

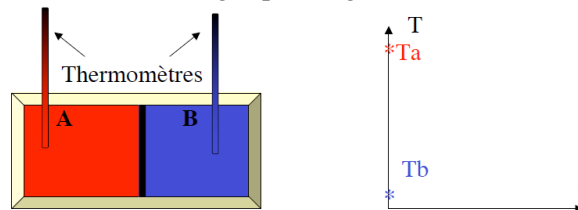
## 1. Notion of heat or quantity of heat Q:

### 1.1) Heat transfer:

Heat (thermal energy) is a form of energy associated with the disordered movement of particles contained in a substance.

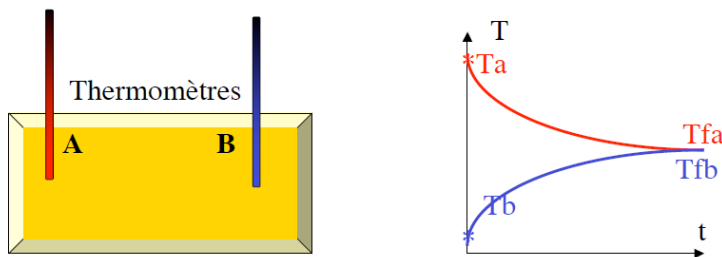
A thermal transfer or heat transfer is a transfer of thermal energy from one system to another due to a difference in temperature.

Consider a system in 2 parts (A and B) made up of the same pure substance (water) with the same mass but different temperatures. An insulating separating wall maintains  $T_a$  and  $T_b$ .



**For example:**  $T_a=80^\circ\text{C}$ ;  $T_b=20^\circ\text{C}$ .

When the insulating wall is removed, thermal equilibrium is established and temperatures become stationary.



### 1.2) Quantity of heat.

The quantity of heat (Q) is the heat required to raise the temperature of a body from  $T_1$  to  $T_2$  or to effect a change of state (e.g. from liquid to gas). At equilibrium temperature, the amount of heat given off by the hot body is equal to the amount of heat received by the cold body.

$$- Q_{\text{released}} = + Q_{\text{absorbed}}$$

**a. Sensible heat** (heat exchanged without changing the state of the system) :

This is the heat that is consumed or produced by a system as its temperature changes.

At constant pressure,  $Q = m \cdot C_p \cdot \Delta T$

Where: m: mass of the body in kg and  $C_p$ : heat capacity of the body in  $\text{J}/\text{kg}^\circ\text{K}$

The mass heat capacity of a substance is the amount of heat required to raise the temperature of a 1 kg mass of that substance by 1K. It is expressed in  $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$

For liquid water:  $C_p = 4185 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$  It can be at constant pressure ( $C_p$ ) or constant volume ( $C_v$ ).

Mayer relationship:  $C_p - C_v = nR$ .

**Example:** heating  $m = 2 \text{ kg}$  of water at constant pressure from  $20^\circ\text{C}$  to  $80^\circ\text{C}$ .

$$Q = 2 \cdot 10^3 \cdot 4,185 (80 - 20) = 502,2 \text{ kJ} = 120 \text{ kcal}$$

**b. Latent heat:** (During a change in the physical state of a body).

It is heat that is consumed or produced by a system that changes phase. Its temperature remains constant.

$$Q = m L = n L$$

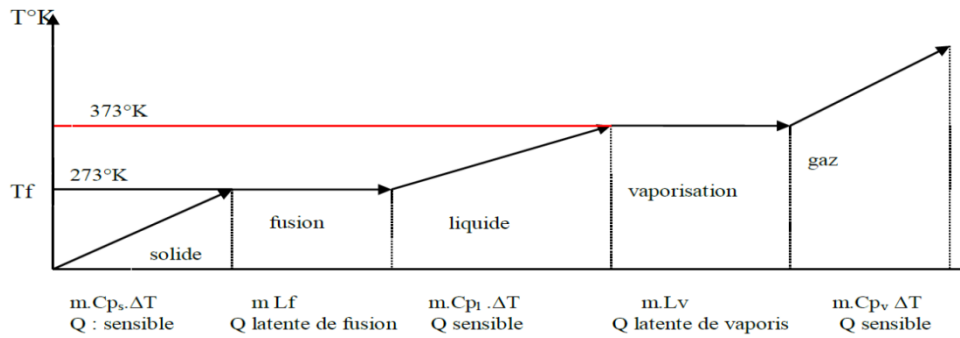
Where  $L_f$ : latent heat of fusion in  $\text{J}/\text{kg}$

$L_v$ : latent heat of vaporization in  $\text{J}/\text{kg}$

Example: melting of ice.  $L_f = 80 \text{ cal/g} = 330 \text{ kJ/kg}$  for water.

Vaporization of water.  $L_v = 2256 \text{ kJ/kg} = 539 \text{ kcal/kg}$  .

