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EQUIVALENT WEIGHTS

Equivalent weight of an element is the number of parts by weight of it that combines with or displaces 1.008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35.45 parts by weight of chlorine. Equivalent weight is merely a number as it is a ratio. Therefore, it does not have any units.

As many metals displace hydrogen from acids, H is used as a reference element in determining equivalent weights of elements. Since most of the elements form compounds with oxygen and chlorine, O and Cl are also used as reference elements.

Gram equivalent weight : It is the equivalent weight of the element expressed in grams. For example, the equivalent weight of Al is 9 and hence, its gram equivalent weight is 9 g.

1.1 DETERMINATION OF EQUIVALENT WEIGHTS OF ELEMENTS

There are mainly 5 methods to determine the equivalent weight of elements.

They are :
1. Hydrogen displacement Method
2. Oxide Method
3. Chloride Method
4. Metal displacement Method
5. Electrolysis Method

1.2 HYDROGEN DISPLACEMENT METHOD

This method is applicable to metals like Fe, Mg and Zn which readily displace hydrogen from dilute acids.

Principle

$$\textit{Equivalent weight of the metal} = \frac{\textit{wt. of metal}}{\textit{wt. of hydrogen}} \times 1.008$$

A known weight of the metal is reacted with excess of a dilute acid. The volume of the hydrogen gas liberated is measured. From the observed volume (at the lab temperature and pressure), the volume at NTP conditions is calculated (NTP means normal temperature and pressure; T = 0°C = 273 K and P = 760 mm = 1 atm). From this volume the weight of the gas is calculated knowing that at NTP 1 litre of hydrogen gas weighs 0.089 g. (It is known that at NTP 1 mole of H_2 (i.e., 2 g) occupies 22.4 litres and so 1 litre of H_2 weighs 0.089 g).

The Method

Using the hydrogen displacement method, equivalent weight of magnesium, for example, may be determined as follows:

A piece of magnesium is wrapped in a copper wire gauze and put into a beaker. A funnel is inverted over the metal piece and some water is poured into the beaker. A graduated glass tube (also known as *eudiometer tube*) filled with water is inverted over the funnel such that the stem of the funnel is inside the tube. Then some conc. HCl is added. The diluted HCl reacts with the metal (Mg) and the hydrogen gas evolved collects at the top of the tube.

$$2HCl + Mg \rightarrow MgCl_2 + H_2 \uparrow$$

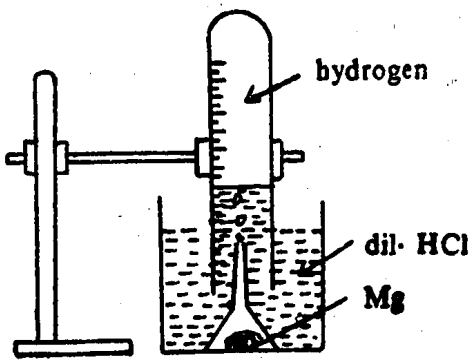

Fig. 1 HYDROGEN DISPLACEMENT METHOD

In fact, the pressure exerted by the gas in the tube is that of the gas and of water vapour (the pressure due to water vapour is known as *aqueous tension*). The tube, closed with thumb, is transferred into a big jar containing water and is adjusted till the levels of water inside and outside the tube are equal. At this stage, the pressure of the gas and the aqueous tension at that lab temperature will be equal to atmospheric pressure. The pressure, the temperature, and the volume of the gas are noted and the value of aqueous tension at that temperature is taken from the tables (aqueous tension has to be subtracted from the observed pressure).

Then the volume is converted to that at NTP conditions and its weight is calculated (at NTP, 1 litre of H_2 weighs 0.089 g).

$$\text{Equivalent weight of magnesium} = \frac{\text{wt. of metal}}{\text{wt. of hydrogen}} \times 1.008$$

Thus the equivalent weight of magnesium may be determined.

