Experiment 8:
Differential Scanning Calorimetry

This experiment is not contained within the required text. The theory and experimental procedures are listed below.

1 Theory

Thermal analysis is defined as the measurement of the change in the chemical or physical properties of a substance as the temperature of the substance is altered. These properties allow the study of (a) thermal decomposition, (b) solid-solid and solid-gas chemical reactions, (c) material specification, purity, and identity, and (d) material adsorption and phase transitions. Thermal analysis is credited to H. Le Chatelier (discovered in 1887). Techniques based on thermal analysis are now used heavily in the plastics industry.

Since solids and liquids do not exhibit an appreciable volume (V) change as the temperature (T) is altered over some predefined range (negligible in comparison to that observed for gases) heat at constant pressure (q_p), change in enthalpy of a system (ΔH_{sys}) and the change in internal energy (ΔU_{sys}) of that system are related through:

$$q_p = \Delta H_{sys} = \Delta U_{sys} + P\Delta V \qquad (1)$$

Where P is pressure. This simplifies to:

$$\Delta H_{sys} \sim \Delta U_{sys} \qquad (2)$$

Certain types of enthalpy changes have special names. For example,

- ✓ When 1mol of substance is formed from its elements the heat of reaction is the Heat of formation, or ΔH_f.
- ✓ When 1mol of substance combines with O_2 in a combustion reaction (that carried out in Experiment 2) the heat of reaction is the Heat of combustion, or ΔH_{comb}.
- ✓ When 1mol of substance vaporizes the change in enthalpy is referred to as the heat of vaporization, or ΔH_{vap}.
- ✓ Finally, when 1mol of substance melts the enthalpy change is the Heat of fusion, or ΔH_{fus} (ΔH_{melt} is also used in some texts so as not to confuse the heat of fusion with ΔH_f, even though this description is sometimes used)

Another important thermodynamic quantity is *entropy*, or S. This determines whether a reaction, inclusive of phase transitions, will spontaneously occur. The entropy is the tendency for a system to proceed towards greater disorder. The second law of thermodynamics stipulates that every system proceeds toward a state of increasing disorder. For a reaction to occur spontaneously, the change in the entropy of the system (ΔS_{sys}) plus the entropy of the surroundings (ΔS_{surr}) must be greater than zero. The third law of thermodynamics reveals entropy of the surroundings is inversely proportional to temperature (in degrees K), i.e.

$$\Delta S_{surr} \geq \int \Delta U_{sys} / T \qquad (3)$$

Thus, equations 2 and 3 reveal that the entropy associated with melting or vaporization can be written as:

$$\Delta S_{surr} = -\Delta H_{sys} / T \qquad (4)$$

ΔS_{surr} in this case would represent the entropy of the heating element causing melting or vaporization. To define spontaneity, ΔS_{sys} must also be defined.

In this experiment, you will be using Differential Scanning Calorimetry (DSC) to derive enthalpy of several substances and the entropy of the surroundings. In this instrument, the difference in heat flow between a sample of interest and a reference are measured while the two are exposed to a predefined temperature program (the *Heat flux* as opposed to *power compensation* method is used). A schematic example of the DSC is shown in Figure 1. An example of a thermal curve, which consists of peaks, troughs, and steps dependent on the sample analyzed and the reactions taking place is shown in Figure 2.

The dips, peaks and troughs seen in a thermal curve indicate whether an *exothermic* or *endothermic* reaction is taking place. Recall; an exothermic reaction is one in which heat is released (feels warm) and an endothermic reaction is one requiring heat (feels cold). When a positive heat flow is recorded, an exothermic reaction is taking place. Likewise when a negative heat flow is recorded, an endothermic reaction is occurring.

Crystallization is an example of an exothermic reaction (releases energy) while melting is an endothermic reaction (requires energy). Thus, these will appear in a thermal curve as peaks and troughs respectively. The glass transition is another type of phase change. This only occurs in polymers and is one of the things that make polymers unique. The glass transition is pretty much what it sounds like. When the polymer is cooled below this temperature, it becomes hard and brittle, like glass. Above this temperature it is rubbery. Since no heat is absorbed or emitted during glass transition (only the heat capacity, C_p, changes), no change in enthalpy results.

