Empirical Formulas

The compound disilicon hexafluoride has the formula Si_2F_6. The percent composition would be calculated from the atomic masses (atomic weights) as follows:

Si $\quad 28.09\times 2 = \quad 56.18 \quad \Rightarrow \quad \frac{56.18}{170.2}\times 100\% = \quad 33.01\ \%\ \text{Si}$

F $\quad 19.00\times 6 = \quad 114.00 \quad \Rightarrow \quad \frac{114.0}{170.2}\times 100\% = \quad 66.99\ \%\ \text{F}$

$\qquad\qquad\qquad\qquad 170.18 \quad \leftarrow$ molecular mass (molecular weight)

To obtain the formula from the percent composition one can convert masses to moles and find the mole ratio. If masses are not given, it is convenient to (arbitrarily) start with 100. g of compound to obtain elemental masses. So in this case 100.0 g would contain 33.01 g Si and 66.99 g F. Convert these masses to moles and scale to simple whole numbers.

$$33.01\ \text{g Si}\times\frac{1\ \text{mol Si}}{28.09\ \text{g Si}} = 1.175 \Rightarrow \frac{1.175}{1.175} = 1$$ Divide both numbers by the smallest number.

$$66.99\ \text{g F}\times\frac{1\ \text{mol F}}{19.00\ \text{g F}} = 3.526 \Rightarrow \frac{3.526}{1.175} = 3.00 \Rightarrow \quad Si_1F_3 \quad \Rightarrow SiF_3$$

SiF_3 is the empirical formula. **The empirical formula is the molecular formula reduced to the simplest whole number ratio of atoms**. It is not possible to get back to the molecular formula, Si_2F_6, from percent composition without further information.

A silicon bromide compound is 11.65% Si and 88.35% Br. Calculate the empirical formula.

$$11.65\ \text{g Si}\times\frac{1\ \text{mol Si}}{28.09\ \text{g Si}} = 0.415 \Rightarrow \frac{0.415}{0.415} = 1 \qquad \Rightarrow \times 3 \Rightarrow 3$$

$$88.35\ \text{g Br}\times\frac{1\ \text{mol Br}}{79.90\ \text{g Br}} = 1.106 \Rightarrow \frac{1.106}{0.415} = 2.667 \quad \Rightarrow \times 3 \Rightarrow 8.00 \Rightarrow Si_3Br_8$$

Notice that the division by the smallest number (0.415) did not give whole numbers in this case, so a further step is required. 2.667 **cannot** be rounded to 3.0 to give the compound $SiBr_3$, because $SiBr_3$ will not agree with the percent composition . ($SiBr_3$ is 10.5% Si and 89.5%Br) Since $2.667 = 2^2/_3$ it is appropriate to **multiply both numbers** by 3. If you are not certain what to multiply by, try multiplying by integers 2, 3, 4, 5… until both subscripts reach integer values or nearly integer values—say within ±0.05. If the final numbers seem unusually large, double-check all calculations. If the numbers came directly from an experiment, it may be necessary to try the experiment again to get better data.

Determination of Waters of Hydration from Percentage Data.

A hydrated compound like $CuCl_2 \cdot 2H_2O$ has a percentage of the compound that is H_2O and a percentage that is the anhydrous (without water) $CuCl_2$. This is easily calculated from the molecular weight:

MW of $CuCl_2 \cdot 2H_2O$ is 134.5 $(= 63.55 + 2\times35.45)$ $+ 2\times18.016 = 170.5$

$$\% \, CuCl_2 = \frac{134.5 \text{ g } CuCl_2}{170.5 \text{ g } CuCl_2 \cdot 2H_2O} \times 100\% = 78.9 \% \, CuCl_2$$

$$\% \, H_2O = \frac{2\times18.016 \text{ g } H_2O}{170.5 \text{ g } CuCl_2 \cdot 2H_2O} \times 100\% = 21.1 \% \, H_2O$$

Problem:
The hydrated compound $CuCl_2 \cdot xH_2O$ is 21.1 % water. Determine the value of x.

The problem can be solved by methods used for determination of an empirical formula. Determine the mole ratio of $CuCl_2$ and H_2O in the compound.

Calculate moles of $CuCl_2$ and H_2O in 100.0 g of the hydrate, $CuCl_2 \cdot xH_2O$.

$$78.9 \text{ g } CuCl_2 \times \frac{1 \text{ mol } CuCl_2}{134.5 \text{ g } CuCl_2} = 0.587 \text{ mol } CuCl_2$$

$$21.1 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.016 \text{ g } H_2O} = 1.17 \text{ mol } H_2O$$

so $\dfrac{1.17 \text{ mol } H_2O}{0.587 \text{ mol } CuCl_2} = 1.99$ so x must equal 2,

i.e, in the hydrate there are 2 moles of water per every mole of $CuCl_2$.

The formula for the hydrate is: $CuCl_2 \cdot 2H_2O$

Try these problems:

1. $VSO_4 \cdot xH_2O$ is 46.175 % water; calculate the value of x.

2. $Mg_2Fe(CN)_6 \cdot xH_2O$ is 45.346 % water; calculate the value of x

3. A compound of neptunium (Np) and oxygen is 15.25% oxygen; determine the empirical formula of the compound.

Answers: 1. x=7 $VSO_4 \cdot 7H_2O$ 2. x= 12 $Mg_2Fe(CN)_6 \cdot 12H_2O$ 3. Np_3O_8

Solutions:

1. For 100.0 g of hydrate $\quad 46.175\text{ g } H_2O \dfrac{1\text{ mol } H_2O}{18.016\text{ g } H_2O} = 2.563\text{ mol } H_2O$

$100.0\text{ g hydrate} - 46.175\text{ g } H_2O = 53.825\text{ g } VSO_4 \times \dfrac{1\text{ mol } VSO_4}{147.00\text{ g } VSO_4} = 0.36616\text{ mol } VSO_4$

so $\dfrac{2.563\text{ mol } H_2O}{0.36616\text{ mol } VSO_4} = 7.00$ so hydrate is $VSO_4 \cdot 7H_2O$

2. For 100.0 g of hydrate $\quad 45.346\text{ g } H_2O \dfrac{1\text{ mol } H_2O}{18.016\text{ g } H_2O} = 2.517\text{ mol } H_2O$

$100.0\text{ g hydrate} - 45.346\text{ g } H_2O = 54.654\text{ g } Mg_2Fe(CN)_6 \times \dfrac{1\text{ mol } Mg_2Fe(CN)_6}{260.56\text{ g } Mg_2Fe(CN)_6} = 0.20975\text{ mol } Mg_2Fe(CN)_6$

so $\dfrac{2.517\text{ mol } H_2O}{0.20975\text{ mol } Mg_2Fe(CN)_6} = 12.00$ so hydrate is $Mg_2Fe(CN)_6 \cdot 12H_2O$

3. For 100.0 g of compound $\quad 15.25\text{ } H_2O \dfrac{1\text{ mol O}}{15.9994\text{ g O}} = 0.95316\text{ mol O}$

$100.0\text{ g compound} - 15.25\text{ g } H_2O = 84.75\text{ g Np} \times \dfrac{1\text{ mol Np}}{237\text{ g Np}} = 0.3576\text{ mol Np}$

$\dfrac{0.95316}{0.3576} = 2.665 \quad \rightarrow \quad x3 \quad = 8.00$

$\dfrac{0.3576}{0.3576} = 1 \quad \rightarrow \quad x3 \quad = 3 \quad$ so Np_3O_8