

**“...BUT A HOT TEMPER
LEAPS O’ER A COLD DECREE”**

**ENTHALPY OF VARIOUS
REACTIONS**

Techniques

- calorimetry
-

MSDS available for

- ammonium nitrate
- ammonium chloride

Principles

- calorimetry
- enthalpy of different reactions
- Hess’ Law
- graphical extrapolation

Recommended Advanced Reading

- Chapter 5 in Silberberg, Lavieri, and Venkateswaran, 1st. CE, McGraw-Hill, 2013.

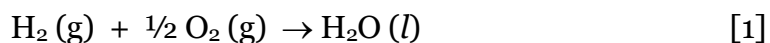
EXPERIMENT 2: *A Tall Cold Drink of Water!*

Introduction

“Currently, a new polymer PEG, polyethylene glycol, is being used to treat certain fabrics. These fabrics, once coated, can generate or absorb heat, depending on air temperature. The day of air-conditioned clothing may not be that far in the future!”

Heat of Formation

The standard heat of formation of a substance, $\Delta_f H^\circ$, is defined as the change in enthalpy when one mole of the substance is formed from its elements in their standard states. The standard state is usually defined at a pressure of one bar and a temperature of 25 °C. The enthalpy of any element that is in its standard state and is in its most stable form is arbitrarily given a value of zero. Thus, graphite, which is the most stable form of carbon, has an enthalpy of zero at 25 °C and 1 bar, whereas diamond, another form of carbon but not the most stable at 25 °C and 1 bar, does not have a zero value for enthalpy in the standard state. The standard heat of formation of most simple compounds can be found in the literature. Most of these have been measured experimentally. For example, the standard enthalpy of formation of liquid water at 25 °C can be found from the reaction,



$$\Delta_f H^\circ = -68.3 \text{ kcal/mol} = -285.8 \text{ kJ/mol}$$

The standard heat of formation of liquid water is -68.3 kcal/mol or in SI units -85.8 kJ/mol. One calorie is defined as 4.184 Joule. The negative sign in front of the value indicates that heat is released or that the reaction is **exothermic**. If the value of the enthalpy is positive, the reaction is **endothermic**.

Hess' Law can be used to determine the enthalpy of a more complex reaction. The enthalpies of certain reactions cannot be measured in the lab directly. However, it is possible to measure the enthalpies of other reactions which, when added chemically together, give the desired chemical reaction. In such cases, the enthalpies of these reactions can also be added together.

Calorimetry

An apparatus called a "calorimeter" is used to measure the quantity of thermal energy gained or lost in a chemical change. A simple calorimeter, also called a "**coffee cup calorimeter**", can be constructed using two nested Styrofoam cups with lids and a thermometer. A more complex type of calorimeter is the bomb calorimeter, which measures thermal energy changes under constant volume conditions. Although not strictly true, we may assume that in this calorimeter, no heat is lost to the surroundings or the calorimeter itself.

Measurement of Thermal Energy

How can thermal energy be measured? One way is to measure a quantity called the specific heat capacity. The specific heat of a substance is the amount of thermal energy required to heat one gram of that substance by one degree. The specific heat capacity of a substance is an intensive property, meaning that it does not depend on the amount of substance present. The specific heat capacity of a drop of water and a pan of water are the same. When we multiply the mass of an object by its specific heat capacity, it is possible to calculate the heat capacity of that object. Heat capacity is an extensive property, meaning that it is dependent on the quantity of substance present. The heat capacity of a drop of water is much, much less than that of a lake. The specific heat capacity of water is unusually high compared to many other substances. This fact has an important impact on us. Cities located near huge bodies of water tend to have more moderate climates. Such cities are cooler in the summer as large water bodies take a long time to absorb the heat of the summer sun, and these cities are warmer in the winter, as the water slowly releases the heat absorbed during the summer. Since our bodies are composed largely of water, we are able to maintain a fairly constant body temperature, in spite of outside temperature fluctuations.

We can determine the specific heat capacity of a metal that does not react with water by heating the metal and then transferring it to cold water. The change in the temperature of the water gives a measure of the heat capacity of the metal. In reality, the specific heat capacity of a substance does vary with temperature.

Specific Heat Capacity of a Metal

In general, we may state that the energy required to change the temperature of a substance can be determined using the following equation:

$$q = m \times c \times \Delta T \quad [2]$$

where c represents the specific heat capacity of the substance, m represents the mass of the substance and ΔT represents the change in temperature of the substance. When a hot metal is added to cold water, the temperature of the metal decreases and the temperature of the water rises. If there is no heat loss to the surroundings or the calorimeter, then the heat lost by the metal must be equal to the heat gained by the water.

$$-q(\text{metal}) = q(\text{water}) \quad [3]$$

Equation [3] follows the convention that when the system loses heat, the sign is negative and when the system gains heat, the sign is positive. If we now substitute Equation [2] into Equation [3],

$$-c_{\text{met}} \times m_{\text{met}} \times \Delta T_{\text{met}} = c_{\text{wat}} \times m_{\text{wat}} \times \Delta T_{\text{wat}} \quad [4]$$

In a calorimeter, since no heat is lost to the surroundings, the heat gain of the water must equal the heat loss of the metal. Do not forget, however, that $\Delta T = T_f - T_i$, so the sign is important! The specific heat capacity of water is $4.18 \text{ J/g}^\circ\text{C}$.

Enthalpy of Solution

The dissolution of a salt may be exothermic or endothermic depending on two main factors. The first factor is the **lattice energy** of the salt. The lattice energy is the energy required to vaporize one mole of the salt to form gaseous ions and this quantity is endothermic. The second factor, the **hydration energy**, is the energy released when one mole of gaseous ions is solvated by water to form aqueous ions and is exothermic. Both these quantities are difficult to measure in the lab. However, their sum, the **enthalpy of solution**, can be measured without much difficulty. The enthalpy of solution can be expressed as

$$\Delta_s H^\circ = (- \text{heat loss of H}_2\text{O}) + (- \text{heat loss of salt}) \quad [8]$$

For a particular salt, if the enthalpy of dissolution is negative, the hydration energy is greater than the lattice energy. If the enthalpy of dissolution is positive, the reverse is true.

One way to calculate the enthalpy of solution is by using the equation below:

$$\Delta_s H^\circ = \frac{q_s}{n_{\text{salt}}} = \frac{-(m_{\text{solution}})(c_{\text{solution}})(\Delta_{\text{solution}} T)}{n_{\text{salt}}} \quad [9]$$

where c is the specific heat capacity, m is the mass, ΔT is the temperature difference and n is the amount (mol).