So, how do we derive, *heat*, *heat capacity*, *enthalpy*, *entropy* and the temperatures associated with phase

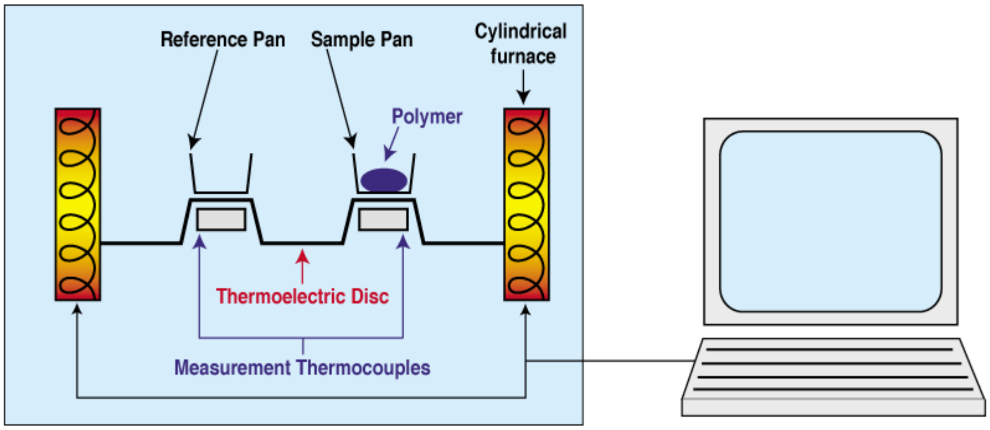


Figure 1. Schematic example of a typical DSC instrument.

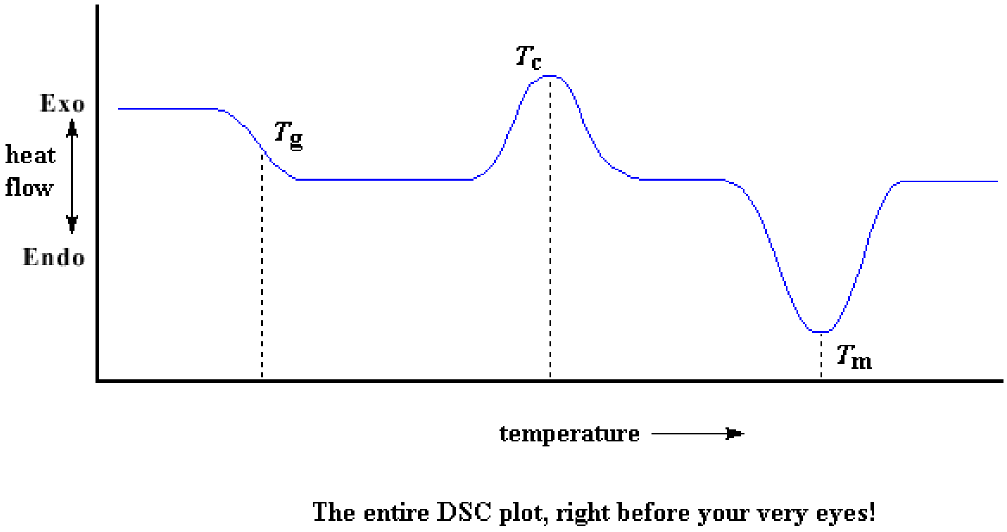


Figure 2. An example of a DSC thermal curve for a typical polymer. The thermal curves you will be recording may differ substantially in structure. Tg, Tc and Tm refer to the glass transition temperature, the temperature at which the system crystallizes and the temperature at which melting occurs, respectively.

changes from a DSC curve? Well first, let's consider what we are doing: we are attempting to heat a substance and a reference pan over a predefined temperature range at a predefined rate, i.e.

