

Video Course : Nonferrous Extractive Metallurgy

Questions and Answers

Modules 1 and 2 (Introduction , occurrence of metals, beneficiation etc.)

Discuss validity/invalidity of the following statements

1. Human civilization progressed through the following Ages : Chalcolithic, Neolithic, Paleolithic, Bronze and Steel

Ans- Statement invalid because there is a mix up. Lithos means stone , Neo means new and Paleo means old. The correct order is : Paleolithic Age (Old Stone Age), Neolithic Age (Neo stone Age), Chalcolithic Age (Chalcos means copper and hence, the word refers to use of copper and stone), Bronze Age and Steel Age.

2. The ancient man knew of only a handful of metals

Ans: Statement valid. The metals known comprised Ag, Au, Cu, Hg, Pb, Sn, Fe and perhaps As. Often alloys such as brass and bronze were thought of as metals. Zn was isolated by Indians around the 5th century AD.

3. Indians are known to have produced copper first.

Ans- Statement invalid . Indians were the first to produce only Zn. Copper was first produced in Egypt. All the pyramids were built using copper tools only.

4. All ores are mixtures of minerals

Ans- The statement is correct only with the exception of metals such as Au, Ag and Pt group metals (precious metals) which are present in some ores not as minerals or compounds but in native or free state. Ag may be sometimes found as weakly stable compound or mineral.

5. The earth's crust (which includes the oceans and the atmosphere) contains many elements but only a few account for the bulk

Ans- This is true. 98% or more is accounted for by only a handful, namely, O₂, Si, Al, Fe, Ca, Na, K and Mg. Of these , the first two account for nearly 75%.

6. In the sea, the sea water is the only source of various metals

Ans- Statement is not complete. While it is true that all elements are present in sea water, there are other sources of metals in the sea. These are : ocean floor nodules and sea organisms i.e. animal and plant life. Elements are also added by volcanic eruptions in sea bed.

7. Ocean floor nodules are called Nickel nodules

Ans – No, although these nodules, often also called multimetal nodules, contain Ni, Co and other valuable metals, by far the most abundant is Mn (~24%) . Hence the nodules are often called manganese modules.

8. Primary metals refer to the more important metals and secondary metals refer to secondary metals refer to metals of minor importance.

Ans – Statement is invalid. Primary metals refer to all metals obtained through extraction processes that process ores and minerals from land, sea water and sea modules. When metals are obtained through processing of scrap then they are called secondary metals.

9. The ore deposits for various metals in India are sufficient for indigenous production of all important metals required by the country.

Ans- This statement is invalid. Metals whose deposits can be classified as adequate to abundant include only the following – Al, Be, Cr, Mn, Fe, Mg, Ti, Zr, Th and R.E. Deposits of base metals are inadequate and ores of many others are very meagre.

10. A spiral used in beneficiation of minerals separates minerals based on magnetic and electrical properties.

Ans: This statement is incorrect. A spiral exploits for minerals separation, properties such as density, particle size and shape.

Module 3

General methods of reduction, Pyrometallurgy and Hydrometallurgy

A. Discuss the correctness of the following statements.

1. **Not all metal compounds are equally stable and there are different criteria to indicate relative stabilities.**

Ans. The statement is correct. The relative stabilities can be expressed in terms of electrode potential values, electronegativity values and free energies of formation of compounds. Greater stability is indicated by higher electrode potential, lower electronegativity and more negative free energies of compounds.

2. **The orders of stability and listing of various metals are identical in the use of all the criteria applied.**

Ans. This is not so and there are minor differences. Generally reactive metals occupy higher positions and less reactive metals occupy lower positions, noble metals coming at the bottom of every list.

3. **Decomposition of a CaCO_3 sample is about 910°C . This means that, during heating, decomposition reaction starts at 910°C**

Ans. This statement is invalid. Decomposition will start at lower temperatures but only at 910°C the partial pressure of CO_2 will reach the atmospheric pressure. Similarly, the boiling point of water implies the temperature when vapour pressure of water will equal to 1 atm. There will be water vapour even at room temperature but at lower temperatures vapour pressure will be lower. At higher altitudes, where atmospheric pressure is lower, the boiling will also be lower.

