1.5 Chemical or Dry Corrosion:

Dry corrosion of metals occurs in non-aqueous solution and in non-humid (dry) atmosphere. It occurs due to direct chemical interaction between the surfaces of metal and corrosive environment like atmospheric gases (e.g., O_2, H_2S, Cl_2, etc.) or anhydrous liquid like HCl, H_2SO_4, etc.

Most common type of dry corrosion is **Oxidation Corrosion.**

Oxidation Corrosion: It occurs when a reactive metal is exposed to O_2 in absence of moisture. Upon oxidation a thin layer of oxide formed on the surface of metal

(i) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
(ii) $Ca + 1/2O_2 \rightarrow CaO$
(iii) $Mg + 1/2O_2 \rightarrow MgO$

1.5.1 Nature of Oxide layer

A thin layer of oxide formed on the surface of metal can be non-porous, porous, unstable or volatile.

(i) *Non-porous oxide layer*: It is stable, impervious and tightly sticks on the surface. It acts as a protective coating and prevents further corrosion.
Example: Metals like Cu, Al, and Cr forms protective oxide layer such as CuO, Al_2O_3, Cr_2O_3, respectively.

(ii) *Unstable oxide layer:* Such layer is formed by gold (Au) and platinum (Pt). As oxide layer decomposes back to metal and oxygen, Au and Pt do not undergo oxidation corrosion.

Example: $4Au + 3O_2 \rightarrow 2Au_2O_3$

(iii) Volatile oxide layer: The moment it is formed it gets volatilized and the metal surface is again gets exposed for further attack leading to continuous and rapid corrosion.
Example: $2Mo + 3O_2 \rightarrow 2MoO_3$ Molybdenum oxide (volatile oxide layer)

$2V + 2.5O_2 \rightarrow V_2O_5$ Vanadium oxide (volatile oxide layer)

✓ *This is the reason why Molybdenum and Vanadium undergo rapid corrosion in oxygen atmosphere.*

(iv) *Porous oxide layer*:Due to porous nature, oxygen attacks the metal through pores and corrosion continues till the entire metal is converted into metal oxide.
Metals like Fe, Ca, Mg, K, etc. form porous oxide layer.

Q.5 Define oxidation corrosion with a suitable example.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

Q.6. How many types of oxide layer can be formed on the surface of metal?

Ans. Four type (Porous, non-porous, unstable, Volatile)

Q.7.Which type of oxide results in rapid and continuous corrosion?

Ans. Volatile

Q.8 Name a metal which can form a volatile oxide layer (mention reaction).

Ans. Molybdenum (Mo); $2Mo + 3O_2 \rightarrow 2MoO_3$

Q.9Name two metals which form porous oxide layer.

Ans. Na, K

Q.9 Name two metals which form non-porous oxide layer.

Ans. Al and Cr

Q.9 Name two metals which form unstable oxide layer.

Ans. Au and Pt

Q 10. Corrosion resistance of iron can be significantly improved by alloying with aluminum. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Al is that alloying element forms a protective layer of Al_2O_3 on the surface of host metal.

Q 10. Corrosion resistance of iron can be significantly improved by alloying with chromium. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Cr is that alloying element forms a protective layer of Cr_2O_3 on the surface of host metal.

Q 11. Stainless steel maintains its luster for a longer period of time. Give reason.

Ans. Stainless steel is an alloy of iron with alloying elements like Al, Cr, etc. This alloying elements upon exposure to oxygen form a protective layer of Al_2O_3/Cr_2O_3 on the surface of it to prevent formation of rust.

Q.13. Which type of oxide film is more protective against corrosion?

Ans. Al_2O_3 form by Al is Non-porous.

1.5.2 Piling-Bedworth Rule (PBR)

PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide film is porous.

[N.B: **Specific Volume Ratio SVR = (Volume of metal oxide/n.Volume of metal)]**

Where 'n' is no of metal per oxide molecule. For example for MgO, n =1.

In general,If,

- SVR ≥ 1 but < 2; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, SnO_2etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.), usually less than or equal to 2
- SVR >>>1 (SVR>2); Oxide layer is less protective in nature (usually > 2), example, Fe_2O_3

SVR: Al_2O_3 (1.27); Cr_2O_3 (2); MgO (0.8), ZnO (1.58), NiO (1.42), etc.