Example: calculate the energy required to heat 1 kg of H<sub>2</sub>O from - 5°C to 110°C.



**Example:** A beaker containing 800 g of water is heated on a hot plate. If the temperature of the water rises from 20°C to 85°C, how much energy has the water absorbed?

**Solution:**

1. Problem data

$$Q = x$$

$$m = 800 \text{ g}$$

$$c = 4.19 \text{ J/(g} \cdot \text{°C)}$$

$$\Delta T = 85 \text{ °C} - 20 \text{ °C} = 65 \text{ °C}$$

2. Calculation of energy

$$Q = m \cdot c \cdot \Delta T$$

$$Q = 800 \text{ g} \cdot 4.19 \text{ J/(g} \cdot \text{°C)} \cdot 65 \text{ °C}$$

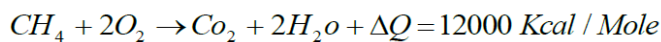
$$Q = 217880 \text{ J}$$

The energy absorbed by the water is 217.880 KJ.

**c. Heat of reaction:**

This is the amount of heat consumed or produced by a system during a chemical reaction.

Example:



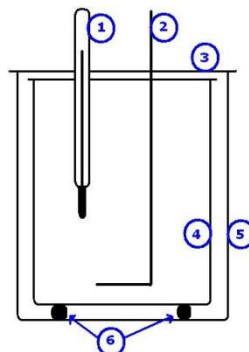
### 1.3. Calorimetry

Calorimetry is used to experimentally determine the quantities of heat involved in a transformation.

#### The calorimeter

A calorimeter is an isolated system used to take the measurements needed to perform calorimetry calculations.

Diagram of a calorimeter used to study a reaction taking place in an aqueous medium (1-thermometer; 2-agitator; 3-cover; 4-inner wall of the calorimeter; 5-outer wall of the calorimeter; 6-insulating feet).



Once the substances have been added to the calorimeter and it has been hermetically sealed, the thermal agitation of the particles involved in the reaction can be transmitted to the water in the calorimeter. So, during the reaction, the temperature of the water is measured. If the chemical reaction generates heat, the temperature of the water rises. If, on the other hand, the reaction is endothermic, the water cools as it transfers some of its thermal energy to the reaction. By measuring the variation in temperature in an isolated system, we can determine the energy involved in the transfer using the formula  $Q=m\cdot c\cdot\Delta T$ .

By convention, a negative energy value ( $-Q$ ) is considered to be energy released, while a positive energy value ( $+Q$ ) corresponds to energy absorbed.

When the temperature variation is positive, this means that the substance has absorbed heat during the transfer.

### Calculating the energy transferred

To calculate the energy transferred between two systems, we assume that the heat given by the first system is equal to the heat received by the second system. The following relationship can therefore be considered:

$$-Q_1 = Q_2 \quad \text{ou} \quad -m_1 \cdot c_1 \cdot \Delta T_1 = m_2 \cdot c_2 \cdot \Delta T_2$$

For the same substance at different temperatures:

$$(m_1 \cdot T_1) + (m_2 \cdot T_2) = (m_{\text{tot}} \cdot T_{\text{eq}})$$

$m_{\text{tot}}$  is the total mass of the two substances;

For two different substances:

$$-m_1 c_1 (T_f - T_1) = m_2 c_2 (T_f - T_2) \rightarrow T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2}$$

### Example:

A calorimeter contains a mass  $m_1 = 250\text{g}$  of water. The initial temperature is  $T_1 = 18^\circ\text{C}$ . A mass  $m_2 = 300\text{g}$  of water is added at temperature  $T_2 = 80^\circ\text{C}$ .

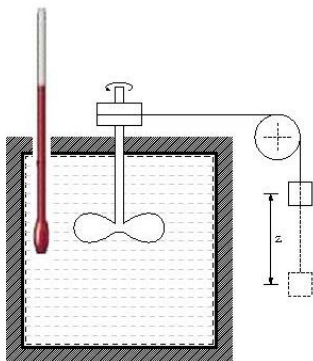
1. What would be the thermal equilibrium temperature  $T_e$  of the assembly if the heat capacity of the calorimeter and its accessories were negligible?

2. in fact, a thermal equilibrium temperature  $T_e = 50^\circ\text{C}$  is measured. Determine the heat capacity  $C$  of the calorimeter and its accessories.

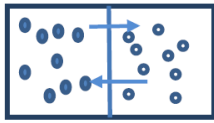
Data: Heat density of water:  $c_e = 4185 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ; Density of water:  $\mu = 1000 \text{ kg}\cdot\text{m}^{-3}$ .