4. **In Ellingham diagrams for oxides all lines showing free energies of formation versus temperature are shown for per mole of the oxide.**

Ans. The answer is not correct. The lines shown are always for one mole of oxygen for forming corresponding metal oxide, CO or CO_2 . Metals have different valencies and thus, while one mole of some oxide needs one half mole of oxygen (e.g. PbO, ZnO, FeO) some other need two moles (e.g. SnO_2 , TiO_2 , ZrO_2 etc) or other amounts. (For Al_2O_3 and Fe_2O_3 it is $3/2$). For one mole of C it can be one (as for CO_2) or half (as for CO). Lines indicate values per mole of oxygen so that one can easily and conveniently calculate the free energy change when oxide of one metal is reduced by carbon to form CO or CO_2 or is reduced by another metal to form a more stable oxide. The required values for change in free energy is obtained by deducting the free energy change corresponding to reduction of the oxide by C (w.r.t. CO or CO_2 as the case may) or the second metal and the oxide being produced. In subtraction O_2 is cancelled out and one is left only with the chemical equation for carbon reduction or metallothermic reaction of one oxide to produce the metal.

5. **The lines in Ellingham diagrams that have positive slopes are nearly parallel because each represents formation of a compound consuming one mole of oxygen.**

Ans. The statement is not correct fully. Moreover, it is not written correctly either. It is true that lines showing free energy change, in the reaction for formation of a metal oxide per mole of oxygen, have all positive slopes that are nearly equal so long as the oxide and the metal are solid. If there is melting of any of the two then the slope changes. For CO formation, the slope is negative and for CO₂ formation the free energy change line has zero slope, i.e. the line is horizontal.

The expression for standard free energy change is written as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

ΔH^0 and ΔS^0 values are almost independent of temperature and, therefore, variation in ΔG^0 is because of the T term, essentially, ΔS^0 giving the slope and ΔH^0 the intercept. For all lines ΔS^0 is constant (when there is no phase change) because it arises out of disappearance of one mole of oxygen. When there is phase change there is greater ΔS^0 and hence change in slope. There is no entropy change for formation of CO₂ because one mole of O₂ is consumed to produce one mole of CO₂. However, there is increase in entropy when we consider CO formation. Here one mole of O₂ is consumed to produce two moles of CO.

6. In theory all metal oxides can be reduced by carbon to produce the metal.

Ans. This statement is partially correct. For carbon reduction to be feasible the product must be thermodynamically more stable. Since the stability of CO₂ remains essentially unchanged with temperature it can intersect lines for some metal oxides which are stabler at lower temperatures but less stable than CO₂ at some temperature where the CO₂ horizontal line intersects the metal oxide line sloped upwards (see Ellingham diagrams) For very stable oxides this cannot happen for two reasons.

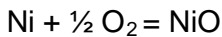
- The temperature of intersection of CO₂ line and metal oxide line is far too high.
- Beyond around 700°C CO becomes more stable than CO₂ and with increasing temperature the ratio of partial pressure of CO to that of CO₂ increases in C – CO – CO₂ system.

Since the CO line has negative slope it crosses all lines for metal oxides and temperatures of intersections are not that high. Yet, for metals which produce very stable oxides, carbon reduction is not recommended because at the high temperatures of reduction the reactive metals also produce stable carbides which will contaminate the metal.

7. The lines in predominance area diagram for metal – sulphur – oxygen – systems are easily obtained through thermodynamic calculations.

Ans. Yes, and that is how the lines that show for a fixed temperature, the relative stabilities of various possible phases (M, MS, MSO₄, MO etc.) are obtained for different partial pressures of O₂ and SO₂.

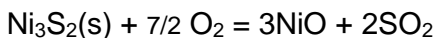
As an example consider how one obtains the lines indicating equilibrium between Ni and NiO and Ni and Ni₃S₂



$$K = \frac{a_{\text{NiO}}}{a_{\text{Ni}} \cdot p_{\text{O}_2}^{0.5}} = p_{\text{O}_2}^{-0.5}$$

The value of K (Eq. const) can be obtained from thermo-dynamic data ($\Delta G^0 = -RT \ln K$) and hence partial pressure of oxygen calculated. The line for Ni / NiO will be parallel to the vertical line for partial pressure of SO₂ in the area diagram (the horizontal axis shows partial pressure for oxygen).

Ni can form Ni₃S₂ and we can consider NiO / Ni₃S₂ equilibrium for which the reaction is



$$K = \frac{p_{\text{SO}_2}^2}{p_{\text{O}_2}^{7/2}}$$

$$\log p_{\text{SO}_2} = \frac{7}{4} \log p_{\text{O}_2} + \frac{1}{2} \log K$$

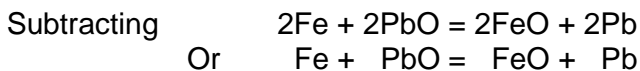
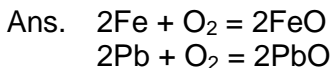
The slope in the log – log plot will be 7/4 and its position can be fixed by the calculated value of K.

