EXPERIMENT 4 - Constructing a Solid-Liquid Phase Diagram Using Differential Scanning Calorimetry

Objective

The purpose of this laboratory is to use a modern differential scanning calorimeter to measure the liquid-solid phase diagram (T-χ) and associated thermodynamic parameters (eutectic point, ΔH, C_p, ΔS, etc..) of a binary compound or elemental system.

Introduction

The objective of calorimetry is the measurement of heat (Q). There are many types of calorimeters used to measure heat in many different situations. These include (i) bomb calorimeters which are used to measure heats of combustion, (ii) drop calorimeters which measure heat capacities or enthalpy differences very quickly, (iii) adiabatic calorimeters which are used to measure heats of transition and heat capacities, (iv) flow calorimeters which are typically used measure the heat generation from biological systems, and (v) isoperibol mixing calorimeters which are used to investigate reactions between two fluids or between a fluid and a solid. Differential scanning calorimeters use a differential method of measurement and all systems have the characteristic feature of having a twin-type design in which the direct in-difference connection of the two measuring systems is measured [1].

Differential Scanning Calorimetry

In all Differential Scanning Calorimeters (DSC), the difference in temperature between a reference pan and a sample pan (ΔT) is expressed as a voltage. In almost all modern instruments, a heat flow rate (Φ_m) is internally assigned to ΔT. All heat flow in the system is approximately proportional to temperature difference, via Newton's law of cooling (often described in this context as the thermal analog of Ohm's law):

$$\frac{d\Phi}{d\tau} = K\Delta T \tag{10.1}$$

where $\frac{d\Phi}{d\tau}$ is the heat flow between two stages separated in temperature (ΔT) by a barrier with a heat transfer coefficient (K). The thermal resistance (R) is the inverse of the heat transfer coefficient.

When a sample (s) is being scanned at a temperature rate $\frac{dT_s}{d\tau}$, the heat flow is also proportional to the heat capacity of the sample (C_s).

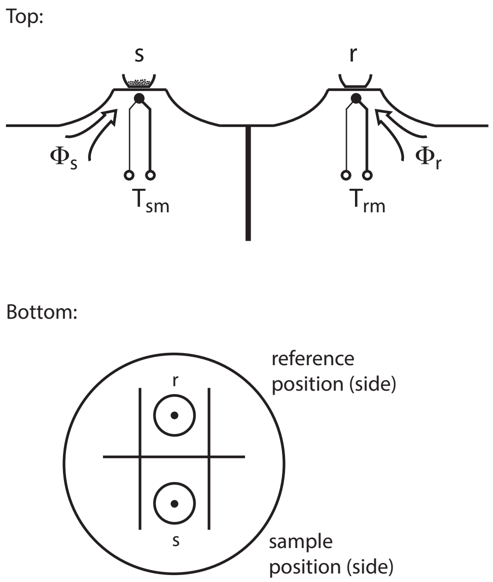

Figure 10.1: Schematic of the sample area in a heat-flow differential scanning calorimeter.

$$\frac{d\Phi_s}{d\tau} = C_s \frac{dT_s}{d\tau} \tag{10.2}$$

A similar expression can be derived for the reference side (r). A more detailed analysis relies on knowing whether the DSC is a heat-flux or a power-compensated electronic design. In the case of TA Instrument DSC's, these are heat-flux designed systems where the primary signal obtained can be expressed as

$$signal \equiv T_{rm} - T_{sm} = R\frac{dT}{d\tau}(C_s - C_r) \tag{10.3}$$

where T_{rm} is the temperature measured (m) at the reference thermocouple, T_{sm} is the temperature measured at the sample thermocouple, $\frac{dT}{d\tau}$ is the scan rate, (C_s) is the sample heat capacity, C_r is the reference position heat capacity, and R is the thermal resistance which is now a **constant of the apparatus** (being dependent on the furnace construction, plate thickness, etc.) and is not dependent on the sample configuration or thermal conductivity. R is still a function of temperature but can be calibrated for this dependence and incorporated into all subsequent measurements. In fact, the manufacturers of heat-flux DSC instruments generally calibrate for this R and incorporate it electronically into the measuring circuit [2].