### 1.4) Joule's experiment

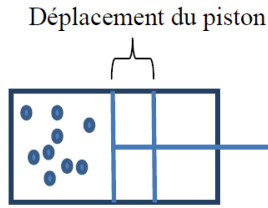
Joule's experiment established the equivalence between work (mechanical energy) and heat (thermal energy). In this experiment, a fluid is agitated by applying a known amount of work and the resulting rise in temperature is measured.



These two forms are interpreted as a manifestation of the agitation of molecules and atoms in disordered form (heat  $Q$ ) or in ordered form (work  $W$ ).



Transfert de chaleur (Q)



Transfert de travail (W) par déplacement du piston

Joule established through a series of carefully conducted experiments that there was a direct proportionality between the work expended and the quantity of heat obtained:  $W=JQ$

J: is the mechanical equivalent of heat= $4.186 \text{ cal}^{-1}$

**Examples:**

- Converting heat into work: mechanical displacement following combustion in an engine.
- Converting work into heat: heating brake pads.

**Work**

**2.1)The concept of pressure**

Pressure is due to the impact of atoms or molecules of matter on the walls of the container. It corresponds to the force per unit area exerted by the gas molecules on the wall.

$P=F/S$

- Pressure: in Pascal [Pa] ou [N/m<sup>2</sup>]

$1 \text{ Pa} = 1 \text{ N/m}^2$  ;  $1 \text{ atm} = 1,013 \text{ bar} = 1,013105 \text{ Pa} = 760 \text{ Torr} = 76 \text{ cmHg}$

$1 \text{ bar} = 10^5 \text{ Pa} = 750 \text{ Torr}$

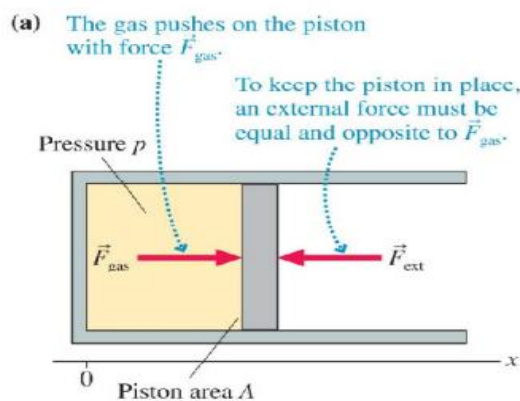
Work is a transfer of energy resulting from the displacement of the point of application of a force exerted by the external environment on the thermodynamic system.

- It is an energy expressed in [J] or [cal].
- On a microscopic scale, it is an energy exchanged in an orderly fashion (thanks to the displacement of a piston, for example, which imparts a certain direction to the atoms).
- It is not a state function.

Work is most often the result of a variation in the volume of a deformable (non-rigid) system, such as the displacement of a piston.

**2.2) Work in Ideal-Gas Processes**

Consider a gas cylinder sealed at one end by a moveable piston.

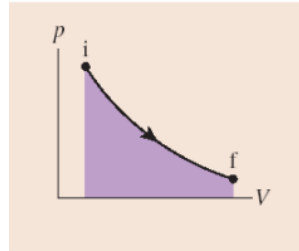


If we let the piston move in a slow quasi-static process from initial volume  $V_i$  to final volume  $V_f$ , the total work done by the environment on the gas is

$$W = - \int_{V_i}^{V_f} P dV$$

or, graphically.

$W$  = the negative of the area under the PV curve between  $V_i$  and  $V_f$



Visualize show the process on a PV diagram. Note whether it happens to be one of the basic gas processes. Isochoric, isobaric, or isothermal.

Solve calculate the work as the area under the PV curve either geometrically or by carrying out the integration:

Work done on the the gas  $W = - \int_{V_i}^{V_f} P dV = -$  (area under the PV curve )

Assess check your signs

- $W > 0$  when the gas is compressed. energy is transferred from the environment to the gas
- $W < 0$  when the gas is expands. energy is transferred from the gas to the environment
- No work is done if the volume doesn't change.  $W = 0$

**In an isochoric process**, when the volume does not change, no work is done.

في عملية متساوية الحجم عندما لا يتغير الحجم، لا يُبذل أي شغل.

$W=0$  (isochotic)

**In an isobaric process**, when pressure is a constant and the volume changes by  $\Delta V = V_f - V_i$ , the work done during the process is process is

$W = -P\Delta V$  (isobaric process)

**In an isothermal process**, when temperature is a constant, the work done during the process is

$$W = -nRT \ln \left( \frac{V_f}{V_i} \right) = -P_i V_i \ln \left( \frac{V_f}{V_i} \right) = -P_f V_f \ln \left( \frac{V_f}{V_i} \right) \quad \text{Isothermal process.}$$

**An Adiabatic process (Q=0)**

$$PV^\gamma = \text{constante et } TV^{(\gamma-1)} = \text{const}$$

$\gamma$  coefficient adiabatique  $\gamma = 1.67$  for monoatomic gases,  $\gamma = 1.4$  for diatomic gases and  $\gamma = 1.3$  for polyatomic gases.

$$W = \frac{nR(T_f - T_i)}{\gamma - 1} = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

### an irreversible process

$$P_{\text{ext}} = P_{\text{int}} = P_2 \rightarrow W_{12} = \int_1^2 P_2 dV$$

#### Example 1

A cylinder contains 7 g of nitrogen gas . how much work must be done to compress the gas at a constant temperature of 80 °C until the volume is halved?