8. Flash roasting gives accelerated reaction compared to hearth roasting.

Ans. This statement is correct. In the former, sulphide particles are suspended mid-air much longer and, therefore, more effectively oxidized.

B. Find, through calculation, answers to the following questions.

1. Can Fe reduce PbO at 1000°C? The free energies of formation for FeO and PbO are given, respectively, as – 364 KJ and – 184 KJ per mole of oxygen.

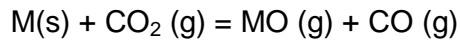


The free energy change for the last reaction is $[-364 + 184] / 2$ i.e. -90 KJ / mol

Since the value is negative the reduction reaction is possible when all the species are in their standard states.

1. The equilibrium constant for oxidation of a metal M to oxide MO is 5.76×10 at 1000 K. That for oxidation of CO to CO₂ is 1.68×10^{10} at 1000 K. Will a gas containing 15% CO₂, 5% CO and 80% N₂ oxidize the metal at 1000 K?

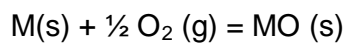
Ans. The reaction is



Eqm. Constants are for standard states only i.e. pure solids and gases under 1 atm.

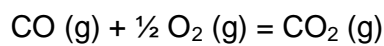
The Eqm. Constant for the above reaction is obtained by considering the data given.

For metal oxidation



$$5.76 \times 10^7 = 1 / P_{O_2}^{0.5} \dots\dots\dots(a)$$

For CO oxidation



$$1.68 \times 10^{10} = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{0.5}} \dots\dots\dots(b)$$

Eqm. Constant for CO₂ oxidation of M is obtained by dividing Eq. (a) with Eq (b)

$$\begin{aligned} \frac{p_{CO}}{p_{CO_2}} &= 5.76 \times 10^7 / 1.68 \times 10^{10} \\ &= 3.43 \times 10^{-3} \text{ at } 1000 \text{ K} \end{aligned}$$

The eqm (p_{CO} / p_{CO₂}) for oxidation of metal is, therefore, 1000 / 3.43 i.e. 291.5

In the actual gas with 15% CO₂ and 5% CO the (p_{CO₂} / p_{CO}) ratio is 15/3 = 3

Obviously, the metal will not be oxidized.

Module 4

Principles of metals refining and Electrometallurgy

A: Discuss the validity/invalidity of the following statements

- 1. A solute is to be transferred from Phase I to another Phase 2 that is in contact. There is a choice between co-current flow and counter current flow. Over extended duration of contact, transfer is more effective when the flows are counter current**

Ans– This statement is correct. When Phase 2 with no solute comes in contact with Phase 1 with the solute, as it happens in cocurrent flow. The initial driving force for transfer of solute from Phase 1 to Phase 2 is high. But this driving force diminishes with time quite rapidly. On the other hand, in counter current contacting Phase 2 with no solute first encounters Phase 2 from which much of solute has been transferred already. As Phase 2 advances in counter current flow with some enrichment in the solute it encounters Phase 1 richer in solute. That is, there is a steady driving force maintained although and thus, over an extended duration solute transfer is more effective.

Counter current flow is employed in solvent extraction and some slag cleaning operation such as by counter current flow of slag and matte in continuous copper smelting.

- 2. Both the electrolytic production of aluminium and its electrorefining are 3 layer processes.**

Ans- No, the electrorefining process is a 3 layer process because there are 3 layers – pure molten Al cathode at the top , an AlF_3 , CaF_2 , cryolite electrolyte at the middle and Al-Cu alloy cathode at the bottom. During electrolysis , there are essentially only 2 layers, molten aluminium at the bottom and then the electrolyte. On top is solid Al_2O_3 charge which is not considered a layer in the sense that it is not liquid.

- 3. The voltage requirement for electrorefining is generally much less than that needed for electrowinning**

Ans- This statement is correct. In electrorefining, metal is not produced by decomposition of a salt, the electrolyte only providing a medium for transfer of metal from an impure anode to a pure cathode. In theory, the required voltage is actually zero because metal potential is the same at both electrodes. However , some voltage is necessary to overcome resistance of the electrolyte and electronic resistances in the circuit and the electrodes.

- 4. The vapour transport process may be schematically written as follows**

Metal(Impure) + vapour 1 \rightarrow vapour 2 (Temp T_1)

Vapour 2 \rightarrow Vapour 1 + Metal (Pure) (Temp T_2)

T_2 is always higher than T_1 .

Ans – This is not correct. For Ni (forming $\text{Ni}(\text{CO}_4)$) $T_2 > T_1$. But for Al (forming AlCl_3) $T_2 < T_1$

The sign of ΔH^0 for the reaction determines this.

