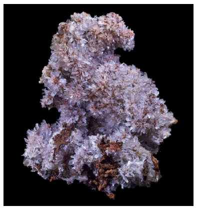
3.3.7: Geology- Using the Acid Test to Distinguish the Minerals in "Calomine"

Calamine is an obsolete name for what is now known to be a mixture of two distinct minerals: zinc carbonate ($ZnCO_3$ or smithsonite) and zinc silicate ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, or hemimorphite). the name "Calamine" is now used only for calomine lotion, which is a suspension of ZnO and Fe_2O_3[1].

Smithsonite and hemimorphite may be similar in appearance to one another, but their appearance may be quite variable depending on location, so two samples of smithsonite (or hemimorphite) may look quite different as shown in the figures:

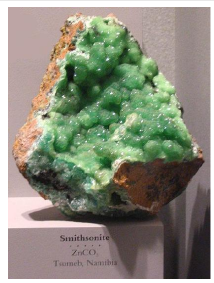


Solid chunk of mineral with many crystalline spikes all around. This mineral has a light purple hue.

Hemimorphite from Mapimi, Durango, Mexico[2]

Hemimorphite[3]

Smithsonite from Tsumeb, Namibia[4]



Smithsonite from Tsumeb, Namibia[5]

The two minerals can only be reliably distinguished through chemical analysis.

Carbonate minerals like calcite or smithsonite react with acids to efforvesce (fizz) while dissolving and producing CO_2(see equation (1) below). This test can be done with 1 M HCl, or household vinegar (crushing the sample will help if vinegar is used). While calcite ($CaCO_3$) bubbles strongly in cold dilute acid, dolomite $CaMg(CO_3)_2$) and rhodochrosite ($MnCO_3$) bubble weakly. Smithsonite (along with Siderite, $FeCO_3$ and Magnesite, $MgCO_3$) require heating to react.

Silicates, like hemimorphite, don't generally react with cold, dilute acids at all. So we could tell if a sample contained just smithsonite, because it would ocmpletely dissolve in acid. hemimorphite would not react, and a mixture of the two would partially dissolve.

It would be necessary to add an excess of HCl to the sample, otherwise it might not all dissolve because there isn't enough HCl, not because it's partially hemimorphite. If we have a 100 g sample that may contain smithsonite, hemimorphite, or both, we need to add enough acid to react with the sample, assuming it's all smithsonite, just to make sure.

Example 4 from Equations and Mass Relationships also illustrates the idea that one reactant in a chemical equation may be completely consumed without using up all of another. Here we want the smithsonite to be completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first (the smithsonite) is the **limiting reagent**.

EXAMPLE 1 When 100.0 g of smithsonite is reacted with 100.0 g of HCl to form carbon dioxide gas, which is the limiting reagent? What mass of product will be formed? (Note: HCl is provided as a solution with a concentration of 1-5% HCl for this purpose. The mass of HCl solution would be much (20-100 times) greater than the mass of HCl given here).

Solution

The balanced equation

$ZnCO_3 + 2\ HCl \rightarrow ZnCl_2 + CO_2 + H_2O$ (1) tells us that according to the atomic theory, 2 mol HCl are required for each mole of $ZnCO_3$. That is, the stoichiometric ratio S($HCl/ZnCO_3$) = 2 mol HCl/ 1 mol $ZnCO_3$. Let us see how many moles of each we actually have

$$n_{\mathrm{HCl}} = 100.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ HCl}}{36.5\ \mathrm{g}} = 2.74\ \mathrm{mol\ HCl} \tag{3.3.7.1}$$

$$n_{\mathrm{ZnCO_3}} = 100.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ ZnCO_3}}{125.4\ \mathrm{g}} = 0.798\ \mathrm{mol\ ZnCO_3} \tag{3.3.7.2}$$

Calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting.

For example, if all the HCl were to react, it would require

$\frac{1\ \mathrm{mol\ ZnCO_3}}{2\ \mathrm{mol\ HCl}}\ x\ \ 2.74\ \mathrm{mol\ HCl} = 1.37\ \mathrm{mol\ ZnCO_3}$

Since there is not this much $ZnCO_3$ present, this is impossible. HCl is in excess, and $ZnCO_3$ is the limiting reactant. In the table, we've crossed out this calculation, and proceeded to calculate how much HCl would be required if all the $ZnCO_3$ reacts (which is what happens).

calculations of how much HCl would be required if all the ZnCO3 reacts

	$ZnCO_3$	+ HCl	→ $ZnCl_2$	+ CO_2	+ H_2O
m (g)	100	100			
M (g/mol)	125.1	36.5	136.3	44.0	18.0
n (mol)	0.798	2.74			
if all $ZnCO_3$ reacts	-0.798	-1.60	+0.798	+0.798	+0.798
~~if all HCl reacts~~	~~-2.74~~	~~-1.37~~			
Actual Reaction Amounts	-0.798	-1.60	+0.798	+0.798	+0.798
Actual Reaction Masses	-100	-58.4	+108.8	+35.1	+14.4

We use the amount of limiting reagent to calculate the amount of product formed.

$\frac{1\ \mathrm{mol\ CO_2}}{1\ \mathrm{mol\ ZnCO_3}}\ x\ \ 0.798\ \mathrm{mol\ ZnCO_3} = 0.798\ \mathrm{mol\ CO_2}$

$0.798\ \mathrm{mol\ CO_2}\ \ x\ \frac{44.0\ \mathrm{g\ CO_2}}{1\ \mathrm{mol\ CO_2}} = 35.1\ \mathrm{g\ CO_2}$

When the reaction ends, 1.60 mol HCl will have reacted with 0.798 mol $ZnCO_3$ and there will be

(2.74 – 1.60) mol HCl = 1.14 mol HCl left over. $ZnCO_3$ is therefore the limiting reagent. The left over HCl will ensure that if any material remains in a mineral test of a 100 g sample, that it can't be a carbonate.

