be understood. Gold nanoparticles have been suggested as an effective transfection agent (a device for introducing exogenous DNA into a cell) and, as such, it is important to understand the interactions of nanoparticles with DNA. Figure 25.37 shows AFM images of complexes of lysine-modified gold nanoparticles and DNA at different nanoparticle/DNA ratios. These results indicate the possibility of developing functionalized gold nanoparticle-DNA into a model system to study DNA condensation in vivo. These smart

nanomaterials have far-reaching consequence for the design of nanoscale self-assembled materials that can be used as building blocks for active nanodevices. Another exciting accomplishment in the synthesis of bionanomaterials is the use of DNA to drive the assembly of inorganic nanoparticles (Fig. 25.38).



First, nanoparticles are functionalized with single strands of DNA. Then, the complementary strand of DNA is introduced from an analyte or bioagent, leading to dimerization with the DNA on the nanoparticles and the self-assembly of the nanoparticles into ordered arrays. Detectable differences in optical properties occur between the disordered and ordered states and result in colour changes. This work has helped to make sophisticated optical-based biosensor arrays with remarkable sensitivity and selectivity for different analytes and bioagents.

Natural and artificial nanomaterials: biomimetics

Key point: Biological materials can be used as templates in the design of nanoinorganics having specific architectures that mimic the structure of the natural material. The formation mechanisms in fossilization, including those for siliceous woods, offer efficient methods to reproduce morphological hierarchies of original plant matter through the replacement of the organic components by silica. Artificial fossilization processes can be realized by carefully lining the morphologically complex surfaces of the biological structure with inorganic layers followed by removal of the organic template. Natural materials such as wood and eggshell membrane have

been used as templates for the preparation of macroporous silica, zeolites, and titanium dioxide from both precursor sol–gel solutions and suspensions of nanocrystals. Unfortunately, morphological replication has been achieved only over the micrometre scale and the nanoscale details of the biological templates have not yet been reproduced. An artificial fossilization process has been developed by taking advantage of a surface sol–gel process that can replicate nanoscale features of biological templates (Box 25.3). The surface sol–gel process consists of two steps. First, metal alkoxides are adsorbed from the solution on to hydroxylated substrate surfaces. Then the adsorbed species are hydrolysed to yield nanometre-thick oxide films. Natural cellulose fibres possess surface –OH groups and provide a template for using the surface sol–gel process. The outer diameter of the TiO₂ nanotube varies from 30 to 100 nm, and the thickness of the tube is uniform along its length, with a wall thickness of about 10 nm. The nanotube assembly exhibits the original morphology of interwoven cellulose fibres. The ‘titania paper’ produced in this way records the morphological information of the original paper at the nanoscale and offers a remarkable example of successful bio templating of metal oxide nanomaterials.

POSSIBLE QUESTIONS
UNIT-II

PART-A (20 MARKS)
(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. Write a note on Carbon nanotubes and
2. Write note on inorganic nanowires
3. What is meant by Bio-inorganic nanomaterials
4. Write a note on Nano materials
5. Give the example of natural and artificial nanomaterial

Part-C (6 Marks)

1. How prepare Gold and Silver nano particles?
2. Give the detail about self-assembled nanostructures-control of nanoarchitecture-one dimensional control
3. Write a note on natural and artificial nanomaterial and bionano composites.
4. How prepare carbon nanotubes and inorganic nano wires
5. Write detail about Bio-inorganic nanomaterials

Unit-III-Multiple choice Questions

S. No	Questions	Option-I	Option-II	Option-III	Option-IV	Answer
1.	Which of the following impurity in cast iron makes it hard and brittle?	Silicon	Sulphur	Manganese	Phosphorus	Sulphur
2.	Tensile strength of steel can be safely increased by	Adding carbon up to 2.8%	Adding carbon up to 6.3%	Adding carbon up to 0.83%	Adding small quantities of copper	Adding carbon up to 0.83%
3.	Resistance developed by surface of any material is known as	Strength	Hardness	Stiffness	Creep	Hardness
4.	Permanent deformation of material with respect to time due to constant load and variable temperature is known as	Elasticity	Isotropy	Hardness	Creep	Creep
5.	Material with same property in all direction may be termed as	Creep	Anisotropy	Isotropy	Orthotropic	Isotropy

KARPAGAM ACADEMY OF HIGHER EDUCATION

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Unit-III-Multiple choice Questions

6.	Property by virtue of which material can absorb strain energy without plastic deformation is called	Creep	Anisotropy	Resilience	Fatigue	Resilience
7.	Steel ball is used as indenter in which of the following test?	Brinell hardness test	Rockwell harness test	Vickers hardness test	All of the mentioned	Brinell hardness test
8.	Which of the following metal is used for nuclear energy?	Uranium	Thorium	Niobium	All of these	All of these
9.	Y-alloy contains	3.5 to 4.5% copper, 0.4 to 0.7% magnesium, 0.4 to 0.7% manganese and rest aluminium	3.5 to 4.5% copper, 1.2 to 1.7% manganese, 1.8 to 2.3% nickel, 0.6% each of silicon, magnesium and iron, and rest aluminium	4 to 4.5% magnesium, 3 to 4% copper and rest aluminium	5 to 6% tin, 2 to 3% copper and rest aluminium	3.5 to 4.5% copper, 1.2 to 1.7% manganese, 1.8 to 2.3% nickel, 0.6% each of silicon, magnesium and iron, and rest aluminium

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Unit-III-Multiple choice Questions

10.	Amorphous material is one	In which atoms align themselves in a geometric pattern upon solidification	In which there is no definite atomic structure and atoms exist in a random pattern just as in a liquid	Which is not attacked by phosphorous	Which emits fumes on melting	In which there is no definite atomic structure and atoms exist in a random pattern just as in a liquid
11.	Brass (alloy of copper and zinc) is an example of	Substitutional solid solution	Interstitial solid solution	Intermetallic compounds	All of the above	Substitutional solid solution
12.	In process annealing, the hypo eutectoid steel is	Heated from 30°C to 50°C above the upper critical temperature and then cooled in still air	Heated from 30°C to 50°C above the upper critical temperature and then cooled suddenly in a suitable cooling medium	Heated from 30°C to 50°C above the upper critical temperature and then cooled slowly in the furnace	Heated below or closes to the lower critical temperature and then cooled slowly	Heated below or closes to the lower critical temperature and then cooled slowly

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13.	Pick up the wrong statement	Aluminium in steel results in excessive grain growth	Manganese in steel induces hardness	Nickel and chromium in steel helps in raising the elastic limit and improve the resilience and ductility	Tungsten in steels improves magnetic properties and hardenability	Aluminium in steel results in excessive grain growth
14.	A coarse grained steel	Is less tough and has a greater tendency to distort during heat treatment	Is more ductile and has a less tendency to distort during heat treatment	Is less tough and has a less tendency to distort during heat treatment	Is more ductile and has a greater tendency to distort during heat treatment	Is less tough and has a greater tendency to distort during heat treatment
15.	Pick up the wrong statement Nickel and chromium in steel help in	Providing corrosion resistance	Improving machining properties	Providing high strength at elevated temperatures	Raising the elastic limit	Improving machining properties

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16.	Normalising of steel is done to	Refine the grain structure	Remove strains caused by cold working	Remove dislocations caused in the internal structure due to hot working	All of the above	All of the above
17.	Steel contains	80% or more iron	50% or more iron	Alloying elements like chromium, tungsten nickel and copper	Elements like phosphorus, sulphur and silicon in varying quantities	50% or more iron
18.	Iron-carbon alloys containing carbon _____ 4.3% are known as hyper-eutectic cast irons	Equal to	Less than	More than	None of these	More than

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19.	When a steel containing _____ 0.8% carbon is cooled slowly below the lower critical point, it consists of ferrite and pearlite	Equal to	Less than	More than	None of these	Less than
20.	The following element can't impart high strength at elevated temperature	Manganese	Magnesium	Nickel	Silicon	Magnesium
21.	The percentage carbon content in wrought iron is about	0.02	0.1	0.2	0.4	0.02
22.	The silicon steel is widely used for	Connecting rods	Cutting tools	Generators and transformers in the form of laminated cores	Motor car crankshafts	Generators and transformers in the form of laminated cores
23.	Blast furnace produces following by reduction of iron ore	Cast iron	Pig iron	Wrought iron	Malleable iron	Pig iron

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24.	For a steel containing 0.8% carbon	There is no critical point	There is only one critical point	There are two critical points	There can be any number of critical points	There is only one critical point
25.	Nickel in steel	Improves wear resistance, cutting ability and toughness	Refines grain size and produces less tendency to carburisation, improves corrosion and heat resistant properties	Improves cutting ability and reduces hardenability	Gives ductility, toughness, tensile strength and anti-corrosion properties	Gives ductility, toughness, tensile strength and anti-corrosion properties
26.	Which of the following has highest specific strength of all structural materials?	Magnesium alloys	Titanium alloys	Chromium alloys	Magnetic steel alloys	Titanium alloys
27.	When steel containing less than 0.8% carbon is cooled slowly from temperatures above or within the critical range, it consists of	Mainly ferrite	Mainly pearlite	Ferrite and pearlite	Pearlite and cementite	Ferrite and pearlite

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28.	Duralumin contains	3.5 to 4.5% copper, 0.4 to 0.7% magnesium, 0.4 to 0.7% manganese and rest aluminium	3.5 to 4.5% copper, 1.2 to 1.7% manganese, 1.8 to 2.3% nickel, 0.6% each of silicon, magnesium and iron, and rest aluminium	4 to 4.5% magnesium, 3 to 4% copper and rest aluminium	5 to 6% tin, 2 to 3% copper and rest aluminium	3.5 to 4.5% copper, 0.4 to 0.7% magnesium, 0.4 to 0.7% manganese and rest aluminium
29.	Admiralty brass used for steam condenser tubes contains copper and zinc in the following ratio	50 : 50	30 : 70	70:30:00	40 : 60	30 : 70
30.	A steel containing 16 to 18% chromium and about 0.12% carbon is called	Ferritic stainless steel	Austenitic stainless steel	Martensitic stainless steel	Nickel steel	Ferritic stainless steel
31.	Which of the following iron exist between 910°C and 1403°C?	α -iron	β -iron	γ -iron	δ -iron	γ -iron

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32.	The presence of hydrogen in steel causes	Reduced neutron absorption cross-section	Improved Weldability	Embrittlement	Corrosion resistance	Embrittlement
33.	Which of the following is added in low carbon steels to prevent them from becoming porous?	Sulphur	Phosphorus	Manganese	Silicon	Silicon
34.	Free cutting steels	Contain carbon in free form	Require minimum cutting force	Is used where rapid machining is the prime requirement	Can be cut freely	Is used where rapid machining is the prime requirement
35.	The aluminium alloy, mainly used, for anodized utensil manufacture, is	Duralumin	Y-alloy	Magnalium	Hindalium	Hindalium
36.	When low carbon steel is heated up to upper critical temperature	There is no change in grain size	The average grain size is a minimum	The grain size increases very rapidly	The grain size first increases and then decreases very rapidly	The average grain size is a minimum

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37.	Sulphur in steel	Acts as deoxidiser	Reduces the grain size	Decreases tensile strength and hardness	Lowers the toughness and transverse ductility	Lowers the toughness and transverse ductility
38.	Structural steel contains following principal alloying elements	Nickel, chromium and manganese	Tungsten, molybdenum and phosphorous	Lead, tin, aluminium	Zinc, sulphur, and chromium	Nickel, chromium and manganese
39.	Aluminium bronze contains	94% aluminium, 4% copper and 0.5% Mn, Mg, Si and Fe	92.5% aluminium, 4% copper, 2% nickel, and 1.5% Mg	10% aluminium and 90% copper	90% magnesium and 9% aluminium with some copper	10% aluminium and 90% copper
40.	The main alloying elements high speed steel in order of increasing proportion are	Vanadium, chromium, tungsten	Tungsten, titanium, vanadium	Chromium, titanium, vanadium	Tungsten, chromium, titanium	Vanadium, chromium, tungsten

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41.	The aluminium alloy made by melting aluminium with 2 to 10% magnesium and 1.75% copper is called	Duralumin	Y-alloy	Magnalium	Hindalium	Magnalium
42.	Brass contains	70% copper and 30% zinc	90% copper and 10% tin	85 - 92% copper and rest tin with little lead and nickel	70 - 75% copper and rest tin	70% copper and 30% zinc
43.	A specimen of aluminium metal when observed under microscope shows	B.C.C. crystalline structure	F.C.C. crystal structure	H.C.P. structure	A complex cubic structure	F.C.C. crystal structure
44.	Which of the following statement is incorrect about duralumin?	It is prone to age hardening	It can be forged	It has good machining properties	It is lighter than pure aluminium	It is lighter than pure aluminium

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45.	The hardness of steel primarily depends on	Percentage of carbon	Percentage of alloying elements	Heat treatment employed	Shape of carbides and their distribution in iron	Shape of carbides and their distribution in iron
46.	The tensile strength of wrought iron is maximum	Along the lines of slag distribution	Perpendicular to lines of slag distribution	Uniform in all directions	Uniform in particular directions	Along the lines of slag distribution
47.	Which of the following represents the allotropic forms of iron?	Alpha iron, beta iron and gamma iron	Alpha iron and beta iron	Body centered cubic iron and face centered cubic iron	Alpha iron, gamma iron and delta iron	Alpha iron, gamma iron and delta iron
48.	In low carbon steels, _____ raises the yield point and improves the resistance to atmospheric corrosion.	Sulphur	Phosphorus	Manganese	Silicon	Phosphorus

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49.	Which of the following impurity in cast iron promotes graphite nodule formation and increases the fluidity of the molten metal?	Silicon	Sulphur	Manganese	Phosphorus	Silicon
50.	An important property of high silicon (12-18%) cast iron is the high	Hardness	Brittleness	Plasticity	Ductility	Hardness
51.	White cast iron contains carbon in the form of	Free carbon	Graphite	Cementite	White carbon	Cementite
52.	A small percentage of boron is added to steel in order to	Increase hardenability	Reduce machinability	Increase wear resistance	Increase endurance strength	Increase hardenability
53.	Brass is an alloy of	Copper and zinc	Copper and tin	Copper, tin and zinc	None of these	Copper and zinc
54.	Iron-carbon alloys containing 1.7 to 4.3% carbon are known as	Eutectic cast irons	Hypoeutectic cast irons	Hypereutectic cast irons	None of these	Hypoeutectic cast irons

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55.	Which is false statement about properties of aluminium?	Modulus of elasticity is fairly low	Wear resistance is very good	Fatigue strength is not high	Creep strength limits its use to fairly low temperatures	Wear resistance is very good
56.	Pure iron is the structure of	Ferrite	Pearlite	Austenite	Ferrite and cementite	Ferrite
57.	The unique property of cast iron is its high	Malleability	Ductility	Surface finish	Damping characteristics	Damping characteristics
58.	Cast iron is characterized by minimum of following percentage of carbon	0.20%	0.80%	1.3%	2%	2%
59.	Chilled cast iron has	No graphite	A very high percentage of graphite	A low percentage of graphite	Graphite as its basic constituent of composition	No graphite

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60.	Carbon steel is	Made by adding carbon in steel	Refined from cast iron	An alloy of iron and carbon with varying quantities of phosphorus and sulphur	Extensively used for making cutting tools	An alloy of iron and carbon with varying quantities of phosphorus and sulphur
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UNIT III

Introduction to engineering materials for mechanical construction:

Composition, mechanical and fabricating characteristics and applications of various types of cast irons, plain carbon and alloy steels, copper, aluminium and their alloys like duralumin, brasses and bronzes cutting tool materials, super alloys thermoplastics, thermosets and composite materials.

Alloys

An alloy is a blend of metallic elements prepared by mixing the molten components and then cooling the mixture to produce a metallic solid. Alloys may be homogeneous solid solutions, in which the atoms of one metal are distributed randomly among the atoms of the other, or they may be compounds with a definite composition and internal structure. Alloys typically form from two electropositive metals, so they are likely to be located towards the bottom left-hand corner of a Ketelaar triangle (Fig. 3.25). Solid solutions are classified as either ‘substitutional’ or ‘interstitial’. A substitutional solid solution is a solid solution in which atoms of the solute metal occupy some of the locations of the solvent metal atoms (Fig. 3.26a). An interstitial solid solution is a solid solution in which the solute atoms occupy the interstices (the holes) between the solvent atoms (Fig. 3.26b). However, this distinction is not particularly fundamental because interstitial atoms often lie in a definite array (Fig. 3.26c), and hence can be regarded as a substitutional version of another structure. Some of the classic examples of alloys are brass (up to 38 atom per cent Zn in Cu), bronze (a metal other than Zn or Ni in Cu; casting bronze, for instance, is 10 atom per cent Sn and 5 atom per cent Pb), and stainless steel (over 12 atom per cent Cr in Fe).

(a) Substitutional solid solutions

Key point: A substitutional solid solution involves the replacement of one type of metal atom in a structure by another. Substitutional solid solutions are generally formed if three criteria are fulfilled:

1. The atomic radii of the elements are within about 15 per cent of each other.
2. The crystal structures of the two pure metals are the same; this similarity indicates that the directional forces between the two types of atom are compatible with each other.
3. The electropositive characters of the two components are similar; otherwise compound formation, where electrons are transferred between species, would be more likely. Thus, although sodium and potassium are chemically similar and have bcc structures, the atomic radius of Na (191 pm) is 19 per cent smaller than that of K (235 pm), and the two metals do not form a solid solution. Copper and

nickel, however, two neighbours late in the d block, have similar electropositive character, similar crystal structures (both ccp), and similar atomic radii (Ni 125 pm, Cu 128 pm, only 2.3 per cent different), and form a continuous series of solid solutions, ranging from pure nickel to pure copper. Zinc, copper's other neighbour in Period 4, has a similar atomic radius (137 pm, 7 per cent larger), but it is hcp, not ccp. In this instance, zinc and copper are partially miscible and form solid solutions known as '-brasses'

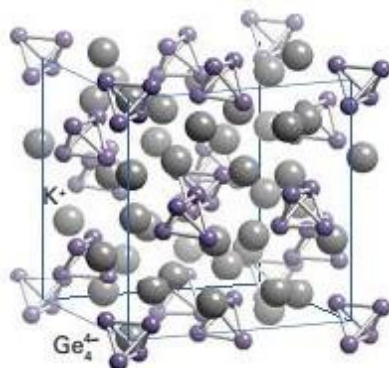
of composition $\text{Cu}_{1-x}\text{Zn}_x$ with $0 \leq x \leq 0.38$ and the same structural type as pure copper.

(b) Interstitial solid solutions of nonmetals

Key point: In an interstitial solid solution, additional small atoms occupy holes within the lattice of the original metal structure. Interstitial solid solutions are often formed between metals and small atoms (such as boron, carbon, and nitrogen) that can inhabit the interstices in the structure. The small atoms enter the host solid with preservation of the crystal structure of the original metal and without the transfer of electrons and formation of ionic species. There is either a simple whole-number ratio of metal and interstitial atoms (as in tungsten carbide, WC) or the small atoms are distributed randomly in the available spaces or holes in the structure between the packed atoms. The former substances are true compounds and the latter can be considered as interstitial solid solutions or, on account of the variation in the atomic ratio of the two elements, nonstoichiometric compounds (Section 3.17). Considerations of size can help to decide where the formation of an interstitial solid solution is likely to occur. Thus, the largest solute atom that can enter a close-packed solid without distorting the structure appreciably is one that just fits an octahedral hole, which as we have seen has radius $0.414r$. For small atoms such as B, C, or N the atomic radii of the possible host metal atom structures include those of the d-metals such as Fe, Co, and Ni. One important class of materials of this type consists of carbon steels in which C atoms occupy some of the octahedral holes in the Fe bcc lattice. Carbon steels typically contain between 0.2 and 1.6 atom per cent C. With increasing carbon content they become harder and stronger but less malleable (Box 3.2).