5. In eletrolysis, it is desirable to have thick and wide electrodes and not thin and deep (long) electrodes.

Ans- This statement is correct. There is less voltage drop in the former case. The width actually is immaterial and , therefore, by increasing the width one can increase more electrode surface area and greater production.

6. An impure metal is thermodynamically more stable than the pure metal

Ans- This statement is correct. Assimilation of impurities increases the entropy of the system (configurational entropy) and decreases free energy. In fact, it becomes increasingly difficult to achieve further purification when impurity level approaches zero, specially so for reactive metals.

7. Zn reacts with acid solutions. Yet zinc metal can be obtained through electrolysis of acid solutions.

Ans – This is correct. Normally Zn is placed higher in the e.m.f. series with hydrogen electrode assigned zero potential. Being more electropositive, zinc will replace hydrogen. During eletrolysis, however, passage of current causes activation overpotential which pushes Zn/Zn^{2+} potential to below hydrogen electrode potential making hydrogen more electropositive.

8. In ionic media there is completely random mixing of anions and cations in the lattice positions.

Ans – This statement is incorrect. In an ionic media, there are two interlocked sub-lattices, one for the anions and the other for the cations. Anions can be randomly distributed only in the anion sublattice and cations in the cation sub-lattice.

9. Limiting current dencisty arises out of concentration overpotential which is dictated by thermodynamics.

Ans- The first part of the sentence is correct but not the second part.

When current flows, cations are pushed to the cathode by a concentration gradient, the cathode surface concentration of cations being lower than their bulk concentration . A limit is reached when cation concentration at the surface falls to zero and no more current can be passed unless electrode area is increased. This limiting current is thus because of kinetic factors.

Of course, concentration overpotential becomes important only when the diffusion of cations towards to cathode surface is slower than the ion discharge at the electrode and , therefore, is rate controlling.

10.Fluidized bed electrolysis enhances the limiting current density during electrolysis by almost one order of magnitude.

Ans- This statement is correct. A fluidized bed of metal particles makes available a larger metal surface area for electro-deposition and hence limiting current can be higher.

11. kinetics has no role in creating activation over potential at the cathode.

Ans- This statement is not correct. Activation over potential comes into play when the rate of discharge of cations at the cathode surface is slower than the rate of diffusion of cations from the bulk to the cathode surface. When the former becomes rate controlling then there is accumulation of cations at the cathode surface and, therefore, a deviation in the thermodynamic M/M^{n+} electrode potential.

12. When a metal tends to dissolve in its molten salt during electrolysis then addition of another salt generally decreases the solubility.

Ans- The statement is correct. Generally this happens more significantly when metal valency is more than one. We can write the following equations for a divalent metal M dissolving in, say, a halide MX_2 .

The dissolution is a 2 step process

Step 1 $M(l) \rightarrow M(\text{solution})$ – atomic/molecular dissolution)

Step 2 $M(\text{solution}) + MX_2 = 2MX$ (subhalide formation)

When a second salt, say NY, is added to MX_2 then the activity of MX_2 is decreased and thus, both the above reactions are encouraged to shift equilibrium to the left.

B. Answer the following equations

1. A fused salt mixture contains equal number of moles of $CaCl_2$ and $NaCl$. If an equal number of moles of $CdBr_2$ are added to the mixture then calculate activities of these salts in the fused salt mixture.

Ans- Activity of any salt is given by the Temkin Model that takes into account ionic fractions and probability of finding association of required number of cations and anions making up to the salt. We remember that cations are randomly distributed only in the cation sublattice whereas anions are randomly distributed only in the anion sublattice.

$$a_{CaCl_2} = X_{Ca^{2+}} [X_{Cl^-}]^2 \\ = [1/3] [3/5]^2 = 3/25 = 0.12$$

$$a_{NaCl} = X_{Na^+} \cdot X_{Cl^-} = \frac{1}{3} \cdot \frac{3}{5} = 0.2$$

$$a_{CdBr_2} = X_{Cd^{2+}} \cdot [X_{Br^-}]^2 \\ = [1/3] [2/5]^2 = 0.053$$

2. From the data given in Problem 1, can one calculate activities of $CaBr_2$, $NaBr$ and $CdCl_2$?

Ans- Yes one can. In the mixture, one only has ions and not what one added in the first place. One can get activities of other salts, such as the ones mentioned here also using the Temkin model.