Assess the work is positive because a force from the environment pushes the piston inward to compress the gas.

Solve

Nitrogen gas is N<sub>2</sub> , with molar mass M<sub>mol</sub> = 28 g/mol, so 7g is 0.25 mol of gas .the temperatue is T = 353 K . although we don't know the actual volume. We do know that V<sub>f</sub> = ½ V<sub>i</sub> . the volume ratio is all we need to calculate the work :

$$W = -nRT \ln(V_f/V_i) = - (0.25 \text{ mol}) (8.31 \text{ J/mol.K}) (353\text{K}) \ln(1/2) = 508 \text{ J}$$

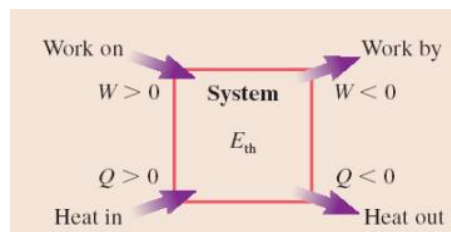
**Examlle 2 :** Gas in a container is at a pressure of 1.50 atm and a volume of 4.00 m<sup>3</sup>. What is the work done by the gas

- (a) if it expands at constant pressure to twice its initial volume?
- (b) If it is compressed at constant pressure to one quarter of its initial volume?

### The First Law of Thermodynamics

The first law of thermodynamics says the change in internal energy of a system is equal to the heat flow into the system plus the work done on the system (conservation of energy).

$$\Delta U = Q + W$$



### Isochoric process

An isochoric process is a constant volume process.

$$dV = 0, \quad \delta W = 0, \quad dU = \delta Q$$

We have hence

$$\left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

for the heat capacity at constant volume  $C_V$  .

**Ideal gas.** An ideal gas containing n moles is defined by its equation of state,

$$PV = N K_B T, \quad NK_B = nR$$

Using the internal energy

$$U = \frac{3}{2} NK_B T = \frac{3}{2} nRT$$

$$dU = \frac{3}{2} nRdT$$

we obtain

$$C_V = \frac{3}{2} nR = \frac{3 PV}{2 T}$$

for the heat capacity of the ideal gas at constant volume.

### Isobaric process

An isobaric process is a constant pressure process. In order to evaluate  $C_p$  we consider

$$\delta Q = dU + P dV$$

which, under an infinitesimal increment of temperature, is written as

$$dQ = \left(\frac{\partial U}{\partial T}\right)_P dT + P \left(\frac{\partial V}{\partial T}\right)_P dT \equiv C_P dT$$

The specific heat at constant pressure,

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

Reduces then for an ideal gas, for which

$$U = 3nRT/2 \text{ and } PV = nRT, \text{ to } C_p = \frac{3}{2}nR + nR = \frac{5}{2}nR = C_V + nR$$

Mayer's relation between  $C_P$  and  $C_V$ .

$$C_P = C_V + \left[ P + \left(\frac{\partial U}{\partial T}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P$$

### Isothermal processes for the ideal gas

An isothermal process takes place at constant temperature. The work performed

$$W = - \int_{V_1}^{V_2} P dV$$

is hence given by the area below  $P = P(T, V)$ . Using the equation of state relation

$PV = nRT$  of the ideal gas we obtain

$$W = -nRT \ln\left(\frac{V_2}{V_1}\right) = -Q$$

### Adiabatic processes for the ideal gas

An adiabatic process happens without heat transfer:

$$\delta Q = 0, dU = -P dV,$$

where the second relation follows from the first law of thermodynamics,

$$dU = \delta Q + \delta W.$$

For the ideal gas we have  $PV = nRT$ ,  $U = 3nRT/2 = 3PV/2$  and hence

$$dU = \frac{3}{2}(PdV + VdP) = -PdV$$

$$\frac{5 dV}{2 V} = \frac{3 dP}{2 P}$$

Which can be solved as?

$$\gamma \log\left(\frac{V}{V_0}\right) = \log\left(\frac{P}{P_0}\right), PV^\gamma = \text{const}, \gamma=5/3$$

Using the ideal gas equation of state,  $P V = nRT$ , we may write equivalently

$$T V^{\gamma-1} = \text{const.}$$

Since  $\gamma > 1$ , an adiabatic path has a steeper slope than an isotherm in a  $P-V$  diagram.

