**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$_4$Si$_2$O$_7$(OH)$_2$·H$_2$O, or hemimorphite). The name "Calamine" is now used only for calamine lotion, which is a suspension of ZnO and Fe$_2$O$_3$[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:

![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 completely 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.

**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

\[
\text{ZnCO}_3 + \text{HCl} \rightarrow \text{ZnCl}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

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

\[
\text{if all HCl reacts} \quad -2.74\quad -1.37
\]

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).

<table>
<thead>
<tr>
<th></th>
<th>ZnCO$_3$</th>
<th>+ HCl</th>
<th>→ ZnCl$_2$</th>
<th>+ CO$_2$</th>
<th>+ H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (g)</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M (g/mol)</td>
<td>125.1</td>
<td>36.5</td>
<td>136.3</td>
<td>44.0</td>
<td>18.0</td>
</tr>
<tr>
<td>n (mol)</td>
<td>0.798</td>
<td>2.74</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>if all ZnCO$_3$ reacts</td>
<td>-0.798</td>
<td>-1.60</td>
<td>+0.798</td>
<td>+0.798</td>
<td>+0.798</td>
</tr>
<tr>
<td>if all HCl reacts</td>
<td>-2.74</td>
<td>-1.37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual Reaction Amounts</td>
<td>-0.798</td>
<td>-1.60</td>
<td>+0.798</td>
<td>+0.798</td>
<td>+0.798</td>
</tr>
<tr>
<td>Actual Reaction Masses</td>
<td>-100</td>
<td>-58.4</td>
<td>+108.8</td>
<td>+35.1</td>
<td>+14.4</td>
</tr>
</tbody>
</table>

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

(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$_2$O$_3$) 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$_2$O$_3$ 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 $2\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 3\text{CO}_2 + 4\text{Fe}$

b) $2323\text{consumed}23\text{nFe}_2\text{O}_3$

$^6$the initial amount of the limiting reagent must be used to calculate the amount of product formed

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
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