# Thermal Analysis

**Manuel Minas da Piedade**

*Departamento de Química e Bioquímica, FCUL, Portugal*

Questions

# Q1

Briefly explain the main differences between differential scanning calorimetry, thermomicroscopy and thermogravimetry.

# Answer Q1

The three methods allow the study of the physical and chemical transformations occurring in a sample as it is subjected to a programmed temperature change. In differential scanning calorimetry the changes are detected and characterized by monitoring the difference between the heat fluxes transmitted to a sample (S) and a reference material (R). In thermomicroscopy variations in morphology, optical properties, gas release phenomena, etc. are monitored with a microscope. In thermogravimetry the changes are detected by the change in mass of the sample.

# Q2

One of the most important analytical applications of differential scanning calorimetry (DSC) is the determination of the purity of solid samples.

a) Explain why this determination is only valid when the sample purity is very high (typically when the weight% is greater than 98%).

b) The fusion of naphthalene was studied by DSC and the corresponding fusion enthalpy was obtained as $\Delta_{fus}H_m$ = 18.17 kJ·mol$^{-1}$. It was also found that a plot of the fusion temperature, $T$, as a function of the melted fraction, $F$, could be described by the equation:

$$T = -\frac{0.09}{F} + 346.57$$

Estimate the molar fraction of impurity contained in the naphthalene sample and the melting temperature of 100% pure naphthalene.
*Note*: $R$ = 8.31451 J·K$^{-1}$·mol$^{-1}$;

# Answer Q2

a) Purity determination by DSC is based on the van't Hoff equation, which is only valid for ideal solutions. This model is all the more valid the more diluted the solution, that is, the smaller the amount of impurity.

b) The fusion temperature, $T$, is related to the melted fraction, $F$, through:

$$T = T_o - \frac{RT_o^2 x}{F\Delta_{fus}H}$$

where $T_o$ is the fusion temperature of the 100% pure compound, $R$ is gas constant, $x$ is the molar fraction of impurity, and $\Delta_{fus}H$ is the enthalpy of fusion. Comparing this equation with the linear relation given in the problem, it is concluded that:

$$T_o = 346.57 \text{ K}$$

$$\frac{RT_o^2 x}{\Delta_{fus}H} = 0.09$$

$$x = \frac{18.17 \times 10^3 \times 0.09}{8.31451 \times 346.57^2} = 1.637 \times 10^{-3}$$

$$\text{purity} = 1 - 1.637 \times 10^{-3} \equiv 99.8\%$$

# Q3

2) A study of the thermal decomposition of a 10 mg calcium oxalate sample by thermogravimetry led to the results in Figure 1. Show that these results are compatible with the following reaction:
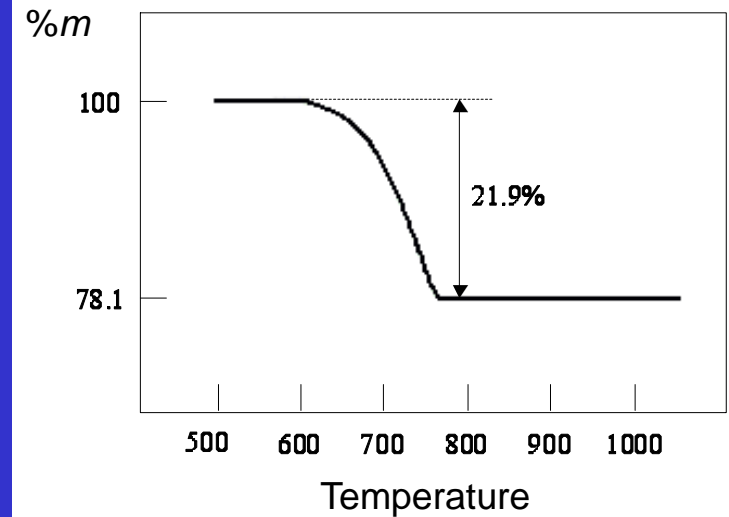
$$CaC_2O_4(s) \rightarrow CaCO_3(s) + CO(g) \qquad (1)$$

*Note*:
$M(CaC_2O_4) = 128.0970 \ g \cdot mol^{-1}$
$M(CaCO_3) = 100.0869 \ g \cdot mol^{-1}$
$M(CO) = 28.0101 \ g \cdot mol^{-1}$

# Answer Q3

The amount of substance (in mol) of $CaC_2O_4$ used is:

$$n(CaC_2O_4) = \frac{0.01}{128.0970} = 7.8066 \times 10^{-5}$$

Taking into account the reaction stoichiometry, it is possible to conclude that the number of moles of CO produced is identical to that of $CaC_2O_4$. Consequently, the mass of CO released will be:

$$m(CO) = (7.8066 \times 10^{-5}) \times 28.0101 = 2.1867 \times 10^{-3} \text{ g} \equiv 2.1867 \text{ mg}$$

This mass corresponds to:

$$\frac{2.1867}{10} = 0.219 \equiv 21.9\%$$

Therefore, given the experimentally observed mass loss, it is concluded that the results are compatible with the indicated reaction for the decomposition of calcium oxalate.