Equation 10.3 shows that the signal being monitored is proportional to the difference in heat capacity between sample and reference sides. The proportionality constant is the operator selected scan rates times R. However, although T_{sm} is maintained equal to T_{rm} by the circuitry, the actual sample temperature (T_s) will differ from the temperature at the thermometer (T_{sm}) by an amount which is determined by three factors: (1) the thermal resistance between the platform and the sample pan, (2) the scan rate, and (3) the sample heat capacity (C_s). Hence, we can derive the following relationship:

$$T_{sm} - T_s = R_s' C_s \frac{dT_s}{d\tau} \tag{10.4}$$

This equation is the basic equation which determines the amount of sample temperature lag with respect to the monitored temperature (T_{sm}).

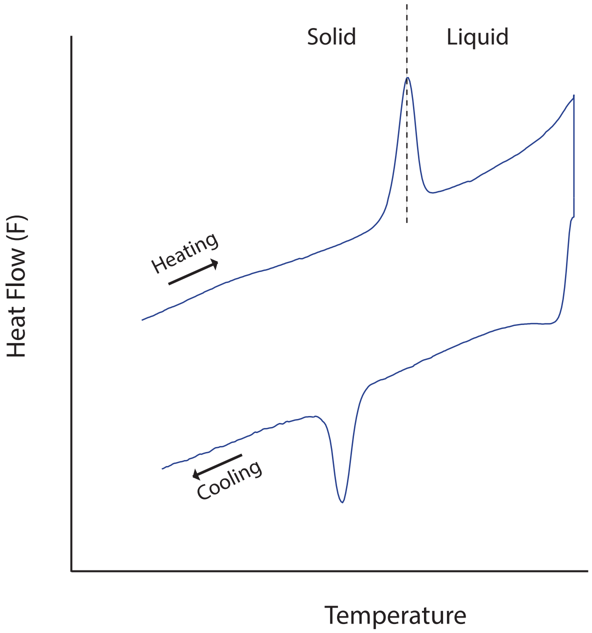

Figure 10.2: A typical DSC run for measurements of the solid-liquid transformation upon heating the material (*top*) and the liquid-solid transformation upon cooling the material from above its melting point (*bottom*). The y-axis is displaced such that an endothermic transition is positive and an exothermic transition is negative.

A schematic of a typical heat-flow DSC is shown in figure 1 (*top*). The reference pan is an empty pan of similar weight, material, and geometry as the pan used to encapsulate the sample. The reference pan is placed on the back platform of the two sample DSC cell and sample pan is placed on the front platform. The pan is typically an Al pan with a lid that is crimped on or hermetically sealed. **WARNING:** *Never exceed 600^{o}C with Al pans and never go to temperatures above the boiling or sublimation point of the material being studied.* DSC typically needs around 1-20 mg of a sample to get good results.

Once the sample and reference pan are placed on the DSC platform and the purge gas flow is started, you are ready to run the instrument and collect data. Typically data is collected while heating, however, both heating and cooling data can be collected. The reason for collecting heating data is because the instrument can control the heat rate very precisely with resistive heating wire placed below the sample just underneath the platform. Cooling, however, it done by letting the sample naturally cool to room temperature or with a cooling gas flowed over the sample. Hence, it is typically not possible to use fast cooling rates and one must insure not to set the DSC instrumental cooling rate faster than the sample can naturally cool off. This becomes particularly slow as one approaches room temperature. A typical heating run followed by a cooling run is shown in figure 2. The top curve is the 'heating run' where the solid sample is taken from room temperature to above its melting point at 20^{o}C per minute. The peak represents melting (fusion) and the area under this peak is proportional to the enthalpy (or heat) of fusion, ΔH_{fus}. The slope of the line is proportional to the heat capacity (C_p) and can be exactly measured by running a baseline sample and a sample with know heat capacity (typically alumina) over the same temperature range (to remove the temp. dependence of R). Conversely, the cooling curve shown at as the bottom curve in figure 2 has a negative peak that is indicative of crystallization of the liquid and the area of this peak is proportional to the enthalpy of crystallization ($-\Delta H_{fus}$).

