Guided Practice Activities

**Module:** Thermodynamics

**Section:** Calorimetry – Key
Coffee Cup Calorimetry

**ACTIVITY 1**

The purpose of this activity is to understand some theory behind calorimetry and coffee cup calorimetry.

1. Define a calorimeter.
   
   A calorimeter is a device that is used to measure the change in temperature during a physical or chemical change.

2. Calorimetry is one method for determining the change in enthalpy of a reaction. It is important to be able to determine this value for many reasons. One is in predicting the spontaneity of a particular change. Can you name another practical reason for determining this value for a change?

   It is often important to know the amount of energy released or absorbed by a certain reaction. Consider how important this would be for the energy sector.

3. A coffee cup calorimeter isolates a chemical or physical change in constant pressure.

4. Heat flow at constant pressure is equivalent to the change in enthalpy for the system.

**ACTIVITY 2**

The purpose of this activity is to help you understand how one can use a coffee cup calorimeter to measure the heat flow into or out of a system (which in our case will be defined as either a chemical change or a physical change) by measuring the change in temperature upon the change.

1. CaCl₂ dissolves in water in an exothermic process. Consider that you place 2.5 grams of solid CaCl₂ in 20 grams of water at 25°C and the temperature of the solution increases to 47°C.

   In this example, what is the system? What are the surroundings?

   **System:** The CaCl₂ is the system. We are focused on how this solid dissolves.

   **Surroundings:** Everything else. Specifically, we can look at water as the surroundings as we consider how heat flows between system and surroundings.
2. Draw a microscopic view of the dissolution process. Also draw an energy level diagram showing how the potential energy of the system changes as a result of the dissolution.

**Microscopic view of the dissolution process:**

![Microscopic view of dissolution process](image1)

**Potential energy diagram for this dissolution process:**

![Potential energy diagram](image2)
3. Given that there are only two types of energy, KE and PE, what must have happened to the PE of the system – an increase, decrease or no change?

   The potential energy must have decreased because the process released energy (exothermic).

4. What must have happened to the energy of the surroundings?

   We know from the First Law of Thermodynamics that energy is neither lost nor destroyed. If the system released the energy – it must have gone into the surroundings. The energy of the surroundings increased.

5. Given that the surroundings is the water in which the CaCl$_2$ dissolved, and knowing the pressure of the system remained constant at 1 atm, how might one calculate the amount of energy that flowed from the system to the surroundings?

   The change in enthalpy ($\Delta H$) at constant pressure is equal to the heat transfer measured in this dissolution process ($q_p$). We know that all of the energy released by the dissolution process flowed into the water. We observed this transfer as a rise in temperature in the water. Additionally, we know the specific heat capacity and mass of the water. The equation that we could use to calculate the energy transfer is therefore:

   \[
   q_p = m_{water} C_{s,water} \Delta T_{water}
   \]

6. Calculate the amount of heat that flowed from the system to the surroundings.

   \[
   q_p = m_{water} C_{s,water} \Delta T_{water}
   \]

   \[
   q_p = (20\,g)(4.184 \, \frac{J}{g\,^\circ C})(T_{final} - T_{initial})
   \]

   \[
   q_p = (20\,g)(4.184 \, \frac{J}{g\,^\circ C})(47\,^\circ C - 25\,^\circ C)
   \]

   \[
   q_p = (20\,g)(4.184 \, \frac{J}{g\,^\circ C})(22\,^\circ C)
   \]

   \[
   q_p = 1841 \, J = 1.841 \, kJ = 1.8 \, kJ
   \]

There are a few things we can note here. Sometimes you’ll find listed specific heat capacities with units of Jg$^{-1}$K$^{-1}$. Students often worry about the temperature unit – good for you! Units are very important in all realms of science. In this case, we need to understand the equation in order to understand the different units we can use. $\Delta T$ measures the change in temperature. You’ll find that the Kelvin and Celsius temperature systems use the same relative scale. This means the difference in two Celsius temperatures will equal the difference in two equivalent Kelvin temperatures. Try it for yourself: Take the difference in 300K and 350K. Convert those to Celsius temperatures by subtracting 273 ($27^\circ C$ and $77^\circ C$). Now take the difference in the two Celsius temperatures. What do you find for the $\Delta T$ in both cases?

Additionally, we are considering the heat flow into the surroundings. We predict that this would be a positive energy value because the system releases energy (a negative change in
energy) and the surroundings absorb this energy (a positive change in energy). Our calculations prove these predictions correct. As long as you are careful when inputting your final and initial temperatures, the sign of \( q \) should match with your predictions.

7. Heat flow at constant pressure is defined as change in enthalpy or \( \Delta H \). Calculate the change in enthalpy of dissolution per mole of \( \text{CaCl}_2 \) using the data given.