$$\text{Heating rate} = \Delta T / t \tag{5}$$

With

$$\text{Heat flow} = q_p / t \tag{6}$$

Where *t* is time. When we put a certain amount of heat into something, its temperature will rise according to its heat capacity, *C*. By dividing the *heat flow* at a given temperature by the heating rate, *t* cancels out to yield the heat capacity under constant pressure defined as C_p (see experiment I for further discussion on heat capacities), i.e.

$$C_p = q_p / \Delta T \tag{7}$$

If the substance undergoes any reaction resulting in the uptake or release in energy (exothermic or endothermic reaction) once a certain temperature is reached, the computer will attempt to compensate for this by altering the applied heat, so that the heating rate remains constant. This change in applied heat (measured in the form of power i.e. milliwatts) reflects the reaction occurring as well as the extent of the reaction. This is directly proportional to the mass, *m*, of the substance being studied.

The enthalpy associated with any reaction can then derived from the area contained between the baseline and the peak (or trough) since:

$$\text{area} = (q_p \times T) / (t \times m) \tag{8}$$

To makes things even easier, the supplied software defines this area by integrating the thermal curve over a user defined range, and rearranges equation 8 to provide enthalpy in units of J/g. Entropy can then be derived using equation 4.

2 Experimental

You will be deriving various thermodynamic properties of In and Naphthalene from the thermal curves obtained using a Du Pont 9900 DSC instrument. Due to the simplicity of use, and type of information relayed, DSC has become one of the most widely used of all the thermal analysis techniques in both industrial and research laboratories. As an example, DSC is routinely in the plastics and pharmaceuticals industry to characterize, among other things, the purity of a material. This is possible since purity dictates the temperature at which crystallization occurs.

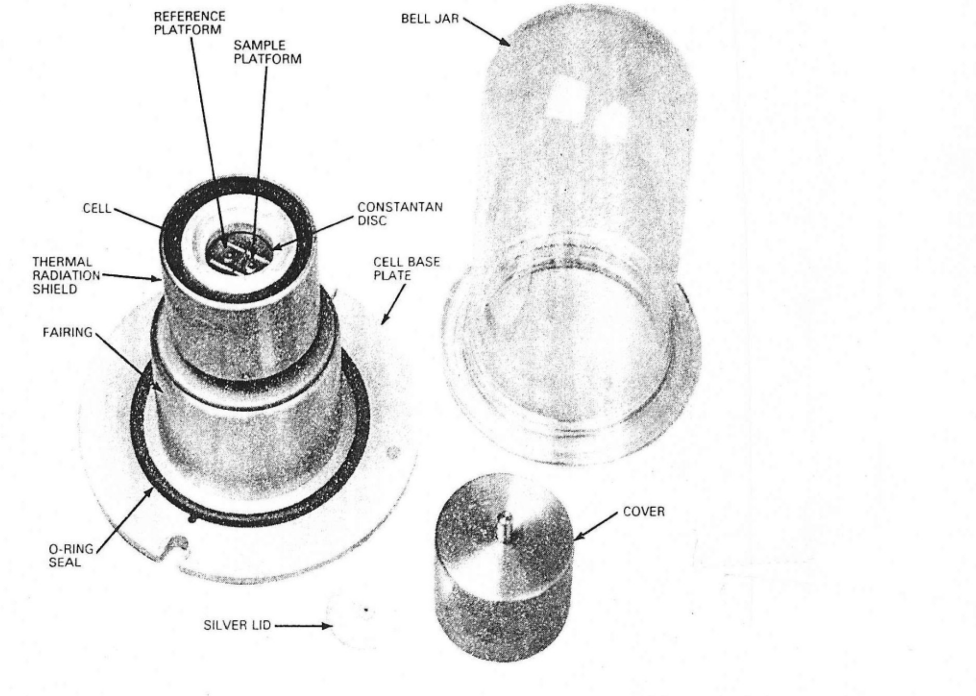
Before starting the experiment, obtain the following:

a. A box containing the DSC Aluminum trays
b. A pair of tweezers
c. Indium foil
d. Naphthalene

2.1 Preparing the samples

Do the naphthalene experiment first and record the exact weight of the sample. Also use the tweezers for handling the Al trays and for handling the DSC components. Do not handle (touch) aluminum trays, samples or DSC components since this will contaminate your samples. Also DSC components will be HOT following analysis.

