Lecture 4:

Stoichiometry

Contents

Key words: stoichiometry, ideal gas law, Dalton's law, mole fraction

Preamble

Many of the materials balance problems that arise in metal extraction processes can be solved easily with either.

a) Knowledge of atomic/molecular weights of reactants and products appearing in a balanced chemical reaction, or
b) From mass of compound contained in a given volume of gas.

Stoichiometry can be used to develop the above relationship.

Basics of stoichiometry

i) Atomic or molecular mass of an element and compound. Molecular weight of a compound is the addition of molecular weight (Atomic weight) of elements comprising the compound.
For example,
Molecular weight of $\mathrm{ZnS} =$ molecular weight of $\mathrm{Zn} +$ molecular weight of S
$$= 65.34 + 32$$
$$= 97.34 \text{ or } \approx 97 \frac{\mathrm{kg}}{\mathrm{kg\ mole}} \text{ or } \frac{\mathrm{g}}{\mathrm{g\ mole}}.$$
Similarly molecular weight of $\mathrm{Fe_2O_3} = 160 \frac{\mathrm{kg}}{\mathrm{kg\ mole}}$

ii) <u>The chemical equation: law of conservation of mass</u>

For any chemical reaction, the number of atoms of elements in the product = No. of atoms of that elements in the reactants.

To avoid confusion and error particularly in thermodynamic calculations, physical forms of reactants and products should also be mentioned in parentheses of chemical symbols e.g.

(s) solid, (l) liquid and (g) gas

$2\ \mathrm{Fe(s)} + \frac{3}{2}(\mathrm{O_2})_\mathrm{g} = \mathrm{Fe_2O_3(s)}$

$\mathrm{Cu_2\ S(l) + O_2(g) = 2Cu(l) + SO_2(g)}$

Balanced equation shows

1) 1 mole of $\mathrm{Cu_2S}$ combines with 1 moles of $\mathrm{O_2}$ to give 2 moles of Cu and 1 mole of $\mathrm{SO_2}$
2) 2 moles of Cu atoms in $\mathrm{Cu_2S}$ from 2 moles of liquid Cu.
3) 1 mole of S in $\mathrm{Cu_2S}$ forms 1 mole of $\mathrm{SO_2}$
4) 1 mole of $\mathrm{O_2}$ forms 1 mole of $\mathrm{SO_2}$
5) 1 mole of $\mathrm{Cu_2S}$ requires 1 mole of $\mathrm{O_2}$to form 2 moles of Cu and 1 mole of $\mathrm{SO_2}$.

How may moles of $\mathrm{SO_2}$ are produced when 1 ton of Cu matte containing $60\%\mathrm{Cu_2S}$ and 40% FeS is converted to liquid Cu and iron oxide

$600\mathrm{Kg\ Cu_2S} = 3.77\mathrm{Kg\ moles}$

$400\mathrm{Kg\ Fe\ S} = 4.551\ \mathrm{Kg\ moles}$

The balanced chemical equation is

$3.77\ \mathrm{Cu_2S} + 3.77\ \mathrm{O_2}\ = 7.54\mathrm{Cu} + 3.77\ \mathrm{S\ O_2}$

Moles of $\mathrm{SO_2}\mathrm{produced}\ =\ 8.32\ \mathrm{Kg\ moles}$

Ideal gas law:

Most gases involved in metallurgical processes at high temperature follow ideal gas behavior.

$\mathrm{PV = nRT}$ (1)

In the equation 1 P is pressure, T is temperature and n is moles of gas. 1 Kg mole gas at $(1.01325 \times 10^5\ \mathrm{atm.\ presssure\ 273K}) = 22.4\ \mathrm{m^3}$and $1\ \mathrm{lb\ mole\ of\ gas}\ =\ 359\mathrm{ft}^3$.

$\frac{\mathrm{V}}{\mathrm{n}} = \frac{\mathrm{RT}}{\mathrm{P}}$ (2)

At any given T and P volume/ mole or no of mole in a given volume of gas is same.

In gas mixtures made up of ideal gases, each component of the mixture obeys the ideal gas law. For $\mathrm{i^{th}}$ component of an ideal mixture contained in a volume V at T

$P_i V = n_i RT$ (3)

Pi= partial pressure and n_i number of moles of component i.

Ideal gases obey Dalton's law

$P_t = \sum_{i=1}^{n} p_i$ (4)

For ideal gas mixture

$V \sum_i^n p_i = (\sum_i^n n_i)RT$ (5)

V is volume, $i =$ number components, R is universal gas constant, n is number of moles of component I and T is temperature p is partial pressure.

Thus for mixture of n component

$VP_t = n_t RT$ (6)

P_t is total pressure as given by equation 4 and n_t is total number of moles of gas in the mixture. The ratio between partial pressure and total pressure is

$\frac{p_i}{p_t} = \frac{n_i}{n_t} = X_i$ (7)

Here X_i is mole fraction of i^{th} component in the mixture. The ratio between volume of a component with total volume at constant temperature and pressure is

$\frac{V_i}{V_t} = \frac{n_i}{n_t}$.

$\therefore \text{volume}(\%i) = 100 \times \frac{V_i}{V_t} = 100 \times X_i$

Therefore for ideal gases volume percent equals mole percent.

Calculate the partial pressure of CO_2 and H_2O on complete combustion of CH_4 with pure stoichiometric amount of oxygen.

$CH_4(g) + 2\ O_2(g) = CO_2\ (g) + 2\ H_2O(g)$

$X_{CO_2} = \frac{nCO_2}{nCO_2 + 2nH_2O} = 0.33$

$X_{H_2O} = \frac{nH_2O}{nCO_2 + 2nH_2O} = 0.67.$

$p_{CO_2} = X_{CO_2} \times P_t = 0.33$ atmoshpere

$p_{H_2O} = X_{H_2O} \times P_t = 0.67$ atmosphere

$$X_{CO_2} = \frac{V_{CO_2}}{V_t} = 0.33;\ \frac{V_{H_2O}}{V_t} = X_{H_2O} = 0.67$$

Thus, in ideal gases partial pressure and volume fraction of a component is same.

Excess and limiting reactants

The exact amount of the reactants can be determined by the stoichiometry of the reaction. In many cases one or more reactants is supplied in excess to complete the reaction. Reactant present in the smallest stoichiometric amount is called the limiting reactant. Reactants supplied in excess of the limiting reactant are called excess reactants.

$$\%\ \text{excess} = \frac{\text{moles in excess}}{\text{moles reqd.for components reaction}} \times 100$$

Oxidation- Reduction Reactions.

Oxidation: Loss of electrons from an atom

Reduction: Gain of electrons by an atom

Oxidation and reduction always occurs simultaneously so that electrons are conserved.

Cementation reaction $Cu^{2+}(\text{in aqueous solution}) \rightarrow Cu(s)$

$$Cu^{2+} + 2\bar{e} = Cu$$

$$Fe = Fe^{2+} + 2\bar{e}$$

$$Cu^{2+}_{(\text{aq sol.})} + (Fe_s) = Cu_{(s)} + Fe^{2+}_{(\text{aq.sol})}.$$

Conclusion

In this lecture basics of stoichiometry are discussed. The concepts are illustrated with suitable examples. The reader may solve more problems to develop skills in stoichiometric calculations. Some problems are discussed in lecture 5.

References

1. R. Schuhmann, JR. Metallurgical engineering, volume 1
2. Geiger: energy balance in metallurgical processes