Thus

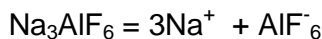
$$a_{\text{CdBr}_2} = X_{\text{Ca}^{2+}} \cdot [X_{\text{Br}^-}]^2 = [1/3] [2/5]^2$$

$$a_{\text{NaBr}} = X_{\text{Na}^+} \cdot X_{\text{Br}^-} = [1/3] \cdot [2/5] = 0.1355$$

$$a_{\text{CdCl}_2} = X_{\text{Cd}^{2+}} \cdot [X_{\text{Cl}^-}]^2 \\ = [1/3] [3/5]^2 = 0.12$$

3. Consider a fused salt solution containing, in mole percent, the following constituents: Al_2O_3 – 15, CaF_2 - 5, NaF – 2 and Cryolite (Na_3AlF_6) – the rest. Calculate the activity of Al_2O_3 the bath and comment on the value.

Ans- First assume that Al_2O_3 and Cryolite are dissociated as follows.



The bath will contain in moles, the following (we omit the charge signs)

Cations (+ ions) – 30 Al, 5 Ca, (2 + 3 x 78) Na

i.e. 30Al, 5 Ca, 236 Na

Anions (- ions) - (3 x 15) O, 78 AlF_6 , (2 x 5 +2)F

i.e. 45 O, 78 AlF_6 , 12 F

$$a_{\text{Al}_2\text{O}_3} = X_{\text{Al}}^2 \cdot X_{\text{O}}^3 \\ = \left[\frac{30}{30+5+236} \right]^2 \cdot \left[\frac{45}{45+78+12} \right]^3$$

$$= (0.110)^2 \cdot (0.333)^3$$

$$= 0.012 \times 0.037 = 0.00044$$

$$= 4.4 \times 10^{-4}$$

This value appears very small indeed. Perhaps the dissociation of cryolite makes available other ions so that this value becomes larger.

Module 5

Extraction of metals from oxides

A. Discuss validity/invalidity of the following statements

1. **Fe-Si reduction of calcined dolomite (CaO.MgO) is a solid –solid reduction reaction.**

Ans- Not quite correct. Though both the reactants are solid and the initiation must be by solid-solid reaction, soon a liquid Ca-Fe-Si alloy formed permeates the solid briquettes and then this liquid reacts with calcined dolomite.

2. **Al_2O_3 cannot be reduced by carbon to produce Al because the required temperature for reduction is too high.**

Ans- The C-CO line intersects Al- Al_2O_3 line in the Ellingham's diagram at about 2000°C . That is beyond 2000°C , CO becomes more stable than Al_2O_3 and therefore, thermodynamically Al_2O_3 can be reduced by carbon beyond 2000°C . This temperature can be achieved in an electric furnace. However, at such high temperatures aluminium will also form stable carbide which will contaminate the metal.

The statement, therefore, is incorrect. However, in the ALCAN process, one reduces Al_2O_3 by carbon in an electric furnace at about 2000°C to produce an alloy containing 50 percent Al, 30 per cent Fe, 10 percent Si, 5 per cent Ti and 5 percent C. The impure Al is purified by a vapour transport process.

3. **The consumable carbon anode used in aluminium electrolysis reduces the decomposition voltage of Al_2O_3 in the electrolyte.**

Ans- This statement is correct. If the decomposition produced only Al at the cathode and oxygen at the anode then the voltage required will be around 2:1. However when the oxygen liberated reacts with carbon anode to produce CO and CO_2 then dissociation of Al_2O_3 is thermodynamically made easier and the required voltage is nearly halved.

4. **In an Al electrolytic cell of the Hall-Heroult process, Al_2O_3 concentration in cryolite is controlled to be within limits to ensure proper heating of the bath.**

Ans: The statement is incorrect and confusing. It is true that heating of the bath is internal i.e. passage of the current provides heat because of ionic resistance of the bath. The ionic resistance is essentially determined by inter-electrode and separation and conductivity of the bath and variation in Al_2O_3 concentration has little role.

However, Al_2O_3 content is restricted for smooth operation because beyond a certain value Al_2O_3 cannot dissolve in cryolite (at 1000°C the solubility is less than 15 per cent). Again, below about 2 percent, Al_2O_3 , there is the 'Anode effect' which stops normal electrolysis, the anode surface being covered by fluorine bubbles. Normally Al_2O_3 percentage is controlled within 5-8.

5. **Some nonferrous metals are produced as ferro-alloys because they are often used as such in the industry.**

Ans- Yes this true but that is not the only reason. Alloys such as Fe-Mn, Fe-Cr, Fe-Ti etc find application as such for alloying additions in steel, deoxidation etc. but there are other reasons for ferroalloy production. In such alloys activities of Mn, Ti, Cr etc are lower and therefore, it becomes thermodynamically easier to reduce the metal oxides. At lower temperatures the formation of their carbides is also discouraged.