In the previous question we calculated the transfer of heat into the surroundings at constant pressure \( q_p \). We can now consider this heat flow from the perspective of the \( \text{CaCl}_2 \) (the system). Again, due to the First Law of Thermodynamics we know that any energy absorbed by the surroundings must have been released from the system. We could represent this idea with this relationship:

\[
q_{\text{system}} = -q_{\text{surroundings}}
\]

So for our particular case we can now determine the heat flow at constant pressure out of the system.

\[
q_{\text{system}} = -q_{\text{surroundings}}
q_{\text{system}} = -1.841 \text{ kJ}
\]

What did we just find? We found that, at a constant pressure, the system loses 1.841 kJ of energy into the surroundings as heat during the process. We also know that heat flow at constant pressure is defined as the change in enthalpy, \( \Delta H \).

\[
q_{\text{system}} = -1.841 \text{ kJ}
\Delta H_{\text{dissolution}} = q_{\text{system}} = -1.841 \text{ kJ}
\]

So we just found the change in enthalpy for the dissolution of \( \text{CaCl}_2 \). However, we found the enthalpy change for exactly 2.5 grams of \( \text{CaCl}_2 \). Our value will only be useful to us and others if we are all considering exactly 2.5 grams of \( \text{CaCl}_2 \). Let’s make our calculation a little more useful by normalizing for 1 mole of \( \text{CaCl}_2 \) instead of just 2.5 grams.

First, let’s find out how many moles \((n)\) are in 2.5 grams of \( \text{CaCl}_2 \).

\[
2.5 \text{g} \text{CaCl}_2 \times \frac{1 \text{mol} \text{CaCl}_2}{111 \text{g} \text{CaCl}_2} = 0.0225 \text{mol} \text{CaCl}_2
\]

If we divide the enthalpy of dissolution for 0.0225 moles by those 0.0225 moles, we have scaled the enthalpy of dissolution to a per mole value:

\[
\Delta H_{n,\text{dissolution}} = \frac{\Delta H_{\text{dissolution}}}{n_{\text{CaCl}_2}}
\Delta H_{n,\text{dissolution}} = -1.841 \text{ kJ}
\Delta H_{n,\text{dissolution}} = \frac{\Delta H_{\text{dissolution}}}{0.0225 \text{mol} \text{CaCl}_2}
\Delta H_{n,\text{dissolution}} = -81.8 \frac{\text{kJ}}{\text{mol}} = -82 \frac{\text{kJ}}{\text{mol}}
\]
Bomb Calorimetry

**ACTIVITY 1**

The purpose of this activity is to understand the theory behind bomb calorimetry.

1. Define bomb calorimeter.
   
   A bomb calorimeter is a device that measures the change in temperature during a physical or chemical change at constant volume. A bomb calorimeter is constructed such that the reaction chamber is tightly constricted and fortified so that it does not expand or contract.

2. Why is it preferable to use a bomb calorimeter when assessing combustion reactions?
   
   Combustion reactions normally occur with a change in volume because gases are typically being consumed or produced during that change. Additionally, a great deal of heat energy is typically released, rendering a coffee cup calorimeter useless for determining the energy change associated with this type of chemical change.

3. Heat flow at constant volume is equivalent to the change in internal energy for the system.

**ACTIVITY 2**

The purpose of this activity is to help you understand how one can use a bomb calorimeter to measure the heat flow into or out of a system (which in our case will be defined as either a chemical change or a physical change) by measuring the change in temperature upon the change.

1. A bomb calorimeter has a calorimeter constant of 10.17 kJ/°C. This constant includes the device and surrounding water. Calculate the heat absorbed by the calorimeter and water when one combests 1.74 grams of naphthalene (C₁₀H₈) in oxygen yielding carbon dioxide and water.

   In a bomb calorimeter, the change in internal energy, \( \Delta U \), is equal to the transfer of heat at constant volume, \( q_v \). The system cannot experience in work because the volume is held constant. Therefore, if we calculate the transfer of heat from the system to the surroundings (calorimeter and water), then we will know the change in internal energy:

   \[
   \Delta U_{\text{combustion}} = q_v = q_{\text{system}} = -q_{\text{surroundings}}
   \]

   We can calculate the heat absorbed by the calorimeter and water with the following equation:

   \[
   q_{\text{surroundings}} = C_{\text{calorimeter}} \Delta T_{\text{calorimeter}}
   \]

   We don't have to account for water separately because the problem specifies that the calorimeter constant, \( C_{\text{cal}} \), includes the surrounding water. Not every calorimetry problem
will be so nice to us! Also, note that the units for the calorimeter constant don’t include mass. That is because the constant given here is specific to this calorimeter. Another calorimeter would have a different constant based on its mass and composition. So in our formula for \( q_{\text{surr}} \) we do not include mass! It wouldn’t make sense with the units we are given.

\[
q_{\text{surr}} = C_{\text{calorimeter}} \Delta T_{\text{calorimeter}} \\
q_{\text{surr}} = C_{\text{calorimeter}} (T_{\text{final}} - T_{\text{initial}}) \\
q_{\text{surr}} = (10.71 \text{ kJ/}^\circ \text{C})(26.150^\circ \text{C} - 19.626^\circ \text{C}) \\
q_{\text{surr}} = (10.71 \text{ kJ/}^\circ \text{C})(6.524^\circ \text{C}) \\
q_{\text{surr}} = 69.87204 \text{ kJ}
\]