1. Weigh and Tare one of the Aluminum trays, and when this reads zero load the tray with naphthalene or a piece of Indium of between 5–60 mg. You will need to cut approx. 1–2 mm long piece of Indium wire.
2. Place the empty tray and the tray containing naphthalene or Indium into the DSC cell (Figure 3). To do this you must first remove the bell jar. Then lift off the cover and silver lid using the tweezers. You will see two sample platforms. The empty tray goes on the rear platform and the tray containing the sample goes on the platform closest to you. Return silver lid, and cover using the tweezers and replace the bell jar and locking ring.



DSC CELL

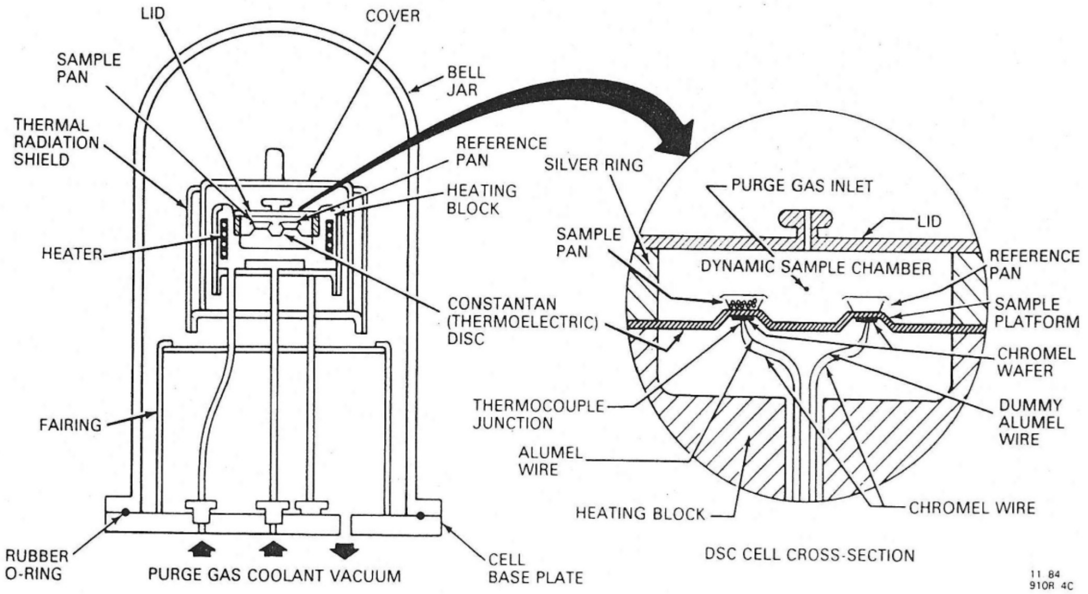


Figure 3. The Du-Pont 9900 DSC cell (top) and a schematic of the cross section of this cell (bottom)..

3. Slowly switch the N_2 gas supply on. To do this you must open up the valve on top of the N_2 bottle. Adjust the regulator such that the out pressure gauge reads ~10psi. This should result in a reading of ~30 on the flow meter which is situated on the white “Temperature Program Interface” box (the white box situated to the left of the DSC instrument). If the reading is above of below 30, adjust either the regulator or the flow meter until this value is attained.

   Note where the N_2 enters the DSC instrument (behind the DSC cell) and ensure the black valve on this line behind the DSC cell, is pointing toward the DSC cell.
   Also, ensure that the switch on the “module switching accessory” (black box on top of the white “Temperature Program Interface” box) is turned to DSC.