6. A high carbon ferrochrome is melted in an electric furnace and oxygen is injected into it. This oxygen will preferentially oxidize carbon and not chromium.

Ans- This statement is true because, as per the Ellingham diagram CO becomes thermodynamically more stable than Cr₂O₃ beyond about 1300°C. In fact oxygen injection is a standard method of decarbonization. By injection, the temperature is also raised making carbon remove more effective kinetically.

7. During any electrolytic process Energy Efficiency can never be greater than Current Efficiency.

Ans- That the answer is correct should be obvious. Current efficiency refers to the level of utilization of current passed in the metal deposition reaction of interest. Loss of current consumed in unwanted side reactions reduce Current Efficiency.

Energy Efficiency is also calculated with reference to the same desired reaction and side reactions will lower this also. However, Energy Efficiency must always be lower than the Current Efficiency because some of it must be lost as voltage losses in overcoming the ionic resistance of the bath and electronic resistance in the circuit . The energy consumed in overcoming the ionic resistance, however, is not always exactly a loss, because the heating required for keeping a fused salt mixture molten is provided by this.

The relationship between energy efficiency (EE) and current efficiency (CE) is as follows:

$$E.E = \frac{V_D}{V_A} \cdot CE$$

Where V_D is decomposition voltage (theoretical) and V_A is actual applied voltage.

B. Calculate the energy efficiency of an electrolytic process when 10 percent of the current passed is wasted into unwanted side reactions and only 80 per cent of the applied voltage of 6V is used in decomposition of the solute for metal deposition.

Ans – Energy Efficiency =[Theoretical energy / Actual Energy X100]

$$= \frac{V_D \cdot I_{Th}}{V_A \cdot I_{Ac}} \times 100$$

Where

V_D = Decomposition voltage

I_{Th} = Theoretical current as per Faraday's Law

V_A = Actual voltate

I_{Ac} = Actual current passed.

$$= \frac{V_D}{V_A} \cdot \text{Current efficiency}$$

$$= \frac{4.8}{6} \times 90 = 72 \text{ percent}$$

Module 6

Extraction of metals from sulphides

A. Discuss the correctness of the following statements

1. During matte smelting of copper by multiple steps, there is no reduction step.

Ans: The steps or stages in traditional copper extraction process are : roasting of sulphides (copper pyrites), reverberatory smelting of roasted product to produce a matte and then converting of matte to blister copper.

During roasting the aim is to oxidize iron sulphide of CuFeS_2 (or $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$) to FeO which can be easily slagged off later. To ensure that higher oxides are not formed some FeS may be left behind.

During reverberating smelting all iron oxide is removed as slag and the product left is essentially a mixture of copper and iron sulphides.

The oxidation process is continued in converting where iron sulphide is first oxidized and slagged off to produce a 'white metal' which is Cu_2S . This is further subjected to oxidation. When Cu_2O formation proceeds sufficiently then Cu_2S and Cu_2O react to produce Cu .

Thus all steps are oxidation steps and the statement made is true.

2. Blister Copper cannot be produced in Bessemer converters used in steelmaking.

Ans : This is correct. Bessemer converter uses bottom blowing of air whereas in copper converters oxygen is blown from the sides. This is so because during blowing copper rich liquid is formed at the bottom. In the converter, heat is generated essentially by exothermic oxidation of Cu_2S . If air is blown from the bottom then some copper produced will get oxidized to Cu_2O . Moreover, the heat will be insufficient to keep the metal molten and the tuyers will get clogged. Neither is desirable. In side blown converter the metal produced collects below the level of air injection.

3. During electrorefining of impure copper anode, all undesirable impurities are rejected as slimes that collect at the bottom of the anode.

Ans : The statement is not valid. The desired reaction is transfer of copper from the impure anode to the pure cathode. Impurities which are more electropositive than copper dissolve in the acid solution and these are metals like Fe , Co , Se etc. Those that do not dissolve and collect as anode slime contain Pb , As , Te , Ni , S , Fe , Se , etc and also precious metals Au , Ag , Pt etc and therefore the slime is not exactly 'undesirable'. Valuable by products are recovered from the slime.

4. Oxygen enrichment during copper smelting and converting consumes more energy because of the energy requirement to produce oxygen in the first place,

Ans – This statement is not valid. It is true that oxygen production consumes energy but this is more than offset by the enhanced intensity of reactions when there is oxygen enrichment. Moreover, there is elimination of heat losses through nitrogen of air which has no useful role in reactions.

5. When a single reactor is used in continuous copper production, then the oxygen partial pressure within the reactor cannot be same all throughout.