(c) Intermetallic compounds

Key point: Intermetallic compounds are alloys in which the structure adopted is different from the structures of either component metal. There are materials formed between two metals that are best regarded as actual compounds despite the similarity of their electropositive nature. For instance, when some liquid mixtures of metals are cooled, they form phases with definite structures that are often unrelated to the parent structure. These phases are called intermetallic compounds. They include β -brass(CuZn) and compounds of composition MgZn_2 , Cu_3Au , NaTl , and $\text{Na}_5\text{Zn}_{21}$. Note that some of these intermetallic compounds contain a very electropositive metal in combination with a less electropositive metal (for example, Na and Zn), and in a Kasper triangle lie above the true alloys (Fig. 3.27). Such combinations are called Zintl phases. These compounds are not fully ionic (although they are often brittle) and have some metallic properties, including lustre. A classic example of a Zintl phase is KGe with the structure shown in Fig. 3.28.



Composition, mechanical and fabricating characteristics and applications of various types of aluminium.

The elements Al, Ga, In, and Tl are metals with many similarities in their chemical properties. Like B, they form electron-deficient compounds that act as Lewis acids. Aluminium forms alloys with many other metals and produces light, corrosion-resistant materials. When Al is alloyed with Ga, the Ga prevents the formation of the tightly held passivating oxide film on the Al. When the alloy is dropped in water the Al reacts with the water, forming aluminium oxide and liberating hydrogen. This reaction has been suggested as a solution to the problem of storing hydrogen for use in fuel cells. However, the energy cost of recycling the aluminium oxide and gallium mixture to metallic Al and Ga makes this application unlikely. Aluminium hydride, AlH_3 , is a solid that is best regarded as saline, like the hydrides of the s-block metals. Unlike CaH_2 and NaH , which are more readily available commercially, AlH_3 has few applications in the laboratory. The alkylaluminium hydrides, such as $\text{Al}_2(\text{C}_2\text{H}_5)_4\text{H}_2$, are well-known molecular compounds and contain AlHAl .

All the elements form trihalides with the metal in its 3 oxidation state. However, as we expect from the inert-pair effect (Section 9.5), the 1 oxidation state becomes more common on descending the group and Tl forms stable monohalides. Because the F ion is so small, the trifluorides are mechanically hard ionic solids that have much higher melting points and sublimation enthalpies than the other halides. Their high lattice enthalpies also result in them having very limited solubility in most solvents, and they do not act as Lewis acids to simple donor molecules. The heavier trihalides of Al, Ga, and In are soluble in a wide variety of polar solvents and are excellent Lewis acids. The trigonal planar MX_3 monomer occurs only at elevated temperatures in the gas phase. Otherwise, the trihalides exist as M_2X_6 dimers in the vapour phase and in solution. The volatile solids are dimeric. An exception is AlCl_3 , which has a six-coordinate layer structure in the solid phase and converts to four-coordinate molecular dimers at its melting point. The dimers contain coordinate MX bonds in which a lone pair on X belonging to one AlX_3 unit completes the octet of M belonging to the second MX_3 unit (3). This

arrangement results in a tetrahedral arrangement of X atoms around each M atom. In contrast to the other elements in the group, Tl(I) is the most stable oxidation state of the halides.

Composition, mechanical and fabricating characteristics and applications of various types of copper

The gap between the valence and conduction bands (Section 3.19) decreases steadily from diamond, which is classed as a wide-band-gap semiconductor but commonly regarded as an insulator, to tin, which behaves like a metal above its transition temperature. Elemental carbon in the form of coal or coke is used as a fuel and reducing agent in the recovery of metals from their ores. Graphite is used as a lubricant and in pencils, and diamond is used in industrial cutting tools. The band gap and consequent semiconductivity of silicon leads to its many applications in integrated circuits, computer chips, solar cells, and other electronic solid-state devices. Silica (SiO_2) is the major raw material used to make glass. Germanium was the first widely used material for the construction of transistors because it was easier to purify than silicon and, having a smaller band gap than silicon (0.72 eV for Ge, 1.11 eV for Si), is a better intrinsic semiconductor. Tin is resistant to corrosion and is used to plate steel for use in tin cans. Bronze is an alloy of tin and copper that typically contains less than 12 per cent by mass of tin; bronze with higher tin content is used to make bells. Solder is an alloy of tin and lead, and has been in use since Roman times. Window glass or float glass is made by floating molten glass on the surface of molten tin. The 'tin side' of window glass can be seen as a haze of tin(IV) oxide when viewed with ultraviolet radiation. Trialkyl and triaryltin compounds are in widespread use as fungicides and biocides. The softness and malleability of lead has resulted in its use in plumbing, although this application is now illegal in many countries due to concerns over lead poisoning. Its low melting point contributes to its use in solder and its high density (11.34 g cm³) leads to its use in ammunition and as shielding from ionizing radiation. Lead oxide is added to glass to raise its refractive index and form 'lead' or 'crystal' glass.

Composition, mechanical and fabricating characteristics and applications of various types of brasses

Key point: A solid solution occurs where there is a continuous variation in compound stoichiometry without a change in structural type.

Because many substances adopt the same structural type, it is often energetically feasible to replace one type of atom or ion with another. Such behaviour is seen in many simple metal alloys such as those discussed in Section 3.8. Thus zinc/copper brasses exist for the complete range of compositions $\text{Cu}_{1-x}\text{Zn}_x$ with $0 \leq x \leq 0.38$, where Cu atoms in the structure are gradually replaced by Zn atoms. This replacement occurs randomly throughout the solid, and individual unit cells contain an arbitrary number of Cu and Zn atoms (but such that the sum of their contents gives the overall brass stoichiometry). Another good example is the perovskite structure adopted by many compounds of stoichiometry ABX_3 (Section 3.9), in which the composition can be varied continuously by varying the ions that occupy the A, B, and X sites. For instance, both LaFeO_3 and SrFeO_3 adopt the perovskite structure and we can consider a perovskite crystal that has, randomly distributed, half SrFeO_3 unit cells (with Sr on the A-type cation site) and half LaFeO_3 unit cells (with La on the A-site). The overall compound stoichiometry is $\text{LaSrFe}_2\text{O}_6$, which is better written $(\text{La}_{0.5}\text{Sr}_{0.5})\text{FeO}_3$, to reflect the normal ABO_3 perovskite stoichiometry. Other proportions of these unit cells are possible and the series of compounds $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ for $0 \leq x \leq 1$ can be prepared. This system is called a **solid solution** because all the phases formed as x is varied have the same perovskite structure. A solid solution occurs when there is a single structural type for a range of compositions and there is a smooth variation in lattice parameter over that range. Solid solutions occur most frequently for d-metal compounds because the change in one component might require a change in the oxidation state of another component to preserve the charge balance. Thus, as x increases in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ and La(III) is replaced by Sr(II) , the oxidation state of iron must change from Fe(III) to Fe(IV) . This change can occur through a gradual replacement of one exact oxidation state, here Fe(III) , by another, Fe(IV) , on a

proportion of the cation sites within the structure. Alternatively, if the material is metallic and has delocalized electrons, then the change can be accommodated by altering the number of electrons in a conduction band, which corresponds to the delocalization of the change in oxidation state rather than its identification with individual atoms. Some other solid solutions

Uses of the elements and their compounds

Key points: The most useful compound of boron is borax; the most commercially important element is aluminium. The main use of B is in borosilicate glasses. Borax has many domestic uses, for example as a water softener, cleaner, and mild pesticide. Boric acid, $B(OH)_3$, is used as a mild antiseptic. Amorphous brown boron is used in pyrotechnics to impart a bright green colour. Boron is an essential micronutrient in plants. Lightweight, strong boron filaments are used in composite materials for the aerospace industry and in sports equipment. Many compounds of B are superhard materials, having hardness approaching that of diamond. Cubic boron nitride is synthesized at high pressures, which makes it expensive. Rhenium diboride does not require high pressures so production is relatively cheap, but Re is an expensive metal. The material known as ‘heterodiamond’, sometimes labelled BCN, is formed from diamond and boron nitride by explosive shock synthesis. These compounds are used as substitutes for diamond in cutting tools and blades. Sodium perborate, $NaBO_3$, is used as a chlorine-free bleach in laundry products, cleaning materials, and tooth whitener. It is less aggressive to textiles than chlorine bleaches and active at low temperatures when mixed with an activator such as tetraacetylenediamine, which is commonly abbreviated to TAED. Boranes used to be popular as fuels for rockets but were found to be too pyrophoric to be handled safely. Boranes are being investigated as possible hydrogen storage materials with the hydrogen stored as the ammonia-borane complex $NH_3:BH_3$. Aluminium is the most widely used nonferrous metal. The technological uses of aluminium metal exploit its lightness, resistance to corrosion, and the fact that it is easily recycled. It is used in cans, foils, utensils, in construction, and in aircraft alloys (Box 13.2). Many Al compounds are used as mordants, in water

and sewage treatment, in paper production, as food additives, and for waterproofing textiles. Aluminium chloride and chlorohydrate are used in antiperspirants and the hydroxide is used as an antacid. Sodium tetrahydridoaluminate, NaAlH_4 , doped with TiF_3 is used as a hydrogen storage material. Because the melting point of Ga (30°C) is just above room temperature, it is used in high-temperature thermometers. Gallium and In form a low-melting-point alloy that is used as the safety device in sprinkler systems. Both elements are deposited on glass surfaces to form corrosion-resistant mirrors, and In_2O_3 doped with Sn is used as a transparent, conducting coating for electronic displays and as a heat-reflective coating for light bulbs. Gallium nitride is used in blue laser diodes and is the basis of Blu-ray technology. It is insensitive to ionizing radiation and is used in solar cells in satellites. Gallium arsenide is a semiconductor and used in integrated circuits, light-emitting diodes and solar cells. Thallium compounds were once used to treat ringworm and as a rat and ant poison. However, this application has been banned because of their very high toxicity, which arises from the transport of Tl ions across cell membranes together with K^+ ions (Section 26.3). Thallium is absorbed more efficiently by tumour cells and has been used in nuclear medicine as an imaging agent.

Composition, mechanical and fabricating characteristics and applications of various types of super alloys thermoplastics,

Key points: Class I inorganic–organic materials have noncovalent interactions and class II have some covalent interactions; sol–gel and self-assembly methods are key chemical routes to hybrid nanocomposite design and synthesis; the properties of polymer nanocomposites are controlled through the nature of the polymeric and inorganic phases, as well as through their dispersions and interactions. Inorganic–organic nanocomposites are a third class of three-dimensional ordered materials that possess chemical and physical properties that can be tuned by using the synergistic association of organic and inorganic components at nanoscales. These hybrid materials originated in the paint and polymer industries where inorganic fillers and pigments were dispersed in organic materials (including solvents, surfactants, and polymers) to fabricate

commercial products with improved materials performance. Hybrid nanomaterials are also of interest because their mechanical properties occupy a niche between glasses and polymers, so achieving enhanced strength and robustness. Hybrid nonmaterial have been reported with excellent laser efficiencies, photostability, and ultrafast photochromic response. They also can have very large second-order and third-order nonlinear optical response, which is important in frequency conversion and optical switching for telecommunications. Nanocomposites have already entered the market-place in sunscreens, fire-retardant fabrics, stain-resistant clothing, thermoplastics, water filters, and automobile parts. Examples include the use of nylon-6/montmorillonite clay nanocomposites for timing-belt covers, television screens that are coated with indigo dyes embedded in a silica/zirconia matrix, organically doped sol-gel glassware, and sol-gel-entrapped enzymes. Hybrid nanomaterials offer the materials chemist novel routes that use rational materials design to optimize structure-property relationships. Their nanoarchitectures and resulting properties depend on the chemical nature of the components and the synergy between them. A key part of the design of these hybrids is the selective tuning of the nature, extent, and accessibility of the interfaces between the inorganic and the organic building blocks.

Key points: The frontier between metals and nonmetals in the periodic table is characterized by the formation of amphoteric oxides; amphoterism also varies with the oxidation state of the element. An **amphoteric oxide** is an oxide that reacts with both acids and bases.⁴ Thus, aluminium oxide reacts with acids and alkalis:

Amphoterism is observed for the lighter elements of Groups 2 and 13, as in BeO, Al₂O₃, and Ga₂O₃. It is also observed for some of the d-block elements in high oxidation states, such as MoO₃ and V₂O₅, in which the central atom is very electron withdrawing, and some of the heavier elements of Groups 14 and 15, such as SnO₂ and Sb₂O₅. Figure 4.6 shows the location of elements that in their characteristic group oxidation states have amphoteric oxides. They lie on the frontier between acidic and basic oxides, and hence serve as an important guide to the metallic or nonmetallic character of an element. The onset of amphoterism correlates with a

significant degree of covalent character in the bonds formed by the elements, either because the metal ion is strongly polarizing (as for Be) or because the metal ion is polarized by the O atom attached to it (as for Sb). An important issue in the d block is the oxidation number necessary for amphotericism. Figure 4.7 shows the oxidation number for which an element in the first row of the block has an amphoteric oxide. We see that on the left of the block, from titanium to manganese and perhaps iron, oxidation state +4 is amphoteric (with higher values on the border of acidic and lower values of the border of basic). On the right of the block, amphotericism occurs at lower oxidation numbers: the oxidation states 3 for cobalt and nickel and 2 for copper and zinc are fully amphoteric. There is no simple way of predicting the onset of amphotericism. However, it presumably reflects the ability of the metal cation to polarize the oxide ions that surround it—that is, to introduce covalence into the metal_oxygen bond. The degree of covalence typically increases with the oxidation number of the metal as the increasingly positively charged cation becomes more strongly polarizing.

POSSIBLE QUESTIONS
UNIT-III
PART-A (20 MARKS)
(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. What is the Composition of cast irons?
2. What is the Composition plain carbon?
3. What are the Composition alloy steels?
4. What is the Composition copper?
5. What is the Composition Aluminium?
6. Define super alloys?
7. Write a note thermoplastics and thermosets?

PART-C (6 MARKS)

1. Give detail about composition, mechanical and fabricating characteristics and applications of cast irons?
2. Give detail about composition, mechanical and fabricating characteristics and applications of brasses?
3. Write the application of alloy steels, copper and aluminium?
4. What are the characteristics of plain carbon and cast iron?
5. Give an account on super alloys thermoplastics, thermosets?

KARPAGAM ACADEMY OF HIGHER EDUCATION

SUBJECT : NOVEL INORGANIC SOLIDS

SEMESTER : V

SUBJECT CODE: 17CHU503B

Class: III-B. Sc Chemistry Batch – (2017-2020)

Unit-IV (Multiple Choice Questions)

S.N O	Questions	Option-I	Option-II	Option-III	Option-IV	Answers
1.	polyethylene is _____?	Colourless liquid	Colourless gas	Gas	Liquid	Colourless gas
2.	Melting Point of Low Density Polyethylene (LDPE) is?	~115oC	~116 oC	~117oC	~118 oC	~115oC
3.	Which is more flexible than HDPE due to lower crystallinity?	Polyethylene	Low Density Polyethylene	Polyamide	Low density polyamide	Low Density Polyethylene
4.	Which one is a natural polymer?	Polyamide	Polyester	Cellulose	PVC	Cellulose
5.	Which is good resistance to acids and alkalis?	High Density Polyethylene	High Density polyamide	Low Density polyamide	Low Density Polyethylene	Low Density Polyethylene
6.	Which is chemically inert?	Low Density Polyethylene	High Density Polyethylene	High Density polyamide	Low Density polyamide	High Density Polyethylene
7.	The characteristic property of HDPE is	More flexible due to lower crystallinity	Irregular packing of polymer chains	Density drops off dramatically above room temperature.	Strong as a result of regular packing of polymer chains	Strong as a result of regular packing of polymer chains
8.	Used as a filler in the polymer industry	Antioxidants	Flame retardants	Colourants	Mgo	Mgo
9.	Synthetic polymers are?	polyamide	Light stabilizers	Fibers	Glass fibre	polyamide

KARPAGAM ACADEMY OF HIGHER EDUCATION

SUBJECT : NOVEL INORGANIC SOLIDS

SEMESTER : V

SUBJECT CODE: 17CHU503B

Class: III-B. Sc Chemistry Batch – (2017-2020)

Unit-IV (Multiple Choice Questions)

10	Which is used as a reinforcing filler for polyester resins?	Fibre	Wood fibre	Glass fibre	Polyamide	Glass fibre
11	Important example of the beneficial effect of fillers is the reinforcement of?	Fibre	Rubber	Wood	Glass	Rubber
12	Principal fillers are classified into how many types?	3 types	4 types	2 types	5 types	2 types
13	Carbon fibers made by?	Pyrolizing materials	Wood	Glass	Polyester	pyrolizing materials
14	Synthetic fibers are?	Rayon	Boron filaments	Glass fibre	Polyvinylalcohol	polyvinylalcohol
15	Which polymer is not an copolymer?	CCDDCCDDCCD	AAAAAAAAA	BBBBBBBAAAAA A	CCDDCCDDCC C	AAAAAAAAA
16	Which, speeds up the oxidation process?	Heat	Catalyst	Initiator	Reactants	Heat
17	Highly unsaturated polymers are much more sensitive to ?	Reduction	Addition	Oxidation	Redox	oxidation
18	Stability depends on?	Physical structure	Chemical properties	Physical properties	Chemical structure	Chemical structure
19	Most polymers are?	Thermally stable	Physically stable	Chemically stable	Unstable	Thermally stable
20	Carbon Black and other colorants may also protect plastics from the effects of?	Temperature	Melting point	Pressure	Light	Light
21	Ultraviolet absorber is?	2-hydroxyphenyl benzotriazoles	Hydroxybenzophenones	Hindered amines	Benzophenones	Hydroxybenzophenones

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Unit-IV (Multiple Choice Questions)

22	Any of a group of substances that are used in plastics to impart viscosity, flexibility, softness to the finished product is defined as?	Light stabilizers	Colourants	Plasticizers	Flame retardants	Plasticizers
23	80-90% of all plasticizers used with?	DOP	DIOP	PVC	Colourants	PVC
24	It must not exude from the plastic material?	Primary plasticizers	Secondary plasticizers	Antioxidants	Colourants	Primary plasticizers
25	Limited compatibility with the polymers are?	Primary plasticizers	Secondary plasticizers	Antioxidants	Colourants	Secondary plasticizers
26	Inhibiting the oxidation of polymers is usually filled by a substance which itself is readily oxidized.	Antioxidants	Flame retardants	Colourants	Mgo	Antioxidants
27	In polymer industry 2-hydroxybenzophones are used as	Light stabilizers	Antioxidants	Polymer initiators	Fillers	Light stabilizers
28	Any of a group of substances that are used in plastics or other materials to impart viscosity, flexibility, softness or other properties to the finished product	Plasticizers	Antioxidants	Polymer initiators	Fillers	Plasticizers
29	28. It often added to semicrystalline polymer to	Light stabilizers	Colourants	Plasticizers	Flame retardants	Plasticizers

