

Equivalent weight

It is defined as the mass of an element/compound/ion which combines or displaces 1 part of hydrogen or 8 parts of oxygen or 35.5 parts of chlorine by mass.

It is not always possible to apply this classic definition to determine equivalent weights of chemical entities. It is so because, we can not conceive of reactions involving chemical entities with three named reference of hydrogen, oxygen and chlorine. Generally, we are limited to determination of equivalent weights of elements and few compounds by using this definition of equivalent weight. A more workable definition is given as :

$$\text{Equivalent weight, } E = \frac{\text{Molecular weight}}{\text{Valence factor}} = \frac{M}{x}$$

Clearly, determination of equivalent weight amounts to determining valence factor "x". Here, we shall classify chemical entities and the techniques to determine "x".

Equivalent weight of an element

In the case of an element, the equivalent weight is defined as :

$$\text{Equivalent weight, } E = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{A}{x}$$

Note that atomic weight substitutes molecular weight and valency substitutes valence factor in the definition. Valencies of hydrogen, calcium and oxygen are 1, 2 and 2 respectively. Hence, their equivalent weights are $1/1 = 1$, $40/2 = 20$ and $16/2 = 8$ respectively.

Equivalent weight of an acid

The valence factor of an acid is equal to its basicity. The basicity of an acid is equal to furnishable hydrogen ion (proton) in its aqueous solution. Importantly, basicity is not same as the number of hydrogen atoms in acid molecule. Consider acetic acid (CH_3COOH). It contains 4 hydrogen atoms in it, but only 1 furnishable hydrogen ion. As such, basicity of acetic acid is 1. With this background, we define equivalent weight of an acid as :

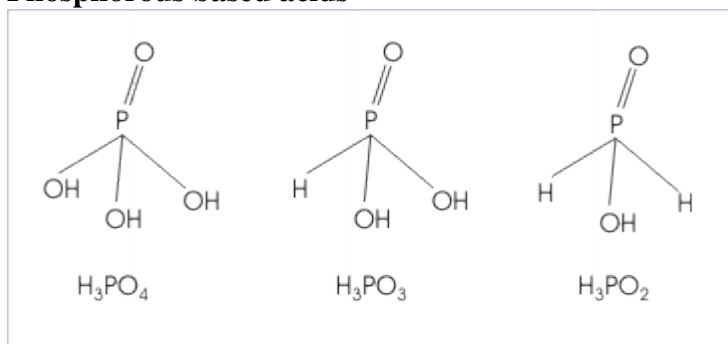
$$\text{Equivalent weight, } E = \frac{\text{Molecular weight of acid}}{\text{Basicity}}$$

Basicity of sulphuric acid is 2. Hence, equivalent weight of sulphuric acid (H_2SO_4) is $(2 \times 1 + 32 + 4 \times 16)/2 = 98/2 = 49$. Similarly, basicity of oxalic acid is 2. Hence, equivalent weight of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is $(2 \times 1 + 2 \times 12 + 4 \times 16)/2 = 90/2 = 45$.

Phosphorous based acids like phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3) and hypo-phosphorous acid (H_3PO_2) need special mention here to understand their basicity. The structures of three acids are shown here. From the structure, it appears that these compounds may furnish OH ions, but bond strengths between phosphorous

and oxygen (P-O) and phosphorous and hydrogen (P-H) are stronger than between oxygen and hydrogen (O-H) in -OH group. As such, these molecules release hydrogen ions from -OH group and behave as acid. Clearly, basicities of phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3) and hypo-phosphorous acid (H_3PO_2) are 3, 2 and 1 respectively.

Phosphorous based acids



Furnishable hydrogen ions of acids

Equivalent weight of a base

The valence factor of a base is equal to its acidity. The acidity of a base is equal to furnishable hydroxyl ion (OH^-) in its aqueous solution. With this background, we define equivalent weight of a base as :

$$\text{Equivalent weight} = \frac{\text{Molecular weight of base}}{\text{Acidity}}$$

Acidity of KOH is 1, whereas acidity of $\text{Ca}(\text{OH})_2$ is 2. Hence, equivalent weight of KOH is $(39 + 16 + 1)/1 = 56/1 = 56$. Similarly, equivalent weight of $\text{Ca}(\text{OH})_2$ is $\{40 + 2 \times (16 + 1)\}/2 = 74/2 = 37$.

Equivalent weight of a compound

The valence factor of a compound depends on the manner a compound is involved in a reaction. The compounds of alkali metal salts and alkaline earth metal salts are, however, constant. These compounds are ionic and they dissociate in ionic components in aqueous solution. In this case, valence factor is equal to numbers of electronic charge on either cation or anion.

$$\text{Equivalent weight} = \frac{\text{Molecular weight of compound}}{\text{Numbers of electronic charge on cation or anion}}$$

The numbers of electronic charge on cation of NaHCO_3 is 1. Hence, equivalent weight of NaHCO_3 is $(23 + 1 + 12 + 3 \times 16)/1 = 84$.

If we look at the defining ratio of equivalent weight of a compound (AB) formed of two radicals (say A and B), then we can rearrange the ratio as :

Equivalent weight, $E = \frac{\text{Molecular weight of Radical A}}{\text{Numbers of electronic charge}}$
 $E = \frac{\text{Molecular weight of Radical B}}{\text{Numbers of electronic charge}}$

Thus,

$\Rightarrow \text{Equivalent weight of AB} = \text{Equivalent weight of A} + \text{Equivalent weight of B}$
 $\Rightarrow \text{Equivalent weight of AB} = \frac{\text{Molecular weight of A}}{\text{Numbers of electronic charge of A}} + \frac{\text{Molecular weight of B}}{\text{Numbers of electronic charge of B}}$

Equivalent weight of an ion

The valence factor of an ion is equal to numbers of electronic charge on the ion. Therefore, we define equivalent weight of an ion as :

Equivalent weight, $E = \frac{\text{Molecular weight of ion}}{\text{Numbers of electronic charge}}$
 $E = \frac{\text{Molecular weight of ion}}{\text{Numbers of electronic charge}}$

The numbers of electronic charge on carbonate ion (CO_3^{2-}) is 2. Hence, equivalent weight of carbonate ion is $(12 + 3 \times 16) / 2 = 60 / 2 = 30$. Similarly, equivalent weight of aluminum ion (Al^{3+}) is $27 / 3 = 9$.