

# Pressure-Volume Work

One way to understand work and its sign convention is to study the expansion and compression of a gas. The most common type of chemical work is pressure-volume work. It consists of:

- work done by a gas (expansion), where  $w > 0$ .
- work done to a gas (compression), where  $w < 0$ .

## Work

Given the following formulas, we can derive the following relationship for work and the application of the force over a distance:

$$w = F\Delta h, P = F/A$$

$$\implies w = P\Delta h$$

$$\implies w = -P\Delta V$$

- if the work is done **by** the gas,  $\Delta V > 0$ , so the sign convention is  $w = -P\Delta V$  (as work is being lost).
- if the work is done **to** the gas,  $\Delta V < 0$ , so the sign convention is still  $w = -P\Delta V$  (as the change in volume is negative).

## Enthalpy

Now, we can measure heat at a constant volume. Starting with the 1st Law of Thermodynamics, we can derive:

$$\Delta U = q + w$$

$$\implies \Delta U = q_{rxn} - P\Delta V$$

$$\implies \Delta U = q_{rxn}, \Delta V = 0$$

At constant pressure, some pressure-volume work will be done:

$$\Delta U = q_p - P\Delta V$$

$$\implies q_p = \Delta U + P\Delta V$$

$$\implies \Delta H = \Delta U + P\Delta V$$

$$\Delta H = q_p$$

Now we have defined enthalpy ( $\Delta H$ ) as the change in heat at **constant pressure**. The enthalpy will be equal to the change in energy only when no work is being done, as  $\Delta V$  would be zero.

We will use ways to calculate  $\Delta H$ :

1. Hess' Law
2. Standard Enthalpies of Formation
3. Bond Dissociation

You can also determine  $\Delta H$  experimentally using calorimetry, for example.

## Properties of Enthalpy

- $\Delta H$  is a state function
- $\Delta H$  depends on phase
- $\Delta H$  is an extensive property (depends on the amount of material undergoing a reaction)

Recall that  $\Delta H > 0$  for an endothermic reaction, while  $\Delta H < 0$  for an exothermic reaction.

## Hess' Law

Hess' law states that the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps:

$$\Delta H_{rxn} = \sum^n \Delta H_n$$

So, an overall reaction can be calculated if the  $\Delta H$  values for the individual steps are known.

## Standard Enthalpy of Formation

Standard Enthalpy of Formation ( $\Delta H_f^\circ$ ) is the change in enthalpy that accompanies the formation of 1 mole of a substance in the standard state (where  $P = 1 \text{ atm}$  and  $T = 298.15 \text{ K}$ ).

- $\Delta H_f^\circ = 0$  for pure elements (such as  $O_{2(g)}$ ), as they are treated as reference points.

## Bond Dissociation Enthalpy

Bond Dissociation energy  $D$  is the energy required to break 1 mole of covalent bonds.

- different bonds have different bond energies (for example, it takes more energy to break a  $C = C$  bond than it does to break a  $C - C$  bond)
- recall that multiple bonds are comprised of  $\sigma$  and  $\pi$  bonds
- some molecules can have bonds with different bond energies than their normal value

In a given reaction, we can calculate  $\Delta H_{rxn}$  because enthalpy is a state function:

$$\Delta H^\circ = \sum n_{react} D_{react} - \sum n_{prod} D_{prod}$$

To use this equation, all reactants and products must be in the gaseous state as the formula doesn't take into account the intermolecular forces present in both liquids and solids.