Ans: This statement is valid. The stages of roasting, smelting and converting accomplished in different regions of the reactor, require increasing partial pressures of oxygen i.e. gradually enhanced oxygen potential. This is controlled by oxygen injection in the converting zone, counter current flow of matte and slag and also outflow of exit gases containing SO_2 .

6. In lead furnace, scrap iron is added to the charge (lead oxide sinter, coke and flux) to recover lead as Fe-Pb alloy.

Ans– This is not correct. Iron and lead do not mix . Iron scrap is added to recover Pb from any PbSiO_3 going into slag. Fe reacts to form FeSiO_3 and helps to recover Pb. Fe also reacts directly with PbO and helps reduction reaction.

7. In the Imperial Smelting Process (ISP) roasted zinc and lead sulphides, i.e. sinters containing the metal oxides, are reduced by carbon in a type of blast furnace. While lead is produced at the bottom, the zinc vapours escaping with the exist gases are dissolved in molten lead to produce a Pb-Zn alloy.

Ans- This statement is only partially correct. ISP does employ a blast furnace to produce impure lead metal (lead bullion as it is called) and the zinc vapours are dissolved in a spray of molten zinc but then zinc recovery is not so simple.

The furnace gases exit at about 1000°C containing about 6 percent Zn. The exit gases are sprayed by liquid lead (containing about 2.15 percent Zn) at around 450°C .The contacting increases lead temperature and zinc content increases to about 2.4% Zn, the gases from the recovery system exiting at 450°C with 0.24% Zn. The lead streams slightly enriched in Zn is cooled to 450°C to produce a Zn-layer which floats up and is separated. The Zn content in Pb falls to 2.15 percent and this is pumped back to contact incoming furnace gases afresh. It is a continuous process of zinc recovery exploited difference in zinc solubility in lead at two different temperatures.

8. During electrolytic production zinc the aim is to first produces as purify it to produce pure zinc.

Ans- This statement is not valid. Production of an impure metal in bulk and then subsequent refining is a common procedure in pyrometallurgy such as in extraction process for iron, copper and lead. In the case of zinc electrowinning it is necessary to produce zinc from an acid solution free of all impurities because if impurities are present then zinc electrolysis is not possible. During passage of current the phenomenon of activation overpotential decreases Zn/Zn^{2+} potential to below H_2 / H^+ potential. If impurity ions are present then activation overpotential will be absent.

As a result of using highly purified leach liquor the Zinc produce is extremely pure (99.99%), in fact the purify is far more than what is required for metals most important application i.e. galvanizing.

Module 7

Extraction of metals from halides

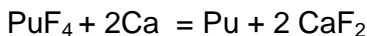
Discuss the correctness of the following statements

- 1. All metal oxides can be chlorinated. This chlorination reaction requires chlorine and carbon.**

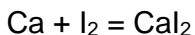
Ans : The statement is correct as far as only the first sentence is concerned. Chlorination can be achieved by other chlorinating agents such as HCl and CCl₄. Oxides which are not very stable are easily chlorinated by chlorine only without any presence of carbon and this is called direct chlorination . For reactive metal oxides such as TiO₂ one needs carbon to make 'indirect' chlorination thermodynamically feasible. One can look upon the reaction as combination of two steps: first , reduction of oxide to metal by carbon and then second, chlorination of the metal to a chlortide.

- 2. A 'booster' reaction helps metallothermic reduction of metal halides by raising the temperature.**

Ans: There is an element of truth in this statement but it is not the entire truth Booster reactions are indeed exothermic and the heat generated does raise the temperature. For example, consider calciothermic reduction of PuF₄.



A booster reaction to provide heat is the following exothermic reaction



This reaction has another important role. CaI₂ dissolves CaF₂ and thus reduces activity of the fluoride. This drives the metallothermic reduction to the right. Enhanced temperatures also helps to drive the reaction to the right and helps in cleaner separation of the metal and the slag (i.e. the mixture of slats).

- 3. Uranium and Thorium are important in nuclear metallurgy because they are fissionable elements.**

Ans- This statement is not valid. Natural uranium contains three isotopes :

U₂₃₈(99.28%), U₂₃₅(0.70%) and U₂₃₄(0.005%). Of these only U₂₃₅ is fissionable. However , U₂₃₈ is a 'fertile' isotope that can be converted by neutron irradiation to a fissionable element Pu₂₃₉. This man-made element is stable with a half life of 24,360 years. Thorium is not fissionable but the element Th₂₃₂ can be converted to a fissionable (man made) isotope of uranium , U₂₃₃.

