A SIMPLE METHOD FOR DETERMINING THE SPECIFIC HEAT OF SOLIDS

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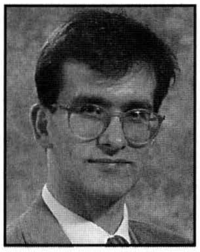
Specific heat is one of those properties that all undergraduate students of chemical engineering would claim at least some measure of familiarity with, often from close and bloody encounters in the performance of energy balances. Our experience has been that this familiarity rarely extends to methods of determining this important intensive property. Many of the sophisticated methods that have been developed over the last century or so are inappropriate to the repertoire of the first-year laboratory, either because they require elaborate and expensive apparatus and/or because they are time consuming and not easily scheduled into what appears to be that universal period of time (3 hours) devoted to laboratory classes. The interested reader should consult any of the texts on classical calorimetry[e.g., 1,2] for a full account of the available methods.

In this paper we describe a simple and inexpensive undergraduate experiment for the determination of the specific heat of solids based on the evaporation calorimeter devised by Dewar in 1904.[3] An added advantage of the experiment is that it introduces some important thermodynamic principles in the development of the theory underlying the evaluation of specific heat. To deflect the charge that we may be over-virtuous in our endeavors, we confine ourselves to a method that will allow the determination of the *average* specific heat of a solid in the range of 80K to 298K.



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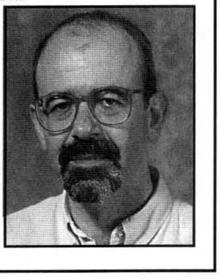

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BACKGROUND[4-8]

The terms "specific heat" and "heat capacity" are often used synonymously. In fact, the term heat capacity is a legacy of the "caloric" theory of heat that Count Rumford essentially laid to rest at the end of the 18th Century. This theory held that heat was a substance that could literally be "poured" from one body to another. We now know that heat cannot be contained within a system, but rather is a manifestation of the interaction of a particular system with its surroundings. The modern concept of specific heat is that it is a measure of the energy changes of a system when energy, in the form of heat, is transferred across its boundaries. Transfers of energy can be conducted under a number of different conditions (*e.g.*, constant pressure or constant volume), each of which can be used to define a specific heat; the concept is further elaborated upon below.

The general change in enthalpy of a system that is in mechanical equilibrium with its surroundings can be obtained with

$$dH = dQ + dW_e + VdP \tag{1}$$

The term W_e is used to denote all forms of work that may be referred to as "non-P,V work." *i.e.*, electrical, gravitational, etc. Now, if we assume that there is no non-P,V work done on the system, and heating or cooling occurs at constant pressure, this equation reduces to

$$dH = dQ \tag{2}$$

Using the relationship

$$dQ = CdT \tag{3}$$

we can then write

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{4}$$

which is the definition of the heat capacity or specific heat (at constant pressure). A similar deduction starting from the description of the internal energy of the system U leads to

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{5}$$

It can be further shown that the relationship between C_p and C_V is

$$C_p - C_V = \left(\frac{\alpha^2}{\kappa}\right) VT \tag{6}$$

Following on from Eq. (4), however, if, at constant pressure, the temperature of a compound, S, is raised by a small increment ΔT, a finite amount of heat needs to be transferred, and

$$Q = \Delta H = n_S C_P^m \Delta T \tag{7}$$

Here, C_P^m is the molar specific heat and n_S is the number of mols of compound S. The specific heat is usually a function of the temperature and approaches zero for very low temperatures (a few degrees Kelvin above absolute zero). In this temperature range, the function $C_p(T)$, or $C_V(T)$ for that matter, is sufficiently accurately described by the theories of Einstein[9] and Debye.[10] At higher temperatures, the rule of Dulong and Petit[11] applies. They observed as early as 1819 that the *molar* heat capacities of elementary solids have values close to 25 J/mol K. The theoretical justification of this law can be drawn from Boltzmann's equipartition theorem. Based on the energy of motion of each oscillating atom in a solid, the internal energy of the system can be described as

$$U = 6\,N_A\left(\frac{1}{2}kT\right) = 3\,RT \tag{8}$$

Differentiation then leads to the constant value 3 R

$$C_V = 24.9\ \text{J/mol K}$$

Quantization of the vibrational energy of the atoms by Einstein led to an expression for C_V,

$$C_V = 3\,Rf^2 \tag{9}$$

that could describe the low temperature behavior of the heat capacity. The application of Debye's continuum theory to the vibrational modes of atoms in a solid predicts a cubic law dependency for the specific heat of elemental solids and is a definite improvement over Einstein's work:

$$C_V = \frac{12}{5}\pi^4 R\left(\frac{T}{T_D}\right)^3 \tag{10}$$

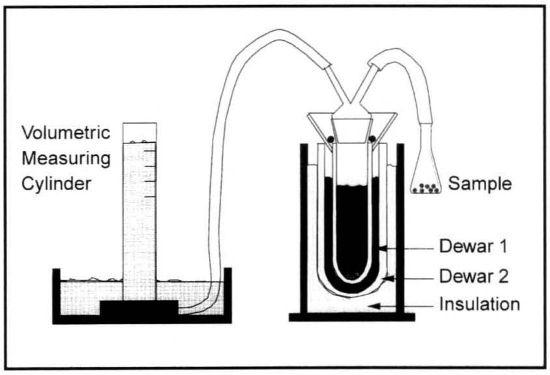

Figure 1. *Set-up of evaporation calorimeter.*

This experiment was designed as a first-year laboratory experiment for undergraduate students in order to familiarize them with the concepts of thermodynamics. Once it is set up, results for a number of different elements can be conveniently obtained and compared.

In our experiment, various solids are cooled from room temperature, T_2, to the temperature of liquid nitrogen, T_1. The *average* molar specific heat between T_2 and T_1 is denoted here as $\overline{C_P^m}$. The enthalpy change for a solid immersed into the liquid nitrogen can then be described as

$$\Delta H = H(T_2) - H(T_1) = n_S \int_{T_1}^{T_2} C_P^m \, dT = n_S \overline{C_P^m}(T_2 - T_1) \tag{11}$$

This change results in the boiling off of n_{N_2} mols of nitrogen. If the molar heat of evaporation of liquid N_2 is known (ΔH_{N_2}), then $\overline{C_P^m}$ simply follows from

$$\overline{C_P^m} = \frac{n_{N_2}\Delta H_{N_2}}{n_S(T_2 - T_1)} \tag{12}$$

EXPERIMENT

A simple evaporation calorimeter was fabricated from two Dewar flasks and additional components mostly comprising standard laboratory items. The entire calorimeter is housed within a PVC container made from a 0.6-m section of 0.2-m diameter PVC pipe, to which is fitted a base plate of 0.4-m diameter. This provides adequate stability for the entire assembly and minimizes the risk of it being knocked over during the experiment. For additional security, we recommend that the PVC container be fastened to the laboratory bench with screws. The large, outer Dewar ("Dewar 2" in Figure 1) has a capacity of 0.5 litre. This Dewar is placed inside the PVC container, and insulating material is poured into the gap between the inside wall of the container and the Dewar. Expanded polystyrene chips of the sort often used in packaging proved to be ideal for this purpose. The smaller Dewar ("Dewar 1" in the figure) has a ground-glass socket at its opening and a capacity of 0.2 liters. The cone closure was modified in our workshop to provide inlet and outlet tubes as shown in the figure. A small glass flask of 50-ml capacity, into which samples are placed, is connected to one branch of the modified cone by clear flexible tubing. A longer length of identical tubing is attached to the other branch and is directed to a "beehive shelf" in a large plastic tray filled with water, which serves to collect the nitrogen gas evaporated during operation. A 2-liter measuring cylinder is used for this purpose.

Operation of the calorimeter requires partially filling Dewar 2 with liquid nitrogen. Dewar 1 is then carefully lowered into the large Dewar. (We recommend that a rubber bung be placed at the bottom of Dewar 2 in order to prevent breakage.) Liquid nitrogen is then added to Dewar 1 and care is taken to ensure that the level of liquid nitrogen in Dewar 1 is lower than that in Dewar 2. Approximately 1 g of solid sample is charged into the small glass flask and connected to the cone. This will result in evolution of nitrogen gas, which must be recorded (using a stopwatch) in order to provide a baseline. Once the baseline has been established, the contents of the flask are steadily discharged into the liquid nitrogen, and the volume of gaseous nitrogen evolved is recorded. Once a steady state has been reestablished, the constant evolution of nitrogen is again recorded (second baseline).

SAFETY

Prior to conducting the experiment, students are briefed on the particular hazards associated with liquid nitrogen and are given eye protectors and insulated gloves. We recommend that students' handling of liquid nitrogen be minimized and that "bulk" transfers from storage Dewars be carried out by suitably qualified laboratory technicians.

Normally, it will not be necessary to replenish the volume of liquid nitrogen during the course of the experiment once the Dewars have been charged. We employed glass Dewar vessels and encountered no difficulties with their use. (It may be of interest to point out that metal Dewar flasks are also available, and that anyone having particular concerns about breakage may wish to consider using them instead.)

One less obvious hazard associated with the use of liquid nitrogen is the condensation of liquid oxygen from the atmosphere during the experiment. The volume contained in the Dewars of the capacity quoted above are sufficiently small to minimize this occurrence. As an additional precaution, we fabricated a simple check valve from a truncated plastic filter funnel and rubber "O" ring (see Figure 1) by which the smaller of the two Dewars is suspended inside the outer one.

