Introduction of Differential Scanning Calorimetry in a General Chemistry Laboratory Course: Determination of Thermal Properties of Organic Hydrocarbons

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General chemistry students are introduced to many of the principles and concepts of thermodynamics. Thermochemistry, which is a branch of thermodynamics, is also commonly discussed. Traditionally, thermochemical properties such as melting points and changes in energy for physical changes of state are introduced. When discussing the melting or fusion of a compound, the thermal properties that can be determined include the melting temperature (T_m), enthalpy of fusion ($\Delta_{fusion}H$), and the entropy of fusion ($\Delta_{fusion}S$). Other thermal characteristics such as polymorphism are rarely introduced or discussed *(1–3)*. In its simplest interpretation, polymorphism is defined as a phenomenon in which a compound exhibits two or more different crystalline forms or polymorphs *(4–5)*. These aforementioned thermal properties are only occasionally reinforced or examined in a laboratory setting.

Instrumental techniques that can routinely and easily be used for thermal analysis are rarely mentioned or implemented. Today, it has become increasingly important to incorporate modern techniques and instrumentation into the general chemistry curriculum to provide a more hands-on and applicable learning environment for the general chemistry students. It is beneficial to introduce students to instrumental techniques early on in the curriculum to prepare them for more advanced chemistry courses and expose them to techniques used in the real world. Differential scanning calorimetry (DSC) is commonly used to determine thermodynamic properties *(6)* and used in a wide variety of applications ranging from food analysis to polymer analysis *(7–9)*. DSC has been used in some physical chemistry experiments and even some general chemistry experiments *(10–13)*. The development of these upper-level DSC experiments suggests that there is a need for more laboratory experiments at the general chemistry level involving the hands-on use of DSC.

An experiment has been developed in our general chemistry laboratories over the course of a year to introduce the use of DSC in determining the thermal properties of organic hydrocarbons and introduce the phenomenon of polymorphism. Students worked individually or in groups to complete the experiment. A survey was given to the students to provide feedback on the quality, usefulness, and relevance of this experiment. A majority of their responses were favorable. Some of their responses are summarized in the learning outcomes section.

The goals of this experiment are

1. To supplement the classroom lecture of thermodynamic properties with a hands-on experiment
2. To determine thermal properties of organic hydrocarbons
3. To introduce the phenomenon of polymorphism
4. To have the students compare their experimental data to accepted data provided by the National Institute of Standards and Technology (NIST)

Learning Outcomes

In using the DSC and doing this experiment students indicated from a survey that some of the concepts learned included (i) how to use the DSC instrument, (ii) how to determine T_m and $\Delta_{fusion}H$ from a DSC thermogram, (iii) how to calculate $\Delta_{fusion}S$ of a compound, (iv) the relationship between the molecular weight and the $\Delta_{fusion}S$ of a compound, (v) the phenomenon of polymorphism and its detection by DSC, and (vi) how to evaluate their experimental data by comparing it to the accepted values obtained from NIST.

Materials

All chemicals were purchased from Aldrich with 99% purity and were used without further purification. Purity was confirmed by gas chromatography analysis with a Hewlett Packard 5890 Series II gas chromatograph.

Experimental Procedures

In this experiment, the thermal properties of three organic hydrocarbons are determined. Each student or group of students analyzes cyclohexane and pentadecane and one other compound assigned by the instructor selected from dodecane, tetradecane, or octadecane. In one laboratory period, a student or group of students determines the T_m, $\Delta_{fusion}H$, and $\Delta_{fusion}S$ of cyclohexane and one other organic hydrocarbon and examines the thermal and polymorphic properties of pentadecane.

A Perkin–Elmer power-compensated DSC model Pyris I is used. All DSC experiments are run with samples ranging from 5 to 15 mg under dry nitrogen flowing at 20 cm^3/min to prevent any moisture pickup or oxidative degradation. All samples are prepared at room temperature (21 °C), weighed on an analytical balance, and placed in reusable stainless steel capsules with an internal volume of 30 μL. To eliminate all thermal history, all the samples are subjected to three thermal cycles: two heating and one cooling. A detailed summary of the thermal cycles and temperature ranges can be found in the Supplementary Material.[W]

All melting point data or endothermic transition temperatures are obtained by taking the onset temperature of the endothermic change from the thermal baseline. All $\Delta_{fusion}H$ data are calculated using the Pyris for Windows software by taking the area under the second heating thermogram. A comparison of experimentally determined values is made to the accepted values as provided by NIST *(14)*.