Problem

0.0899 g of a metal is treated with dil. HCl and the liberated hydrogen is collected over water. The volume of hydrogen is measured as 128.9 ml at 27°C and 752 mm. What is the equivalent weight of the metal? (aqueous tension at 27°C is 26.75 mm)

Volume of hydrogen collected, $V_1 = 128.9$ ml

Temperature, $T_1 = 27°C = 27+273 = 300$ K

Aqueous tension at $27°C = 26.75$ mm

$\therefore$ Pressure exerted by the gas, $P_1 = 752-26.75 = 725.25$ mm

At NTP,

Temperature, $T_0 = 273$ K

Pressure, $P_0 = 760$ mm

Volume of hydrogen $= V_0$

According to the gas equation,

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$\therefore V_0 = \frac{P_1 V_1 \times T_0}{T_1 \times P_0}$$

$$= \frac{725.25 \times 128.9 \times 273}{300 \times 760} = 112.0 \text{ ml}$$

It is known that at NTP 1000 ml of hydrogen gas weighs 0.089 g.

$\therefore$ Weight of 112.0 ml of hydrogen gas

$$= \frac{112.0}{1000} \times 0.089 = 0.0099 \text{ g}$$

i.e., weight of hydrogen gas evolved = 0.0099 g

Weight of the metal reacted = 0.0899 g (given)

$\therefore$ Equivalent weight of the metal

$$= \frac{\text{wt. of metal}}{\text{wt. of hydrogen}} \times 1.008$$

$$= \frac{0.0899}{0.0099} \times 1.008 = 9.153$$

1.3 OXIDE METHOD

Principle

In this method, a known weight of the metal is directly or indirectly oxidised and the weight of the oxide is determined.

Direct oxidation by heating in the air is done in the case of metals like Mg and Ca and non-metals like C and S.

e.g., $2Mg + O_2 \longrightarrow 2MgO$

Equivalent weight of metals like copper may be determined by indirect oxidation method. In this method, the metal is converted into its nitrate by adding conc. HNO_3 and then on strong heating, the nitrate is converted into the metal oxide.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

$$\text{Equivalent weight of the element} = \frac{\text{wt. of element}}{\text{wt. of oxygen}} \times 8$$

1.3.1 Direct Oxidation

The Method

Equivalent weights of metals like magnesium and non-metals like sulphur and carbon can be determined by the direct oxidation method.

Example : Magnesium (Mg)

A piece of magnesium metal is taken in a crucible (with lid) of known weight and weighed. It is carefully heated, moistened and again heated to get magnesium oxide. It is then cooled in a desiccator and weighed. Heating, cooling and weighing are repeated until a constant weight is obtained.

Calculation

Weight of the crucible = W_1 g
Weight of the crucible + metal = W_2 g
Weight of the crucible + metal oxide = W_3 g
Weight of the metal = $(W_2 - W_1)$ g
Weight of oxygen = $(W_3 - W_2)$ g

$$\text{Equivalent weight of the metal} = \frac{\text{wt. of metal}}{\text{wt. of oxygen}} \times 8$$

$$= \frac{(W_2 - W_1)}{(W_3 - W_2)} \times 8$$

Problem

1.18 g of a metal on oxidation gave 1.5 g of the oxide. Calculate the equivalent weight of the metal.

Weight of the metal = 1.18 g
Weight of the oxide = 1.5 g
Weight of oxygen = 1.5 − 1.18
= 0.32 g

Equivalent weight of the metal

$$= \frac{\text{wt. of metal}}{\text{wt. of oxygen}} \times 8$$

$$= \frac{1.18}{0.32} \times 8 = 29.5$$

1.3.2 Indirect Oxidation

The Metho

Metals e copper and mercury will not evolve hydrogen on treatment with dil. HCl Equivalent weight of these metals may be determined by the indirect oxidation method.

For example, to determine the equivalent weight of copper by this method, a piece of it is taken in a china dish of known weight and weighed. Then 1:1 HNO_3 is added. A vigorous reaction takes place forming copper nitrate solution. It is then carefully evaporated over a water bath. The dry nitrate is strongly heated on a sand bath to get copper oxide residue. The dish is cooled in a desiccator and weighed. Heating, cooling and weighing are repeated till a constant weight is obtained.