ANALYSIS

By extrapolating the volumetric flow rates before and after the experiment, the actual gas volume ΔV evolved can be determined (see Figure 2). The value of ΔV is the distance between the two baselines at the point where the two areas, A1 and A2, shown in the figure are equal. Using the ideal gas law, the number of mols of evaporated N_2 can be calculated. The partial pressure of nitrogen follows from

$$P_{Air} = P_{N_2} + P_{H_2O} + P_{hydrostatic} \qquad (13)$$

The atmospheric pressure in the laboratory has to be determined very accurately, and the partial pressure of water at room temperature is taken from the appropriate tables. The correction for the hydrostatic pressure is given by

$$P_{hydrostatic} = \rho_{H_2O} g h \qquad (14)$$

When the heat of evaporation of liquid nitrogen ($\Delta H_V = 5.56 \frac{kJ}{mol}$)[12,13] and the molecular weight of the sub-

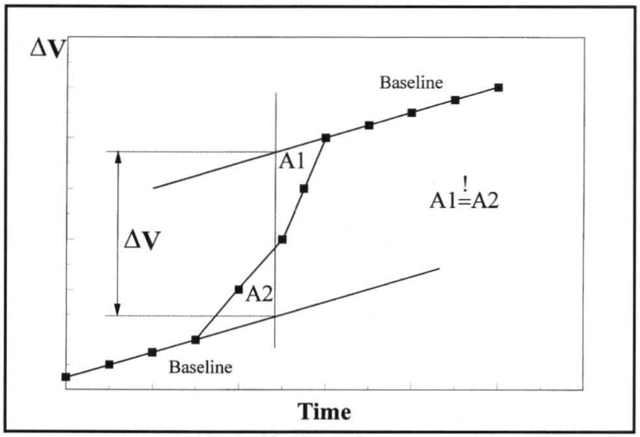

Figure 2. *N_2 evolution; determination of the volume of evaporated gas.*

TABLE 1

Comparison of Specific Heat Values for Gold, Tin, Silver, Zinc, and Silicon[14-22]

Element	Experimental Values [J/mol K]	Data from Literature [J/mol K]
Gold	25.95 [77K - 293K]	25.35 [290K]; 25.42 [298K]; 25.38 [298K]; 19.54 [80K]; 19.63 [80K]
Tin	25.55 [77K - 293K]	26.98 [298K]; 25.32 [298K]; 20.71 [80K]
Silver	23.45 [77K - 293K]	25.28 [290K]; 25.35 [298K]; 25.54 [298K]; 17.91 [80K]; 17.87 [80K]
Zinc	22.85 [77K - 293K]	25.4 [298k]; 25.38 [298K]; 16.86 [80K]
Silicon	13.55 [77K - 293K]	19.99 [298K]; 19.74 [298K]; 5.28 [80K]

stance investigated are known, the heat capacity can be calculated according to Eq. (12).

RESULTS

We have used the above apparatus to measure the specific heats of gold, silver, silicon, tin, and zinc. The experimental results that we determined are compared with data obtained from various sources in Table 1.

It is clear from Table 1 that the average C_p values found from our experiments lie somewhere between the values quoted in the literature for the distinct temperature limits of the experiment. The specific heats of all elements considered (with the exception of silicon) seem to obey the rule of Dulong and Petit and are close to 3R as mentioned above.

The somewhat lower value obtained for silicon is due to the fact that the C_p value for Si approaches lower values at much higher temperatures than is observed for the other metals. This is presumably because the highest frequency for the 3N normal modes of vibration for a silicon crystal is larger than for the other elements due to the intrinsic bond strength.[5,8,23]

CONCLUSIONS

This experiment was designed as a first-year laboratory experiment for undergraduate students in order to familiarize them with the concepts of thermodynamics. Once it is set up, results for a number of different elements can be conveniently obtained and compared. In order to further develop the concepts introduced by this experiment, students could be asked to compare their results with the rule of Dulong and Petit as well as the predictions provided by the theories of Einstein and Debye. The definition of degrees of freedom and their contribution to the specific heats C_p and C_V of gases could also be addressed. For especially keen students, the process of achieving very low temperatures by adiabatic demagnetization could be elaborated on.

NOMENCLATURE

α	thermal expansivity (K^{-1})
C_p	specific heat at constant pressure (J $mol^{-1} K^{-1}$)
C_V	specific heat at constant volume (J mol^{-1} K^{-1})
$\overline{C_p^m}$	average molar specific heat (J mol^{-1} K^{-1})
F	frequency factor
g	gravitational acceleration (ms^{-2})
h	height (m)
H	enthalpy of a system (J mol^{-1})
ΔH_V	heat of evaporation (J mol^{-1})
κ	compressibility (bar^{-1})
k	Boltzmann's constant (J K^{-1})
n	number of mols (mol)
N_A	Avogadro's constant
P	pressure (bar)
Q	heat (J)
ρ	density (kg m^{-3})
R	universal gas constant (J mol^{-1} K^{-1})
T	temperature (K)
T_D	Debye temperature (K)
U	internal energy of a system (J mol^{-1})
V	volume (m^3)
W_c	non P,V work on system (J)

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