MSE 310 Lecture 4

Differential Thermal Analysis (DTA)

It is well known that, at a given temperature, every system has a tendency to attain the state of minimum free energy. For example, the transition of a substance to another, which ever has a lower free energy that is more stable. The formation of a more stable substance with a lower free energy may take place on gradually heating the sample via intermediate steps such as melting, sublimation, change of crystalline structure, chemical reaction etc.. Such a transformation is characterized by the temperature at which it occurs and by a change in the heat content, manifested by an increase or decrease in temperature, depending on whether the reaction is exo- or endothermic. This is the basis of differential thermal analysis.

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

Every physico-chemical transformation is accompanied by liberation or absorption of heat, causing a change in temperature of the sample. The method of Differential Thermal Analysis (DTA) is capable of detecting temperature changes accompanying a change in weight (e.g. decomposition of a substance) as well as the changes not 6.1 accompanied by change in weight (e.g. change in crystal structure, or melting), the latter being the main advantage of DTA over thermogravimetry. Thus DTA is the recording of every enthalpy change (exo- or endothermic) caused by any structural or chemical change. DTA is a dynamic method in which the equilibrium condition is not attained. The temperature determined in this way therefore does not correspond to a thermodynamic equilibrium temperature.

Principle

The basic **principle** involved in DTA is the temperature difference (ΔT) between the test sample and an inert reference sample under controlled and identical conditions of heating or cooling is recorded continuously as a function of temperature or time, thus the heat absorbed or emitted by a chemical system is determined.

Instrumentation and working of DTA

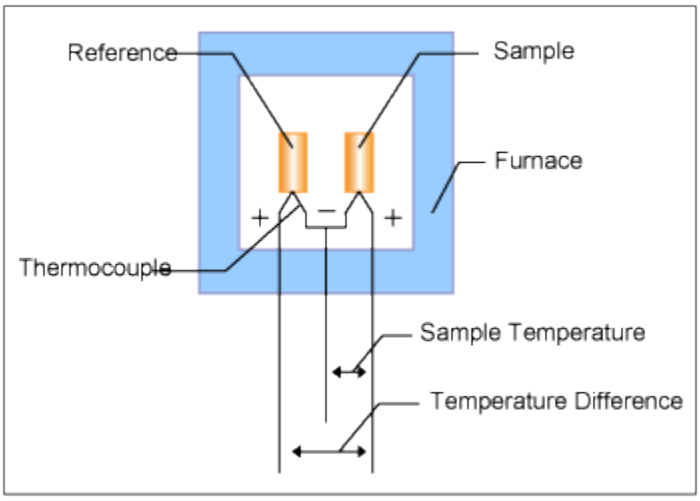
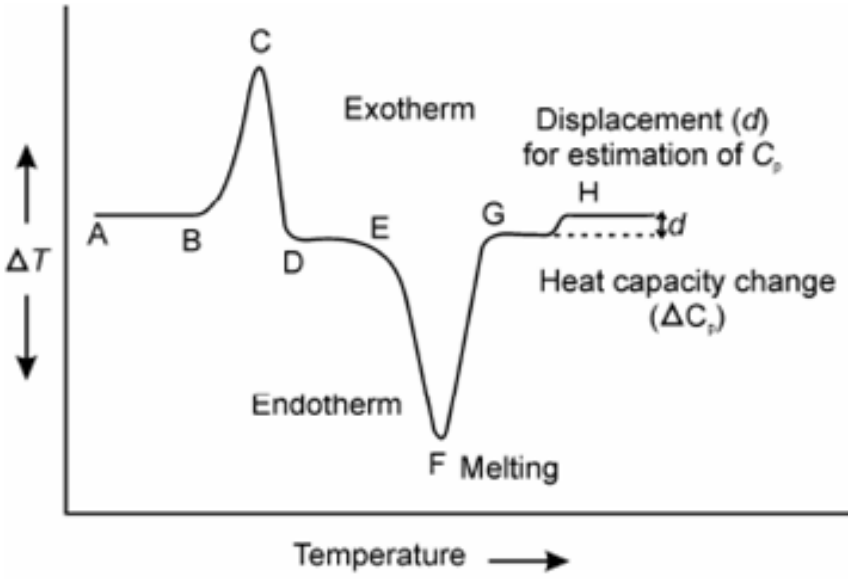


Figure 1 shows the block diagram of DTA.

Differential thermal analysis is usually performed in a furnace, as this is the most efficient way to obtain a uniform temperature in the surrounding environment—especially with modern-day furnaces. The sample and the reference are placed symmetrically in the furnace. The furnace is controlled under a temperature program and the temperature of the sample and the reference are changed. Matters that do not change in the measurement temperature range (usually α-alumina) are used as reference.

The temperature itself is recorded using two thermocouples, which are specialist (and versatile) types of temperature sensors that use metal wires to form hot and cold junctions. The hot junction measures the temperature of the material while the cold junction provides a reference to compare the analysis temperature against. This is what happens inside every thermocouple to determine the temperature of a material. The reference, in this case, is not the reference temperature of the DTA analysis, rather, it is the reference inside each thermocouple device. So, two thermocouples are needed because one thermocouple measures the temperature of the sample, and the other measures the reference.

Aside from the thermocouples and the furnace, voltmeters are also employed to measure the voltages across the thermocouples (which is how they determine the temperature), as well as crucibles that are often used to hold the material—especially when small samples are under analysis. Inside the furnace, inert gases such as argon or helium are also used, as they don't react with the sample or the reference materials, and this ensures that there is no interference during the measurements. In most cases, the analysis environment is air-tight to prevent any contaminants from affecting the results. Most furnaces used in modern-day DTA approaches can also provide a temperature environment from -150 °C and 2400 °C. Additionally, many different crucibles can be used, and the combination of these two factors enable a wide range of materials to be analyzed—and this is why differential thermal analysis spans many different industrial sectors.



To perform the analysis itself, both the sample material and the reference material are placed symmetrically in the furnace. The two materials then undergo a controlled program of heating and cooling, where both temperatures are kept as constant as possible (within a reasonable error) during each cycle. There is usually

a slight delay in the recording of data due to the furnace heating up (and the length of delay typically depends on the heat capacity of the material).

DTA Graph

During the analysis, the temperature difference is plotted on a graph against time. In some cases, it can also be plotted against temperature. From here (and how the curve manifests itself), the endothermic and exothermic transition temperatures of a material can be determined, and these larger classification categories include the glass transition temperature of the material, the crystallization temperature of a material, the melting temperature of a material, and the sublimation temperature of the material. These are often deduced because the changes in the temperature against the reference material can determine whether the material is absorbing heat (endothermic) or is giving out heat (exothermic). The presence of the thermocouples also helps to easily identify if a phase transition has occurred, because the voltmeter attached to the reference thermocouple will jump slightly when the phase change happens. This is due to the latent heat which arises from the material phase change causing the temperature of the inert gas to raise slightly (which in turn affects the voltage of the reference thermocouple).

Aside from conventional temperature phase transitions, differential thermal analysis can also be used to measure two inert samples when their responses to the heat cycle are not identical. In these specific cases, DTA can also be used to identify any phase changes that are not based around a change in enthalpy. These are often identified by discontinuities in the curve on a DTA graph.

Conclusion

While differential thermal analysis is formally defined as a method of determining the temperature difference between sample and reference materials, in practice, it can tell the user a lot about the phase properties of a material at different temperatures. The amount of information obtainable is of great benefit to many industries, hence it’s widespread use.