Table 1. Summary of Student Obtained Thermal Analysis Data

Sample	T_m/K	T_m/K	Error (%)	$\Delta_{fusion}H$/ (kJ/mol)	$\Delta_{fusion}H$/ (kJ/mol)	Error (%)	$\Delta_{fusion}S$/ (J/mol K)	$\Delta_{fusion}S$/ (J/mol K)	Error (%)
Cyclohexane	279.7 (±0.1)	279.6	0.036	2.71 (±0.18)	2.68	1.05	9.69 (±0.90)	9.57	1.22
Dodecane	261.3 (±0.3)	263.5	–0.84	36.9 (±1.2)	36.8	0.256	141 (±5.4)	138.8	1.13
Tetradecane	278.5 (±0.1)	278.7	–0.072	45.0 (±2.9)	45.1	–0.074	162 (±10.)	161.5	0.155
Octadecane	300.1 (±0.2)	301.0	–0.30	60.4 (±3.3)	60.8	–0.524	201 (±11.)	203.6	-1.08

N.B. The accepted values for T_m, $\Delta_{fusion}H$, and $\Delta_{fusion}S$ are given by NIST.

Hazards

Cyclohexane, dodecane, tetradecane, pentadecane, and octadecane can be harmful if inhaled or ingested. Care should be taken to avoid contact with the skin and eyes as mild irritation may occur upon contact. Cyclohexane is extremely flammable and should be kept away from open flames and sparks. Small quantities of samples are used help to minimize these risks.

Results and Discussion

Determination of Thermal Properties of Cyclohexane Using DSC

Cyclohexane was chosen for thermal analysis because of its purity and its use as a DSC calibrant. A typically obtained thermogram of cyclohexane is shown in Figure 1 with a T_m of 6.55 °C. The $\Delta_{fusion}H$ of 32.2 J/g (2.71 kJ/mol) is determined as described above. A $\Delta_{fusion}S$ is calculated from

$$\Delta_{fusion}S = \frac{\Delta_{fusion}H}{T_m} \qquad (1)$$

where $\Delta_{fusion}S$ is the entropy of fusion, $\Delta_{fusion}H$ is the enthalpy of fusion, and T_m is the melting point in Kelvin. A $\Delta_{fusion}S$ of 9.69 J mol^{-1} K^{-1} was calculated for cyclohexane and was in good agreement with the reported literature value *(14)*. The experimentally obtained average with standard deviation data, accepted data, and relative percent errors for cyclohexane are summarized in Table 1. The student data shown was obtained from eight groups of students.

Determination of Thermal Properties of Another Organic Hydrocarbon Using DSC

Either dodecane, tetradecane, or octadecane was used as another compound for analysis. A typical thermogram of tetradecane is shown in Figure 2. Analogous to the cyclohexane analysis, a T_m and $\Delta_{fusion}H$ were determined and are in excellent agreement with the accepted values (Table 1). The $\Delta_{fusion}S$ was calculated using eq 1 as previously described. As can be seen from Table 1, as the molecular weight of the organic hydrocarbon increases (from dodecane to tetradecane to octadecane), so do the values of T_m and the $\Delta_{fusion}H$. Additionally, as the molecular weight of the sample increases (from dodecane to tetradecane to octadecane) so does the $\Delta_{fusion}S$. A summary of the thermal data for all three compounds and a comparison to their accepted values taken from NIST is shown in Table 1.

Introduction of Polymorphism of Pentadecane Using DSC

Pentadecane was used to demonstrate the phenomenon of polymorphism. When determining pentadecane's thermal

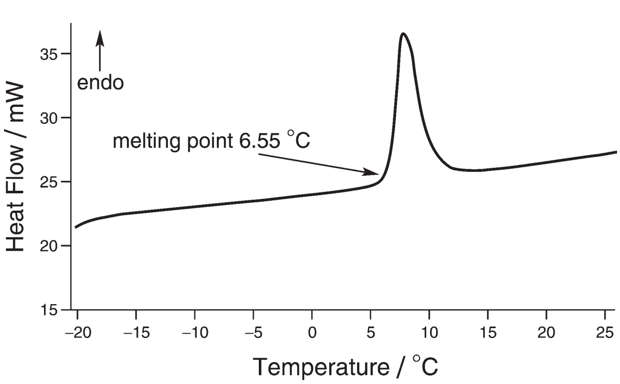

Figure 1. A heating DSC thermogram of pure cyclohexane. The melting point was determined to be 6.55 °C (279.7 K) by taking the onset temperature of the heating curve. A $\Delta_{fusion}H$ of 32.2 J/g (2.71 kJ/mol) is determined from the area under the heating curve.

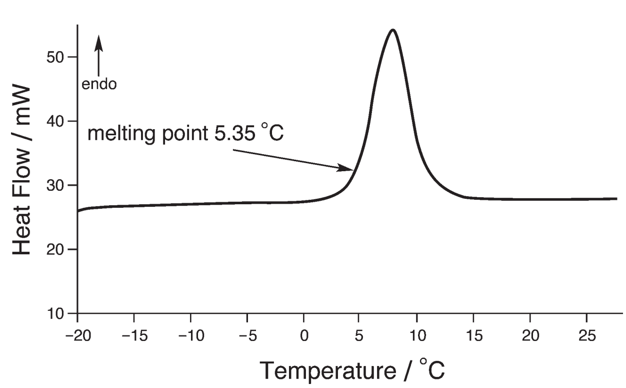

Figure 2. A heating DSC thermogram of tetradecane. The melting point was determined to be 5.35 °C (278.5 K) by taking the onset temperature of the heating curve. A $\Delta_{fusion}H$ of 227.0 J/g (45.0 kJ/mol) is determined from the area under the heating curve.