$$W = \frac{nR(T_f - T_i)}{\gamma - 1} = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

### Diferentielle totale exacte

$f(x,y)$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$A(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx, B(x,y) = \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$df = A(x,y)dx + B(x,y)dy$$

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$$

$$dU = dQ + dW$$

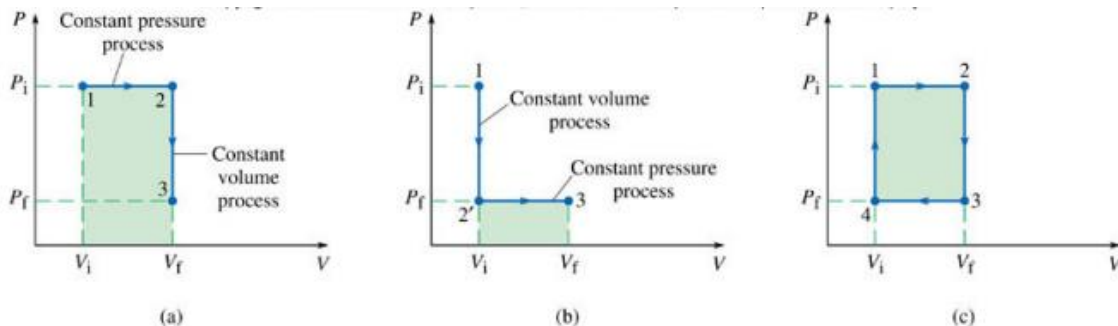
$$dU = mc dT - PdV$$

$$A = mc, B = -p, U(T,V)$$

$$\frac{\partial A}{\partial V} = 0, \frac{\partial B}{\partial T} = \frac{\partial(-P)}{\partial T} = 0$$

### Work for Different Pathways

To go from the state  $(V_i, P_i)$  by the path (a) to the state  $(V_f, P_f)$  requires a different amount of work than by path (b). To return to the initial point (1) requires the work to be nonzero.

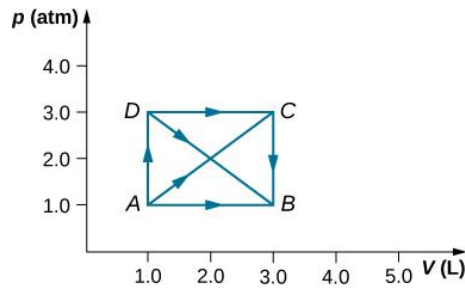


The work done on a system depends on the path taken in the  $PV$  diagram. The work done on a system during a closed cycle can be nonzero.

Example :



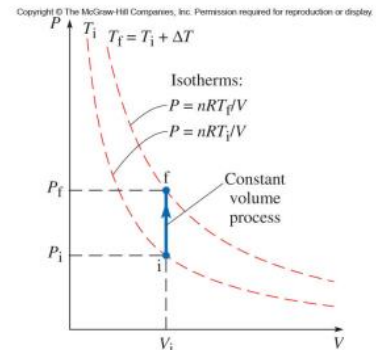
As shown below, calculate the work done by the gas in the quasi-static processes represented by the paths (a) AB; (b) ADB; (c) ACB; and (d) ADCB.



### Isochoric Process

No work is done on a system when its volume remains constant (isochoric process). For an ideal gas (provided the number of moles remains constant), the change in internal energy is

$$Q = \Delta U = nC_v \Delta T .$$

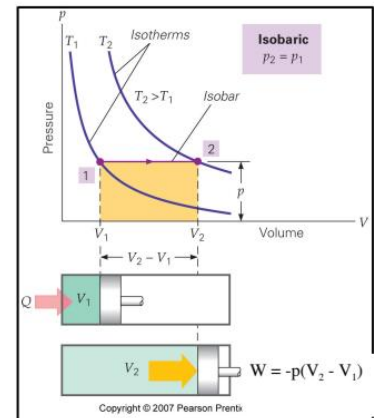


### Isobaric Process

For a constant pressure (isobaric) process, the change in internal energy is

$$\Delta U = Q + W$$

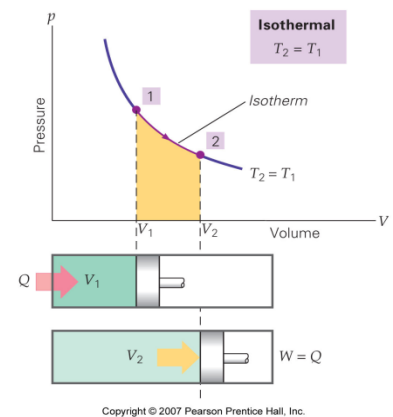
Where  $W = -P\Delta V = -nR \Delta T$



### Isothermal Process

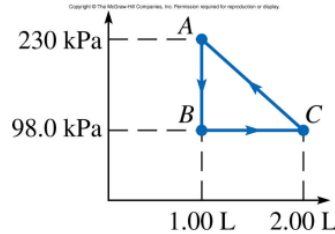
For a constant temperature (isothermal) process,  $\Delta U = 0$  and the work done on an ideal gas is

