

## Thermochemistry

**Thermochemistry deals with the physical and chemical changes of matter due to work and heat flow (i.e. it's an idealized model of real life)**

The nature of the study, therefore, is to define chemical changes in terms of the energy transfer that occurs in a process (i.e. from some beginning (step 1) to some ending (step 2) in terms of two forms of energy, work (W) and heat (Q).

In order to do this we need a few ground rules:

First, we need to simplify things for ourselves and define what we'd like to study (**system**) because, in its entirety, the universe is very difficult to understand.

We then need to view this system as separate from everything else; in other words, we need to make a distinction between it and its **surroundings**.

A few examples of systems that you've already created in class are: the reactants in an Erlenmeyer flask, which were mixed together to form new compounds; the contents of a coffee-cup calorimeter; and the balloon that we dipped into liquid nitrogen. All of these things were of particular interest to you and so you studied them in terms of the physical changes that occurred from the beginning to the end of the experiment.

In thermochemistry, the physical changes that are of particular interest to us are changes in volume, pressure, temperature and mass. And to help us understand how these changes relate to each other in a process we have the first law of thermodynamics:

$$\Delta E = Q + W$$

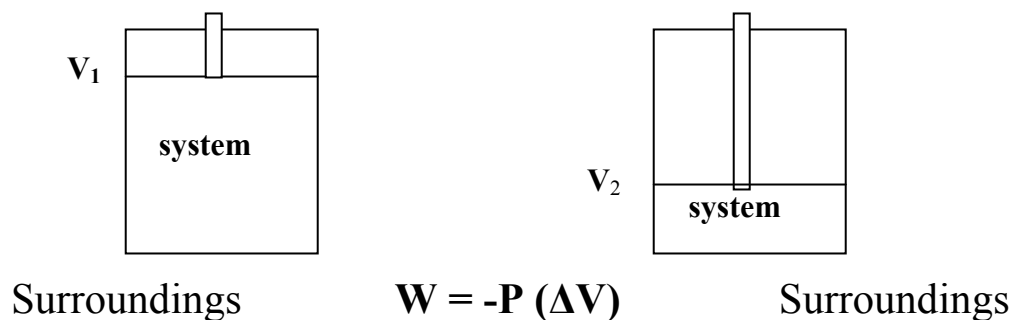
This is just a restatement of the law of conservation of energy which says that energy can neither be created or destroyed, but does change form. The energy forms are heat and work and hence the units of heat and work are the same as that of energy (e.g. joules (J)).

### Work

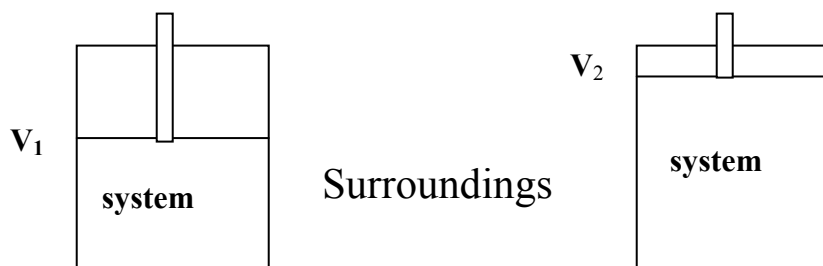
We all know it takes work to do something, but for our purposes let's restrict ourselves to work in terms of pressure and volume.

Put simply,  $W = -P(\Delta V)$ , because we define work to be positive for work done on the system and negative for work done by the system on the surroundings. The following example of a piston (system) undergoing compression and expansion illustrates this concept.

## Surroundings



$\Delta V = V_2 - V_1 \longrightarrow$  negative  $\longrightarrow$  work done on the system is positive  $W = (-)(-) = +$



$\Delta V = V_2 - V_1 \longrightarrow$  positive  $\longrightarrow$  work done by the system is negative  $W = (-)(+) = -$

## Heat

In order to understand  $Q$ , you can apply the same principles to a problem that you did for work. Therefore, heat that flows into a system from the surroundings is positive (+ because heat is added) and heat that flows out of a system to its surroundings is negative (- because heat is being removed). Heat is a slightly more abstract form of energy because its physical meaning relies solely on the change in temperature from step 1 to step 2, and thus if we wish to examine heat changes we have to conduct experiments in a specialized environment called a calorimeter.

Question: But why do we do this?

Answer: Bomb calorimeters allow us to conduct experiments at constant volume (i.e.  $\Delta V = 0$ ), and as a result we can measure  $\Delta E$  for a reaction in terms of the change in temperature because heat is solely responsible for energy change in the system

For example, recall the equation for the first law of thermodynamics:

$$\Delta E = Q + W$$

if we insert our definition of  $W$  into the equation it becomes  $\Delta E = Q - P(\Delta V)$ . In a calorimeter (process at constant volume)  $\Delta V=0$ , so the work term is eliminated from the equation to yield: energy equals heat measured at constant volume.

$$\Delta E = Q_v$$

If we conducted our experiment under conditions of constant volume and constant pressure (e.g. coffee cup calorimeter at 1 atm) we would, again, be able to measure the amount of heat evolved in terms the change in temperature. However, heat measured at constant pressure is given the name **ENTHALPY** ( $\Delta H$ ):

$$\Delta H = Q_p$$

And the complete equation for enthalpy is officially:

$$\Delta H = \Delta E + P(\Delta V)$$

This is why calorimeters are so very important. When we conduct an experiment under conditions of constant volume and constant pressure we get a direct relationship between energy and enthalpy; hence we can figure out whether a system is losing energy or gaining energy depending on the sign of  $\Delta H$ .

**As it was with  $Q$  and  $W$ , so it is with  $H$ :**

$\Delta H = \text{negative} \rightarrow$  energy moves from the system to the surroundings? **exothermic**

$\Delta H = \text{positive} \rightarrow$  energy moves from the surroundings to the system? **endothermic**

**So here are my keys to solving thermodynamics problems:**

- 1.) Approach a problem by defining what is the system and what are its surroundings? (This will give you the signs of  $Q$ ,  $W$  and  $H$  !)
- 2.) Make each problem into a step-wise process (i.e. what were the characteristics of a system at step 1 and what are they at step 2)
- 3.) Draw a diagram to help make this clearer. Make sure to label the physical characteristics of the system at each of the steps: e.g. temperature, volume, pressure and mass of each step.
- 4.) Know the above equations, and supplement as needed with those given to you in the book chapter. e.g.  $\Delta H = m \cdot C \cdot \Delta T$ ;  $\Delta H_{\text{rxn}} = \sum H_{\text{f prod}} - \sum H_{\text{f react}}$
- 5.) See how these fit into the given values of the problem and solve.
- 6.) Go back to #1 and make sure that your answer makes physical sense (Do you have the signs correct?)

