

THEMODYNAMICS AND THERMOCHEMISTRY

(SILBERBERG CHAPTER 6)

1. Introduction

The world is becoming more and more energy conscious. With ever increasing energy costs it becoming more and more important to minimize energy use and thus save energy. A change in the form of energy (i.e. conversion from one type of energy to another) does not only take place in chemical reaction (e.g. in a forest fire) but also when a physical change takes place e.g. when a gas is compressed for example when you pump your bicycle tire.

Firstly we are going to concentrate on certain aspects of thermodynamics (which is regarded as the science of energy in all its forms) and then we will focus on thermo-chemistry, which is the subsection of thermodynamics that describes reaction heat effects. The mechanical, mechatronic and chemical engineering students will have follow-up modules in their 2nd and 3rd years where most of the aspects of thermodynamics will be investigated in more detail.

To be able to understand the typical questions that need to be answered, it is required to be aware of the various forms of energy associated with a specific quantity of matter, namely:

- (a) Internal energy
- (b) Displacement work
- (c) Kinetic energy
- (d) Potential energy
- (e) Flow work
- (f) Technical work
- (g) Heat
- (h) Chemical energy

The creation of energy by nuclear reactions or due to the effects of external electrical or magnetic fields will not be considered in this course.

2. Open and Closed systems

A system is the quantity of matter of a constant identity or of a constant area that is selected. Everything outside the system is regarded as the surrounding (i.e. the remainder of the universe). All the real or imaginary surfaces that separate the system from the surroundings are known as the system boundaries. If the boundary is constant, we refer to the systems as a control volume, i.e. a control volume is a fixed area in space.

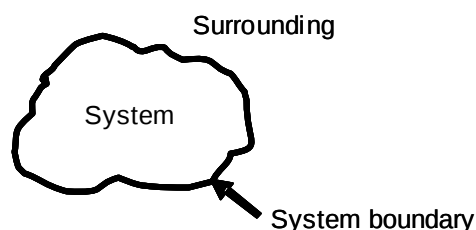


Figure 2.1: System

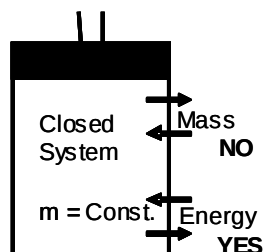


Figure 2.2: Closed System

A closed system consists of a fixed mass of matter and no mass is able to move across the system boundary. However, energy can move across the system boundary and the volume of the closed system can also change. If energy is also not able to pass the system boundary, then the system is said to be isolated.

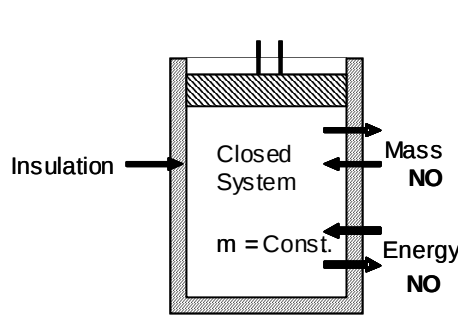


Figure 2.3: Isolated System

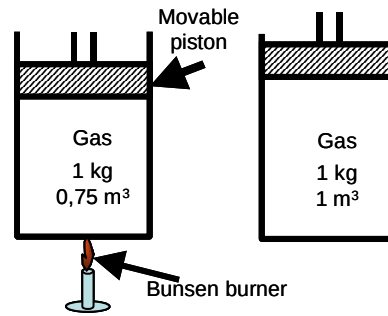


Figure 2.4: Closed system with movable system boundary.

An open system (or a control volume) is a constant volume in space where both mass and energy is able to pass through the system boundary. The boundary of the control volume is known as the control surface. An open system is also known as a flow system.