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Class: III-B. Sc Chemistry Batch – (2017-2020)

Unit-IV (Multiple Choice Questions)

	lower the value of Tg below room temperature.					
30	The basic requirement that must be met by a plasticizer are	Compatibility	Prevent oxidation	Retard flame	Impart a colour	Compatibility
31	Porosity increased as plasticizers content?	Increased	Decreased	Suddenly decreased	Never change	Increased
32	The substances which weaken the intermolecular forces between the polymer chains and decrease Tg.	Plasticizers	Antioxidants	Polymer initiators	Fillers	Plasticizers
33	Which content did not have a significant effect on the rate of erosion?	Light stabilizers	Colouarants	Plasticizers	Flame retardents	Plasticizers
34	Which type of compound is not used as a flame retardants in polymers	Aluminum Hydroxide	Halogen compounds	Phosphorous compounds	Ferrocene	Ferrocene
35	Chemical compounds capable of interfering with the physical and chemical processes of UV light-induced degradation .	Plasticizers	Antioxidants	Polymer initiators	Light stabilizer	Light stabilizer
36	35. which one of the following polymers is the product of a condensation polymerisation reaction?	Polypropylene	Polytetrafluoroethene	Polyacetic acid	PVC	Polyacetic acid

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SUBJECT : NOVEL INORGANIC SOLIDS

SEMESTER : V

SUBJECT CODE: 17CHU503B

Class: III-B. Sc Chemistry Batch – (2017-2020)

Unit-IV (Multiple Choice Questions)

37	The phenol-formaldehyde resins are formed by polymerisation of phenol and formaldehyde by	Addition polymerisation	Cationic polymerisation	Condensation polymerisation	Anionic polymerisation	Condensation polymerisation
38	The addition of polyethylene glycol in dielectric property significantly improves?	Electrolytic conductivity	Dielectric conductivity	Electric conductivity	Ionic conductivity	Ionic conductivity
39	Melamine is	White crystalline solid	Gas	Colourless liquid	Yellow liquid	White crystalline solid
40	Plastics are ?	Hydrocarbons	Aldehyde	Ester	Amide	Hydrocarbons
41	Which one is inorganic pigment?	Barium sulfate	Perylenes	Pyrroles	Arylamides	Barium sulfate
42	Poly vinyl chloride is?	An allotrope polymer of vinyl chloride	An addition product of vinyl chloride	An isomer of vinyl chloride	A polymer of hydrated vinyl chloride	An addition product of vinyl chloride
43	Which one is more , active flame retardant?	Aluminum hydroxide	Antimony oxychloride	Phosphorous	Halogen compounds	Antimony oxychloride
44	The most useful material imparting flame retardance to plastics is?	Antimony trioxide	Aluminum hydroxide	Halogen compounds	Antimony oxychloride	Antimony trioxide
45	Which one of the following flame retardant forms a gas shield layer?	Calcium	Phosphorous	Ammonium	Aluminium oxide	Phosphorous
46	Which one of the following flame retardant breaks	Phosphorous	Ammonium	Aluminium oxide	Aluminum Hydroxide	Aluminum Hydroxide

KARPAGAM ACADEMY OF HIGHER EDUCATION

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Class: III-B. Sc Chemistry Batch – (2017-2020)

Unit-IV (Multiple Choice Questions)

	down endothermic reaction?					
47	Melting Point of Low Density Polyethylene (LDPE) is?	~115°C	~116 °C	~135°C	~148 °C	~135°C
48	Which one is a synthetic polymer?	Cellulose	Cotton	Polyamide	Fibers	Polyamide
49	Polymethyl methacrylate is colourless transparent_____?	Plastic	Rubber	Cotton	Nylon	Plastic
50	Polymethyl methacrylate can be prepared by acetone cyanohydrin is treated with_____?	Nitric acid	Acetic acid	Sulphuric acid	Hydrochloric acid	Sulphuric acid
51	Silicones was commercially introduced in_____?	1943	1930	1936	1947	1943
52	Polyvinyl chloride was commercially introduced in_____?	1943	1930	1936	1947	1936
53	Polyvinyl acetate monomer is prepared by the reaction between acetic anhydride with_____?	Benzaldehyde	Acetaldehyde	Acetic acid	Sodium acetate	Acetaldehyde
54	Polyvinyl acetate is used for the manufacture of_____?	Polyvinyl chloride	Polyvinyl alcohol	Poly methyl methacrylate	Polyvinyl acetate	Polyvinyl alcohol

KARPAGAM ACADEMY OF HIGHER EDUCATION

SUBJECT : NOVEL INORGANIC SOLIDS

SEMESTER : V

SUBJECT CODE: 17CHU503B

Class: III-B. Sc Chemistry Batch – (2017-2020)

Unit-IV (Multiple Choice Questions)

55	Styrene(butadiene rubber) was commercially introduced in_____?	1943	1930	1936	1947	1930
56	Polyvinyl acetate is insoluble in_____?	Alcohols	Aromatic solvents	Esters	Water	Water
57	Polythene was first synthesied in_____?	1877	1853	1890	1898	1898
58	Polythene was first produced in_____?	German	England	India	USA	England c
59	Polyethylene was first synthesized by_____?	Pechmann	Fawcett	Karl ziegler	Walter	Pechmann
60	Which one of the compound is used in the manufacture of terylene ?	Vinyl chloride	Ethylene glycol	Vinyl alcohol	Ethylene	Ethylene glycol

UNIT IV

Composite materials:

Introduction, limitations of conventional engineering materials, role of matrix in composites, classification, matrix materials, reinforcements, metal-matrix composites, polymer-matrix composites, fibre-reinforced composites, environmental effects on composites, applications of composites.

Introduction

There is an unabated quest for new materials which will satisfy the specific requirements for various applications like structural, medical, house-hold, industrial, construction, transportation, electrical; electronics, etc. Metals are the most commonly used materials in these applications. In the yore of time, there have been specific requirements on the properties of these materials. It is impossible of any material to fulfil all these properties. Hence, newer materials are developed. In the course, we are going to learn more about composite materials. First, we will deal with primary understanding of these materials and then we will learn the mechanics of these materials.

In the following lectures, we will introduce the composite materials, their evolution; constituents; fabrication; application; properties; forms, advantages-disadvantages etc. In the present lecture we will introduce the composite materials with a formal definition, need for these materials, their constituents and forms of constituents.

Definition of a Composite Material

A composite material is defined as a material which is composed of two or more materials at a microscopic scale and has chemically distinct phases. Thus, a composite material is heterogeneous at a microscopic scale but statistically homogeneous at macroscopic scale. The materials which form the composite are also called as constituents or constituent materials. The constituent materials of a composite have significantly different properties.

Further, it should be noted that the properties of the composite formed may not be obtained from these constituents. However, a combination of two or more materials with significant properties will not suffice to be called as a composite material. In general, the following conditions must be satisfied to be called a composite material: The combination of materials should result in significant property changes. One can see significant changes when one of the constituent material is in platelet or fibrous form.

2. The content of the constituents is generally more than 10% (by volume).
3. In general, property of one constituent is much greater than the corresponding property of the other constituent.

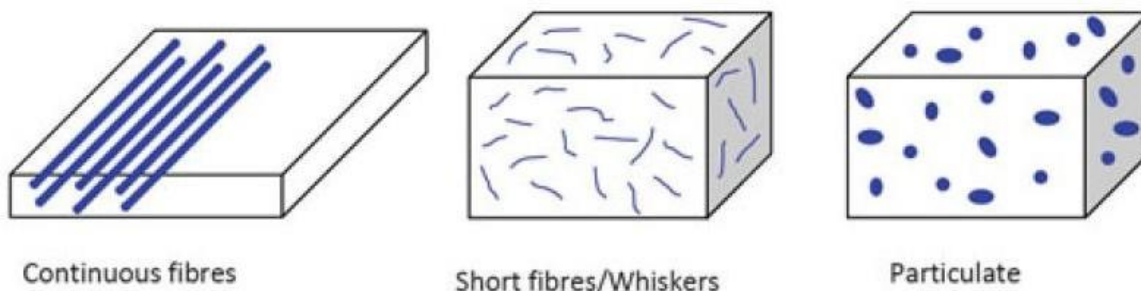
The composite materials can be natural or artificially made materials. In the following section we will see the examples of these materials.

Why we need these materials?

There is unabated thirst for new materials with improved desired properties. All the desired properties are difficult to find in a single material. For example, a material which needs high fatigue life may not be cost effective. The list of the desired properties, depending upon the requirement of the application, is given below.

1. Strength
2. Stiffness
3. Toughness
4. High corrosion resistance
5. High wear resistance
- High chemical resistance
7. High environmental degradation resistance
8. Reduced weight
9. High fatigue life
10. Thermal insulation or conductivity
11. Electrical insulation or conductivity
12. Acoustic insulation
13. Radar transparency
14. Energy dissipation
15. Reduced cost
16. Attractiveness

The list of desired properties is in-exhaustive. It should be noted that the most important characteristics of composite materials is that their properties are tailorable, that is, one can design the required properties.



Types of reinforcement in a composite

What are the constituents in a typical composite?

In a composite, typically, there are two constituents. One of the constituent acts as a reinforcement and other acts as a matrix. Sometimes, the constituents are also referred as phases.

What are the types of reinforcements?

The reinforcements in a composite material come in various forms.

Fibre: Fibre is an individual filament of the material. A filament with length to diameter ratio above 1000 is called a fibre. The fibrous form of the reinforcement is widely used. The fibres can be in the following two forms: a. Continuous fibres: If the fibres used in a composite are very long and unbroken or cut then it forms a continuous fibre composite. A composite, thus formed using continuous fibre is called as fibrous composite. The fibrous composite is the most widely used form of composite.

b. Short/chopped fibres: The fibres are chopped into small pieces when used in fabricating a composite. A composite with short fibres as reinforcements is called as short fibre composite. In the fibre reinforced composites, the fibre is the major load carrying constituent. 2. Particulate: The reinforcement is in the form of particles which are of the order of a few microns in diameter. The particles are generally added to increase the modulus and decrease the ductility of the matrix materials. In this case, the load is shared by both particles and matrix materials. However, the load shared by the particles is much larger than the matrix material. For example, in an automobile application carbon black (as a particulate reinforcement) is added in rubber (as matrix material). The composite with reinforcement in particle form is called a particulate

composite. 3. Flake: Flake is a small, flat, thin piece or layer (or a chip) that is broken from a larger piece. Since these are two dimensional in geometry, they impart almost equal strength in all directions of their planes. Thus, these are very effective reinforcement components. The flakes can be packed more densely when they are laid parallel, even denser than unidirectional fibres and spheres. For example, aluminum flakes are used in paints. They align themselves parallel to the surface of the coating which imparts the good properties. 4. Whiskers: These are nearly perfect single crystal fibres. These are short, discontinuous and polygonal in cross-section.

Composite materials:

Introduction

Composite: Two or more chemically different constituents combined macroscopically to yield a useful material. Examples of naturally occurring composites – Wood: Cellulose fibers bound by lignin matrix – Bone: Stiff mineral “fibers” in a soft organic matrix permeated with holes filled with liquids – Granite: Granular composite of quartz, feldspar, and mica

Some examples of man-made composites

- Concrete: Particulate composite of aggregates (limestone or granite), sand, cement and water
- Plywood: Several layers of wood veneer glued together
- Fiberglass: Plastic matrix reinforced by glass fibers
- Cemets: Ceramic and metal composites
- Fibrous composites: Variety of fibers (glass, kevlar, graphite, nylon, etc.) bound together by a polymeric matrix

These are not composites:

- Plastics: Even though they may have several “fillers”, their presence does not alter the physical properties significantly.
- Alloys: Here the alloy is not macroscopically heterogeneous, especially in terms of physical properties.
- Metals with impurities: The presence of impurities does not significantly alter physical properties of the metal.

Automotive industry: Lighter, stronger, wear resistance, rust-free, aesthetics

- Car body
- Brake pads
- Drive shafts
- Fuel tanks
- Hoods
- Spoilers

Aerospace: Lighter, stronger, temperature resistance, smart structures, wear resistance

- Aircraft: Nose, doors, struts, trunnion, fairings, cowlings, ailerons, outboard and inboard flaps, stabilizers, elevators, rudders, fin tips, spoilers, edges
- Rockets & missiles: Nose, body, pressure tanks, frame, fuel tanks, turbo-motor stators, etc.
- Satellites: Antennae, frames, structural parts
- Sports: Lighter, stronger, toughness, better aesthetics, higher damping properties

- Tennis
- Bicycles
- Badminton
- Boats
- Hockey
- Golfing
- Motorcycles ...

Transportation & Infrastructure: Lighter, stronger, toughness, damping

- Railway coaches
- Bridges
- Ships and boats
- Dams
- Truck bodies and floors
- RV bodies

And many more industry sectors

- Biomedical industry
- Consumer goods
- Agricultural equipment
- Heavy machinery
- Computers
- Healthcare



Composite material is formed by the combination of two or more different materials which combined together generate enhanced properties of the developed material this we have already seen that why we are combining two materials together because, we want to develop a material which has certain properties, which we cannot attain by the individual macro constituents or the individual constituents. For example, the roofs there are bars and there is concrete.

They have been blended together because we need certain properties which are not easily attainable by the bars alone or attainable by the concrete alone. So, both these two constituents have been combined together to make a third material which is offering a certain properties which are not attainable with individual constituents.

So, here on your screen you can see a very simple diagram a very simplistic view of a composite material. So, there is reinforcement and there is a matrix. So, any composite material will have two constituents. Now, we are coming on to defining the constituents. Till now we are saying composite is made up of two or three different macro constituents. What are these constituents called and what their rules that we are going to see now. The macro constituents are basically called the reinforcement and the matrix. So, one of the macro constituent is a

reinforcement another one is a matrix and when the reinforcement and the matrix join together they make a composite material.

Matrix provides the bulk form of the part or product made of the composite material. So, majorly the major portion will be the matrix or the continuous phase would be the matrix, provides the bulk form. So, you can say it will give shape or the size to the composite when the load is applied on the composite, the matrix shares this load with the reinforcement. Again we can see the example of the roof. In the roof, the concrete is the matrix and the bars are the reinforcement. So, whenever some load will act on this particular roof, the concrete will share this load with the reinforcement or in a very plain term, we can say it will transfer the load among the various reinforcing agents or the reinforcements or the different types of reinforcement as may be the case in some other composite materials. So, we need to understand that composite material is made up of different constituents and these constituents are called that matrix and the reinforcement.

The reinforcing element reinforces the matrix. So, the major load bearing member in a composite material is the reinforcement and the matrix provides support to the reinforcement. Sometimes the reinforcement may be abrasive in nature.

The role of matrix is to support the reinforcing elements and provide or transfer a media between the load bearing or transfer media of load acting on the various individual reinforcing elements and reinforcing elements have a prime aim of taking the load or the major portion of the load or the maximum load. So, reinforcing elements take the load and matrix provides support to the reinforcing elements and help to transfer the load among the various reinforcing elements.

The reinforcements can be given in the form of a fibre, it can be in the form of a particle or it can be in terms of flakes. So, you have a continues or a bulk form matrix and you put some fibres into this matrix or you can put some particles into this matrix or for that matter flakes into this matrix and this will give you another material which is a composite material. You have a bulk form, you are adding certain reinforcement into that bulk form and the final material that you are getting is a composite material.

The reinforcement or the matrix or the proportion of the reinforcement of the matrix should not be less than 5 percent or the material which is present in lesser quantity should be more than 5 percent of the total quantity. So, basically both constituents are present in reasonable proportion, the proportion of the material or the matrix of the reinforcement which is lesser should even be higher than 5 percent. It can be a ratio may be 60 to 40. The 60 percent proportion of reinforcement and 40 percent proportion of matrix or it can be vice versa, 60 percent proportion of matrix and 40 percent proportion of reinforcement.

So, it should be reasonable, it should not be like 99.99 percent of matrix and only 0.01 percent of reinforcement. So, that type of material we cannot broadly classify as a composite material. Then, the second important point, the composite properties are noticeably different from the properties of the constituents. So, the resultant properties that we are getting out of a composite material should be substantially different from the properties of the individual components or the individual constituents that go into making a composite material. So, manmade composite is usually produced or for that matter we can very easily say a synthetic composite is usually produced by intimately mixing and combining the constituents. So, what does this mean? This means that the constituents are mixed together, but, they are not soluble in one another. Again, I am emphasizing when they are

Mixed together they form a composite material, with the interface separating the two constituents. By now, we know what are the two constituents- the constituents are the reinforcement and the matrix. Let me give you another example of a composite material. From history, the mud walls which are these days also made in the villages, have some vegetable waste or some wheat straw or rice husk, added to the mud in order to improve its property. Now what is the role of this rice husk or wheat straw or any other vegetable waste which is put into the mud?

Types of composites

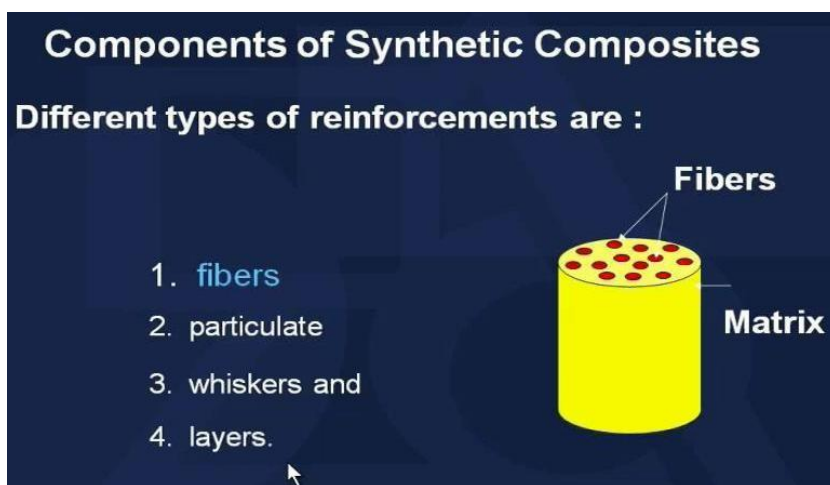
Natural composites and

Synthetic composites.

So, synthetic composites are basically a man made composites and natural composites are those which are existing in nature. One of the natural composite one example I am showing on

screen that is wood. So, in this we have a matrix and the reinforcement. The reinforcement is in terms of in type of a fiber. The matrix is lignin matrix and the fiber is the hemicelluloses fiber. So, here you can see one particular block of wood, in this wood a annular rings are seen. So, a wood has got different properties along the length of the grains and across or in the radial direction. So, the properties are different in the radial direction and in the longitudinal direction. Therefore, we can see that wood is a naturally occurring composite material because it has a matrix; it has got a reinforcement in the type of fibers which are hemicelluloses or cellulosic fibers.

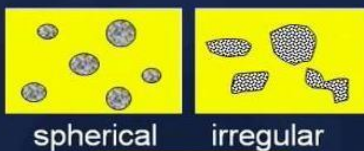
The first and the foremost is the reinforcement in the type of fibers or in the shape of fibers, then you can have particulate type of reinforcement, you can have whisker type of reinforcement and we can have the reinforcement in the terms of layers. So, in this particular diagram you can see this bulk is the material, it is a cylindrical shape and these red portion shows the ends of the fibers. These fibers are running all along the length of the matrix. Now you can see I will just draw a diagram, to explain the running of this particular fiber in the bulk of the matrix.



Components of Synthetic Composites

Different types of reinforcements are :

1. fibers
2. **particulate**
3. whiskers and
4. layers.



Particulate reinforcement morphology

Components of Synthetic Composites

Different types of reinforcements are :

1. fibers
2. particulate
3. **whiskers and**
4. layers.



aligned





randomly
oriented

Whisker reinforcement
morphology

Components of Synthetic Composites

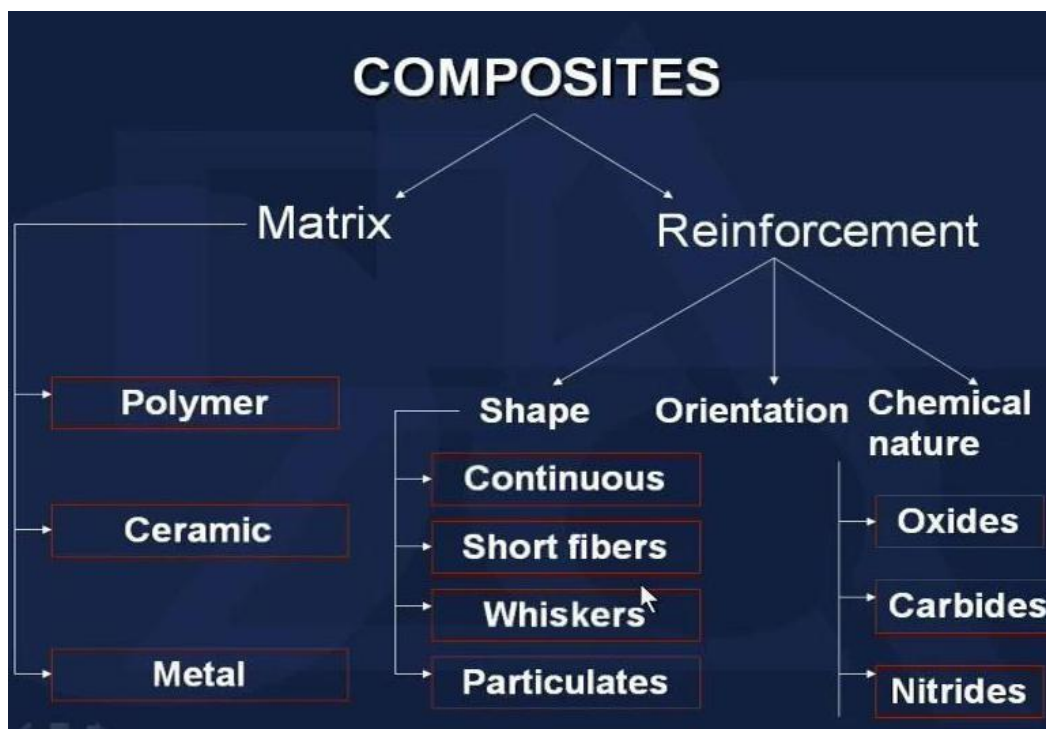
Different types of reinforcements are :

1. fibers
2. particulate
3. whiskers and
4. **layers.**



Continuous layers in matrix

The reinforcement can be in terms of layers also. So, you can see we have different layers of fibres and this yellow portion indicates the matrix. So, continuous layers are put in the matrix to make a composite material. So, this is one of the important types of polymer matrix composites in which the reinforcement is in the form of the layers, the layers are made up of fibers. The fibers basically can be glass fiber those can be carbon fiber those can be aramid fiber or other different types of fiber, but, these are three main types of fibers which are used as reinforcing materials in the polymer matrix composite.



This is another classification of composites particle reinforced, fiber reinforced and structural composites. Structural composites in terms of laminates and sandwiched panels. We can have a fiber reinforced in continuous reinforcement and discontinuous short fiber reinforcement, which can further be aligned or randomly oriented which we have already seen. We can have particle reinforcement in terms of large particles or dispersion strengthened reinforcement. So, we can see we have a matrix and we have reinforcement. Matrix can be of different types. Reinforcement can be of different types, reinforcement can further be sub classified into based on their shape based on their orientation and based on their chemical nature. Broadly we can classify the synthetic composite materials into three categories, that is polymeric matrix composites, metal matrix composites and ceramic matrix composites. So, you can see ceramics, metals and polymers. So, these three types of composites are broadly used and in our series of lectures we would be focusing primarily on polymer matrix composites and metal matrix composites.

Alumina Fibre

These are ceramics fabricated by spinning a slurry mix of alumina particles and additives to form a yarn which is then subjected to controlled heating. Fibers retain strength at high temperature. It also shows good electrical insulation at high temperatures. It has good wear resistance and high hardness. The upper continuous use temperature is about 1700. Fibers of glass, carbon and alumina are supplied in the form of tows (also called rovings or strands) consisting of many individual continuous fiber filaments. Du Pont has developed a commercial grade alumina fibre, known as Alumina FP (polycrystalline alumina) fibre. Alumina FP fibres are compatible with both metal and resin matrices. These fibres have a very high melting point of 2100 . They can withstand temperatures up to 1000 without any loss of strength and stiffness properties at this elevated temperature. They exhibit high compressive strengths, when they are set in a matrix. The Alumina whiskers are available and they exhibit excellent properties. Alumina whiskers can have the tensile strength of 20700 MPa and the tensile modulus of 427 GPa.

What are the applications of Alumina fibres?

The Alumina has a unique combination of low thermal expansion, high thermal conductivity and high compressive strength. The combination of these properties gives good thermal shock Resistance. These properties make Alumina suitable for applications in furnace use as crucibles, tubes and thermocouple sheaths. The good wear resistance and high hardness properties are harnessed in making the components such as ball valves, piston pumps and deep drawing tools.

Aramid Fibre

These fibres are from Aromatic polyamide, that is, nylons family. Aramid is derived from “Ar” of Aromatic and “amid” of polyamide. Examples of fibres from nylon family: Polyamide 6, that is, nylon 6 and Polyamide 6.6, that is, nylon 6.6 These are organic fibers. Melt-spun from a liquid solution. Du Pont developed these fibers under the trade name Kevlar. From poly (p-phenylene terephthalamide (PPTA) polymer. Morphology – radially arranged crystalline sheets resulting into anisotropic properties.

Filament diameter about 12 and partially flexible.

High tensile strength.

Intermediate modulus.

Significantly lower strength in compression.

5 grades of Kevlar with varying engineering properties are available.

Kevlar-29, Kevlar-49, Kevlar-100, Kevlar-119 and Kevlar-129.

Silicon Carbide Fibre (SiC)

Silicon carbide fibres are ceramic fibers. These fibres are produced in similar fashion as boron fibres are produced. The fibres are produced by two methods as follows:

CVD on Tungsten or Carbon Core

NICALON™ by NIPPON Carbon Japan

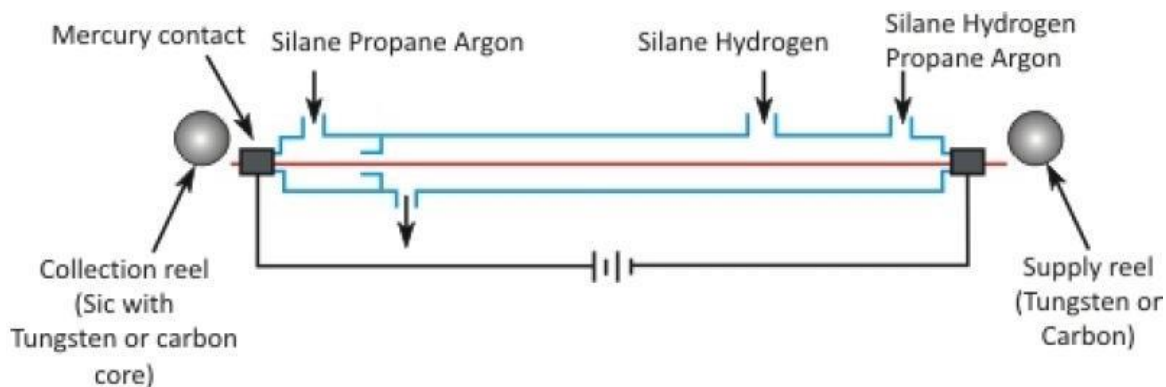
CVD on Tungsten or Carbon Core:

This fiber is similar in size and microstructure to boron. The fibres are produced on both tungsten and carbon cores. These fibres are relatively stiff due to thicker diameter of the fibres. The diameter of the fibres is about 140 μ m.

The fibres have strength in the range of 3.4 – 4.0 GPa.

Failure strain is in the range of 0.8 - 1%. The Young's modulus is about 430 GPa. The fibres show high structural stability and strength retention even at temperatures above 1000 $^{\circ}$ C.

The CVD for SiC fibres is shown in Figure



POSSIBLE QUESTIONS

UNIT-IV

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. What are the functions of a reinforcing agent?
2. What are the functions of a matrix material?
3. What are the types of fibres?
4. What are the advanced fibres?
5. What are the applications of Alumina Fibres?
6. What is the role of matrix in composites?
7. Give two examples of metal-matrix composites

PART-C (6 MARKS)

1. Write the limitations of conventional engineering materials?
2. Give account on following terms role of matrix in composites, matrix materials and reinforcements
3. What are the environmental effects on composites?
3. Give detail about metal-matrix composites and polymer-matrix composites?
5. Write the applications Composites material?

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SUBJECT : NOVEL INORGANIC SOLIDS

SEMESTER : V

SUBJECT CODE: 17CHU503B

Class: III-B. Sc Chemistry Batch – (2017-2020)

Unit-V (Multiple Choice Questions)

S. No	Questions	Option-I	Option-II	Option-III	Option-IV	Answer
1.	Which is obtained from the reaction of diamines with diacids?	Polyamides	b) polyester	Acrylicfibre	poly vinyl chloride	Polyamides
2.	In step polymerization the reactivity of a functional group depends on_____?	The collision frequency of the group	b. diffusion rate of the whole molecule	Nature of the functional group	Size of the group	The collision frequency of the group
3.	The alkyl resins are condensation polymers obtained from dibasic acids and	phenol	formaldehyde	Acetaldehyde	Glycol	Phenol
4.	Reactivity of a functional group depends on_____?	Collision frequency	diffusion rate	Size	Molecular weight	Collision frequency
5.	In a polymer chain the functional group has appreciable mobility due to	the conformational rearrangements	different stereochemical forms	Tautomeric arrangements	Optical activity	The conformational rearrangements
6.	The first step in the reaction of the diol and diacid monomers to form ?	dimer	trimer	Pentamer	Tetramer	Dimer

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Unit-V (Multiple Choice Questions)

7.	The rate of a step polymerization is conveniently expressed in terms of the	Concentrations of the reacting functional groups.	concentration of the monomeric	Concentration of monomer and the solvent	Concentration of the functional groups and monomers	Concentration of the functional groups and monomers
8.	Dimer + monomer → ?	Trimer	Dimer	Pentamer	Tetramer	Trimer
9.	In thermal catalyzed polymerizations the most widely used mode of generating radicals to initiate polymerization ?	Homolytic dissociation of initiators	Heterolytic dissociation of initiators	Decomposition of the initiator	Association of the initiator	Homolytic dissociation of initiators
10.	The Polyesterification of a diol and a diacid to illustrate the general of the kinetics of a typical ?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalyzed polymerization	Step polymerization
11.	The carboxyl concentration is comprised of two, first-order dependencies, one for the carboxyl as the reactant and another one as?	Product	Reactant	Reagent	Catalyst	Catalyst
12.	The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an _____ ?	Base	Acid	Alkali	Neutral	Acid

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Unit-V (Multiple Choice Questions)

13.	Example for radical sources for the polymerization reactions?	Peroxides	Epoxides	Nitrenes	Carbenes	Peroxides
14.	A titanium atom at the surface is bonded by?	Five chlorines	Six chlorines	Three chlorines	Two chlorines	Five chlorines
15.	In free radical vinyl polymerization	The electrons in the pi bond split up	The electrons in the sigma bond split up	Non bonding electrons are used	Electrons from the functional group splits.	The electrons in the pi bond split up
16.	The general linearity of the plot in the higher conversion region is a strong confirmation of the concept of functional group reactivity independent of?	Frequency	Molecular Weight	Density	Molecular size	Molecular size
17.	The catalyst used for the Ziegler–Natta polymerizations?	TiCl ₃ with Al(C ₂ H ₅) ₂ Cl	BCl ₃ with Al(C ₂ H ₅) ₂ Cl	TiCl ₃ with Fe(C ₂ H ₅) ₂ Cl	TiF ₃ with Al(C ₂ H ₅) ₂ F	TiCl ₃ with Al(C ₂ H ₅) ₂ Cl
18.	In the acid hydrolysis of cellulose there is no effect of ?	Frequency	Molecular wight	Density	Molecular size	Molecular size
19.	Isotactic polymerization depends intimately on the ?	Crystal structure of the initiator surface	Surface area of the initiator	Volume of the initiator	Concentration of the initiator	Crystal structure of the initiator surface
20.	In isotactic polymerization the	Edges (surfaces) of elementary	Edges of the basal planes	Corners of the basal planes	Inside the pores of the catalyst	Edges (surfaces) of elementary

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Unit-V (Multiple Choice Questions)

	polymerization occurs at active sites found on the ?	sheets of the crystal				sheets of the crystal
21.	Which find extensive use as radical sources?	Peroxides	Epoxides	Nitrenes	Carbenes	Peroxides
22.	The enantiomorphic site control model attributes stereo control in ?	Isospecific polymerization	Isotactic polymerization	Free radical polymerization	Ionic polymerization	Isospecific polymerization
23.	The C—N bond dissociation energy is?	$\sim 190 \text{ kJ mol}^{-1}$	$\sim 390 \text{ kJ mol}^{-1}$	$\sim 290 \text{ kJ mol}^{-1}$	$\sim 360 \text{ kJ mol}^{-1}$	$\sim 290 \text{ kJ mol}^{-1}$
24.	The various initiators are used at different temperatures depending on their rates of	Reaction	Decomposition	Composition	Entropy	Decomposition
25.	The azobisisobutyronitrile (AIBN) is commonly used at?	60-70 °C	50–70°C	80-90 °C	40-50 °C	50–70°C
26.	Teflon is a polymer of the monomer or Teflon is obtained by the polymerisation of ?	Monofluoroethene	Difluoroethene	Trifluoroethene	Tetrafluoroethene	Tetrafluoroethene
27.	Which of the following is an example of condensation polymer?	PVC	Polyamide	Terylene	Polyester	Terylene
28.	Trimer + trimer is_____?	Trimer	Hexamer	Monomer	Heptamer	Hexamer

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Unit-V (Multiple Choice Questions)

29.	Ionic vinyl polymerizations are very similar to	Free radical vinyl polymerizations	Step polymerizations	Self catalyzed vinyl polymerization	Free radical polymerizations	Free radical vinyl polymerizations
30.	Tetramer + trimer is _____?	Trimer	Dimer	Pentamer	Heptamer	Heptamer
31.	Pentamer + trimer is →?	Trimer	Dimer	Pentamer	Octamer	Octamer
32.	Monomer concentration decreases steadily throughout reaction is _____?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalyzed polymerization	Ionic polymerization
33.	Polymer molecular weight rises steadily throughout reaction is _____?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalyzed polymerization	Step polymerization
34.	In Cationic vinyl polymerization electron flow is _____?	Same direction	Same and opposite direction	Opposite direction	Same or opposite direction	Opposite direction
35.	Ionic polymerization necessarily carry along a?	Counter ion	Cation	Anion	Cation or anion	Counter ion
36.	The fraction of the radicals produced in the	Initiator efficiency	High efficiency	Low efficiency	Closer efficiency	Initiator efficiency

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Unit-V (Multiple Choice Questions)

	homolysis reaction that initiate polymer chains is defined as?					
37.	Dimer + dimer is _____?	Trimer	Dimer	Pentamer	Tetramer	Tetramer
38.	In most polymerizations, the second step is?	Much faster than the first step	Much slower than the first step	Less faster than the first step	Slower than the first step	Much faster than the first step
39.	Which is impossible under any and all reaction conditions if it does not pass the test of thermodynamic feasibility?	Cationic vinyl polymerization	Ionic polymerization	Polymerization	Wastage reactions	Polymerization
40.	The _____ alternating copolymer contains ?	2 monomer units	3 monomer units	4 monomer units	1 monomer units	2 monomer units
41.	The copolymer is not an _____?	Alloy	Trimer	Monomer	Initiator	Alloy
42.	Monomers show high selectivity towards?	Cationic initiators	Cationic and anionic initiators	Ionic initiators	Anionic initiators	Ionic initiators
43.	Most monomers will undergo polymerization with a radical initiator, although at?	Varying rates	Reliable rates	Stable rates	Positive rates	Varying rates
44.	Polymerization is possible only if the free-	Positive	Negative	Both negative and positive	Neither negative nor positive	Negative

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Unit-V (Multiple Choice Questions)

	energy difference -G between monomer and polymer is?					
45.	The polyethene polymer formed by the addition polymerisation process using the Ziegler- Natta catalyst is a_____?	High density and high melting point	Low density and high melting point	High density and low melting point	Low density and low melting point	High density and high melting point
46.	The property of fabric which influences drape the most is?	Tensile	Compressional	Shear	Surface	Shear
47.	The Q–e scheme is best considered as an empirical approach to placing monomer reactivity on a?	Qualitative basis	Quantitative basis	Qualitative radical	Quantitative radical	Quantitative basis
48.	To remove the residual metals, a process referred as _____?	Ashing	Reashing	Ashing and reashing	Deashing	Deashing
49.	The polyethene polymer formed by the addition polymerisation process using the Ziegler-Natta catalyst is a_____?	Non linear polymer	Linear polymer	Chain polymer	Cross linked polymer	Linear polymer
50.	Ziegler Natta catalyst is used in the polymerization of ?	Nylon	PET	Acetate	Polypropylene	Polypropylene

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Unit-V (Multiple Choice Questions)

51.	3,4-Difluorophenylamine is a weaker base than_____?	Phenylamine	Phenylacetate	Phenol	Henephthyl alcohol	Phenylamine
52.	What method would you use to synthesize a triblock copolymer?	Free radical polymerization	Anionic polymerization	Using a Ziegler Natta catalyst	Condensation polymerization	Free radical polymerization
53.	Suspension free radical polymerization of styrene would be preferred over bulk polymerization to overcome the problem of ?	Branching	Cross-linking	Stereo-isomerism	Polymeric impurities	Branching
54.	Polymers are_____?	Large molecule	Small molecule	Small chain molecule	Large chain molecule	Large chain molecule
55.	Polymers are high molecular weight in the range of_____?	10^4 to 10^7	10^3 to 10^7	10^2 to 10^7	10^5 to 10^7	10^3 to 10^7
56.	Tetramer + monomer is _____?	Trimer	Dimer	Pentamer	Tetramer	Pentamer
57.	Which one is not a polymer?	Carbohydrates	Proteins	Carboxylic acid	Nucleic acid	Carboxylic acid
58.	Due to the presence of carbon atom in polymers all large biological molecules are made	Ionic bond	Covalent bond	Triple bond	Metalic bond	Covalent bond

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Unit-V (Multiple Choice Questions)

	of _____?					
59.	Amino acids are building blocks of _____?	Carbohydrates	Proteins	Carboxylic acid	Lipids	Proteins
60.	polyethylene is _____?	Colourless liquid	Colourless gas	Gas	Liquid	Colourless gas

UNIT V

Syllabus

Speciality polymers:

Conducting polymers - Introduction, conduction mechanism, polyacetylene, polyparaphenylene and polypyrrole, applications of conducting polymers, Ion-exchange resins and their applications. Ceramic & Refractory: Introduction, classification, properties, raw materials, manufacturing and applications.

Introduction

Polymers have long been used as insulating materials. For example, metal cables are coated in plastic to insulate them. However, there are at least four major classes of semiconducting polymers that have been developed so far. They include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers. The conductively filled conducting polymers were first made in 1930 for the prevention of corona discharge. The potential uses for conductively filled polymers have since been multiplied due to their ease of processing, good environmental stability and wide range of electrical properties. Being a multi-phase system in nature, however, their lack of homogeneity and reproducibility has been an inherent weakness for conductively filled polymers. Therefore, controlling the quality of dispersion to obtain homogeneous conducting polymer composites is critically important.

Conjugated Conducting Polymers

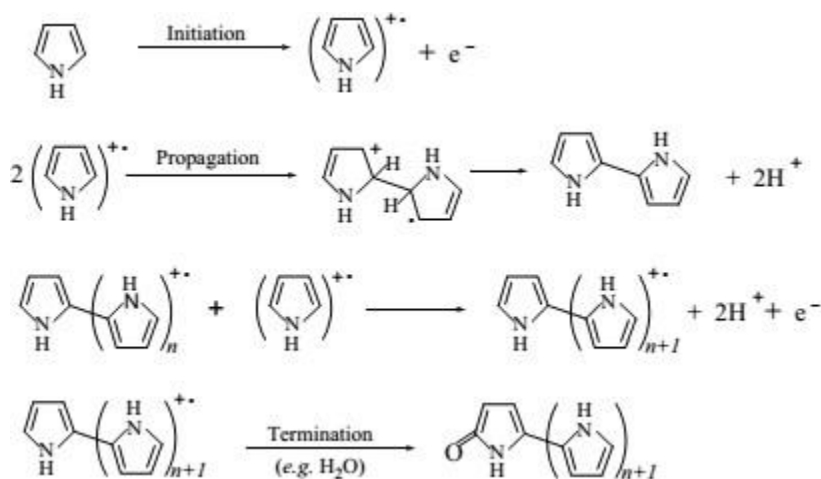
Structure and Properties

d-d* Conjugation

Table 2.1 lists the repeat units and conductivities for some common conjugated polymers (Dai, 1999). As can be seen in Table 2.1, the conjugated structure with alternating single and double bonds or conjugated segments coupled with atoms providing p-orbitals for a continuous orbital overlap (e.g. N, S) seems to be necessary for polymers to become intrinsically conducting. This is because just as metals have high conductivity due to the free movement of electrons through their structure, in order for polymers to be electronically conductive they must possess not only charge carriers but also an orbital system that allows the charge carriers to move. The conjugated structure can meet the second requirement through a continuous overlapping of S-orbitals along the polymer backbone. Due to its simple conjugated molecular structure and fascinating electronic properties, polyacetylene has been widely studied as a prototype for other electronically conducting polymers (Chien, 1984).

Electro polymerization

Apart from the electrochemical doping, both the potentiostatic method with a constant potential and potentiodynamic technique by scanning the potential within a certain range of voltages have been used for electrochemical polymerization of electronically conducting polymers (Chien, 1984). For instance, pyrrole can be oxidatively polymerized on a suitable anode using a simple two-electrode electrochemical cell. Equation (2.23) shows the mechanism for electropolymerization of pyrrole, which is also valid for many other conjugated conducting polymers (Skotheim et al., 1986).



As can be seen from Equation the electrochemical oxidation initially produces radicals. This is followed by the formation of dimers via the radical-radical recombination. Subsequent electrochemical oxidation of the dimer intermediates results in the formation of “oligomeric” radicals with a higher molecular weight, which could also combine with monomer radicals. Repeating the above steps yields a polypyrrole film on the anode electrode. The growth of polypyrrole macromolecules is believed to be governed by the radical-radical coupling and can be terminated via the exhaustion of reactive radical species in the vicinity of the electrode or by

other chain termination processes. To balance the charge on the polymer backbone, counter ions are normally incorporated into the polymer film during the chain growth process.

Introduction

Ceramics comes from the Greece word *keramicos*, which means burnt stuff. Among the key materials of new technologies and technical solutions there also belong so called "progressive ceramics", "advanced ceramics" and "high-tech ceramics". These new ceramics are definitely different from traditional ceramics. Progressive ceramics = synthetic polycrystalline material with a predominant content of inorganic, non-metallic phases prepared by sintering. The main factors raising interest in these materials are:

- ☐ their wide range of exceptional properties,
- ☐ the availability of raw materials,
- ☐ the lower energy demand for preparation,
- ☐ the more favourable ecological aspects of production compared to various metals.

With the development of technology and materials engineering, ceramics have an important role in many areas, including: electronics, communications, aviation, astronautics, environment, energy, etc. Many of the newly proposed and developed ceramic products are of a great importance both for daily and industrial use.

Since the mid-20th century there have been many kinds of ceramics produced with the use of raw materials and with a strictly controlled chemical composition. This represents ceramics which provide products of completely specific characteristics. These ceramics are characterized by their thermal, mechanical, electromagnetic, optical and biological functions. Their production is based on synthetic, even analytical pure raw materials, special forming techniques and a method of firing at a very high temperature. The products of special and structural ceramics show such extraordinary properties that directly caused reversals in certain fields.

- ☐ Special ceramics

Special ceramic materials include the area of materials having their own characteristics e.g.,

magnetic, electrical, dielectric, pyroelectric, piezoelectric, conductivity, semi conductivity, superconductivity and other areas. A large group is represented by so-called electro ceramics and also materials for electrical engineering. Another group is represented by the magnetic properties of the ceramics. The electrical and magnetic properties of ceramics vary considerably due to the difference in composition and the crystal structure. Many ceramics have a high insulation quality and are used for cable insulation, while some of them have excellent high temperature superconductivity. Certain ceramics are biocompatible and are used for biomedical applications. These materials are used e.g. in orthopaedics, cardio surgery, vascular surgery, plastic surgery and other areas.

- ☐ Characteristics of special ceramics:
- ☐ ceramic materials are defined as non-metallic materials,
- ☐ the preparation of classic ceramics is based on natural raw materials with a different granulometry,
- ☐ special (progressive) ceramics puts an emphasis on the creation of structures (microstructure) of a so-called regulated particle-size (grain-size) composition,
- ☐ special ceramics are made from synthetically produced materials with a predominant content of an inorganic, non-metallic phase (one phase can be glass),
- ☐ special ceramics are prepared by special methods of forming
- ☐ (Other) Characteristics of special ceramics:
- ☐ a wide range of materials with irreplaceable properties,
- ☐ mainly made of synthetic materials,
- ☐ production with relatively low energy requirements,
- ☐ production is basically environmentally-friendly,
- ☐ usable in almost all industrial areas.

Common properties

High melting point and high refractoriness (except glass)

- ☐ Generally electrical and thermal insulators

- ☐ Generally hard and strong with low plasticity
- ☐ Low fracture toughness (brittle)
- ☐ Chemically inert
- ☐ Many are low cost (bricks)
- ☐ Wide range of appearance

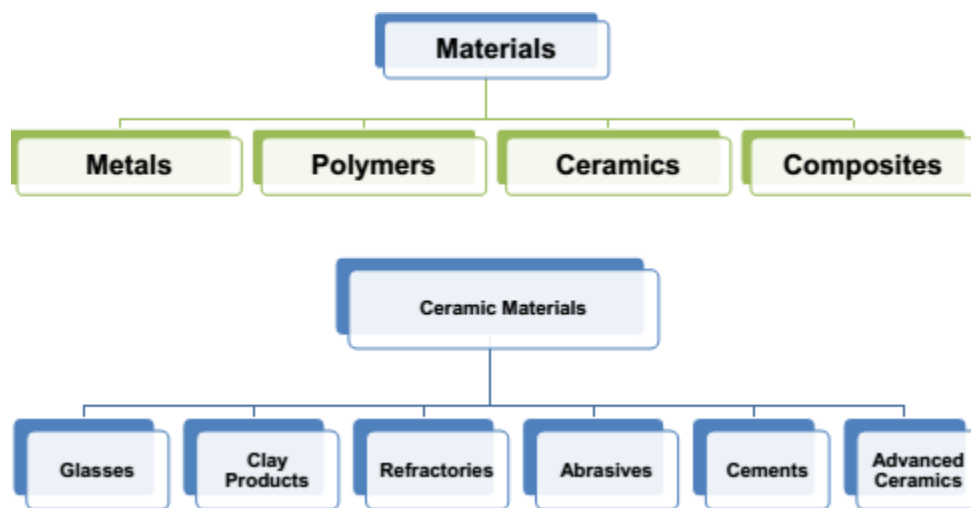
CLASSIFICATION OF ADVANCED CERAMICS

Many authors divide this type of ceramics in different ways. Table 1 gives a more detailed classification of special ceramics according to several criteria. At the same time, there are representatives named after each type of ceramics. Special products of special and structural ceramics can be divided into:

Table show Classification of advanced ceramics by selected criteria

According to the chemical composition	
Oxide ceramics	Al ₂ O ₃ , SiO ₂ , ZrO ₂ , MgO, Fe ₂ O ₃ , BeO, CaO, TiO ₂ , SnO ₂ , ThO ₂ , PuO ₂ , UO ₂ and oxides of rare earth elements
Non-oxide ceramics	Carbides (SiC, B ₄ C, TiC, ZrC, Mo ₂ C, VC, WC, ThC, HfC, NbC) Borides (Ti ₂ B, ZrB ₂ , TaB ₂ , HfB ₂ , ThB ₂) Nitrides (BN, Si ₃ N ₄ , TiN, ZrN, TaN, UN, ThN, SiAlON), Silicides (MoSi ₂ , ZrSi, ZrSi ₂ , Ti ₅ Si ₃ , TaSi ₂ , TiSi ₂)
Titanic ceramics (Titanium)	BaTiO ₃ , SrTiO ₃ , CaTiO ₃
Sulphidic ceramics	BaS, CeS, US, ThS, CdS, ZnS
Metal ceramics (Cermets)	Al ₂ O ₃ , ZrO ₂ , MgO, BeO, ThO ₂ , Y ₂ O ₃ + W, V, Mo, Ta, Ti, Zr, Si, Cr, Co, Ni, Nb

CLASSIFICATION OF MATERIALS



Ceramic materials are inorganic compounds consisting of metallic and nonmetallic elements which are held together with ionic and/or covalent bonds.

Ceramics are

- ☐ inorganic, nonmetallic, solids, crystalline, amorphous (e.g. glass), hard, brittle, stable to high temperatures, less dense than metals, more elastic than metals, and very high melting.
- ☐ Ceramics can be covalent network and/or ionic bonded

Metals	ceramics	polymers
High density Medium to high	Low density High melting	Very low density Low melting

melting point	point	point
Medium to high	Very high elastic	Low elastic
elastic modulus	modulus	modulus
Reactive	Unreactive	Very reactive
Ductile	Brittle	Ductile and brittle types

Material	Melting Point (°C)	Density (g/cm ³)	Hardness (Mohs) ^a	Modulus of Elasticity ^b	Coefficient of Thermal Expansion ^c
Alumina, Al ₂ O ₃	2050	3.8	9	34	8.1
Silicon carbide, SiC	2800	3.2	9	65	4.3
Zirconia, ZrO ₂	2660	5.6	8	24	6.6
Beryllia, BeO	2550	3.0	9	40	10.4
Mild steel	1370	7.9	5	17	15
Aluminum	660	2.7	3	7	24

Ceramic materials have now become the cornerstone of such advanced technologies as energy transformation, storage and supply, information technology, transportation systems, medical technology, and manufacturing technology Design of materials having specific desired characteristics directly from our knowledge of atomic structure.

- Miniaturization: "Nanostructured" materials, with microstructure that has length scales between 1 and 100 nanometers with unusual properties. Electronic components, materials for quantum computing.
- Smart materials: airplane wings that deice themselves, buildings that stabilize themselves in earthquakes...

- Environment-friendly materials: biodegradable or photodegradable plastics, advances in nuclear waste processing, etc.
- Learning from Nature: shells and biological hard tissue can be as strong as the most advanced laboratory-produced ceramics, molluscs produce biocompatible adhesives that we do not know how to reproduce...
- Materials for lightweight batteries with high storage densities, for turbine blades that can operate at 2500 C, room-temperature superconductors? chemical sensors (artificial nose) of extremely high sensitivity, cotton shirts that never require ironing...

Ceramic Materials		
Advanced Ceramics		Traditional Ceramics
Structural Ceramics	Functional Ceramics	Whitewares
Bioceramics	Electronic substrate, package ceramics	Cement
Ceramics used in automotive industry	Capacitor dielectric, piezoelectric ceramics	Abrasives
Nuclear ceramics	Magnetic ceramics	Refractories
Wear resistant ceramics (tribological)	Optical ceramics	Brick and tile
	Conductive ceramics	Structural clay products

Traditional Ceramic Products



Clay pipes are sustainable products and last longer than other materials



Well Known Glass Products



Tempered glass table



<http://www.ifjk.org>



<http://freshome.com>



www.tripsadvisor.com

Glass sink cabinets in the bathroom



www.aartcommercial.com/products.php

Laminated Windscreen Glass



Heat resistant glass door



Special Glass Products

Laminated Glass

Laminated glass is widely used for

bullet proof

burglar-proof

showcase

counter

aquarium

skylight

long corridor

sidelite, etc.

If the laminated glass is made from “ordinary” float glass, it is still workable (cutting and drilling is possible) and the PVB helps the fractured glass to stay put inside the construction.

Bulletproof glass is made of laminated glasses and films which have special shielding capability towards bullets. The different levels of bullet proof glasses are able to shield the bullets from penetration and prevent the broken parts from injuring people. They are widely applied in bank, counters of jewelry and gold shops, cash trucks and other regions requiring special safety prevention.

Applications of Advanced Ceramics



Ceramic filter



Foam ceramic molten metal filter

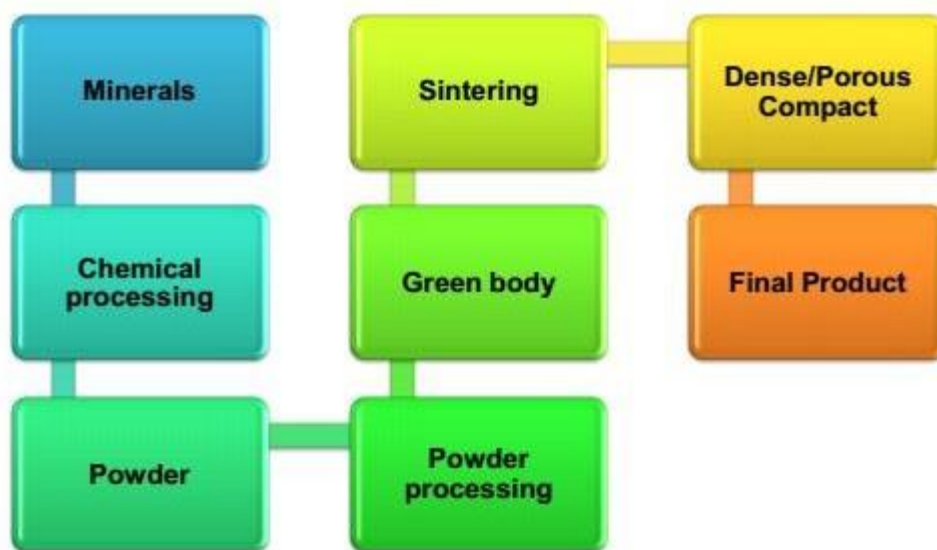


Ceramic Knife



Ceramic Fiber Boards As The Heat Insulation

CERAMIC PROCESSING



Other Ceramic Materials

Cements - Ceramic raw materials are joined using a binder that does not require firing or sintering in a process called cementation.

- ☐ Coatings - Ceramics are often used to provide protective coatings to other materials.
- ☐ Thin Films and Single Crystals - Thin films of many complex and multi-component ceramics are produced using different techniques such as sputtering, sol-gel, and chemical-vapor deposition (CVD).
- ☐ Fibers - Fibers are produced from ceramic materials for several uses: as a reinforcement in composite materials, for weaving into fabrics, or for use in fiber-optic systems.
- ☐ Joining and Assembly of Ceramic Components - Ceramics are often made as monolithic components rather than assemblies of numerous components.

Ceramics form an important part of materials group. Ceramics are compounds between metallic and nonmetallic elements for which the inter-atomic bonds are either ionic or predominantly ionic. The term ceramics comes from the Greek word *keramikos* which means ‘burnt stuff’. Characteristic properties of ceramics are, in fact, optimized through thermal treatments. They exhibit physical properties those are different from that of metallic materials. Thus metallic materials, ceramics, and even polymers tend to complement each other in service.

Types and applications of ceramics

Ceramics greatly differ in their basic composition. The properties of ceramic materials also vary greatly due to differences in bonding, and thus found a wide range of engineering applications. Classification of ceramics based on their specific applications and composition are two most important ways among many. Based on their composition, ceramics are classified as:

Oxides,
Carbides,
Nitrides,
Sulfides,
Fluorides, etc.

The other important classification of ceramics is based on their application, such as:

Glasses,
Clay products,
Refractories,
Abrasives,
Cements,

In general, ceramic materials used for engineering applications can be divided into two groups: traditional ceramics, and the engineering ceramics. Typically, traditional ceramics are made from three basic components: clay, silica (flint) and feldspar. For example bricks, tiles and porcelain articles. However, engineering ceramics consist of highly pure compounds of aluminium oxide (Al_2O_3), silicon carbide (SiC) and silicon nitride (Si_3N_4).

Glasses: glasses are a familiar group of ceramics – containers, windows, mirrors, lenses, etc. They are non-crystalline silicates containing other oxides, usually CaO , Na_2O , K_2O and Al_2O_3 which influence the glass properties and its color. Typical property of glasses that is important in engineering applications is its response to heating. There is no definite temperature at which the liquid transforms to a solid as with crystalline materials. A specific temperature, known as glass transition temperature or fictive temperature is defined based on viscosity above which material is named as super cooled liquid or liquid, and below it is termed as glass.

Clay products: clay is the one of most widely used ceramic raw material. It is found in great abundance and popular because of ease with which products are made. Clay products are mainly two kinds – structural products (bricks, tiles, sewer pipes) and whitewares (porcelain, chinaware, pottery, etc.).

Refractories: these are described by their capacity to withstand high temperatures without melting or decomposing; and their inertness in severe environments. Thermal insulation is also an important functionality of refractories. Abrasive ceramics: these are used to grind, wear, or cut away other material. Thus the prime requisite for this group of materials is hardness or wear resistance in addition to high toughness. As they may also exposed to high temperatures, they need to exhibit some refractoriness. Diamond, silicon carbide, tungsten carbide, silica sand, aluminium oxide / corundum are some typical examples of abrasive ceramic materials. Cements: cement, plaster of paris and lime come under this group of ceramics. The characteristic property of these materials is that when they are mixed with water, they form slurry which sets subsequently and hardens finally. Thus it is possible to form virtually any shape. They are also used as bonding phase, for example between construction bricks.

Advanced ceramics: these are newly developed and manufactured in limited range for specific applications. Usually their electrical, magnetic and optical properties and combination of properties are exploited. Typical applications: heat engines, ceramic armors, electronic packaging, etc.

Some typical ceramics and respective applications are as follows:

Aluminium oxide / Alumina (Al_2O_3): it is one of most commonly used ceramic material. It is used in many applications such as to contain molten metal, where material is operated at very high temperatures under heavy loads, as insulators in spark plugs, and in some unique applications such as dental and medical use. Chromium doped alumina is used for making lasers. Aluminium nitride (AlN): because of its typical properties such as good electrical insulation but high thermal conductivity, it is used in many electronic applications such as in electrical circuits operating at a high frequency. It is also suitable for integrated circuits. Other electronic ceramics include – barium titanate (BaTiO_3) and Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$).

Diamond (C): it is the hardest material known to available in nature. It has many applications such as industrial abrasives, cutting tools, abrasion resistant coatings, etc. it is, of course, also used in jewelry. Lead zirconium titanate (PZT): it is the most widely used piezoelectric material, and is used as gas igniters, ultrasound imaging, in underwater detectors.

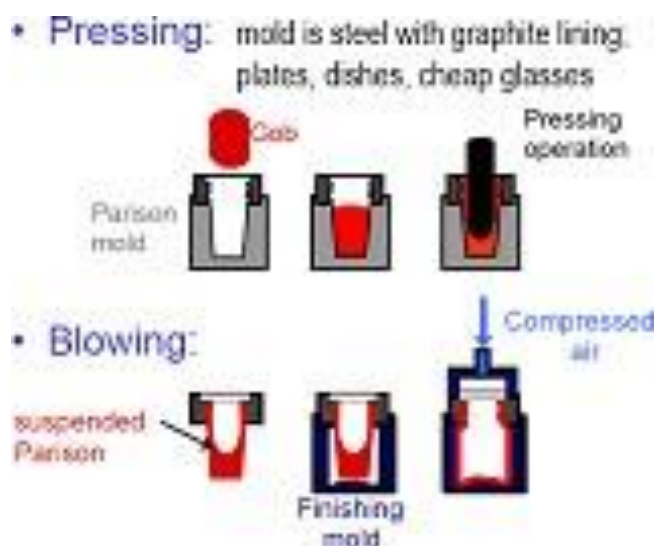
Silica (SiO_2): is an essential ingredient in many engineering ceramics, thus is the most widely used ceramic material. Silica-based materials are used in thermal insulation, abrasives, laboratory glassware, etc. it also found application in communications media as integral part of optical fibers. Fine particles of silica are used in tires, paints, etc. Silicon carbide (SiC): it is known as one of best ceramic material for very high temperature applications. It is used as coatings on other material for protection from extreme temperatures. It is also used as abrasive material. It is used as reinforcement in many metallic and ceramic based composites. It is a semiconductor and often used in high temperature electronics. Silicon nitride (Si_3N_4) has properties similar to those of SiC but is somewhat lower, and found applications in such as automotive and gas turbine engines. Titanium oxide (TiO_2): it is mostly found as pigment in paints. It also forms part of certain glass ceramics. It is used to making other ceramics like BaTiO_3 . Titanium boride (TiB_2): it exhibits great toughness properties and hence found applications in armor production. It is also a good conductor of both electricity and heat. Uranium oxide (UO_2): it is mainly used as nuclear reactor fuel. It has exceptional dimensional stability because its crystal structure can accommodate the products of fission process.

Yttrium aluminium garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$): it has main application in lasers (Nd-YAG lasers).

Zirconia (ZrO_2): it is also used in producing many other ceramic materials. It is also used in making oxygen gas sensors, as additive in many electronic ceramics. Its single crystals are part of jewelry.

Fabrication and processing of ceramics

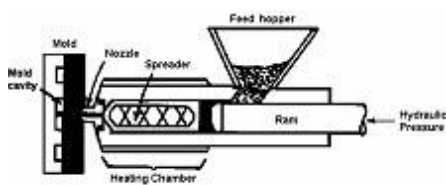
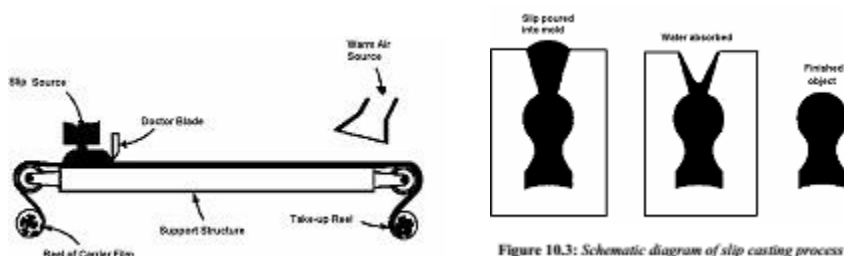
Ceramics melt at high temperatures and they exhibit a brittle behavior under tension. As a result, the conventional melting, casting and thermo-mechanical processing routes are not suitable to process the polycrystalline ceramics. Inorganic glasses, though, make use of lower melting temperatures due to formation of eutectics. Hence, most ceramic products are made from ceramic powders through powder processing starting with ceramic powders. The powder processing of ceramics is very close to that of metals, powder metallurgy. However there is an important consideration in ceramic-forming that is more prominent than in metal forming: it is dimensional tolerance. Post forming shrinkage is much higher in ceramics processing because of the large differential between the final density and the as-formed density. Glasses, however, are produced by heating the raw materials to an elevated temperature above which melting occurs. Most commercial glasses are of the silica-soda-lime variety, where silica is supplied in form of common quartz sand, soda (Na_2O) in form of soda ash (Na_2CO_3) while the lime (CaO) is supplied in form of limestone (CaCO_3). Different forming methods- pressing, blowing, drawing and fiber forming- are widely in practice to fabricate glass products. Thick glass objects such as plates and dishes are produced by pressing, while the blowing is used to produce objects like jars, bottles and light bulbs. Drawing is used to form long objects like tubes, rods, fibers, whiskers etc. The pressing and blowing process is shown in figure



Ceramic powder processing consists of powder production by milling/grinding, followed by fabrication of green product, which is then consolidated to obtain the final product. A powder is a collection of fine particles. Synthesis of powder involves getting it ready for shaping by crushing, grinding, separating impurities, blending different powders, drying to form soft agglomerates. Different techniques such as compaction, tape casting, slip casting, injection molding and extrusion are then used to convert processed powders into a desired shape to form what is known as green ceramic. The green ceramic is then consolidated further using a high-temperature treatment known as sintering or firing. As-mined raw materials are put through a milling or grinding operation in which particle size is reduced to and physically 'liberate' the minerals of interest from the rest of the 'gangue' material. Wet milling is much more common with ceramic materials than with metals. The combination of dry powders with a dispersant such

as water is called slurry. Ball- and vibratory- milling is employed to further reduce the size of minerals and to blend different powders.

Ceramic powders prepared are shaped using number of techniques, such as casting, compaction, extrusion/hydro-plastic forming, injection molding. Tape casting, also known as doctor blade process, is used for the production of thin ceramic tapes. The schematic diagram of tape casting process is shown in figure. In this technique slurry containing ceramic particles, solvent, plasticizers, and binders is then made to flow under a blade and onto a plastic substrate. The shear thinning slurry spreads under the blade. The tape is then dried using clean hot air. Later-on the tape is subjected to binder burnout and sintering operations. Tape thickness normally range between 0.1 and 2 mm. Commercially important electronic packages based on alumina substrates and barium titanate capacitors are made using this technique. A schematic diagram of doctor blade process is shown in the figure.



Slip casting is another casting technique widely used. This technique uses aqueous slurry, also known as slip, of ceramic powder. The slip is poured into a plaster of Paris ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) mold. As the water from slurry begins to move out by capillary action, a thick mass builds along the mold wall. When sufficient product thickness is built, the rest of the slurry is poured out (drain casting). It is also possible to continue to pour more slurry in to form a solid piece (solid casting). The schematic diagram of slip casting process is shown in figure 10.3 Extrusion and injection molding techniques are used to make products like tubes, bricks, tiles etc. The basis for extrusion process is a viscous mixture of ceramic particles, binder and other additives, which is fed through an extruder where a continuous shape of green ceramic is produced. The product is cut to required lengths and then dried and sintered.

Injection molding of ceramics is similar to that of polymers. Ceramic powder is mixed with a plasticizer, a thermoplastic polymer, and additives. Then the mixture is injected into a die with use of an extruder. The polymer is then burnt off and the rest of the ceramic shape is sintered at suitable high temperatures. Ceramic injection molding is suitable for producing complex shapes. Figure 10.4 shows schematically the injection molding process. Most popular technique to produce relatively simple shapes of ceramic products in large numbers is combination of compaction and sintering. For example: electronic ceramics, magnetic ceramics, cutting tools, etc. Compaction process is used to make green ceramics that have respectable strength and can be handled and machined. Time for compaction process varies from within a minute to hours depending on the complexity and size of the product. Basically compaction process involves applying equal pressure in all directions to a mixture ceramic powder to increase its density. In some cases, compaction involves application of pressure using oil/fluid at room temperatures, called cold iso-static pressing (CIP). Then the green ceramic is sintered with or without pressure. CIP is used to achieve higher ceramic density or where the compaction of more complex shapes is required. In some instances, parts may be produced under conditions in which compaction and sintering are conducted under pressure at elevated temperatures. This technique is known as hot

iso-static pressing (HIP), and is used for refractory and covalently bonded ceramics that do not show good bonding characteristics under CIP. HIP is also used when close to none porosity is the requirement. Another characteristic feature of HIP is high densities can be achieved without appreciable grain growth. Sintering is the firing process applied to green ceramics to increase its strength. Sintering is carried out below the melting temperature thus no liquid phase presents during sintering. However, for sintering to take place, the temperature must generally be maintained above one-half the absolute melting point of the material. During sintering, the green ceramic product shrinks and experiences a reduction in porosity. This leads to an improvement in its mechanical integrity. These changes involve different mass transport mechanisms that cause coalescence of powder particles into a more dense mass. With sintering, the grain boundary and bulk atomic diffusion contribute to densification, surface diffusion and evaporation condensation can cause grain growth, but do not cause densification. After pressing, ceramic particles touch one another. During initial stages of sintering, necks form along the contact regions between adjacent particles thus every interstice between particles becomes a pore. The pore channels in the compact grow in size, resulting in a significant increase in strength. With increase in sintering time, pores become smaller in size. The driving force for sintering process is the reduction in total particle surface area, and thus the reduction in total surface energy. During sintering, composition, impurity control and oxidation protection are provided by the use of vacuum conditions or inert gas atmospheres.

POSSIBLE QUESTIONS

UNIT-V

PART-A (20 MARKS)

(Q.NO 1 TO 20 Online Examination)

PART-B (2 MARKS)

1. What is meant by conducting polymers?
2. How prepare polyacetylene?
3. Give four examples of Ion-exchange resins
4. What are the applications of conducting polymers?
5. What is meant by Ceramic and Refractory?
6. How prepare polypyrrole?
7. Give some examples of ceramic products?
8. How prepare polypyrrole?

PART-C (6 MARKS)

1. What is the conduction mechanism involved in polyacetylene, polyparaphenylene?
2. Write the applications of conducting polymers?
3. Write briefly about Ceramic and Refractory?
4. How classification and properties of Ceramic and Refractory?
5. How will manufacturing Ceramic material and its application?

[17CHU503B]

Reg. No-----

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University, Established Under Section 3 of UGC Act 1956)

(For the candidates admitted from 2017 onwards)

B.sc Degree Examination

III B.Sc. Chemistry

Internal Exam-I

Novel Inorganic Solids

Date:

Maximum: 50 marks

Time: 2 hrs

Part A

Answer all the questions (20 x 1 = 20 marks)

1. Carbon nanotubes are

a. Large molecules b. small molecules c. long chain molecule d. small chain molecule

2. Sol-gel method is _____ chemical process

a. Wet b. Dry c. Semi Solid d. Semi liquid

3. The ionic solids shows brittleness because they are arranged in

a. Linear layers b. Parallel layers c. Combined layers **d. Closely packed**

4. In sol-gel process the starting material is processed to form a dispersible oxide and forms a sol in contact with?

a. Water b. Dilute acid c. **Water or dilute acid** d. Acid or alkali

5. Ion exchange resins are made of

a. Polystyrene b. Lutein c. Teflon d. **Sulphonated Bakelite**

6. Which of the ceramics can be used as pigment in paints?

a. Silicon carbide b. Silicon oxide c. Aluminum oxide **d. Titanium oxide**

7. Gelation resulting from the formation of an oxide- or alcohol- bridged network by which reaction?

a. Polycondensation b. Substitution c. Addition d. Decomposition

8. Which one is not a characteristic property of ceramic material?

a. high temperature stability b. high mechanical strength c. low elongation **d. low hardness**

9. Major ingredients of traditional ceramics

a. SiC **b. SiO₂** c. Si₃N₄ d. Al₂O₃

10. Monolith is termed as?

a. Xerogel b. Gel c. Sol d. Syneresis

11. Which of the following is not a form of carbon?

a. Diamond b. fullerene c. **microtubules** d. graphite

12. Colloidal suspension is known as?

a. Gel b. Gel and sol **c. Sol** d. Electrical

13. During sintering densification is not due to

a. Atomic diffusion **b. surface diffusion** c. bulk diffusion d. grain growth

14. The size of nanoparticles is between

a. 100 to 1000 nm b. 0.1 to 10 nm **c. 1 to 100 nm** d. 0.01 to 1 nm

15. How many nanotubes are in the sample shown by Dr. Baughman?

a. two **b. many** c. four d. one

16. Calcination of the gel produces?

a. Calcium oxide b. sulphur c. oxygen **d. oxide**

17. Since the ions are held in fixed positions by strong forces, electricity is not conducted by

a. electrodes b. electrolytes **c. insulators** d. metals

18. Soluble substances that do not easily dissociate into ions in solutions are

a. Weak electrolytes b. Strong electrolytes c. Strong acids d. Electrodes

19. Which of the following pairs of compounds are examples of strong electrolytes?

a. sugar and calcium hydroxide **b. calcium hydroxide and hydrochloric acid** c. Hydrochloric acid and vinegar d. vinegar and sugar

20. Upon dissolving ionic substances or melting them,

a. it become good conductor of electricity b. it become new crystal c. it loose electrical conductivity d. solute increases

PART-B (3 x 2 = 6 MARKS)

21. Give two examples of anionic and cationic electrolytes?

22. Give examples of white and black pigments?

23. Write any two advantages of Ion exchange method?

PART-C (3 x 8 = 24 MARKS)

24. a. Write detail about Solid electrolytes and colour solids

OR

b. Explain the Co-precipitation method for synthesis of inorganic solids?

25. a. Discuss about molecular materials and fullerides?

OR

b. Write about black and white pigments?

26. a. Give the detail about self-assembled nanostructures-control of nanoarchitecture-one dimensional control?

OR

b. How will prepare gold and silver nano particles?

Reg. No.....

[17CHU503B]

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-21

(For the candidates admitted from 2017 & onwards)

B. Sc DEGREE EXAMINATION- AUGUST 2018

III-B.Sc., CHEMISTRY

Internal Exam-II

NOVEL INORGANIC SOLIDS

DATE: 28/08/2019 & SESSION: AN

SUBJECT CODE: 17CHU503B

TIME: 2Hrs

TOTAL: 50 MARKS

PART-A ANSWER ALL THE QUESTIONS

(20 x 1 = 20 Marks)

1. Buckyballs are a type of
a. **fullerene** b. diamond c. graphite d. composites
2. The ionic solids shows brittleness because they are arranged in
a) Parallel layers b) combined layer
c) **closely packed** d) Linear layers
3. A steel containing 16 to 18% chromium and about 0.12% carbon is called
a) **Ferritic stainless steel** b) Austenitic stainless steel
c) Martensitic stainless steel d) Nickel steel
4. Sulphur in steel
a) Acts as deoxidiser b) **Lowers the toughness and transverse ductility**
c) Reduces the grain size d) Decreases tensile strength and hardness
5. The silicon steel is widely used for
a) Connecting rods b) Cutting tools c) Motor car crankshafts
d) **Generators and transformers in the form of laminated cores**
6. Brass is an alloy of
a) **Copper and zinc** b) Copper and tin c) Copper, tin and zinc d) tin
7. Pure iron is the structure of
a) Pearlite b) **Ferrite** c) Austenite d) Ferrite and cementite

8. Brass contains

- a) 70 - 75% copper and rest tin
- b) 90% copper and 10% tin
- c) 85 - 92% copper and with little lead
- d) 70% copper and 30% zinc**

9. The percentage carbon content in wrought iron is about

- a) 0.02**
- b) 0.1
- c) 0.2
- d) 0.4

10. Resistance developed by surface of any material is known as

- a) Strength
- b) Hardness**
- c) Stiffness
- d) Creep

11. Permanent deformation of material with respect to time due to constant load and variable temperature is known as

- a) Elasticity
- b) Isotropy
- c) Hardness
- d) Creep**

12. Material with same property in all direction may be termed as

- a) Creep
- b) Anisotropy
- c) Isotropy**
- d) Orthotropic

13. In process annealing, the hypo eutectoid steel is

- a) Heated from 30°C to 50°C above the upper critical temperature and then cooled in still air
- b) Heated from 30°C to 50°C above the upper critical temperature and then cooled suddenly in a suitable cooling medium
- c) Heated from 30°C to 50°C above the upper critical temperature and then cooled slowly in the furnace
- d) Heated below or closes to the lower critical temperature and then cooled slowly**

14. Nickel in steel

- a) Improves wear resistance, cutting ability and toughness
- b) Refines grain size and produces less tendency to carburisation, improves corrosion and heat resistant properties
- c) Improves cutting ability and reduces hardenability
- d) Gives ductility, toughness, tensile strength and anti-corrosion properties**

15. Which form of carbon has the highest melting point?

- a) graphite
- b) fullerene
- c) diamond**
- d) microtubules

16. A carbon nanotube is

- a) Tube shaped material**
- b) plain shape material
- c) square shape material
- d) no shape

17. Single Walled Carbon Nano tubes are

- a) excellent conductors**
- b) Poor conductor
- c) Poor conductor
- d) semi-conductor

18. Carbon nanotubes have the ability to sustain temperature as high as

- a) 800 °C b) 2800 °C c) 3000 °C d) 1000 °C

19. Carbon nanotubes are

- a) **Less toxicity** b) High toxicity c) no toxicity d) medium toxicity

20. In diamond, carbon atoms are arranged in the shape of

- a) Flat layers b) a geodesic dome c) a hollow cylinder **d) a crystal**

PART-B ANSWER ALL THE QUESTIONS

(3 x 2 = 6 MARKS)

21. Define inorganic nanowires.

22. What is the Composition of cast irons?

23. Define super alloys?

PART-C ANSWER ALL THE QUESTIONS

(3 x 8 = 24 MARKS)

24. a. How will you prepare carbon nano tubes and its applications?

OR

b. What are the inorganic-organic components involved in natural and artificial nano material. Explain?

25. a. What are the characteristics of plain carbon and cast iron?

OR

b. Give detail about composition, mechanical and fabricating characteristics and applications of copper?

26. a. What is meant by thermoplastics and thermosets and its properties and application?

OR

b. How will you fabricating the alloy steels?

[17CHU503B]

Reg. No-----

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University, Established Under Section 3 of UGC Act 1956)

(For the candidates admitted from 2017 onwards)

B.sc Degree Examination, September 2019

III B.Sc. Chemistry

Internal Exam-III

Novel Inorganic Solids

Date:

Maximum: 50 marks

Time: 2 hrs

PART -AAnswer all the questions (20 x 1 = 20 marks)

1. Which is chemically inert?

- a) Low Density Polyethylene **b) High Density Polyethylene** c) High Density polyamide
d) Low Density polyamide

2. Plastics are ?

- a) Hydrocarbons** b) Aldehyde c) Ester d) Amide

3. Polyvinyl chloride was commercially introduced in_____?

- a) 1943 b) 1930 **c) 1936** d) 1947

4. Polythene was first produced in_____?

- a) German **b) England** c) India d) USA

5. Melting Point of Low Density Polyethylene (LDPE) is?

- a) ~115°C b)~116 °C **c)~135°C** d)~148 °C

6. In polymer industry 2-hydroxybenzophones are used as

- a) Light stabilizers** b)Antioxidantsc) Polymer initiators d) Fillers

7. Which polymer is not a copolymer?

- a) CCDDCCDDCCD **b) AAAAAAAAAAA** c) BBBAAB d) CCDDCCDDCC

8. Which is used as reinforcing filler for polyester resins?

a) Fibre b) Wood fibre **c) Glass fibre** d) Polyamide

9. Polymethyl methacrylate can be prepared by acetone cyanohydrin is treated with_____?

a) Nitric acid b) Acetic acid **c) Sulphuric acid** d) Hydrochloric acid

10. Polyvinyl acetate monomer is prepared by the reaction between acetic anhydride with_____?

a) Benzaldehyde **b) Acetaldehyde** c) Acetic acid d) Sodium acetate

11. Polyvinyl acetate is insoluble in_____?

a) Alcohols b) Aromatic solvents c) Esters **d) Water**

12. Which one of the compound is used in the manufacture of terylene?

a) Vinyl chloride **b) Ethylene glycol** c) Vinyl alcohol d) Ethylene

13. Which one is not a polymer?

a) Carbohydrates b) Proteins **c) Carboxylic acid** d) Nucleic acid

14. The word ceramic means

a) Soft **b) Burnt** c) Hard d) soft and hard

15. Which of the ceramics can be used as pigment in paints?

a) Silicon carbide b) Silicon oxide c) Aluminum oxide **d) Titanium oxide**

16. Porcelain is made for making crockery which is itself being prepared by

a) Mud b) soil **c) clay** d) silicon

17. Materials which can retain their strength above 550°C are known as

a) Ceramics **b) refractories** c) metals d) non-metals

18. Glass, furnace lining and abrasive for grinding is done by the ceramic which contain

a) Magnesium oxide b) **aluminum oxide** c) silicon oxide d) Titanium oxide

19. Ceramics bear the properties of

a) High melting and boiling point b) soft c) chemically reactivated) soluble in water

20. Ceramics can conduct

- a)Partially conduct heat b) conduct electricity
c)Conduct heat d) **do not conduct heat and electricity**

PART-B Answer all the Questions (3 x 2 = 6 MARKS)

21. What is the function of a reinforcing agent in composite material?
22. . What is the role of matrix in composites?
23. Give two examples of metal-matrix composites?

PART-C Answer all the Questions (3 x 8 = 24 MARKS)

24. a. Write the limitations of conventional engineering materials?

OR

- b. Write the applications Composites material?

25. a. Give account on metal-matrix composites and polymer-matrix composites

OR

- b. What are the environmental effects on composites?

- 26.a. Write the applications of conducting polymers?

OR

- b. How to manufacture Ceramic material and explain its application?

[17CHU503B]

Reg. No-----

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University, Established Under Section 3 of UGC Act 1956)

(For the candidates admitted from 2017 onwards)

B.sc Degree Examination

III B.Sc. Chemistry

Internal Exam-I

Novel Inorganic Solids

Date:

Maximum: 50 marks

Time: 2 hrs

Part A

Answer all the questions (20 x 1 = 20 marks)

- 1.a. Large molecules
- 2.a. Wet
3. d. Closelypacked
- 4..c. Water or dilute acid
5. d. Sulphonated Bakelite
6. d. Titanium oxide
7. a. Polycondensation
8. d. low hardness
9. b. SiO₂
10. Sol
11. c. microtubule d. graphite
- 12.c. Sol
13. b. surface diffusion
14. c. 1 to 100 nm
15. b. many

16.d. oxide

17.c. insulators

18. a. Weak electrolytes

19. b. calcium hydroxide and hydrochloric

20. a. it become good conductor of electricity

PART-B (3 x 2 = 6 MARKS)

21. Give two examples of anionic and cationic electrolytes?

Cationic electrolytes Ag_2HgI_4 and AgI and RbAg_4I_5

Anionic electrolytes Zirconia, ZrO_2 and 'yttrium stabilized zirconia' (YSZ)

22. Give examples of white and black pigments?

Molecular solids containing individual molecules, clusters, or linked chains of molecules can show bulk magnetic effects such as ferromagnetism.

Molecular inorganic magnetic materials, in which individual molecules, or units constructed from such molecules, contain d-metal atoms with unpaired electrons, is a class of compounds of growing interest.

23. Write any two advantages of Ion exchange method?

Ion exchange is widely used for water treatment in both industrial and municipal water treatment systems. The process provides many advantages over other treatment methods.

It is environment friendly, can provide high flow rate of treated water and has low maintenance cost.

PART-C (3 x 8 = 24 MARKS)

24. a. Write detail about Solid electrolytes and colour solids

Anion mobility can occur at high temperatures in certain structures that contain high levels of anion vacancies. Michael Faraday reported in 1834 that red-hot solid PbF_2 is a good

conductor of electricity. Much later it was recognized that the conductivity arises from the mobility of F ions through the solid. The property of anion conductivity is shared by other crystals having the fluorite structure. Ion transport in these solids is thought to be by an interstitial mechanism in which an F ion first migrates from its normal position into an interstitial site (a Frenkel-type defect, Section 3.16) and then moves to a vacant F site.

Structures that have large numbers of vacant sites generally show the highest ionic conductivities because they provide a path for ion motion (although at very high levels of defects, clustering of the defects or the vacancies can lower the conductivity). These vacancies, which are equivalent to extrinsic defects, can be introduced in fairly high numbers into many simple oxides and fluorides by doping with appropriately chosen metal ions in different oxidation states. Zirconia, ZrO_2 , at high temperature has a fluorite structure, but on cooling the pure material to room temperature it distorts to a monoclinic polymorph. The cubic fluorite structure may be stabilized at room temperature by replacing some Zr^{4+} with other ions, such as the similarly sized Ca^{2+} and Y^{3+} ions.

OR

b. Explain the Co-precipitation method for synthesis of inorganic solids?

In this process the desired component is precipitated from the solution. Co precipitation is used for simultaneous precipitation of more than one component. Catalysts based on more than one component can be prepared easily by co-precipitation. The precipitation process is used for preparation of bulk catalysts and support material such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 etc.

Process

In general, the metal hydroxides are precipitated from their precursor salt solution because of their low solubility. The precipitation of hydroxides can be performed either by starting from an alkaline solution which is acidified or from acidic solution by raising the pH. However, most hydroxides for technical application are precipitated from an acidic solution by the addition of an alkaline precipitating agent. Usually, ammonia or sodium bicarbonate is used as the precipitating agent. Highly soluble inorganic salts such as nitrates, carbonates or chlorides are generally used as metal precursors. For example, preparation of alumina is done by precipitating aluminium hydroxide from aluminium nitrate solution by addition of ammonium hydroxide.

25. a. Discuss about molecular materials and fullerides?

Key points: Solid C₆₀ can be considered as a close-packed array of fullerene molecules interacting only weakly through van der Waals forces; holes in arrays of C₆₀ molecules may be filled by simple and solvated cations and small inorganic molecules. The chemical properties of C₆₀ span many of the conventional borders of chemistry and include the chemistry of C₆₀ as a ligand (Section 14.6). In this section we describe the solidstate chemistry of solid fullerene, C₆₀(s), and the MnC₆₀ fulleride derivatives that contain discrete C₆₀ⁿ molecular anions. The synthesis and chemistry of the more complex carbon nanotubes are discussed in Section 25.7. Crystals of C₆₀ grown from solution may contain included solvent molecules, but with the correct crystallization and purification methods—for example, using sublimation to eliminate the solvent molecules—pure C₆₀ crystals may be grown. The solid structure has a face-centred cubic array of the C₆₀ molecules as shown in Fig. 24.67, as would be expected on the basis of efficient packing of these almost spherical molecules. At room temperature the molecules can rotate freely on their lattice positions and powder X-ray diffraction data collected from crystalline C₆₀ are typical of an fcc lattice with a lattice parameter of 1417 pm. The molecules are separated by a distance of 296 pm, which is similar to the value found for the interlayer separation in graphite (335 pm). On cooling the solid, the rotation halts and adjacent molecules align relative to each other such that an electron-rich region of one C₆₀ molecule is close to an electron-poor region in its neighbor.

OR

b. Write about black and white pigments?

Key point: Titanium dioxide is used almost universally as a white pigment. White inorganic materials can also be classified as pigments and vast quantities of these compounds are synthesized for applications such as the production of white plastics and paints. Important commercial compounds of this class that have been used extensively historically are TiO₂, ZnO, and ZnS, lead(II) carbonate, and lithopone (a mixture of ZnO and BaSO₄); note that none of the metals in these materials has an incomplete d-electron shell that might otherwise induce colour through dd transitions. Titanium dioxide, TiO₂, in either its rutile or anatase forms (Fig. 24.66), is produced from titanium ores, often ilmenite, FeTiO₃, by the sulfate process (which involves dissolution in concentrated H₂SO₄ and subsequent precipitation through hydrolysis) or the chloride process (which is based on the reaction of mixed complex titanium oxides with chlorine to produce TiCl₄, which is then combusted with oxygen at over 1000°C). These routes produce very high quality TiO₂ free from impurities (which is

essential for a bright white pigment) of controlled particle size. The desirable qualities of TiO_2 as a white pigment derive from its excellent light scattering power, which in turn is a result of its high refractive index ($n_r \approx 2.70$), the ability to produce very pure materials of a desired particle size, and its good light-fastness and weather resistance. Uses of titanium dioxide, which nowadays dominates the white pigment market, include paints, coatings, and printing ink (where it is often used in combination with coloured pigments to increase their brightness and hiding power), plastics, fibers, paper, white cements, and even foodstuffs (where it can be added to icing sugar, sweets, and flour to improve their brightness).

Black, absorbing, and specialist pigments

Key points: Special colour, light absorbing, and interference effects can be induced in inorganic materials used as pigments. The most important black pigment is carbon black, which is a better defined, industrially manufactured form of soot. Carbon black is obtained by partial combustion or pyrolysis (heating in the absence of air) of hydrocarbons. The material has excellent absorption properties right across the visible region of the spectrum and applications include printing inks, paints, plastics, and rubber. Copper (II) chromite, CuCr_2O_4 , with the spinel structure (Fig. 24.18), is used less frequently as a black pigment. These black pigments also absorb light outside the visible region, including the infrared, which means that they heat up readily on exposure to sunlight. Because this heating can have drawbacks in a number of applications, there is interest in the development of new materials that absorb in the visible region but reflect infrared wavelengths; $\text{Bi}_2\text{Mn}_4\text{O}_{10}$ is one compound that exhibits these properties.

26. a. Give the detail about self-assembled nanostructures-control of nanoarchitecture-one dimensional control?

Key point: Dimensionality plays a crucial role in determining the properties of materials. The elongated one-dimensional morphology of nanorods, nanowires, nanofibres, nanowhiskers, nanobelts, and nanotubes has been studied extensively because one-dimensional systems are the lowest dimensional structures that can be used for efficient transport of electrons and optical excitation. They are therefore expected to be crucial to the function and integration of nanoscale devices. Not much is known, however, about the nature of localization that could preclude transport through one-dimensional systems. Such systems should possess discrete molecular-like states extending over large distances and exhibit some exotic phenomena, such as the effective separation of the spin and

charge of an electron. There are also many applications where one-dimensional nanostructures could be exploited, including nanoelectronics, very strong and tough composites, functional nanostructured materials, and novel probe microscopy tips. To address these fascinating fundamental scientific issues and potential applications, two important questions pose key challenges to the fields of condensed matter chemistry and physics research. First, how can atoms or other building blocks be assembled rationally into structures with nanometre-sized diameters but much greater lengths? Second, what are the intrinsic properties of these quantum wires and how do these properties depend, for example, on their diameter and their structure? A key class of nanomaterials that offers potential answers to these questions is carbon nanotubes (CNTs). Carbon nanotubes are perhaps the best example of novel nanostructures fabricated through bottom-up chemical synthesis approaches. They have very simple chemical composition and atomic bonding configuration but exhibit remarkably diverse structures and unparalleled physical properties. These novel materials have found application as chemical sensors, fuel cells, field-effect transistors, electrical interconnects, and mechanical reinforcers. The structure and properties of buckminsterfullerene, C₆₀, and related species have produced much activity in the chemistry and materials sciences communities. The now familiar soccer-ball structure of C₆₀ itself was discussed in Chapter 14. Carbon nanotubes were discovered in the early 1990s by electron microscopy. The bonding, local coordination, and general structure of CNTs are similar to those of buckminsterfullerene, but CNTs can have a greatly extended length, leading to a tube rather than a ball structure (Fig. 25.16). Carbon nanotubes are cylindrical shells formed conceptually by rolling graphene (graphitelike) sheets into closed tubular nanostructures with diameters matching that of C₆₀ (0.5 nm) but lengths up to micrometres. A single-walled nanotube (SWNT) is formed by rolling a sheet of graphene into a cylinder along an (m,n) lattice vector in the graphene plane (Fig. 25.17). The (m,n) indices determine the diameter and chirality of the CNT, which in turn control its physical properties.

OR

b. How will prepare gold and silver nano particles?

Chemical methods

Gold nanoparticles: Chemical technique was suggested by Gimenez et al. to prepare Au/NPs by the reduction process of the H₂AuCl₄ through a solution of thiolate chitosan. The method of

thermal citrate reduction used in the preparation of Au/NPs via Raman spectroscopy (SERS) by using inositol hexakisphosphate (IP6) to reduce HAuCl_4 . In addition, the preparation of Au/NPs is by trisodium citrate, and hydrogen tetrachlorocuprate (III) tetrahydrate (chloroauric acid). Au/NPs can be grown in encapsulated immersed in polyethyleneglycol dendrimers and reduced by formaldehyde under near infra-red. Gold nanoparticles are prepared by utilizing peptide-biphenylhybrids (PBHs) as a stabilizer for gold, and in this method the size range 1.8 to 3.7 nm was reported [56]. The dendrimers/Au nanoparticles can be prepared by the reduction of a solution of HAuCl_4 and sodium borohydride. The synthesis Au/NPs with size less than 10 nm can be by two various thiols involved ethylene glycol and dodecanethiol.

Silver nanoparticle preparation: The chemical methods are important to synthesize of Ag-NPs because of the simplicity of preparation in aqueous solution. Monodisperse silver nanobrewery prepared by polyol process, by using a polyvinylpyrrolidone (PVP) polymer with Ag (NO_3) in the presence of ethylene glycol as reducing agent. Furthermore, the shape and size of the nanotubes were based on the molar ratio of Ag (NO_3) and PVP. In this method, the particle size of Ag/NPs with 20 nm was prepared. On the other hand, monodispersed Ag-NPs were prepared by using Ag NO_3 , oleyl amine, and liquid paraffin. Oleyl amine-paraffin was utilized to control temperature and liquid paraffin was utilized in avoiding the solvents [62]. The preparation of Ag-NPs by the chemical method is based on three factors (a) stabilizing agent (b) reducing agents, and (c) Ag precursor. However, the synthesis process and shape of Ag-NPs depend on the Ag nucleus with various sizes and monodispersed which can be obtained by controlling the nucleation of Ag. This is based on factors like a precursor, pH, temperature, and reducing agents. Ag/NPs can be synthesized by utilizing Ag NO_3 as a precursor; and sodium borohydride and trisodium citrate as reducing and stabilizing agents.

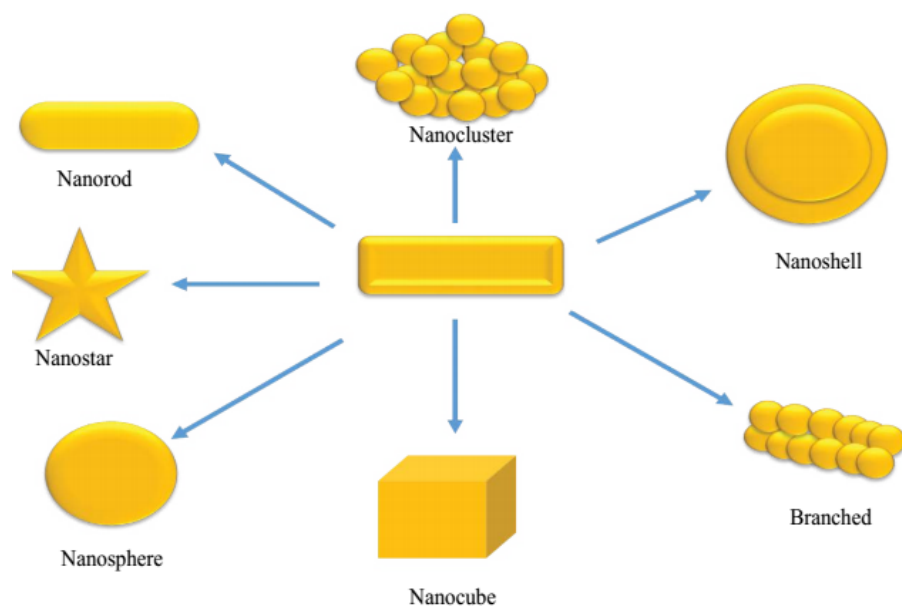


Figure 1: Various shapes of gold nanoparticles.

Reg. No.....