2.2 Running the DSC software

Note, this instrument is fully computer controlled. The computer is situated to the left of the DSC instrument. The temperature of the DSC cell is automatically saved and displayed at all times during a DSC analysis cycle (see top of screen).

1. The DSC analysis program is started by double clicking on the “Thermal Analysis Program” icon. A “TA-PC for windows” box will appear.
2. Click onto the DSC 910 box to get into the acquire mode
3. Click “OK” once you have verified that the switch box is in the correct position (DSC not TGA). This will get you into the “data acquisition setup” box.
4. Click onto the setup icon and the “method” box will appear.
5. In the Method box specify which temperature ramp to use.
   For the naphthalene experiment use a start temperature of 30ºC and end temperature of 120ºC
   For the In experiment use a start temperature of 50ºC and end temperature of 200ºC.
   And use 10ºC per minute instead of the default value of 20ºC.
   Also ensure the calibrate box is checked
6. In addition you will need to specify
   a. The description of the sample (In or naphthalene)
   b. The operator (you)
   c. The sample weight should be ~5 mg but you need to enter the exact weight in mg.
7. Then press the “start” button and specify a filename (use the default directory).
8. The first step where nothing appears to be happening takes about 2 to 5 minutes (the system is in “idle” mode). After than the data is collected and plotted in real time (system is in “segment 1”). This step takes about 10 minutes. Following this the system will go through its cool down cycle (“idle” mode). This is the longest step and is much longer for In (up to 1hr), thus the reason you run naphthalene first. This data is automatically saved for subsequent analysis which you will carry out once you have finished collecting the data for In (next step).
9. Once the DSC has cooled down to ~50ºC you can get ready to do the In experiment (the heat of fusion of In is much higher than this). Use new Al trays and put the old ones aside (do not dispose of these).
10. For the In experiment proceed through steps 5 onwards.
11. Once you have finished recording the thermo curve for In, you can proceed to data analysis. To do this, exit the acquisition program (this can be done while the In is still in its cooling cycle) and click on the analysis icon in the “TA-PC for windows” box.
12. Open your file using the file pull down menu
13. Look for the main peak/trough in your thermal curve (there should only be one)
14. Click on the “analysis” pull down menu (top of screen) and click onto “DSC peak area”.
15. Double click on some point on your thermal curve just before the peak/trough starts and again just after it has finished. This will tell the computer to derive the melting point in ºC and the heat of Fusion in J/g. This will appear on the screen beside the peak/trough. You will need to record these values.
16. You will also need to make a trace of the thermal curve you recorded for both naphthalene and Indium. Now you are finished with today’s experiment.

Once you have completed this experiment show the TA your results.

The TA will then switch off the instrument (please don't attempt to do this yourself).

3 Calculations and Discussion

1. Comment on the shape of the thermal curves above 60°C. Do these imply an exothermic or endothermic reaction is taking place? Would you expect this?
2. What is the melting point (the extrapolated onset of the peak/trough) for both Naphthalene and Indium, and how do these compare with the literature values?
3. The literature value for ΔH_{fus} for Indium is 779 cal/mol. How does this compare with the value you obtained?
4. Can errors be introduced into your heat of fusion value, and if so, how?
5. Derive the change in entropy (ΔS_{surr}) associated with the phase changes you have measured for both naphthalene and Indium, and discuss why these phase changes do not occur spontaneously at room temperature. What does this say about the value of ΔS_{sys}.
6. Discuss and schematically illustrate how the purity of a substance will affect the DSC thermal curve around the phase transition temperature, i.e. indicate whether these will become broader or sharper and why you would expect this (Hint; look up the Clapyron equation and examine its implications)\
7. In experiment 2 a *bomb calorimeter* is used to derive enthalpy. In this experiment *Differential Scanning Calorimetry* is used to define enthalpy. Discuss how the enthalpy values derived using these two techniques differ?

4 Useful texts

Principles of Instrumental analysis by Douglas Skoog, 5th Edition Saunders, Philadelphia (1998).

Physical Chemistry by P Atkins, 5th Edition, W.H. Freeman and Co., New York (1994).