2. From the data, determine the change in internal energy of naphthalene per mole combusted.

The heat absorbed by the surroundings is equal to the heat lost by the system:

\[
q_{\text{system}} = -q_{\text{surr}} \\
q_{\text{system}} = -69.87204 \text{ kJ}
\]

The transfer of heat at constant volume equals the change of internal energy of the system:

\[
\Delta U_{\text{combustion}} = q_v = q_{\text{system}} = -q_{\text{surr}} \\
\Delta U_{\text{combustion}} = -69.87204 \text{ kJ}
\]

This value for the change in internal energy, \( \Delta U \), was calculated for the combustion of exactly 1.74 grams of naphthalene. Let’s find out the change in internal energy per mole so that the value is more usable:

\[
1.74 \text{ g naphthalene} \times \frac{1 \text{ mol naphthalene}}{128.17 \text{ g naphthalene}} = 0.0135757 \text{ mol naphthalene}
\]

If we divide the change in internal energy for 0.0135757 moles by those 0.0135757 moles, we have scaled the change in internal energy to a per mole value:

\[
\Delta U_{n,\text{combustion}} = \frac{\Delta U_{\text{combustion}}}{n_{\text{naphthalene}}} \\
\Delta U_{n,\text{combustion}} = \frac{-69.87204 \text{ kJ}}{0.0135757 \text{ mol naphthalene}} \\
\Delta U_{n,\text{combustion}} = -5146.846 \text{ kJ/mol} \approx -5.15 \times 10^3 \text{ kJ/mol}
\]
You could also choose the “train tracks” method of stoichiometry to arrive at the same value for $\Delta U_{n \text{ combustion}}$.

3. Based on the change in gas moles for the combustion of naphthalene, starting and ending at room temperature, determine the change in enthalpy of the reaction.

Using the bomb calorimeter we eliminated the opportunity for the system to do any work. Therefore, the change in internal energy was measured only as a transfer of heat. Remember that the transfer of heat at constant volume, $q_v$, is equal to internal energy, $\Delta U$, not enthalpy, $\Delta H$. So how would we solve for the change in enthalpy of reaction?

All is not lost. We know that:

$$\Delta U = q_v$$

But we also know that:

$$\Delta U = q_v + w = \Delta H + w$$

Here we see that if we can solve for the work, $w$, experienced by the system, we could solve for the enthalpy!

So let’s solve for work....
First, let’s take a look at the reaction:

$$C_{10}H_8 (s) + \frac{12}{2} O_2 (g) \rightarrow \frac{10}{2} CO_2 (g) + \frac{4}{2} H_2O (l)$$

We need to balance:

$$1C_{10}H_8 (s) + 12O_2 (g) \rightarrow 10CO_2 (g) + 4H_2O (l)$$

The change in the number of gas moles is the difference between the moles of carbon dioxide gas (CO$_2$) and oxygen gas (O$_2$). Here the difference in moles of gas is:

$$\Delta n_{gas} = 10 \text{ moles} - 12 \text{ moles} = -2 \text{ moles gas mol}^{-1}$$

The equation for expansion and compression work that we know is:

$$w = -P_{\text{external}} \Delta V$$

However, if you look at the right-hand side of the above equation, we can see how it relates to the ideal gas law: $PV = nRT$. If the pressure, temperature and gas constant are all constant numbers then the change in volume must be due to the change in the number of gas moles!

$$w = -P_{\text{external}} \Delta V = -\Delta n_{\text{gas}}RT$$
So let’s use our new equation for work to determine the work that the system would have experienced had it not been inside a constant volume environment (bomb calorimeter). We choose to use the gas constant 8.314 Jmol⁻¹K⁻¹ because it has joules in its units. Also, room temperature is approximately 298 K:

\[
w = -\Delta n_{\text{gas}}RT
\]

\[
w = -(-2 \text{ moles gas mol}^{-1})(8.314 \frac{J}{\text{mol K}})(298.15K)
\]

\[
w = 4955 \text{ J mol}^{-1} = 4.955 \text{ kJ mol}^{-1}
\]

So 4.955 kJ of work was done ON the system. We know this because a positive value for work indicates that work was done on the system.

Finally, we can return to our equation for internal energy. We know that for the combustion of one mole of naphthalene the change in internal energy is −5146.846 kJ. The calculated work was for one mole of reaction, which is equivalent to the combustion of one mole of naphthalene. So:

\[
\Delta U = q_p + w = \Delta H + w
\]

\[
-5146.846 \frac{kJ}{\text{mol}} = \Delta H + 4.955 \frac{kJ}{\text{mol}}
\]

\[
\Delta H = -5151.80 \frac{kJ}{\text{mol}} = -5.15 \times 10^3 \frac{kJ}{\text{mol}}
\]

This value of \(\Delta H\) reflects the change described by our chemical equation:

\[
\text{C}_{10}\text{H}_8 (s) + \text{O}_2 (g) \rightarrow 10\text{CO}_2 (g) + 4\text{H}_2\text{O} (l)
\]

Therefore for the combustion of one mole of naphthalene, the enthalpy of reaction is approximately −5.15 \times 10^3 kJmol⁻¹.