$$W = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

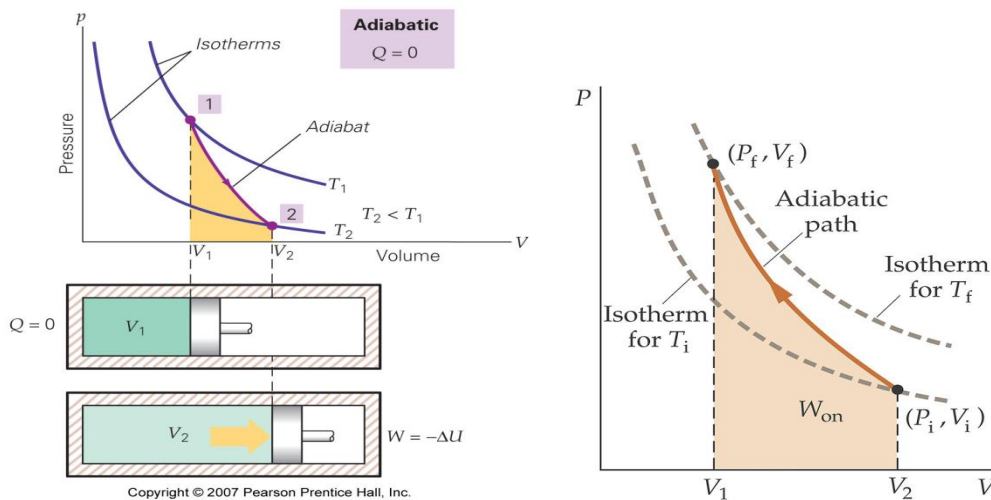


**Example:** An ideal monatomic gas is taken through a cycle in the PV diagram.

- (a) If there are 0.0200 mol of this gas, what are the temperature and pressure at point C?
- (b) What is the change in internal energy of the gas as it is taken from point A to B?
- (c) How much work is done by this gas per cycle?
- (d) What is the total change in internal energy of this gas in one cycle?



### Adiabatic Process



### Example

- Two moles of a monatomic ideal gas such as helium is compressed adiabatically and reversibly from a state (3 atm, 5 L) to a state with pressure 4 atm. (a) Find the volume and temperature of the final state. (b) Find the temperature of the initial state of the gas. (c) Find the work done by the gas in the process. (d) Find the change in internal energy of the gas in the process.

### Reversible and Irreversible Processes

A reversible process is one in which both the system and its environment can return to exactly the states they were in by following the reverse path.

An irreversible process is one in which the system and its environment cannot return together to exactly the states that they were in.

The irreversibility of any natural process results from the second law of thermodynamics. For a process to be reversible each point on the curve must represent an equilibrium state of the system

State an example of a process that occurs in nature that is as close to reversible as it can be.

Some possible solutions are frictionless movement; restrained compression or expansion; energy transfer as heat due to infinitesimal temperature nonuniformity; electric current flow through a zero

resistance; restrained chemical reaction; and mixing of two samples of the same substance at the same state.

An irreversible process can be defined as a process in which the system and the surroundings do not return to their original condition once the process is initiated. Take an example of an automobile engine that has travelled a distance with the aid of fuel equal to an amount 'x'. During the process, the fuel burns to provide energy to the engine, converting itself into smoke and heat energy. We cannot retrieve the energy lost by the fuel and cannot get back the original form. There are many factors due to which the irreversibility of a process occurs, namely:

The friction that converts the energy of the fuel to heat energy

The unrestrained expansion of the fluid prevents from regaining the original form of the fuel Heat transfer through a finite temperature, the reverse of which is not possible as the forward process, in this case, is spontaneous

Mixing of two different substances that cannot be separated as the intermixing process is again spontaneous in nature, the reverse of which is not feasible.

## **Enthalpy.**

### **Definition**

Enthalpy is total energy of heat in the system which is equivalent to the sum of total internal energy and resulting energy due to its pressure and volume.

The system has internal energy because of the molecule in motion and the state of molecules as well. The molecules in motion generate kinetic energy and due to vibrations and electric energy of atoms, the system can have energy in the potential form as well.

Other than this, internal energy also includes energy stored in the form of chemical bonds as we know the breaking of bonds releases energy in an exothermic reaction.

### **Enthalpy Symbol**

In thermodynamics and physical chemistry, Enthalpy is denoted as H. The enthalpy change ( $\Delta H$ ) plays a crucial role in quantifying the heat exchange between a system and its surroundings.