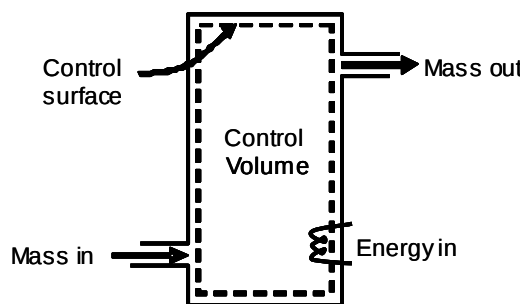


Figure 2.5: Open System

The format of the thermodynamic equations differ for an open system and a closed system. It is thus important to identify at the start of the analysis of a problem if it is an open or a closed system.

3. Types of Energy

Internal Energy

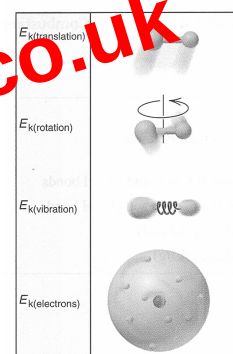
The internal energy of a mass of matter is the sum total of the movement energies of the random movement and vibration of the molecules or atoms and the subatomic energy of the electrons in the atoms (attractive and repulsive potentials). [See figure 3.1].

There exists no instrument that is able to calculate the internal energy on macroscopic level. The internal energy is thus calculated from properties that can be measured on a macroscopic level, such as pressure, volume, temperature and composition.

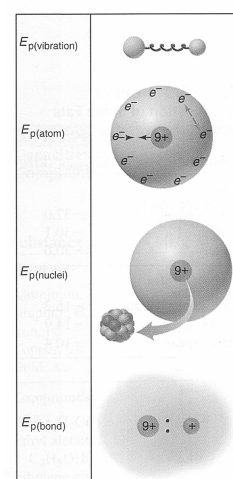
Let E = total internal energy of a body [J]

m = total mass of a body [kg]

e_i = internal energy per unit mass or the specific internal energy of a body [J/kg]



A Contributions to kinetic energy (E_k)



B Contributions to potential energy (E_p)

Figure 3.1

This for an isothermal process it is true that:

$$\begin{aligned} w_{1-2} &= P_1 v_1 \ln \left(\frac{v_1}{v_2} \right) = P_1 v_1 \ln \left(\frac{P_2}{P_1} \right) \\ &= RT \ln \left(\frac{P_2}{P_1} \right) \left[\frac{\text{J}}{\text{kg}} \right] \end{aligned} \quad (4.32)$$

and:

$$\begin{aligned} q_{1-2} &= P_1 v_1 \ln \frac{v_2}{v_1} = P_1 v_1 \ln \left(\frac{P_1}{P_2} \right) \\ &= RT \ln \left(\frac{P_1}{P_2} \right) \left[\frac{\text{J}}{\text{kg}} \right] \end{aligned} \quad (4.33)$$

Isothermal process

If the state change proceeds from (2) to (1) and equivalent amount of work needs to be added and heat removed from the process.

Adiabatic State Change, $q = 0$

If a gas is expanded in a completely isolated cylinder ($q = 0$), the work done by the system done can only be changed into internal energy, which must thus decrease.

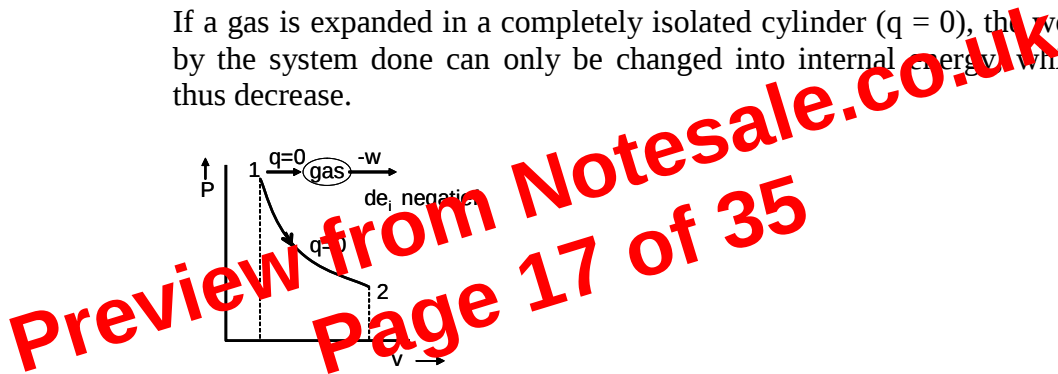


Figure 4.7: Adiabatic state change

1st law for a closed system:

$$de_i = dq + dw$$

$$\therefore de_i = dw \quad \left[\frac{\text{J}}{\text{kg}} \right] \quad (4.32)$$

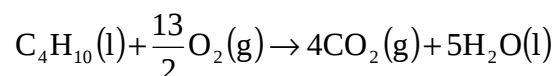
Thus for an adiabatic process:

$$w_{1-2} = - \int_1^2 P dv = e_{i2} - e_{i1} = c_v (T_2 - T_1)$$

It can be proven that for an adiabatic state change of an ideal gas $Pv^\gamma = \text{constant}$ (The mechanical, mechatronic and chemical engineering students will do that in second year thermodynamics).

Heat of Combustion:

If 1 mole of a compound is reacted with oxygen in a combustion reaction and the reactants and products are at 25 °C and 1 atm abs, the heat of reaction is called the heat of combustion. For example:



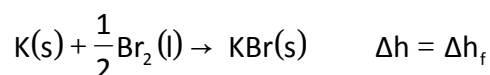
$$\Delta h_{\text{rxn}} = \Delta h_{\text{c}}$$

where Δh_{c} is the heat of combustion.

If the heat of combustion is given at the standard reference conditions (25°C and 1 atm), it is notated as $\Delta h_{\text{c}}^{\circ}$.

Heat of Formation

If 1 mole of a compound is formed from its elements, the heat of reaction is known as the heat of formation, for example:



with Δh_{f} being the heat of formation. If the heat of formation is given at the standard reference conditions (25°C and 1 atm), it is noted as $\Delta h_{\text{f}}^{\circ}$.

Latent Heat of Fusion

If 1 mole of a compound melts, the enthalpy change is known as the latent heat of fusion for example:



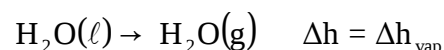
The opposite of the melting process is the solidification process. The enthalpy change is numerically the same except that it has the opposite sign. Note that the latent heat of fusion and the latent heat of evaporation are often

given in $\frac{\text{kJ}}{\text{kg}}$ and in all cases you need to check that the units you are using

are consistent. Remember that phase changes (e.g. melting, boiling and condensation) are isothermal processes and thus the enthalpy of the matter changes although the temperature remains the same.

Latent Heat of Evaporation

When 1 mole of a compound is evaporated, the enthalpy change is known as the latent heat of evaporation, for example:



The same principle applies here as for the latent heat of evaporation.

General Principles Regarding Formulation and Writing of Heats of Reaction

- For an exothermic reaction ΔH_{rxn} is negative and positive for an endothermic reaction.

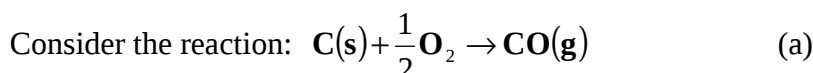
$$= 0,050 \cdot 4,184 \cdot (28,49 - 25,1) \left[\text{kg} \cdot \frac{\text{kJ}}{\text{kg K}} \cdot \text{K} \right] = 0,7092 \text{ kJ} = 709,2 \text{ J}$$

Heat liberated by the solid:

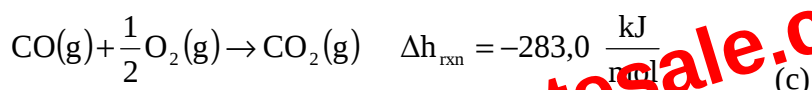
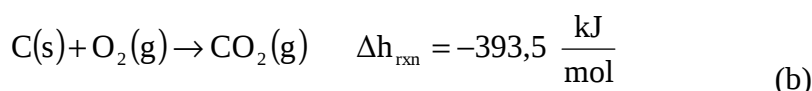
$$Q = m C \Delta T = -709,2 \text{ [J]} = 0,02564 \cdot c \cdot [28,49 - 100,0] \left[\text{kg} \cdot \frac{\text{J}}{\text{kg K}} \cdot \text{K} \right]$$

$$c = \frac{-709,2}{0,02564 \cdot (-71,51)} \frac{\text{J}}{\text{kg K}} = 386,8 \frac{\text{J}}{\text{kg K}}$$

Calculating the Heat of Reaction with the Use of the Hess's Law

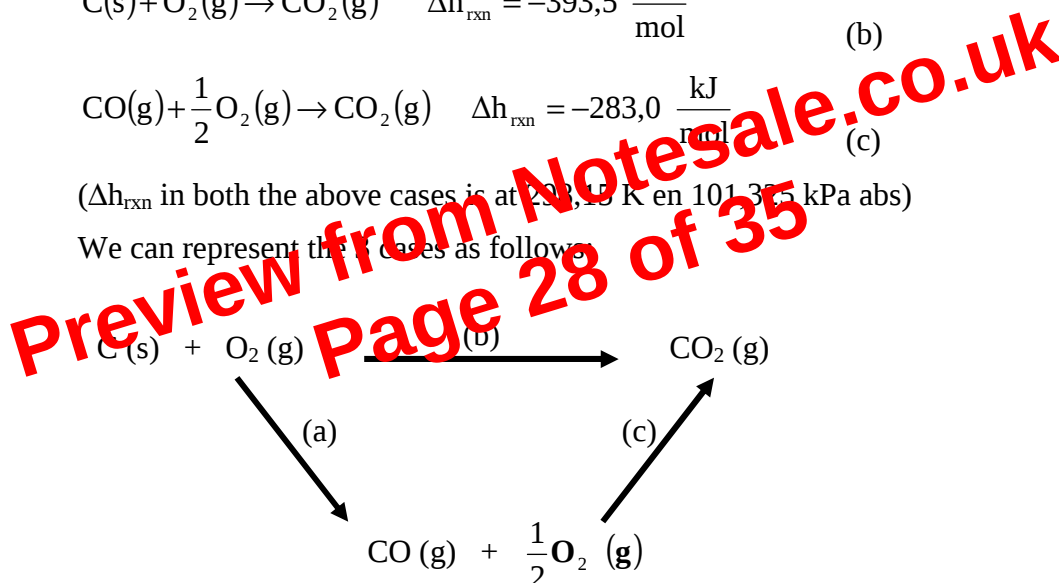


It is very difficult to convert graphite completely to CO without the formation of some CO_2 . It is this not possible to calculate the heat of reaction with the use if a calorimeter. However, it is possible to study the complete combustion of graphite and CO in a bomb calorimeter.



(Δh_{rxn} in both the above cases is at 298,15 K en 101,325 kPa abs)

We can represent the 3 cases as follows:



Because enthalpy is a state function, the enthalpy change must be the same irrespective of the path followed:

$$\therefore \Delta h_{\text{rxn}} (\text{b}) = \Delta h_{\text{rxn}} (\text{a}) - \Delta h_{\text{rxn}} (\text{c})$$

For reaction (a) the following thus holds true:

$$\begin{aligned} \therefore \Delta h_{\text{rxn}} (\text{a}) &= \Delta h_{\text{rxn}} (\text{b}) + \Delta h_{\text{rxn}} (\text{c}) \\ &= -393,5 \left[\frac{\text{kJ}}{\text{mol}} \right] - (-283,0) \left[\frac{\text{kJ}}{\text{mol}} \right] = -110,5 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

This fact was already discovered in 1840 by WG Hess and his law states: