

## 15.6: Enthalpy

In chemistry we are interested not only in those changes occurring in a closed container at constant volume but also in those occurring in an open container at constant (i.e., atmospheric) **pressure**. When a change occurs at constant pressure, there is another energy factor we must consider in addition to the heat absorbed and the change in **internal energy**. This is the *expansion work*  $w_{\text{exp}}$  which the system does as its volume expands against the external pressure.

In order to understand the nature and magnitude of this expansion work, let us consider the simple example illustrated in Figure 15.6.1. Here a sample of oxygen gas is heated at a constant pressure  $P$  from an initial temperature  $T_1$  to a final temperature  $T_2$  by means of an electrical heating coil. The **gas** is confined in a cylinder by a piston, and the **pressure** is maintained by placing a weight of the correct magnitude on top of the piston. The whole apparatus is maintained in a vacuum so that there is no atmospheric pressure to consider in addition to the effect of the weight and piston.

When the heating coil in this apparatus is switched on, the temperature rises and the gas expands in compliance with Charles' law, lifting the piston and weight in the process. Energy must be supplied from the heating coil not only to increase the energy of the oxygen molecules but also to *lift the weight*. In other words,

$$q_P = \Delta U + w_{\text{exp}} \quad (15.6.1)$$

where

- $q_p$  = heat absorbed
- $\Delta U$  = change in internal energy
- $w_{\text{exp}}$  = expansion work, i.e., work done in lifting the weight

To calculate the magnitude of this expansion work, we begin with the definition of pressure:

$$P = \frac{\text{force}}{\text{area}} = \frac{F}{A}$$

or

$$F = PA$$

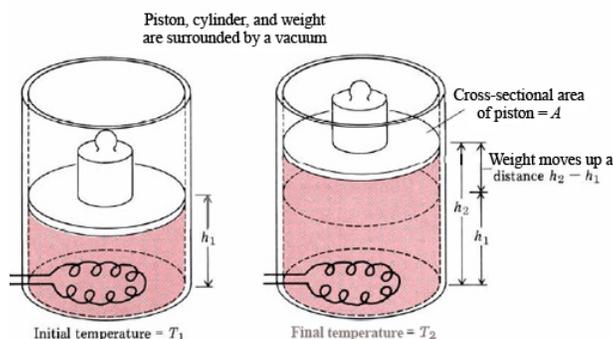


Figure 15.6.2: When a sample of gas is heated at constant pressure, energy must be supplied to expand the gas as well as to increase its internal energy.

where  $F$  is the total force exerted by the weight and piston on the oxygen gas and  $A$  is the area of the piston. As the gas sample is heated, the volume increases from an initial value  $V_1$  to a final value  $V_2$ , while the piston and its weight move from a height  $h_1$  to a height  $h_2$ . The work done is thus given by the expression

$$w_{\text{exp}} = \text{force exerted} \times \text{distance moved}$$

$$= (P * A) * (h_2 - h_1)$$

$$= P * (A * h_2 - A * h_1)$$

However, since the volume of a cylinder is the area of the base times the height,

$$A * h_1 = V_1 \quad \text{initial volume of gas}$$

$$\text{and } A * h_2 = V_2 \quad \text{final volume}$$

Thus  $w_{exp} = P * (V_2 - V_1)$

or

$$w_{exp} = P\Delta V \quad (15.6.2)$$

Inserting this value for  $w_{exp}$  into Eq. 15.6.1, we obtain the final result

$$q_P = \Delta U + P\Delta V \quad (15.6.3)$$

It is important to realize that the expansion work  $P \Delta V$  does not depend on our sample being in the apparatus of Figure 15.6.1 in which there is an obvious gain in the potential energy of a weight. If instead of a weight we allowed the atmosphere to exert a pressure  $P$  on the gas, the result would still be  $P \Delta V$ . In this second case, instead of lifting a visible weight, the expanding gas would push back the atmosphere and hence be lifting invisible air molecules. The work done, and hence the *increase in the potential energy of the atmosphere*, would still be  $P \Delta V$ .

This simple example of an expanding gas helps us to see what is involved in the general case of a chemical or physical change occurring at constant pressure. In any such case the heat energy absorbed by the system,  $q_p$ , will always exactly account for the increase in internal energy  $\Delta U$  and the expansion work  $P \Delta V$ . In other words the relationship  $q_P = \Delta U + P\Delta V$  is valid in the general case.

#### ✓ Example 15.6.1

When 1 mol liquid  $H_2O$  is boiled at  $100^\circ C$  and 101.3 kPa (1.000 atm) pressure, its volume expands from  $19.8 \text{ cm}^3$  in the liquid state to  $30.16 \text{ dm}^3$  in the gaseous state. The heat energy absorbed by the vaporization process is found experimentally to be 40.67 kJ. Calculate the increase in internal energy  $\Delta U$  of  $H_2O$ .

#### Solution

We must first calculate the expansion work  $P \Delta V$ .

$$\begin{aligned} w_{exp} &= P * (V_2 - V_1) \\ &= 101.3 \text{ kPa} * (30.16 \text{ dm}^3 - 0.0198 \text{ dm}^3) = 3053 \text{ kPa dm}^3 \end{aligned}$$

In the section on [Pressure](#), we see that  $1 \text{ Pa} \times 1 \text{ dm}^3 = 1 \text{ J}$ , and we have

$$w_{exp} = 3053 \text{ J} = 3.055 \text{ kJ}$$

Also, since

$$q_P = \Delta U + P\Delta V$$

we have

$$\Delta U = q_P - P\Delta V = 40.67 \text{ kJ} - 3.05 \text{ kJ} = 37.63 \text{ kJ}$$

*Note:* As we see in the sections on [Properties of Organic Compounds and Other Covalent Substances](#) and [Solids, Liquids, and Solutions](#), the vaporization of a liquid is always an endothermic process. Since the molecules attract each other, energy must be supplied to separate them as vaporization occurs. However, not all the energy supplied when a liquid boils goes to increasing the potential energy of the molecules. A significant proportion is needed to increase the potential energy of the air as well.

It is far easier to carry out most chemical reactions in a container open to the atmosphere than in a closed system like a bomb calorimeter. However, when a reaction is carried out at constant atmospheric pressure, it is necessary to measure  $P$ ,  $V_1$  and  $V_2$  (as in Example 15.6.1) as well as  $q_p$  in order to calculate the change in [internal energy](#) from the equation  $\Delta U = q_p - P \Delta V$ . These extra measurements are a nuisance, and they can be avoided by introducing a new quantity which is related to the internal energy but also includes the potential energy of the atmosphere. This quantity is also used in the sections on [Using Chemical Equations in Calculations](#). It is called the enthalpy, symbol  $H$ , and is defined by

$$H = U + PV \quad (15.6.4)$$

From Eq. 15.6.4 we can see that the enthalpy is always larger than the internal energy by a quantity  $PV$ . This extra energy is added to take account of the fact that whenever a body of volume  $V$  is introduced into the atmosphere, the potential energy of the atmosphere is increased by  $PV$  [by the same argument used to derive Eq. 15.6.2]. The enthalpy is thus of the form

Enthalpy = internal energy + potential energy of atmosphere

When a system undergoes a chemical or physical change at constant pressure, the change in enthalpy is given by

Change in enthalpy = change in internal energy + change in potential energy of atmosphere

The change in enthalpy thus includes *both* the energy changes for which heat energy must be supplied from the surroundings. In more formal language

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$

If we consider conditions of constant pressure,  $P_2 = P_1 = P$ , and

$$\Delta H = \Delta U + (PV_2 - PV_1) = \Delta U + P(V_2 - V_1) = \Delta U + P\Delta V$$

but from Eq. [15.6.3](#)

$$q_P = \Delta U + P\Delta V$$

Thus

$$q_P = \Delta H$$

In other words, *the heat energy absorbed by a system in any change at constant pressure is equal to the increase in its enthalpy.* The change in enthalpy  $\Delta H$  can be obtained from a single experimental measurement: the heat energy absorbed at constant pressure.

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