Empirical Formulas

The compound disilicon hexafluoride has the formula Si₂F₆. The percent composition would be calculated from the atomic masses (atomic weights) as follows:

\[
\begin{align*}
\text{Si} & \quad 28.09 \times 2 = 56.18 \quad \Rightarrow \quad \frac{56.18}{170.2} \times 100\% = 33.01\% \text{ Si} \\
\text{F} & \quad 19.00 \times 6 = 114.00 \quad \Rightarrow \quad \frac{114.00}{170.2} \times 100\% = 66.99\% \text{ F}
\end{align*}
\]

170.18 \leftarrow \text{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 100.0 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.

\[
\begin{align*}
33.01 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} & = 1.175 \quad \Rightarrow \quad \frac{1.175}{1.175} = 1 \quad \text{Divide both numbers by the smallest number.} \\
66.99 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} & = 3.526 \quad \Rightarrow \quad \frac{3.526}{1.175} = 3.00 \quad \Rightarrow \quad \text{Si}_3\text{F}_3 \quad \Rightarrow \quad \text{SiF}_3
\end{align*}
\]

SiF₃ 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, Si₂F₆, from percent composition without further information.

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

\[
\begin{align*}
11.65 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} & = 0.415 \quad \Rightarrow \quad \frac{0.415}{0.415} = 1 \quad \Rightarrow \times 3 \Rightarrow 3 \\
88.35 \text{ g Br} \times \frac{1 \text{ mol Br}}{79.90 \text{ g Br}} & = 1.106 \quad \Rightarrow \quad \frac{1.106}{0.415} = 2.667 \quad \Rightarrow \times 3 \Rightarrow 8.00 \Rightarrow \text{Si}_3\text{Br}_8
\end{align*}
\]

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 SiBr₃, because SiBr₃ will not agree with the percent composition. (SiBr₃ is 10.5% Si and 89.5% Br) Since 2.667 = 2\frac{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 CuCl₂·2H₂O has a percentage of the compound that is H₂O and a percentage that is the anhydrous (without water) CuCl₂. This is easily calculated from the molecular weight:

MW of CuCl₂·2H₂O is \( 134.5 = 63.55 + 2 \times 35.45 + 2 \times 18.016 = 170.5 \)

\[
\% \text{ CuCl}_2 = \frac{134.5 \text{ g CuCl}_2}{170.5 \text{ g CuCl}_2 \cdot 2\text{H}_2\text{O}} \times 100\% = 78.9 \% \text{ CuCl}_2
\]

\[
\% \text{ H}_2\text{O} = \frac{2 \times 18.016 \text{ g H}_2\text{O}}{170.5 \text{ g CuCl}_2 \cdot 2\text{H}_2\text{O}} \times 100\% = 21.1 \% \text{ H}_2\text{O}
\]

Problem:
The hydrated compound CuCl₂·xH₂O 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 CuCl₂ and H₂O in the compound.

Calculate moles of CuCl₂ and H₂O in 100.0 g of the hydrate, CuCl₂·xH₂O.

\[
78.9 \text{ g CuCl}_2 \times \frac{1 \text{ mol CuCl}_2}{134.5 \text{ g CuCl}_2} = 0.587 \text{ mol CuCl}_2
\]

\[
21.1 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.016 \text{ g H}_2\text{O}} = 1.17 \text{ mol H}_2\text{O}
\]

so \[
\frac{1.17 \text{ mol H}_2\text{O}}{0.587 \text{ mol CuCl}_2} = 1.99 \text{ so x must equal 2,}
\]

i.e., in the hydrate there are 2 moles of water per every mole of CuCl₂.

The formula for the hydrate is: CuCl₂·2H₂O

Try these problems:
1. VSO₄·xH₂O is 46.175 % water; calculate the value of x.
2. Mg₂Fe(CN)₆·xH₂O 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 VSO₄·7H₂O  2. x= 12 Mg₂Fe(CN)₆·12H₂O  3. Np₇O₄