The baseline, even outside of the melting or crystallization transition, does not coincide with the abscissa $\Delta T = 0$ nor is it straight, because the reference and sample thermal resistivity (constants) are not strictly equal; and moreover, the reference and sample do not possess exactly the same heat capacities and thermal conductivities. Extrapolation of the baseline in the region of the 'transition' of interest can yield a step

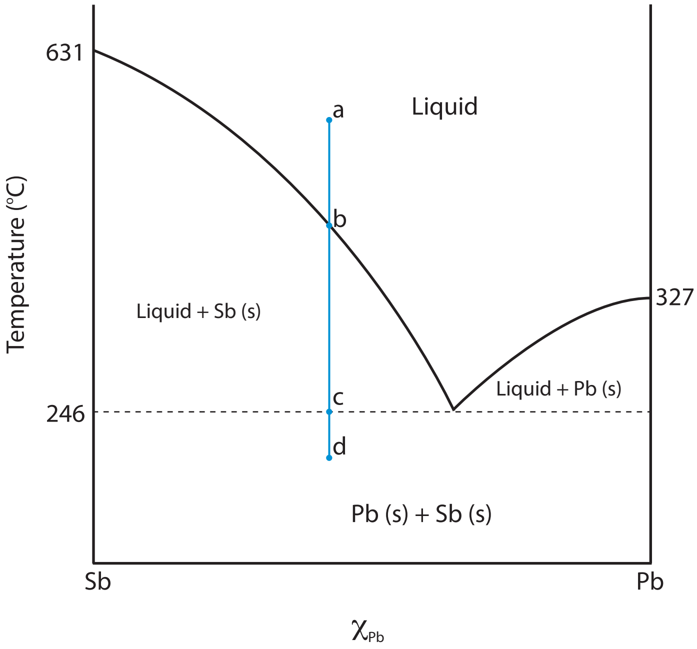

Figure 10.3: The antimony-lead system

because of the difference in the specific heats of the two phases and also as a result of the fact that heat transfer between substance and container may change considerably at the phase transition point. There are a series of procedures for finding the "correct" baseline, and the one most commonly used it a simple fitting of the baseline on each side of the transition to subtract this effect from the data.

Therefore, after calibrating the DSC with materials of known melting temperature, heat capacity [3], and enthalpy of fustion, one can determine the temperature of solid-liquid phase diagram of any binary system by the position of the peaks as well as the enthalpy of the transitions by the area of the peaks. From this data, the entropy of fusion can be determined.

Thermodynamics of Liquid-Solid Equilibrium

If a liquid solution of two substances A and B is cooled to a sufficiently low temperature, a solid will appear. This temperature is the freezing or crystallization point of the solution, which depends on the composition [4]. In a typically discussion of freezing-point depression (colligative properties), we commonly find

$$ln\chi_A = -\frac{\Delta H_{fus,A}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \tag{10.5}$$

where χ_A is the mole fraction of component A, $\Delta H_{fus,A}$ is the enthalpy of fusion of component A, R is the gas constant, T is the freezing temperature of the binary mixture, and T_o is the freezing temperature of the pure solvent. This assumes an ideal dilute solution limit. Hence, this cannot hold true over the entire composition range of a binary mixture. However, as $\chi_B \to 1$, we would expect solid B to freeze out with a melting point depression similar to the expression above for component A (just substitute B for A in the above equation). These two curves intersect at a temperature T_e, the eutectic temperature. The composition χ_e is the eutectic composition. If a crystal-crystal transition also occurs in the binary system at a temperature between the eutectic and melting of the pure substance, this will cause a peritectic point in the phase diagram [5].

An example of a simple eutectic type phase diagram is shown in figure 3. The binary system is composed of lead (Pb) and antimony (Sb) and illustrates a nearly ideal mixing type of binary phase diagram. The regions of the phase diagram are labeled with Sb (s) and Pb (s) indicating pure solid antimony and pure solid lead, respectively. The eutectic temperature is 246^oC; the eutectic composition is 87 mass percent lead. In the lead-antimony system, the values of the eutectic temperature (T_e) and composition (χ_e) calculated from equation 10.5 agree satisfactorily with the experimental values. This implies that the liquid is nearly an ideal solution.