### **Enthalpy Units**

Enthalpy is typically measured in units of energy per mole, such as joules per mole (J/mol) in the International System of Units (SI) or calories per mole (cal/mol) in the calorie-based system.

### **Enthalpy Formula**

Enthalpy can be represented as:

$$H = U + PV$$

where,

**H** is Enthalpy

**U** is Internal Energy

**P** is Pressure

**V** is Volume

## Enthalpy Change

Enthalpy is a state function (those functions which are only dependent on the initial and final state of the process, not the path taken by the process) as its constituents U, P, and V are state functions. As enthalpy is a state function, change in enthalpy ( $\Delta H$ ) will depend on the initial and the final states of the system. Thus, change in enthalpy is represented by  $\Delta H$  and is given by the following formula:

$$\Delta H = H_2 - H_1$$

As we know, the formula for Enthalpy is  $H = U + PV$ , and then

$$H_1 = U_1 + P_1V_1$$

$$H_2 = U_2 + P_2V_2$$

Using, the values of  $H_1$  and  $H_2$ , value of  $\Delta H$  will be,

$$\Delta H = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$\Rightarrow \Delta H = U_2 + P_2V_2 - U_1 - P_1V_1$$

$$\Rightarrow \Delta H = (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$\Delta H = \Delta U + \Delta(PV)$$

Now, at a constant pressure  $P_1 = P_2 = P$  (Isobaric Process)

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

Consider pressure inside and outside are the same for this isobaric process (i.e.  $P_{ex} = P$ ) then the formula for the isobaric process will become,

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

Thus from the above two equations, we get,

$$\Delta H = Q_p$$

Thus from this derived formula, we understand that the increase in enthalpy of a system is equal to the heat absorbed by it at a constant pressure.

## Enthalpy of Fusion

Enthalpy of Fusion is the amount of heat energy required to convert a unit mass of a solid at its melting point into a liquid without an increase in temperature. It changes with the increase in temperature and other parameters.

## Enthalpy of Vapourization

Enthalpy of Vaporization is the amount of heat energy required to convert a unit mass of a liquid at its boiling point into a vapour state without an increase in temperature. Its symbol is  $\Delta H_{\text{vap}}$ . Enthalpy of Vaporization changes with increases with temperature and other parameter.

## Enthalpy of Freezing Water

Enthalpy of freezing water is the heat change required to change liquid ice to water and the its is equal to  $-6.00 \text{ kJ/mole}$ .

## Ionization Enthalpy

Ionization Enthalpy of an element is defined as the amount of energy required to remove an electron from the isolated gaseous in its gaseous state. Ionization energy depends on the force of attraction of electrons and the nucleus.

- Ionization Enthalpy decreases from top to down in a Group.
- Ionization Enthalpy increases from left to right in a Group

### **Activation Enthalpy**

Activation Enthalpy of the reaction is defined as the energy required to proceed a reaction. It is the minimum amount of energy that is necessary for the reactants in a chemical reaction to proceed and form the product.

### **Relationship between $\Delta H$ and $\Delta U$**

As we already established that  $\Delta H$  and  $\Delta U$  are related by the equation  $\Delta H = \Delta U + P\Delta V$ , at constant pressure. For reactions between solids and liquids,  $\Delta V$  is very small because as pressure varies, solids or liquids won't get affected significantly. So, for these reactions remove  $P\Delta V$  from the equation and write  $\Delta H = \Delta U$

However, for the reactions involving gases, which are easily affected by the change in pressure,  $\Delta V$  should strictly be considered.

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

Here we consider the reactants and the product to be ideal, so we can use the ideal gas equation ( $PV = nRT$ ).

Let's consider there are  $n_1$  moles of gaseous reactants that produce  $n_2$  moles of gaseous products. The ideal gas equation becomes

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$

$$\Delta H = \Delta U + n_2RT - n_1RT$$

$$\Delta H = \Delta U + RT (n_2 - n_1)$$

$$\Delta H = \Delta U + RT \Delta n$$

### **Requirements for $\Delta H$ to be equal to $\Delta U$**

There are two cases when  $\Delta H$  and  $\Delta U$  becomes equal, which are as follows:

When the reaction is conducted inside a closed container it prevents the alteration of the volume of the system ( $\Delta V = 0$ ). Then change in enthalpy will change as  $\Delta H = \Delta U$ .

When there are only solids or liquids involved in the reactions then we can neglect  $\Delta V$  as the change in them due to the pressure is significant. So,  $\Delta H = \Delta U$ .

