

Thermodynamics

Introduction :

Chemical thermodynamics is a part of chemistry which is interested in study of energy exchanges which accompany changes of state and chemical reactions, it makes it possible to evaluate the energy exchanged and predict the evolution of systems studied.

It is based on study of the macroscopic properties of matter such as pressure, temperature, volume,.... etc.

Thermodynamics is based on two notions, energy and entropy introduced using principles which are assertions deduced from experience.

The first principle: studies the transfers of energy, in the form of heat (Q) and work (W) between studied system and external environment.

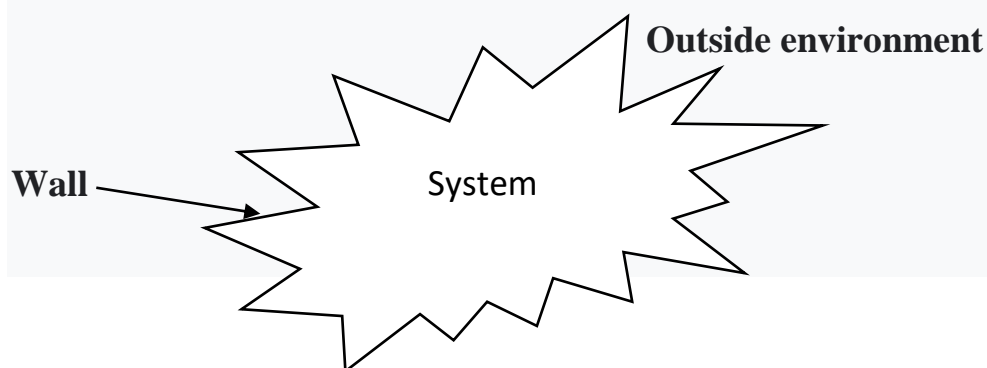
The second principle: predicts direction of chemical evolution processes.

The third law : Entropy of elements and pure compounds in the state of perfect crystals is zero at absolute temperature (0°K).

I. Definitions

1. System

Part of space subject to theoretical or experimental studies is called a system.



The wall can be real (permeable, semi-permeable or impermeable) or it can be fictitious.

A system can be:

Open: when it exchanges energy and matter with the external environment.

Closed: when it exchanges energy with the external environment.

Isolated: when it exchanges neither energy nor matter with the external environment.

2. State quantity

it is a physical quantity which may or may not be directly measurable and which describes the system.

State of a system: represents all values corresponding to state quantities of the system at given moment.

Intensive quantity: it is a quantity that does not depend on the quantity of matter.

Example:

pressure, temperature, chemical composition are intensive quantities

Extensive quantity: it is a quantity which depends on the quantity of matter.

Example:

number of moles, mass, volume are extensive quantities

3. State function

the number of quantities which characterize a system is generally quite large; it is not necessary to determine them all because they are linked.

For example, the fundamental equation for ideal gases $PV = nRT$ corresponds to a state function of n moles.

To define the state of n moles of ideal gas, it is enough to know two quantities among the three (P, V, T) and deduce the third.

4. Mathematical properties of state functions

- During an infinitely small transformation variation of state function is an exact total differential.

if $f(x,y)$ state function : $dF = (dF/dx)_y dx + (dF/dy)_x dy = A dx + B dy$

Example:

free enthalpy $G(P,T)$ is a state function : $dG = VdP - SdT$

- Value of integral depends only on initial and final states:

$$\int_{state1}^{state2} dF(x, y) = F(x_2, y_2) - F(x_1, y_1)$$

- if studied system describes a cycle:

$$\int_{state1}^{state2} dF(x, y) = 0$$

5. Transformations

Transformation is the passage of a system from state1 called initial state to state2 called final state.

- **Isochoric transformation:** this is a transformation which takes place at constant volume.

- **Isobaric transformation:** this is a transformation which takes place at constant pressure.

- **Isothermal transformation:** this is a transformation which takes place at constant temperature.

6. State of equilibrium

System is said to be in thermodynamic equilibrium when the state variables which characterize it are the same at every point of the system and remain fixed over time.

Thermodynamic reversibility:

A transformation is invertible if it can be performed in both directions.

Example :

- a. heating of a matter and its cooling.
- b. Compression of gas and its decompression.

- Reversible transformation

It is a transformation during which the system passes from one state of equilibrium to another state of equilibrium via a succession of equilibrium states.

- Irreversible transformation

It is an abrupt, uncontrolled (spontaneous, natural) transformation.

II. Energy exchanges (Heat, work)

Energy can manifest in several forms:

Mechanical, calorific, nuclear, radiant...etc.

Our study involves only heat energy (Q) and mechanical energy (W).

Energy units

W: quantity of work (mechanical energy)

Q: quantity of heat (heat energy)

In the **MKSA (IS)** system, energy is expressed in joules (J).

In the **CGS** system, energy is expressed in erg.