Calculation

Weight of china dish = W_1 g

Weight of china dish + copper = W_2 g

Weight of china dish + copper oxide = W_3 g

Weight of copper = $(W_2 - W_1)$ g

Weight of oxygen = $(W_3 - W_2)$ g

$$\text{Equivalent weight of copper} = \frac{\text{wt of copper}}{\text{wt. of oxygen}} \times 8 = \frac{(W_2 - W_1)}{(W_3 - W_2)} \times 8$$

Problem

1.62 g of zinc is dissolved in conc. HNO_3 to prepare its nitrate. On strongly heating the nitrate, 2.02 g of the oxide is formed. Find the equivalent weight of zinc.

Weight of zinc = 1.62 g

Weight of zinc oxide = 2.02 g

$\therefore$ Weight of oxygen = 2.02 − 1.62

= 0.40 g

$$\therefore \text{Equivalent weight of zinc} = \frac{\text{wt. of zinc}}{\text{wt. of oxygen}} \times 8$$

$$= \frac{1.62}{0.40} \times 8 = 32.4$$

i.e., equivalent weight of zinc = 32.4

1.3.3 By reduction of the oxide

Equivalent weight of metals like copper can also be determined by reducing a known weight of the metal oxide in a current of dry hydrogen and on weighing the metal formed.

$$CuO + H_2 \longrightarrow Cu + H_2O$$

Weight of the metal oxide = W_1 g

Weight of the metal = W_2 g

Weight of oxygen = $(W_1 - W_2)$ g

Equivalent weight of the metal

$$= \frac{\text{wt. of metal}}{\text{wt. of oxygen}} \times 8 = \left(\frac{W_2}{W_1 - W_2}\right) \times 8$$

Problem

0.04 g of a metallic oxide is reduced in a current of hydrogen. If the weight of water formed is 0.09 g, what will be the eq. wt. of the metal? If the metal is divalent, what will be its atomic weight?

The reduction equation is

$$MO + H_2 \longrightarrow M + H_2O$$

i.e., for every 16 g of oxygen present in the oxide, 18 g of water is formed.

Weight of water formed = 0.09 g.

$\therefore$ Weight of oxygen $= \frac{0.09}{18} \times 16 = 0.08$ g

Weight of the metal oxide = 0.40 g

$\therefore$ Weight of the metal $= 0.40 - 0.08 = 0.32$ g

Equivalent weight of the metal $= \frac{\text{wt. of metal}}{\text{wt. of oxygen}} \times 8$

$$= \frac{0.32}{0.08} \times 8 = 32.0$$

Valency of the metal = 2

Atomic weight (A) = Valency (n) × equivalent weight (E)

(see *Sec. 2.2.1*)

$$= 2 \times 32.0$$

$$= 64.0$$

$\therefore$ Atomic weight of the metal is 64.0.

1.4 CHLORIDE METHOD

1.4.1 For metals forming soluble chlorides

Principle

When a solution of a metal chloride reacts with silver nitrate solution, silver chloride precipitates.

e.g., $NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$

From the weight of the chloride of the element and the weight of AgCl, the equivalent weight (E) of the element can be calculated.

$$E = \left(\frac{\text{wt. of the metal chloride} \times \text{eq. wt. of AgCl}}{\text{wt. of AgCl}}\right) - 35.45$$

Equivalent weights of sodium and potassium may be determined by this method.

The Method

An accurately weighed amount of the metal chloride is dissolved in water and precipitated as AgCl by adding excess of silver nitrate solution. The precipitate is filtered, dried and weighed. The process of drying and weighing is continued until constant weight is obtained. From these data the equivalent weight of the element can be calculated.

Let the equivalent weight of the element be E.

Equivalent weight of chlorine = 35.45

Equivalent weight of silver = 107.88

Equivalent weight of AgCl = 107.88+35.45 = 143.33

Equivalent weight of the metal chloride = E+35.45

It is known that one equivalent of a compound will always react with one equivalent of another compound.

i.e., 143.33 g of AgCl is formed for every E+35.45 g of the metal chloride.