There reaction in which the moles of gaseous products and reactants are the same (i.e.  $n_2 = n_1$ ). So,  $\Delta H = \Delta U$

### **Endothermic and Exothermic Reactions**

A reaction is a process in which two or more two reactants react to form some products we can have a reaction in which we are required to give some energy on the other hand some redactions can give energy to the products. So on this basis, we can have two types of reactions that include

Endothermic Reactions

Exothermic Reactions

**Problem 1:** For a reaction, the system absorbs 10 kJ of heat and does 3 kJ of work on its surroundings. What are the changes in the Internal energy and Enthalpy of the system?

**Solution:**

According to the First law of thermodynamics,

$$\Delta U = Q + W$$

$$Q = +10 \text{ kJ and } W = -3 \text{ kJ}$$

( $W = -3 \text{ kJ}$  because the work is done on the surrounding by the system so the system has lose that energy)

$$\Delta U = 10 \text{ kJ} - 3 \text{ kJ}$$

$$\Delta U = +7 \text{ kJ}$$

and,  $Q_p = \Delta H$

$$Q_p = +10 \text{ kJ}$$

Thus, the Internal energy increases by 7 kJ and Enthalpy by 10 kJ.

**Problem 2:** An Ideal gas expands from a volume of 5 dm<sup>3</sup> to 15 dm<sup>3</sup> against a constant external pressure of  $3.036 \times 10^5 \text{ Nm}^{-2}$ . Find  $\Delta H$  if  $\Delta U$  is 400 J.

**Solution:**

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

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

Assume that  $P_{\text{ext}} = P$ ,  $P = 3.036 \cdot 10^5 \text{ N m}^{-2}$

$$\Delta U = 400 \text{ J}$$

$$V_1 = 5 \text{ dm}^3 = 5 \times 10^{-3} \text{ m}^3$$

$$\text{and } V_2 = 10 \text{ dm}^3 = 10 \times 10^{-3} \text{ m}^3$$

Substituting the values in the equation

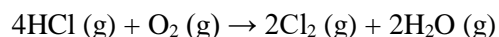
$$\Delta H = 400 \text{ J} + 3.036 \times 10^5 \text{ Nm}^{-2} \cdot (10 \times 10^{-3} \text{ m}^3 - 5 \times 10^{-3} \text{ m}^3)$$

$$\Delta H = 400 \text{ J} + 3.036 \times 10^5 \text{ Nm}^{-2} \cdot (10 - 5) \times 10^{-3} \text{ m}^3$$

$$\Delta H = 400 \text{ J} + 3.036 \times 10^3 \text{ J}$$

$$\Delta H = 3436 \text{ J.}$$

**Problem 3:** Calculate the work done in the following reaction when 2 moles of HCl are used at Constant pressure at 420 K.



State, whether the work done, is by the system or on the system.

**Solution:**

According to the Formula to calculate the work done in chemical reactions,.

$$W = - \Delta n RT$$

$$W = - RT (n_2 - n_1)$$

2 moles of HCl react with 0.5 mole of O<sub>2</sub> to give 1 mole of Cl<sub>2</sub> and 1 mole of H<sub>2</sub>O

Hence, n<sub>1</sub> = 2.5, n<sub>2</sub> = 2, R = 8.314 J.K<sup>-1</sup> .mol<sup>-1</sup> , T = 420 K

Substituting the values in the equation,

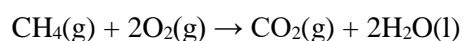
$$W = - 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 420 \text{ K} \times (2 - 2.5) \text{ mol}$$

$$W = -8.314 \times 420 \times (-0.5) \text{ J}$$

$$W = 1745.94 \text{ J}$$

**Problem 4:** Calculate the change in enthalpy ( $\Delta H$ ) for the combustion of methane (CH<sub>4</sub>) if the standard enthalpy of formation of methane is -74.8 kJ/mol.

The combustion reaction of methane is:



The standard enthalpy of the formation of CO<sub>2</sub>(g) is -393.5 kJ/mol and the standard enthalpy of the formation of H<sub>2</sub>O(l) is -285.8 kJ/mol.

**Solution:**

To calculate the  $\Delta H$  for the combustion of methane, we need to use the standard enthalpies of formation of the reactants and products. The  $\Delta H$  can be calculated using the formula:

$$\Delta H = \sum n\Delta H_f(\text{products}) - \sum n\Delta H_f(\text{reactants})$$

where n is the stoichiometric coefficient of each species in the balanced chemical equation.

$$\Delta H = [1 \times (-393.5 \text{ kJ/mol}) + 2 \times (-285.8 \text{ kJ/mol})] - [1 \times (-74.8 \text{ kJ/mol}) + 2 \times (0 \text{ kJ/mol})]$$

[Standard enthalpy of formation of O<sub>2</sub>(g) is 0]

$$\Delta H = -802.2 \text{ kJ/mol} - (-74.8 \text{ kJ/mol})$$

$$\Delta H = -727.4 \text{ kJ/mol}$$

**Therefore, the change in enthalpy for the combustion of methane is -727.4 kJ/mol.**