Energy can also be expressed in **calories(cal)**(**1cal = 4.18J , 1J = 10⁷erg**)

Sign convention

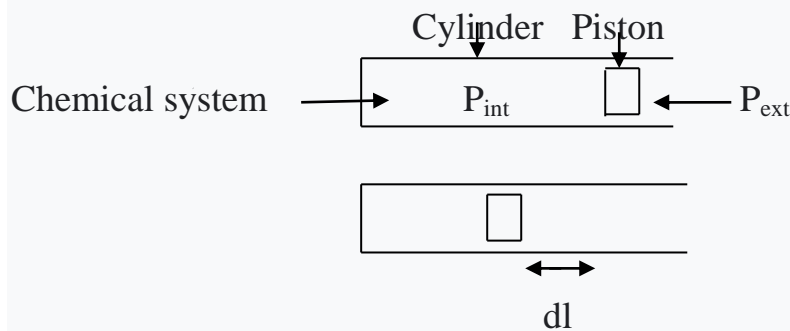
If the system receives energy, it is taken **positive** (+).

If the system releases energy, it is taken **negative** (-).

1. Concept of work W

Energy produced by the movement of an object subjected to a force:

Work = force . distance



Work of an elementary external force, moving a piston at distance dl , on a chemical system.

The piston of surface S , moves over a distance dl under the action of the force F (Force = Pressure . surface). Then the work exchanged is:

$$|\delta W| = |F \cdot dl| = |P_{ext} \cdot S \cdot dl| = |P_{ext} \cdot dV|$$

If the system gains or receives mechanical energy (force from external pressures) dV decreases: $W \uparrow \Rightarrow \delta W > 0 \leftrightarrow \delta W = -P_{ext} \cdot dV$

If the system loses or gives up mechanical energy (force of internal pressures) dV increases: $W \downarrow \Rightarrow \delta W < 0 \leftrightarrow \delta W = -P_{ext} \cdot dV$

Finally the work of a finite transformation passing from state1 to state2 is given by the following relation: $W = \int_{V_1}^{V_2} -P_{ext} dV$

• **Work of a reversible transformation:**

If the system moves slowly from an equilibrium state to another through a succession of equilibrium states, the transformation is reversible. We will then have at every point of the system ; internal pressure of gas is equal to external pressure: $P_{\text{int}} = P_{\text{ext}}$

For a supposedly perfect gas we have:

$$PV = nRT \Rightarrow P_{\text{int}} V = nRT \Rightarrow P_{\text{int}} = n RT/V$$

$$W_{\text{rev}} = \int_{V_1}^{V_2} -P_{\text{ext}} dv = -nRTLn (V_2/V_1)$$

$$W_{\text{rev}1 \rightarrow 2} = -nRTLn (V_2/V_1)$$

• **work of an irreversible (spontaneous) transformation:**

on the other hand if we move the piston suddenly the internal pressure varies quickly, it is not the same at every point of the system during this transformation which is then an irreversible transformation.

Then: $P_{\text{int}} \neq P_{\text{ext}} \rightarrow P_{\text{ext}} = P_{\text{final}} = P_2 = \text{constant}$

The work in this case is: $W_{\text{irrev}} = \int_{V_1}^{V_2} -P_2 dv = -P_2(V_2 - V_1)$

2. Concept of heat Q

- The heat Q (calorific or thermal energy), exchanged, is the energy in movement whose flow from hot environment to cold environment.
- The heat received by a system (>0) can cause a variation in its temperature.

Proportionality relationship between the heat received δQ and the temperature variation dT:

For 1 mole we have: $\delta Q = \int_{T_1}^{T_2} C dT$

For n mole we have: $\delta Q = n \int_{T_1}^{T_2} C dT$

C: molar heat capacity of substance = quantity of heat that must be supplied to 1 mole of substance to raise its temperature by 1 degree (C is expressed in $\text{J mol}^{-1} \cdot \text{K}^{-1}$).

Molar heat capacities at constant volume (C_v) and constant pressure (C_p).

In the interval of temperatures T_1 and T_2 and for a finite transformation we have:

$$\text{Heat of reaction at constant volume : } Q_v = \int_{T_1}^{T_2} nC_v dT$$

$$\text{Heat of reaction at constant pressure : } Q_p = \int_{T_1}^{T_2} nC_p dT$$

If we consider that C_v and C_p are constant in the temperature interval:

$$Q_v = nC_v (T_2 - T_1) = nC_v \cdot \Delta T \quad \text{and} \quad Q_p = nC_p (T_2 - T_1) = nC_p \cdot \Delta T$$

Mayer relationship

Case of monatomic ideal gases:

$$C_v = 3/2 R \quad \text{and} \quad C_p = 5/2 R \Rightarrow C_p - C_v = R$$

Case of diatomic ideal gases: $C_v = 5/2 R$ and $C_p = 7/2 R \Rightarrow C_p - C_v = R$

III. Perfect gas

An ideal gas obeys the following laws:

1. Boyle-Mariotte law:

At a given temperature, for a given mass the product of pressure and volume is constant : **$P \cdot V = \text{constant}$**

2. Charles' Law:

At constant pressure, the volume of a gas is proportional to the absolute temperature : **$V = \text{constant} \cdot T$**

3. Gay-Lussac law:

At constant volume, the pressure of a gas is proportional to the temperature : **$P = \text{constant} \cdot T$**

4. Joule's law:

The internal energy of an ideal gas depends only on temperature.