Weight of the metal chloride = W_1 g

Weight of AgCl = W_2 g

Then, $\frac{E+35.45}{W_1} = \frac{143.33}{W_2}$

$\therefore E = \left(\frac{143.33 \times W_1}{W_2}\right) - 35.45$

Thus the equivalent weight of the metal can be determined by the chloride method.

Problem

1.492 g of a metal chloride on treatment with excess silver nitrate solution gave 2.87 g of silver chloride precipitate. Calculate the equivalent weight of the metal (eq. wts: Ag=108, Cl = 35.45)

Weight of the metal chloride, $W_1 = 1.492$ g

Weight of silver chloride, $W_2 = 2.87$ g

$\therefore$ Equivalent weight of the metal, E

$$= \left(\frac{143.33 \times W_1}{W_2}\right) - 35.45$$

$$= \left(\frac{143.33 \times 1.492}{2.87}\right) - 35.45 = 39.06$$

1.4.2. For metals forming insoluble chlorides

Principle

Equivalent weight of metals like silver and lead, which form insoluble chlorides, may be determined in this way: a known weight of the metal is converted into its chloride and weighed again.

$$\textit{Equivalent weight} = \frac{\textit{wt. of the metal}}{\textit{wt. of chlorine}} \times 35.45$$

The Method

A small piece of the metal is taken in a china dish of known weight and weighed. Dil. HNO_3 is added to it and heated over a steam bath until the metal is completely dissolved forming the metal nitrate. It is then treated with excess of dil. HCl to precipitate the metal chloride. The contents are evaporated to dryness over a steam bath followed by gentle heating on a sand bath. It is cooled and then weighed. Drying, cooling and weighing are repeated until a constant weight is obtained.

Calculation

Weight of empty china dish $= W_1$ g

Weight of the dish+metal $= W_2$ g

Weight of the metal $= (W_2 - W_1)$ g

Weight of the dish+metal chloride precipitate $= W_3$ g

Weight of chlorine $= (W_3 - W_2)$ g

Equivalent weight of the metal

$$= \frac{\text{wt. of the metal}}{\text{wt. of chlorine}} \times 35.45 = \frac{(W_2 - W_1)}{(W_3 - W_2)} \times 35.45$$

Problem

0.36 g of silver is dissolved in dil. HNO_3 and treated with excess dil. HCl to get 0.478 g of silver chloride. Calculate the equivalent weight of silver.

Weight of silver = 0.36 g

Weight of silver chloride = 0.478 g

$\therefore$ Weight of chlorine = 0.478 − 0.36 = 0.118 g

Equivalent weight of the metal, E

$$= \frac{\text{wt. of the metal}}{\text{wt. of chlorine}} \times 35.45$$

$$= \frac{0.36 \times 35.45}{0.118} = 108.15$$

1.5 METAL DISPLACEMENT METHOD

Principle

One equivalent weight of an element always displaces an equivalent weight of another element. So by determining the weight of an element displaced by a known weight of another element, the equivalent weight of an element can be calculated provided that the equivalent weight of the other element is known.

For example, zinc displaces copper from $CuSO_4$ solution.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

$$\text{Equivalent weight of copper} = \frac{\text{wt. of copper}}{\text{wt. of zinc}} \times \text{eq. wt. of zinc}$$

The Method

Equivalent weights of copper, zinc, silver, *etc.* can be determined using this method.

For example, to determine the equivalent weight of copper, an accurately weighed piece of zinc is placed in $CuSO_4$ solution contained in a china dish. It is stirred well. Copper slowly precipitates out which sticks on to the zinc piece. It is scrapped with a glass rod, thoroughly washed and collected in a weighed sintered crucible. It is then dried, cooled and weighed. Drying, cooling and weighing are repeated until a constant weight is obtained. The unreacted zinc piece is well washed, dried and weighed. Using these data, the equivalent weight of copper can be calculated as follows:

Weight of crucible = W_1 g

Weight of copper + crucible = W_2 g

Weight of copper = $(W_2 - W_1)$ g

Weight of zinc taken = W_3 g

Weight of zinc unreacted = W_4 g

Weight of zinc reacted = $(W_3 - W_4)$ g

Equivalent weight of zinc = 32.69

$$\text{Equivalent weight of copper} = \frac{\text{wt. of copper}}{\text{wt. of zinc}} \times 32{\cdot}69$$

$$= \left(\frac{W_2 - W_1}{W_3 - W_4}\right) \times 32{\cdot}69$$

Thus, the equivalent weight of copper can be determined by the metal displacement method.