Table 2. Summary of Student Obtained Thermal Analysis Data for Pentadecane

Sample	T_{trs}/K	T_{trs}/K	Error (%)	$\Delta_{trs}H$/ (kJ/mol)	$\Delta_{trs}H$/ (kJ/mol)	Error (%)	$\Delta_{trs}S$/ (J/mol K)	$\Delta_{trs}S$/ (J/mol K)	Error (%)
Pentadecane (polymorph II)	270.0 (±0.4)	270.9	–0.332	8.71 (±0.45)	9.17	–4.98	32.3 (±1.6)	33.85	-4.661
Sample	T_m/K	T_m/K	Error (%)	$\Delta_{fusion}H$/ (kJ/mol)	$\Delta_{fusion}H$/ (kJ/mol)	Error (%)	$\Delta_{fusion}S$/ (J/mol K)	$\Delta_{fusion}S$/ (J/mol K)	Error (%)
Pentadecane (polymorph I)	282.6 (±0.4)	283.1	–0.177	34.4 (±1.3)	34.6	–0.634	122 (±4.6)	122.17	–0.409

N.B. The accepted values for T_{trs}, T_m, $\Delta_{fusion}H$, and $\Delta_{fusion}S$ are given by NIST.

properties in the temperature range studied, two distinct peaks are identified, one for each of the two polymorphic forms of pentadecane as shown in Figure 3. The lower transition temperature is polymorphic form II and the higher transition temperature is polymorphic form I. For each polymorph a transition temperature, ΔH, and ΔS can be determined. By the strictest of definitions, $\Delta_{fusion}H$ and $\Delta_{fusion}S$ are values associated with the physical change of state from a solid to a liquid upon the melting of polymorph I. In the case of the endothermic transition of polymorph II, this is a solid-to-solid transition and is termed an enthalpy of transition ($\Delta_{trs}H$). A summary of these data is shown in Table 2.

Conclusion

With this experiment the thermal properties T_m and $\Delta_{fusion}H$ of organic hydrocarbons can be determined by DSC. This experiment demonstrates that as the molecular weight of the noncyclic organic hydrocarbons increases so does the T_m and $\Delta_{fusion}H$. A $\Delta_{fusion}S$ can be calculated from the experimentally determined T_m and $\Delta_{fusion}H$ values. The calculated $\Delta_{fusion}S$ values increases as the molecular weight increases from C_{12} to C_{18}. The phenomenon of polymorphism is demonstrated by the two distinct DSC endothermic peaks in pentadecane. The importance of comparing experimental data to the accepted values by using the NIST Web site allows students to calculate percent relative errors in their experiments. Overall, this experiment reinforces the teaching of thermodynamic properties in general chemistry. Using the DSC in the general chemistry laboratory setting allows for a hands-on experience with more sophisticated instrumentation providing students the foundation for more complex experiments and the use of instrumentation in advanced chemistry classes.

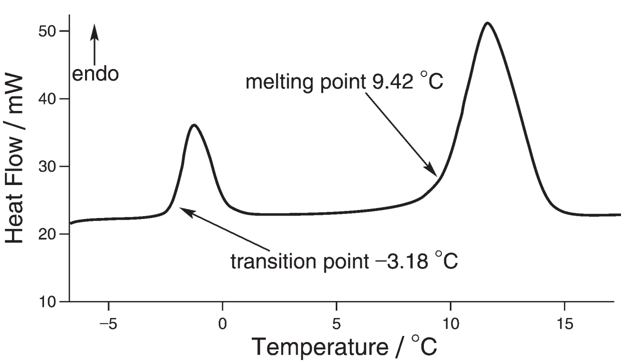

Figure 3. A heating DSC thermogram of pentadecane. There are two peaks indicating polymorphism for pentadecane. The two transition points were determined to be -3.18 °C (270.0 K) for polymorphic form II and 9.42 °C (282.6 K) for polymorphic form I by taking the onset temperature of the heating curve. A $\Delta_{trs}H$ of 41.0 J/g (8.71 kJ/mol) and a $\Delta_{fusion}H$ 161.9 J/g (34.6 kJ/mol) were determined for polymorphic form II and polymorphic form I respectively from the area under the heating curve.

Acknowledgment

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wSupplemental Material

Instructor notes, student handouts, fact sheet on thermal analysis, and safety precautions using the DSC are available in this issue of *JCE Online.*

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