[17CHU503B]

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-21

(For the candidates admitted from 2017 & onwards)

B. Sc DEGREE EXAMINATION-November-2019

III-B.Sc., CHEMISTRY

Internal Exam-II

NOVEL INORGANIC SOLIDS

DATE:

SUBJECT CODE: 16CHU504B

TIME: 2Hrs

TOTAL: 50 MARKS

PART-A ANSWER ALL THE QUESTIONS

(20 x 1 = 20 Marks)

- 1.a) Brinell hardness test
- 2.Adding carbon up to 0.83%
- 3.a) Ferritic stainless steel
- 4.b) Lowers the toughness and transverse ductility
- 5.d) Generators and transformers in the form of laminated cores
- 6.a) Copper and zinc
- 7.b) Ferrite
- 8.d) 70% copper and 30% zinc
- 9.a) 0.02
10. b) Hardness
11. d) Creep
- 12.c) Isotropy
- 13.d) Heated below or closes to the lower critical temperature and then cooled slowly
- 14.d) Gives ductility, toughness, tensile strength and anti-corrosion properties
- 15.c) diamond
- 16.a) Tube shaped material
- 17.a) excellent conductors
- 18.a) Large molecules
- 19.a) Less toxicity
20. d) a crystal

PART-B ANSWER ALL THE QUESTIONS

(3 x 2 = 6 MARKS)

21. What is meant by Bio-inorganic nano materials?

Novel bioactive or biocompatible hybrid systems and composite nanomaterials with new structural organization, properties and functionalities. Integration of biological structures and systems into novel devices, functional and information systems and new materials or vice versa. They include carbon black and titanium dioxide nanoparticles

Bioinorganic nanomaterials Biological phenomena, such as DNA condensation, intercellular transport, tissue assembly, respiration, photosynthesis, and reproduction, originate and operate at the nanoscale.

22. What is the Composition of cast irons?

Most cast irons have a chemical composition of 2.5–4.0% carbon, 1–3% silicon, and the remainder iron. Grey cast iron has less tensile strength and shock resistance than steel, but its compressive strength is comparable to low- and medium-carbon steel.

23. Define super alloys?

Superalloys are heat-resisting alloys based on nickel, nickel-iron, or cobalt that exhibit a combination of mechanical strength and resistance to surface degradation.

Superalloys are primarily used in gas turbines, coal conversion plants, and chemical process industries, and for other specialized applications requiring heat and/or corrosion resistance.

PART-C ANSWER ALL THE QUESTIONS

(3 x 8 = 24 MARKS)

24. Nanotube synthesis and processing: Carbon nanotubes are consisting of rolled graphite sheets with different nanometer range in diameters and micrometer range in lengths. They are different from those of other carbon allotropes, such as diamond, graphite and fullerenes. There are two types of carbon nanotubes (a) single walled carbon nanotubes (SWCNTs) (b) multiwalled carbon nanotubes (MWCNTs). Both SWCNTs and MWCNTs are usually

made by various types of composition such as laser ablation of carbon, carbon-arc discharge and chemical vapor deposition. Carbon nanotubes properties can be tuned by changing the diameter. SWCNTs consist of a cylindrical tube which wrapped by a single graphite seamless sheet. But SWCNTs are presently production only on a small scale and extremely very expensive. MWCNTs comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk 22-23.

The MWCNTs is composed of 3–25 layers of concentric graphite, the range of diameters from 10 to 55 nm and length more than 15 μm . The other way, SWCNTs is much thinner than the MWCNTs, with diameter ranging from 1.0 to 1.5 nm. All the current synthesis methods which used production of SWCNTs result found in major concentrations of impurities 24.

Applications of Carbon nanotube (CNT):

Cancer Treatment: Cancer is one of the most ravaging diseases that approximately more than 10 million new cases found every year from different countries. There are current treatments of cancer by various methods such as radiation, surgery and chemotherapy that successful in several cases. These appropriate methods are also killing healthy cells and cause toxicity to the patient. The spread of cancer cells between organs, a process called as metastasis which is responsible to cause of most cancer death. It would therefore be desirable to develop methods to directly target cancerous cells without affecting normal ones 25. In the drug delivery systems used recent advances to promise for enhance cancer therapy 26.

In advanced drug delivery system there are CNT's considered as antitumor agents when conventional drug combined with in, then obtained enhancement their chemotherapeutic effect. It has been found that Paclitaxel loaded PEG-- carbon nanotube sare promising for cancer therapeutics 27.

There are aqueous solutions of SWCNTs on exposure to radiofrequency (RF) field experiences efficient heating. This property has been achieved by Gannon et al for a noninvasive and selective thermal destruction of treatment for human cancer cells with very less effect or no toxic effects to normal cells. There are carbon nanotubes capable of leading to new suitable directions and approaches in therapeutic human cancer cells 28.

In the next generation of cancer treatments the photo-thermal therapy used and nanomaterials technology has been recently important as an efficient strategy for cancer treatments. SWCNTs are used for potent candidate for the photo-thermal therapeutic agent. It generates sufficient amounts of heat when goes to excitation state with near infrared light (NIR, $\lambda = 700-1100$ nm) which is easily cross to biological systems including skins.

SWCNTs sidewall is highly hydrophobic; they are practically not soluble in water. So SWCNTs are functionally active by covalent or non covalent routes that will help in open the CNT bundles and make them soluble in water 29. There are demonstrated that DOX loaded SWCNTs (PL- SWCNT- DOX) induced significant treatment for U87 cancer cell death and cell apoptosis. There are the main advantages of SWCNTs which used as drug deliver at the particular site such as drug carrier compared to free drug which is the potential to target delivery for selective destruction of different types of cells and reduce the toxicity to non-targeted cells of different site.

The above method used for the treatment of cancer cells provides an easily to make formulation of the SWCNT–DOX complex which extremely high drug-loading efficiency. They are highly higher than obtained conventional liposome's and dendrimer drug carriers 30. Carbon nanotubes are an important new stings and this work as a boost to control against cancer after researchers adopted this technology and found that they can improve a treatment against cancer called adoptive immunotherapy.

Apply conventional adopted immunotherapy techniques which can take few weeks, but using carbon nanotubes technology then reduced this time up to two thirds. The researchers found that the antigens of the cancer cell collected around defects on the surface of the carbon nanotubes by using fluorescence resonance energy transfer (FRET) microscopy 31.

Bioengineering: There are many applications of bioengineering proposed by the carbon nanotubes technology, such as energy storage and conversion devices, conductive and high strength composite, radiation sources, sensors, nanometer-sized semiconductor devices and hydrogen storage media 32-33. The principal of SWCNTs and MWCNTs applied in the industrial and academic for research activity. There are different electronic device focused using in the research activity such as field emission electron source for, lamps, flat panel display and gas discharge tubes applied for surge protection, microwave generations and x-rays.

or

B What are the inorganic-organic components involved in natural and artificial nano material. Explain?

Natural and artificial nanomaterials: biomimetics

Biological materials can be used as templates in the design of Nano inorganics having specific architectures that mimic the structure of the natural material. The formation mechanisms in fossilization, including those for siliceous woods, offer efficient methods to reproduce morphological hierarchies of original plant matter through the replacement of the organic components by silica. Artificial fossilization processes can be realized by carefully lining the morphologically complex surfaces of the biological structure with inorganic layers followed by removal of the organic template. Natural materials such as wood and eggshell membrane have been used as templates for the preparation of microporous silica, zeolites, and titanium dioxide from both precursor sol-gel solutions and suspensions of nanocrystals. Unfortunately, morphological replication has been achieved only over the micrometre scale and the nanoscale details of the biological templates have not yet been reproduced. An artificial fossilization process has been developed by taking advantage of a surface sol-gel process that can replicate nanoscale features of biological templates (Box 25.3). The surface sol-gel process consists of two steps. First, metal alkoxides are adsorbed from the solution on to hydroxylated substrate surfaces. Then the adsorbed species are hydrolysed to yield nanometre-thick oxide films. Natural cellulose fibres possess surface -OH groups and provide a template for using the surface sol-gel process. The outer diameter of the TiO₂ nanotube varies from 30 to 100 nm, and the thickness of the tube is uniform along its length, with a wall thickness of about 10 nm. The nanotube assembly exhibits the original morphology of interwoven cellulose fibres. The 'titanium paper'

produced in this way records the morphological information of the original paper at the nanoscale and offers a remarkable example of successful bio templating of metal oxide nanomaterials.

25. a. Write the application of alloy steels, plain carbon and aluminum?

Cast irons are used in wide variety of application owing to the properties like good fluidity, ease of casting, low shrinkage, excellent machinability, wear resistance and damping capacity.

Applications

Car parts – cylinder heads, blocks and gearbox cases.

Pipes, lids (manhole lids)

Foundation for big machines (good damping property)

Bridges, buildings

Cook wares – Excellent heat retention

Corrosion resistance can be excellent owing to a thin surface layer of aluminum oxide that forms when the metal is exposed to air. Therefore, aluminum is always used in manufacturing chemical reactors, medical equipment, refrigeration equipment, petroleum refining units, oil and gas pipelines etc

As aluminum stores are abundant in the Earth's crust, and it has certain advantages compared to other metals, it will continue to be used widely in the future. For instance, manufacturers are discussing using more aluminum alloy to replace steel in order to make cars lighter. As technology advances, so aluminum alloy products will rapidly find applications in new areas beyond the traditional fields of aerospace, transportation, electronics, electricity and construction.

OR

b. Give detail about composition, mechanical and fabricating characteristics and

Applications of copper?

Copper Usage

The building industry is the largest single consumer of Copper alloys. The following list is a breakdown of Copper consumption by industry on an annual basis:

~ Building industry – 47%

~ Electronic products - 23%

~ Transportation - 10%

~ Consumer products - 11%

~ Industrial machinery - 9%

There are around 370 commercial compositions for Copper alloys. The most common alloy tends to be C106/ CW024A - the standard water tube grade of Copper. World consumption of Copper and Copper alloys now exceeds 18 million tonnes per annum.

Applications

Copper and Copper alloys can be used in an extraordinary range of applications. Some of the applications for Copper include:

~ Power transmission lines

~ Architectural applications

~ Cooking utensils

~ Spark plugs

~ Electrical wiring, cables and bus bars

~ High conductivity wires

~ Electrodes

~ Heat exchangers

~ Refrigeration tubing

~ Plumbing

~ Water-cooled Copper crucibles

In addition, there are many more applications for the Copper Alloys - Brass and Bronze

26. a. What is meant by thermoplastics and thermosets and its properties and application?

Thermoplastics vs. Thermosets

A thermoplastic is a polymeric material or plastic that becomes soft and formable when heated and rigid when cooled. This process may be repeated a number of times without chemically altering the material.

A thermoset is a polymeric material that undergoes irreversible chemical changes when it is cured through heat, catalysts, or ultraviolet light: cross-linking prevents movement of molecular chains after curing. Once cured, the structure cannot be altered.

Thermoplastic Materials		
Name	Properties	Applications and Uses
Acetal	Extremely rigid, high melting point, high strength, good frictional properties, resistance to fatigue	Gears, bearings, bushings, cams, housings, conveyors, plumbing fixtures, gas tank caps, automotive door handles, seat belt components, and zippers
Acrylics	Exceptional resistance to long-term exposure to sunlight and weathering, outstanding clarity, good light transmission	Swimming pools, skylights, sinks, washbasins, room dividers, and the tail lights on automobiles
Acrylonitrile-Butadiene-Styrene (ABS)	Outstanding impact strength and high mechanical strength, great as a substrate for metalizing	Appliances, automotive parts, pipe, business machines, telephone components, shower heads, door handles, faucet handles, and automotive front grilles
Nylon	Known for their stability and adaptability	Automotive parts, electrical and electronic applications, and packaging

Thermoset Materials		
Name	Properties	Applications and Uses
Alkyds	Excellent heat resistance, dimensionally stable under components, excellent dielectric strength	Electrical applications like circuit breaker insulation, switchgear, cases, housings, capacitor and resistor encapsulation, automotive parts, and coatings
BMC (Bulk Molding Compound)	Highly rigid, impact resistant, exceptional physical and aesthetic properties, high strength-to-weight ratio	Appliance parts, electric and electrical components, HVAC components, industrial light housings, automotive, recessed lighting baffles
Diallyl Phthalate (DAP)	Virtually no post-mold shrinkage, high impact resistance, resistant to sudden and extreme jolts and severe stresses, recommended for very high temperatures, chemical resistant, fungus resistant	Cross-linking agent, thermosetting molding powders, casting resins, and laminates, military, electronic components
Epoxy	Virtually no post-mold shrinkage, high impact resistance, resistant to sudden and extreme jolts and severe stresses, recommended for very high temperatures, chemical resistant, fungus resistant	Adhesives, protective coatings in appliances, industrial equipment, aircraft components, pipes, tanks, pressure vessels, tooling jigs, and tooling fixtures

OR

b. How will you fabricating the alloy steels?

Alloy steel is steel that is alloyed with a variety of elements in total amounts between 1.0% and 50% by weight to improve its mechanical properties. Alloy steels are broken down into two groups: low alloy steels and high alloy steels. The difference between the two is disputed. Smith and Hashemi define the difference at 4.0%, while Degarmo, *et al.*, define it at 8.0%.^{[1][2]} Most commonly, the phrase "alloy steel" refers to low-alloy steels.

Strictly speaking, every steel is an alloy, but not all steels are called "alloy steels". The simplest steels are iron (Fe) alloyed with carbon (C) (about 0.1% to 1%, depending on type). However, the term "alloy steel" is the standard term referring to steels with *other* alloying elements added deliberately *in addition to* the carbon. Common alloyants include manganese (the most common one), nickel, chromium, molybdenum, vanadium, silicon, and boron. Less common alloyants include aluminium, cobalt, copper, cerium, niobium, titanium, tungsten, tin, zinc, lead, and zirconium.

The following is a range of improved properties in alloy steels (as compared to carbon steels): strength, hardness, toughness, wear resistance, corrosion resistance, hardenability, and hot hardness. To achieve some of these improved properties the metal may require heat treating.

Some of these find uses in exotic and highly-demanding applications, such as in the turbine blades of jet engines, in spacecraft, and in nuclear reactors. Because of the ferromagnetic properties of iron, some steel alloys find important applications where their responses to magnetism are very important, including in electric motors and in transformers.

[17CHU503B]

Reg. No-----

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University, Established Under Section 3 of UGC Act 1956)

(For the candidates admitted from 2017 onwards)

B.sc Degree Examination, September 2019

III B.Sc. Chemistry

Internal Exam-III

Novel Inorganic Solids

Date:

Maximum: 50 marks

Time: 2 hrs

PART -AAnswer all the questions (20 x 1 = 20 marks)

1. b) High Density Polyethylene

2.a) Hydrocarbons

3. c) 1936

4. b) England

5.c)~135°C

6.a) Light stabilizers

7.b) AAAAAAAAAAAAA

8.c) Glass fibre

9. c) Sulphuric acid

10. b) Acetaldehyde

11. d) Water

12.b) Ethylene glycol

13.c) Carboxylic acid

14. b) Burnt

15. d) Titanium oxide

- 16.c) clay
- 17.b) refractories
- 18.b) aluminum oxide
19. a) High melting and boiling point
20. d) do not conduct heat and electricity

PART-B Answer all the Questions (3 x 2 = 6 MARKS)

21. It provides strength and stiffness to the **composite material** in one direction as **reinforcement** carries the load along the length of the fiber. It increases the mechanical properties of the **composite**.
22. The primary functions of the matrix are to transfer stresses between the reinforcing fibers (hold fibers together) and protect the fibers from mechanical and/or environmental damages.
23. Aluminum **matrix**. Continuous fibers: boron, silicon carbide, alumina, graphite. ...
Magnesium **matrix**. Continuous fibers: graphite, alumina. ...
Titanium **matrix**. Continuous fibers: silicon carbide, coated boron.

PART-C Answer all the Questions (3 x 8 = 24 MARKS)

24. a. Write the limitations of conventional engineering materials?

The non-conventional manufacturing processes are not affected by hardness, toughness or brittleness of material and can produce any intricate shape on any workpiece material by suitable control over the various physical parameters of the processes. The non-conventional manufacturing processes may be classified on the basis of type of energy namely, mechanical, electrical, chemical, thermal or magnetic, apply to the workpiece directly and have the desired shape transformation or material removal from the work surface by using different scientific mechanism. Thus, these non-conventional processes can be classified into various groups according to the basic requirements which are as follows : (i) Type of energy required, namely, mechanical, electrical, chemical etc. (ii) Basic mechanism involved in the processes, like erosion, ionic dissolution, vaporisation etc. (iii) Source of immediate energy required for material removal, namely, hydrostatic pressure, high current density, high voltage, ionised

material, etc. (iv) Medium for transfer of those energies, like high velocity particles, electrolyte, electron, hot gases, etc. On the basis of above requirements, the various processes

OR

b. Write the applications Composites material?

Most widely used form of FRP is a laminar structure, made by stacking and bonding thin layers of fiber and polymer until desired thickness is obtained • By varying fiber orientation among layers, a specified level of anisotropy in properties can be achieved in the laminate • Applications: parts of thin cross-section, such as aircraft wing and fuselage sections, automobile and truck body panels, and boat hulls – Aerospace Industries (Carbon/Epoxy PMCs) Automobile Industry (Epoxy based PMCs) – Springs and bumper systems (Reinforced Thermosets) – Tooling (Epoxy based PMCs) – Fiberglass reinforced plastic has been used for boat hulls, fishing rods, tennis rackets, golf club shafts, helmets, skis, bows and arrows

25. a. Give account on metal-matrix composites and polymer-matrix composites

Metal matrix composites with short or continuous fibrous reinforcements are usually produced by infiltration of preforms, in a process that also defines the final shape of the metal matrix composite, and which can also produce fully or partially reinforced components. Recycling of such composites would thus require preservation of the shape of the component. For example, the alumina short fiber preform ring reinforcing the crown of an aluminum alloy piston can be recuperated during remelting. Although the matrix is molten, such MMCs are mechanically stable up to about 850°C (Burkhard 1995) and can be handled. The integrity of such MMC rings can be confirmed by nondestructive testing and inserted again into the casting of a piston, which has only to achieve bonding between the composite and the matrix, as the primary casting process had already infiltrated the preform. Recycling of MMC sections of defined shape can be envisaged for alumina fiber reinforced aluminum (or magnesium alloys, provided that recuperation of the composite from the melt is rapid enough to restrict interface reactions), SiC reinforced aluminum–silicon alloys, carbon fiber reinforced magnesium, and, with some reservations, for monofilament reinforced titanium alloys.

OR

b. What are the environmental effects on composites?

Moisture absorption characteristics and its effects on the mechanical properties and failure process of polymers (neat epoxy and polyester resins) and composites with simple (glass, carbon and kevlar) and hybrid (glass-carbon, carbon-kevlar and kevlar-glass) fibres were experimentally determined before and after immersion in water at 343 K for 20 days. The maximum moisture content (M_m) and diffusion coefficient (D_x) of these composites were determined. The degradation in ultimate tensile strength and Young's modulus due to the moisture content were experimentally determined and found to be quite significant. Acoustic emissions, from specimens before and after exposure, were monitored during the load cycle, and revealed a significant change in the failure process of these composites. Scanning Electron Microscope (SEM) studies on failed exposed and unexposed specimens revealed resin leach out and fibre prominence.

26.a. Write the applications of conducting polymers?

Typically conventional polymers such as plastics, rubbers, Even for rugged applications including LED lighting and electrical supercapacitors, conducting polymers have advantages over other materials candidates such as conductive metal oxides

OR

b. How to manufacture Ceramic material and explain its application?

Ceramics are an incredibly diverse family of materials whose members span traditional ceramics (such as pottery and refractories) to the modern day [engineering ceramics](#) (such as alumina and silicon nitride) found in electronic devices, aerospace components and cutting tools.

Whilst the most extravagant claims of the 1980s in favour of advanced ceramic materials (such as the all ceramic engine) have largely proved inaccurate, it is true to say that ceramics have established themselves as key engineering materials.

When used in conjunction with other materials, usually metals, they provide added functionality to components thereby improving application performance, once the appropriate joint design and technology have been identified.