- 4. Zirconium is called a reactor metal because nuclear energy is obtained by its fission reaction**

Ans : This statement is wrong. Zr is not a fissionable element and it does not, therefore, produce energy. However, it makes an important contribution indirectly. The high temperature strength and corrosion resistance of zirconium (alloyed with minor amounts of Cr, Fe, Ni, Sn or 2.5 per cent Nb) makes the metal ideally suited for use as a cladding Material for the fissionable materials The charges are kept in Zr alloy tubes

and the group of such tubes is called a pile. Zr alloys do not absorb neutrons generated by fission and allow their free movement from one location in a pile to another.

The role of a 'moderator' is to slow down very fast moving neutrons and minimize escape of neutrons altogether by increasing the size and the mass of the fissionable charge. For a given mixture of fissionable and nonfissionable atoms, there is a proportion of neutrons so reduced that the condition for a nuclear reaction to take place is attained.

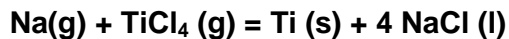
Zr alloys, which have a very low capacity for neutron absorption (or low neutron absorption (or low neutron absorption cross section) allows the pile to be kept as small as possible.

5. BeO is reduced by carbon in presence of copper for easy refining operation subsequently for production of pure Be.

Ans- The statement is totally wrong. Be-Cu alloys with 1.8-2.2 percent BeO and a slight amount of other metals are heat treatable high strength alloys with high fluidity in the molten state. Thus there is demand for such Be-Cu alloys in the industry for manufacture of items such as springs, diaphragms and pump components. There are Be-Cu alloys with other Be levels. Thus these alloys find direct use and no purification is required for pure Be production. For pure Be, there are other routes.

Additionally, the presence of a large excess of Cu during carbon reduction of BeO achieves two important objectives. When Be produced dissolves in copper, its activity is greatly reduced, specially because Be concentration is very low. This makes the reduction reaction thermodynamically far easier and feasible at lower temperatures and the possibility of formation of carbide of Be is also eliminated.

6. The pentamolecular reaction at 1000°C



is slow because it is a gas phase reaction.

Ans. It is correct to say that a gas phase reaction which implies bringing together at one point 4 atoms of Na and one molecule of TiCl₄ in the gas phase may be expected to be slow. However, during the reaction subchlorides of TiCl₄ are formed (TiCl₃, TiCl₂, TiCl etc.) which dissolve in reduction through Na(g) reacting with species in the liquid phase.

B. 10 mole percent of a salt MCl₂ is being electrolyzed at 1000K in a fused electrolyte contains 90 mole percent NaCl. The decomposition voltage is V₁. How will V₁ change if the electrolyte is composed of 20 mole percent MCl₂ and the rest composed of equal mole percents of NaF and CaCl₂. The metal M is neither Na nor Ca.

Ans. Activity of MCl₂ in the first electrolyte

$$a_1 = X_{\text{M}^{2+}} \cdot (X_{\text{Cl}^-})^2 = \frac{10}{10+90} \cdot 1^2 = 0.1$$

Activity of MCl₂ in the second electrolyte

$$a_2 = X_{\text{M}^{2+}} \cdot (X_{\text{Cl}^-})^2$$

$$= \frac{20}{20+40+40} \cdot \frac{[2 \times 20 + 2 \times 40]^2}{[2 \times 20 + 40 + 40 \times 2]}$$

$$= 0.15$$

$$V_1 = V^{\circ} - \frac{RT}{zF} \ln \frac{a_M \cdot p_{Cl_2}}{a_1}$$

$$V_2 = V^{\circ} - \frac{RT}{zF} \cdot \ln \frac{a_M \cdot p_{Cl_2}}{a_2}$$

Assume a_M (pure metal) = 1
 p_{Cl_2} (1 atm.) = 1.

$$V_1 - V_2 = -\frac{RT}{zF} \left[\ln \frac{1}{a_1} - \ln \frac{1}{a_2} \right]$$

$$= \frac{RT}{zF} \cdot \ln \frac{a_2}{a_1}$$

$$= \frac{2.303 RT}{zF} \cdot \log [a_2/a_1]$$

Since a_2/a_1 is positive the decomposition voltage decreases in the second case. This should be obvious, because it will be easier to decompose the solute if the activity is higher.

To get a quantitative value we note the following. In calorie units

Faraday const, $F = 23062$ Cal/Volt . Equiv.

Gas const . , $R = 1.98719$ Cal / Deg . mole

$$\frac{2.303 \cdot R}{F} = \frac{2.303 \cdot 1.98719}{23062}$$

$$= 0.0001985$$

$$V_1 - V_2 = 0.0001985 \cdot 1000 \cdot \log 1.5$$

$$= 0.1985 \cdot 0.1761 / 2$$

$$= 0.017478 \text{ V}$$

$$= 17\text{mV}$$