Problem

0.515 g of zinc displaces 0.50 g of copper from copper sulphate solution. If the equivalent weight of copper is 31.8, find the equivalent weight of zinc.

Weight of copper = 0·50 g

Weight of zinc = 0.515 g

Equivalent weight of copper = 31·8

$$\text{Equivalent weight of zinc} = \frac{\text{eq. wt. of copper} \times \text{wt. of zinc}}{\text{wt. of copper}}$$

$$= \frac{0{\cdot}515 \times 31{\cdot}8}{0{\cdot}50} = 32.75$$

1.6 ELECTROLYSIS METHOD

Principle

When an electric current is passed through an electrolytic solution, chemical reaction takes place. This process is known as *electrolysis*.

According to *Faraday's second law of electrolysis*, when the same quantity of electricity is passed through different electrolytes, the amounts of substances deposited or liberated will be proportional to their equivalent weights.

$$i.e., \quad \frac{E_1}{E_2} = \frac{W_1}{W_2}$$

Applying this principle, the equivalent weight of a metal can be determined. This method is very useful to determine equivalent weights of metals like copper, silver, mercury, gold and lead.

The Method

Example : Copper

A water voltameter containing acidified water is connected in series to a copper voltameter containing copper sulphate solution. The cathode of the copper voltameter is cleaned, dried and weighed before the experiment. When electricity is passed, copper is deposited on the weighed cathode of the copper voltameter while hydrogen gas is liberated at the cathode of the water voltameter. The electrolysis is then stopped. The weight of the copper cathode and the volume of hydrogen gas are measured. From these data, the equivalent weight of copper can be calculated.

Volume of H_2 at NTP $= V_0$ ml

Weight of V_0 ml of $H_2 = \frac{V_0}{1000} \times 0{\cdot}089$ g $= x$ g

Weight of copper cathode before experiment $= W_1$ g

Weight of copper cathode after experiment $= W_2$ g

Weight of copper deposited $= (W_2 - W_1)$ g

$$\text{Equivalent weight of copper} = \frac{\text{wt. of copper}}{\text{wt. of hydrogen}} \times 1.008$$

$$= \frac{(W_2 - W_1)}{x} \times 1.008$$

Thus the equivalent weight of copper may be determined by the electrolysis method.

Equivalent weight of silver may also be determined by this method using silver cathode and $AgNO_3$ solution in place of copper cathode and $CuSO_4$ solution, respectively.

Problem

A copper voltameter and a water voltameter are connected in series and the same quantity of electricity is passed. The weight of copper deposited is 0.202 g and the volume of dry hydrogen produced in the water voltameter is 75 ml at 17°C and 750 mm. Calculate the equivalent weight of copper.

Temperature, $T_1 = 17°C = 290$ K
Pressure, $P_1 = 750$ mm
Volume of hydrogen evolved, $V_1 = 75$ ml

At NTP,

Temperature, $T_0 = 273$ K
Pressure, $P_0 = 760$ mm
Volume of the gas $= V_0$

According to the gas equation,

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

i.e.,
$$V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$

$$= \frac{750 \times 75}{290} \times \frac{273}{760} = 69{\cdot}69 \text{ ml}$$

It is known that at NTP, 1000 ml of hydrogen gas weighs 0.089 g.

$\therefore$ Weight of 69.69 ml of the gas

$$= \frac{69.69}{1000} \times 0.089 = 0.0062 \text{ g}$$

Weight of copper deposited = 0.202 g
Weight of hydrogen evolved = 0.0062 g