An *isopleth* is a line of constant composition such as *abcd* in figure 10.3. At *a*, the system is entirely liquid. As the system cools, solid antimony appears at *b*; as the antimony crystallizes out, the saturated liquid becomes richer in lead, and the liquid composition moves along the solid curve toward the eutectic point. At *c* the solution has the eutectic composition and is saturated with respect to lead also, so lead begins to precipitate. The temperature remains constant even though heat flows out since, in this condition, the system is invariant. The amount of liquid diminishes and the amounts of solid lead and antimony increase. Finally the liquid solidifies, and the temperature of the mixed solids decreases along the line *cd*. If the process is done in reverse, heating a mixture of solid lead and solid antimony from *d*, the state point moves from *d* to *c*. At *c*, liquid forms having the composition χ_e. Note that the liquid formed has a different composition than the solid mixture. The system is invariant (recall Gibbs phase rule), so the temperature remains at 246^oC until all of the lead melts; since the liquid was richer in lead than the original mixture, the lead melts completely leaving a residue of solid antimony. After the lead has melted the temperature rises, and the antimony that melts moves the liquid composition toward *b*. At *b* the last bit of antimony melts and the system is a homogeneous liquid above *b*.

The eutectic (Greek for 'easily melted') point gets its name from the fact that the eutectic composition has the lowest melting point. The eutectic mixture melts sharply at T_e to form a liquid of the same composition, while *all other mixtures melt over a range of temperature.*

Experimental

The objective is to determine the liquid-solid phase diagram and associated thermodynamic parameters of a two component (binary) compound system. To accomplish this, you must first run calibration runs with materials that have know melting points and heats of fusion. Because of time constraints, this data will be available on the class website. Therefore, you are only responsible for collecting data on your binary compound during the laboratory period.

Never touch the DSC sample pans with your hands. Therefore, always wear gloves or handle all samples and pans with tweezers. The first thing you need to do is weigh out 5-10 mg of each of the pure components and seal them in an Al DSC pan for measurement. Make sure to record the weight of the Al pan as well as the weight of the sample. Measure the weights as accurately as possible. Now make 5-10 binary mixtures, mix them thoroughly, weigh out 5-10 mg of each mixture and seal it in an Al DSC pan. Again, make sure to record the weight of the sample mixture as well as the weight of the Al pan. Lastly, an empty sealed Al pan will be used as a reference. This pan is provided and should be in or next to the DSC instrument.

Ok, you have your samples ready. Now its time to run them on the DSC. The DSC is a very very sensitive instrument and can easily be damaged or contaminated, so please be extremely careful when operating this instrument. First rule, **never ever touch your sample pan or any part of the DSC cell with your hands!** The oil will give tons of addition signals and will make it impossible to collect accurate data. Next rule, never ever put anything into the DSC that could evaporate, sublimate, or react at the temperatures you are planning to heat the sample too. Last rule, never ever heat the DSC past 400^oC. Ok, with that out of the way we are ready to put our first sample into the DSC and collect the heat flux data. You will be asked to set a scan rate and a temperature profile. This will be done using the following considerations. First, you want to melt your sample to allow for a well fused solid as the starting point for all runs. This can be achieved by equilibrating at a temperature above the melting point for 1-2 minutes. Second, you want to cool the sample at a known rate and collect the cooling curve data. You can stop collecting data once the sample is completely in the solid phase (below the eutectic temperature). If you are NOT using an actively cooled DSC system, then it is often recommended that you collect only heating data. If this is the case, you need to first heat the sealed samples above their melting temperature to make sure the binary mixture has fused.

Repeat this procedure for both pure samples and your 3 mixture samples. Download the calibration data off the web and now you are done and ready to proceed to data analysis.

Data Analysis

- Use the calibration data to calibrate the temperature and the enthalpy (or include information about how the instrument was calibrated).
- Calculate the liquid to crystal transition temperature and enthalpy.
- If, the sample contains any crystal to crystal transitions then calculate the transition temperature and enthalpy of this transition.
- From the transition temperature data, construct a $\chi - T$ phase diagram and label on areas of the plot.
- Determine and report the eutectic point (temperature and composition) as well as any perectic points.
- Calculate the change in enthalpy for the pure compounds and the mixtures. From a standard ideal solution model, construct the theoretical phase diagram and eutectic point. How does this compare to your measured results?

Safety

You must wear gloves at all times when handling DSC sample pans, lids, or any other part of the DSC instrument or sample assembly.

References

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