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together. In Example 1 this ratio of initial amounts $\frac{n_{\mathrm{ZnCO_3}}(\mathrm{initial})}{n_{\mathrm{HCl}}(\mathrm{initial})} = \frac{0.798\ \mathrm{mol\ ZnCO_3}}{2.74\ \mathrm{mol\ HCl}} = \frac{0.291\ \mathrm{mol\ ZnCO_3}}{1\ \mathrm{mol\ HCl}}$ was less than the stoichiometric ratio $\mathrm{S}\left(\frac{\mathrm{ZnCO_3}}{\mathrm{HCl}}\right) = \frac{1\ \mathrm{mol\ ZnCO_3}}{2\ \mathrm{mol\ HCl}} = \frac{0.5\ \mathrm{mol\ ZnCO_3}}{1\ \mathrm{mol\ HCl}}$ This indicated that there was not enough Hg to react with all the bromine and mercury was the limiting reagent. The corresponding general rule, for any reagents X and Y, is

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is less than S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right)\text{, then X is limiting.} \tag{3.3.7.3}$$

$$\tag{3.3.7.4}$$

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is greater than S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right)\text{, then Y is limiting.} \tag{3.3.7.5}$$

(Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.). This general rule for determining the limiting reagent is applied in the next example.

EXAMPLE 2 Iron can be obtained by reacting the ore hematite (Fe_2O_3) with coke (C). The latter is converted to CO_2. As manager of a blast furnace you are told that you have 20.5 Mg (megagrams) of Fe_2O_3 and 2.84 Mg of coke on hand. (a) Which should you order first—another shipment of iron ore or one of coke? (b) How many megagrams of iron can you make with the materials you have?

Solution

a) Write a balanced equation $2Fe_2O_3 + 3C \rightarrow 3CO_2 + 4Fe$

The stoichiometric ratio connecting C and Fe_2O_3 is $\mathrm{S}\left(\frac{\mathrm{C}}{\mathrm{Fe_2O_3}}\right) = \frac{3\text{ mol C}}{2\text{ mol Fe}_2\mathrm{O}_3} = \frac{1.5\text{ mol C}}{1\text{ mol Fe}_2\mathrm{O}_3}$ The initial amounts of C and Fe_2O_3 are calculated using appropriate molar masses

$$n_{\mathrm{C}}(\text{initial}) = 2.84 \times 10^6\text{g} \times \frac{1\text{ mol C}}{12.01\text{ g}} = 2.36 \times 10^5\text{mol C} \tag{3.3.7.6}$$

$$\tag{3.3.7.7}$$

$$n_{\mathrm{Fe_2O_3}}(\text{initial}) = 20.5 \times 10^6\text{g} \times \frac{1\text{ mol Fe}_2\mathrm{O}_3}{159.69\text{ g}} = 1.28 \times 10^5\text{mol Fe}_2\mathrm{O}_3 \tag{3.3.7.8}$$

Their ratio is $\frac{n_{\mathrm{C}}(\text{initial})}{n_{\mathrm{Fe_2O_3}}(\text{initial})} = \frac{2.36\times10^5\text{mol C}}{1.28\times10^5\text{mol Fe}_2\mathrm{O}_3} = \frac{1.84\text{ mol C}}{1\text{ mol Fe}_2\mathrm{O}_3}$ Since this ratio is larger than the stoichiometric ratio, you have more than enough C to react with all the Fe_2O_3. Fe_2O_3 is the limiting reagent, and you will want to order more of it first since it will be consumed first. b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant C will be left over, but all the initial amount of Fe_2O_3 will be consumed. Therefore we use n_{Fe2O3} (initial) to calculate how much Fe can be obtained $n_{\mathrm{Fe_2O_3}} \xrightarrow{S(\mathrm{Fe/Fe_2O_3})} n_{\mathrm{Fe}} \xrightarrow{M_{\mathrm{Fe}}} m_{\mathrm{Fe}}$ $m_{\mathrm{Fe}} = 1.28 \times 10^5 \text{ mol Fe}_2\mathrm{O}_3 \times \frac{4\text{ mol Fe}}{2\text{ mol Fe}_2\mathrm{O}_3} \times \frac{55.85\text{ g}}{\text{mol Fe}} = 1.43 \times 10^7 \text{ g Fe}$ This is 1.43×10^6 g, or 14.3 Mg, Fe. As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

The concept of a limiting reagent was used by the nineteenth century German chemist Justus von Liebig (1807 to 1873) to derive an important biological and ecological law. **Liebig's law of the minimum** states that the essential substance available in the smallest amount relative to some critical minimum will control growth and reproduction of any species of plant or animal life. When a group of organisms runs out of that essential limiting reagent, the chemical reactions needed for growth and reproduction must stop. Vitamins, protein, and other nutrients are essential for growth of the human body and of human populations. Similarly, the growth of algae in natural bodies of water such as Lake Erie can be inhibited by reducing the supply of nutrients such as phosphorus in the form of phosphates. It is for this reason that many states have regulated or banned the use of phosphates in detergents and are constructing treatment plants which can remove phosphates from municipal sewage before they enter lakes or streams.

References

1. ↑ en.Wikipedia.org/wiki/Calamine_lotion
2. ↑ en.Wikipedia.org/wiki/Hemimorphite
3. ↑ en.Wikipedia.org/wiki/Hemimorphite
4. ↑ en.Wikipedia.org/wiki/Smithsonite
5. ↑ en.Wikipedia.org/wiki/Smithsonite