5. Characteristic equation of an ideal gas:

The previous laws allowed us to establish the formalism of the fundamental equation of an ideal gas: $P.V = nR.T$

P: pressure

V: volume

T: absolute temperature

n: number of moles **R**: ideal gas constant

Avogadro's proposal

One mole of ideal gas occupies under normal conditions of temperature and pressure ($P = 1 \text{ atm}$, $T = 0^\circ\text{C} = 273,15^\circ\text{k}$) a volume of 22.4 l

$$P.V = nR.T \rightarrow R = PV/nT$$

For $n = 1$ $R = (1 \times 22.4)/(1 \times 273,15) \approx 0.082 \text{ l.atm K}^{-1}\text{mol}^{-1}$

And as : $1 \text{ atm} = 1.01325 \cdot 10^5 \text{ Pa} \approx 10^5 \text{ Pa}$, we find:

$$R = (1,01325 \cdot 10^5 \cdot 22,4 \cdot 10^{-3})/1.273,15 \approx 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

First law of thermodynamics:

Statement of the first principle "The variation of internal energy U of a closed system evolving from state1 to a state2 is equal to the algebraic sum of the quantities of work W and heat Q exchanged with the external environment".

The variation of internal energy of a system does not depend on the path followed but only on initial and final states.

Mathematical expression of the 1st principle : $\Delta U = U_2 - U_1 = Q + W$

U is a **state function**, **W** and **Q** are **not**.

Differential expression

$$dU = dQ + dW \rightarrow \Delta u = \int_{state1}^{state2} du = \int_{state1}^{state2} dQ + \int_{state1}^{state2} dW$$

Special cases :

Closed transformation:

If the system undergoes a series of transformations such that its final state is identical to its initial state ($U_2 = U_1$): $\Delta U = U_2 - U_1 = 0 \Rightarrow \mathbf{W} = -\mathbf{Q}$

Isolated system:

If the system does not exchange neither energy nor heat with the external environment ($W = 0$ and $Q = 0$) $\rightarrow \Delta U = Q + W = 0$

2.Constant volume transformation:

We have: $dU = dQ + dW$ on the other hand: $dW = -P_{ext} dv = 0 (v=ct)$

Then: $dU = dQ + dW = dQ + 0 = dQ$

and $\int_{state1}^{state2} du = \int_{state1}^{state2} dQ \Rightarrow \Delta U = Q_v$

Q_v is the quantity of heat exchanged during a transformation at constant volume.

3.Constant pressure transformation:

We have: $dU = dQ + dW$ on the other hand: $dW = -P_{ext} dv$

$$\begin{aligned} \text{Then: } \int_{state1}^{state2} dU &= \int_{state1}^{state2} dQ + dW = \int_{state1}^{state2} dQ + \int_{state1}^{state2} dW \\ &= Q_p + \int_{state1}^{state2} dW = Q_p + \int_{state1}^{state2} -P_{ext} dV \end{aligned}$$

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

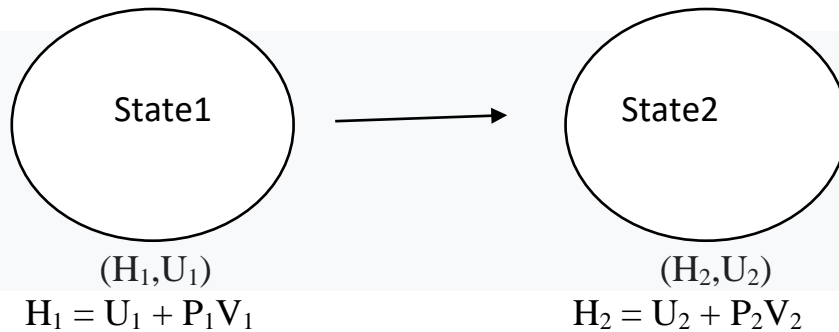
$$U_2 - U_1 = Q_p - PV_2 + PV_1 \rightarrow Q_p = (U_2 + PV_2) - (U_1 - PV_1)$$

We note that :

Q_p only depends on the initial state and the final state, it is a state function that we note **H**: $\mathbf{H} = \mathbf{U} + \mathbf{PV} \longrightarrow \mathbf{Q_p} = \Delta \mathbf{H}$

Relationship between ΔH and ΔU (or Q_p and Q_v):

we consider a system evolving from state1 to state2.



$$\Delta H = H_2 - H_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$\Delta H = (U_2 - U_1) + (P_2V_2 - P_1V_1) = \Delta U + P\Delta V \text{ or } Q_p = Q_v + P\Delta V$$

By applying ideal gas law to the initial and final states of the system:

$$P_1V_1 = n_1RT \quad \text{and} \quad P_2V_2 = n_2RT$$

$$Q_p = Q_v + \Delta nRT \quad \text{or} \quad \Delta H = \Delta U + \Delta nRT$$