Q. 12. What is PBR?

Ans. PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the SVR; greater is the rate of oxidation corrosion.

Q 13. What is specific volume ratio (SVR). Mention its significance.

Ans. Specific Volume Ratio SVR = (Volume of metal oxide formed/n x Volume of metal)

Where n = no of metal per oxide molecule

In general, If,

- SVR ≥ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is less protective in nature (usually > 2), example, Fe_2O_3

Numerical on SVR:

Example-1 What is the nature of the oxide layer (MO) formed on the surface of a metal 'M'? Given that: density of Metal and Metal oxide is 1.74 & 3.65 g/cc, respectively. The At. Mass of Metal is 24 and molecular mass of metal oxide is 40.

Ans. SVR =**(Volume of metal oxide formed/n x Volume of metal)**, **here, n = number of metal per metal oxide, here n = 1**

Volume of MO = Mass of MO/Density of MO = (40/3.65) =10.958

Volume of Metal = **Mass of Metal/Density of Metal = (**24/1.74) =13.793

Now, **SVR = 10.958/(1x13.793) = 0.7944** which is less than 1. So, oxide layer is porpus and non-protective in nature.

Example-2 What is the nature of the Zinc oxide layer formed on the surface of Zinc? Given that: density of Zn and ZnO are 7.13 & 5.61 g/cc, respectively. The At. Mass of Zn is 65 and molecular mass of Zinc oxide is 81.

Ans. SVR =(Volume of metal oxide formed/n x Volume of metal), here, n = number of metal per metal oxide, here n = 1

Volume of MO = Mass of MO/Density of MO = (81/5.61) =14.438

Volume of Metal = **Mass of Metal/Density of Metal =** (65/7.13) =9.116

SVR = (14.438)/(1x9.116) = 1.583 >1 => Oxide layer is non-porous and Protective

Example-3 What is the nature of the Aluminum oxide layer formed on the surface of aluminum? Given that: density of Al and Al_2O_3 are 2.7 & 4.0 g/cc, respectively. The At. Mass of Metal is 27 and molecular mass of metal oxide is 102.

Ans. SVR = **(Volume of metal oxide formed/n x Volume of metal), here, n = number of metal per metal oxide, here n = 2**

SVR= 1.27 >1

=>The oxide layer is protective

Example-4 What is the nature of the Chromium oxide layer formed on the surface of chromium? Given that: density of Cr and Cr_2O_3 are 7.19 & 5.22 g/cc, respectively. The At. Mass of Cr is 52 and molecular mass of metal oxide is 152.

Ans. SVR = **(Volume of metal oxide formed/n x Volume of metal), here, n = number of metal per metal oxide, here n = 2**

SVR= 2.02>1

=>oxide layer is protective

Other Numerical

Q.1. How much rust ($Fe_2O_3.3H_2O$) will be formed when 10 kg of iron (Fe) have completely rusted away? (At. mass: Fe = 56, H =1, O =16)

Ans. Mol. Mass of rust ($Fe_2O_3.3H_2O$) = 214 g

Here, rust contains 2 Fe-atoms.

So, 214g of rust contains 2 x 56 = 112 g Fe

Or, 112 g Fe produces 214 g rust

Then, 10 kg = 10,000g of Fe will form = (214/112) x 10,000 = 19107 g = 19.1 kg.

Q.2. An iron piece has formed 30 Kg of rust ($Fe_2O_3.3H_2O$) after complete corrosion. Find the weight of iron piece. (At. mass: Fe = 56, H =1, O =16)

Ans. Mol. Mass of rust ($Fe_2O_3.3H_2O$) = 214 g

Here, rust contains 2 Fe-atoms.

So, 214g of rust is formed by 112 g Fe

Or, Then, 30 kg = 30,000g of rust will be formed by = (112/214) x 30,000 = 157009 g = 15.7 kg Fe.

Assignment:

Nickel, with an atomic mass of 59, forms an oxide layer (NiO) with a molecular mass of 75. The density of the metal is 8.9 g/cc, and the density of the oxide layer is 6.67 g/cc. Can nickel be used as a coating to control the corrosion of iron?