Lecture – 15

Volatilization Gravimetry

A second approach to gravimetry is to thermally or chemically decompose a solid sample. The volatile products of the decomposition reaction may be trapped and weighed to provide quantitative information. Alternatively, the residue remaining when decomposition is complete may be weighed. In thermogravimetry, which is one form of volatilization gravimetry, the sample's mass is continuously monitored while the applied temperature is slowly increased.

Theory and Practice

Whether the analysis is direct or indirect, volatilization gravimetry requires that the products of the decomposition reaction be known. This requirement is rarely a problem for organic compounds for which volatilization is usually accomplished by combustion and the products are gases such as CO_2, H_2O, and N_2. For inorganic compounds, however, the identity of the volatilization products may depend on the temperature at which the decomposition is conducted.

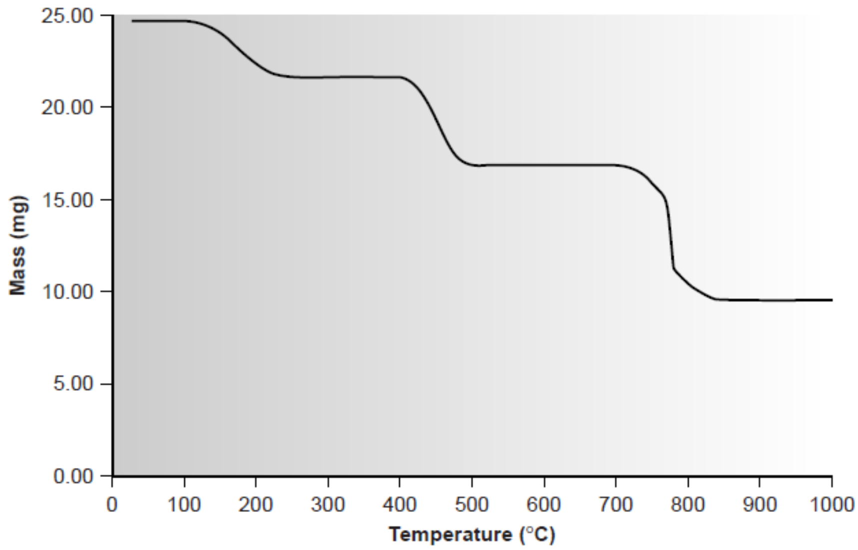

Figure.15.1 Thermogram for $CaC_2O_4.H_2O$

Thermogravimetry: The products of a thermal decomposition can be deduced by monitoring the sample's mass as a function of applied temperature. (Figure 15.1). The loss of a volatile gas on thermal decomposition is indicated by a step in the **thermogram**. As shown in Example 15.1, the change in mass at each step in a thermogram can be used to identify both the volatilized species and the solid residue.

EXAMPLE 15.1

The thermogram in Figure 15.1 shows the change in mass for a sample of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$. The original sample weighed 24.60 mg and was heated from room temperature to 1000 °C at a rate of 5 °C min. The following changes in mass and corresponding temperature ranges were observed:

Loss of 3.03 mg from 100–250 °C
Loss of 4.72 mg from 400–500 °C
Loss of 7.41 mg from 700–850 °C

Determine the identities of the volatilization products and the solid residue at each step of the thermal decomposition.

SOLUTION:

The loss of 3.03 mg from 100–250 °C corresponds to a 12.32% decrease in the original sample's mass.

$$\frac{3.03 \text{ mg}}{24.60 \text{ mg}} \times 100 = 12.32\%$$

In terms of $CaC_2O_4 \cdot H_2O$, this corresponds to a loss of 18.00 g/mol.

0.1232×146.11 g/mol = 18.00 g/mol

The product's molar mass, coupled with the temperature range, suggests that this represents the loss of H_2O. The residue is CaC_2O_4.
The loss of 4.72 mg from 400–500 °C represents a 19.19% decrease in the original mass of 24.60 g, or a loss of

0.1919×146.11 g/mol = 28.04 g/mol

This loss is consistent with CO as the volatile product, leaving a residue of $CaCO_3$.
Finally, the loss of 7.41 mg from 700–850 °C is a 30.12% decrease in the original mass of 24.60 g. This is equivalent to a loss of

0.3012×146.11 g/mol = 44.01 g/mol

suggesting the loss of CO_2. The final residue is CaO.

Once the products of thermal decomposition have been determined, an analytical procedure can be developed. For example, the thermogram in Figure 15.1 shows that a precipitate of $CaC_2O_4 \cdot H_2O$ must be heated at temperatures above 250 °C, but below 400 °C if it is to be isolated as CaC_2O_4. Alternatively, by heating the sample to 1000 °C, the precipitate can be isolated as CaO. Knowing the identity of the volatilization products also makes it possible to design an analytical method in which one or more of the gases are trapped. Thus, a sample of $CaC_2O_4 \cdot H_2O$ could be analyzed by heating to 1000 °C and passing the volatilized gases through a trap that selectively retains H_2O, CO, or CO_2.

Practice Exercise

Under the same conditions as Figure 8.9, the thermogram for a 22.16 mg sample of $MgC_2O_4 \cdot H_2O$ shows two steps: a loss of 3.06 mg from 100–250°C and a loss of 12.24 mg from 350–550°C. For each step, identify the volatilization product and the solid residue that remains.

Solution

From 100–250°C the sample loses 13.8% of its mass, or a loss of

$$0.138 \times 130.35 \text{g/mol} = 18.0 \text{g/mol}$$

consistent with the loss of $H_2O(g)$, leaving a residue of MgC_2O_4. From 350–550°C the sample loses 55.23% of its original mass, or a loss of

$$0.5523 \times 130.35 \text{g/mol} = 71.99 \text{g/mol}$$

This weight loss is consistent with the simultaneous loss of $CO(g)$ and $CO_2(g)$, leaving a residue of MgO.

References:

- Modern of Analytical Chemistry by David Harvey (DePauw University)