Introduction to thermodynamics

Thermodynamics:→ Is the scientific study of the inter conversion of heat and other kinds of energy.

In thermodynamics, we study changes in the state of a system.

State of a system: The value of all relevant macroscopic properties.

Ex: Composition energy, temperature, pressure and volume.

- Energy, volume, pressure and temperature are said to be **state functions**.

  →Properties that are determined by the state of the system, regardless of how that condition was achieved.

- When the state of a system changes, the magnitude of change in any state function depends only on the initial and final states of the system and not how the change is accomplished.

The first law of thermodynamics:→ Is based on the law of conservation of energy which state that energy can be converted from one form to another but can't be created or destroyed.

- we can test the validity of the first law of thermodynamics by measuring only the change in internal energy of a system between its initial state and its final state in a process.

The change in internal energy ΔE is given by:

$\Delta E = E_f - E_i$

E_i →The internal energy of initial state

E_f→The internal energy of final state.

Internal energy of the system has two components:

1-Kinetic energy: Is consists of various types of molecular motion and the movement of electrons within molecules.

2-Potential energy: Is determined by the attractive interactions and repulsive interactions between electrons and between nuclei in individual molecules as well as by interactions between molecules.

- Changes in energy can be determined experimentally.

EX:

Consider the reaction between 1 mole of Sulphur and 1 mole of oxygen gas to produce 1 mole of Sulphur dioxide.

$$S_{(s)} + O_{2\,(g)} \rightarrow So_{2\,(g)}$$

In this case: system is composed of S and O_2 and the product molecules So_2 .

- we don't know the internal energy content of either the reactant molecules or the product molecules, but we can accurately measure the change in energy content.

ΔE is given by:`

$$\Delta E = E_{(product)} - E_{(reactant)}$$

ΔE=Energy content of 1 m of $So_{2\,(g)}$ – Energy content of [1 m $S_{(s)}$+ 1 m $O_{2\,(g)}$]

- ✓ We found that this reaction gives off heat (exothermic).
- ✓ Energy of product is less than energy of reactant ΔE is negative we conclude that the transfer of energy from the system to the surroundings doesn't change the total energy of the universe that is, sum of energy changes must be zero.

$$\Delta E_{sys} + \Delta E_{surr} = 0 \quad , \quad \Delta E_{sys} = -\Delta E_{surr}$$

Where "sys" → System

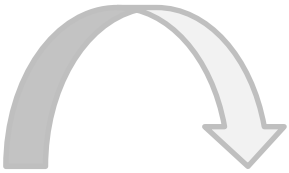
"surr" → surroundings

- If one system undergoes any energy change ΔE, the rest of universe or surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign ($-\Delta E_{surr}$).
- In chemistry, we are normally interested in the energy changes associated with the system (which may be a flask containing reactants and products). Not with its surroundings.

Thus a more useful form of the first law is:

ΔE= q+w

$$\Delta E = q + w$$



❖ This equation say that change in the internal energy ΔE of a system is the sum of the heat exchange (q) between the system and the surroundings and the work done (w) on or by the system.

❖ The sign conventions for q and w are as follows:

- q is positive for an endothermic process.
- q is negative for an exothermic process.
- w is positive for work done on the system by the surroundings.
- w is negative for work done by the system on the surroundings.

ΔE increase → If q, w are positive

ΔE decrease → If q, w are negative

Work and Heat

Work: Can be defined as force (f) multiplied by distance (d).

$$W = fd$$

- In thermodynamics, work has a broader mean that includes: mechanical work, electrical work and surface work.

❖ Mechanical work includes the study of the expansion or compression of a gas.

❖ **Gas in a cylinder fitted with a weightless, frictionless and movable piston at a certain temperature, pressure and volume.**

❖ **As it expands, the gas pushes the piston upward against a constant opposing external atmospheric pressure P.**

- The work done by the gas on the surroundings is: $W = -P\Delta V$
- ΔV (change in volume), given by $(v_f - v_i)$.
- for gas expansion $\Delta V > 0$ So, $-P\Delta V$ is a negative quantity.
- For gas compression (work done on the system), $\Delta V < 0$ and $-P\Delta V$ is a positive quantity.

Note that

✓ The work done depends on the magnitude of the external, opposing pressure (P).

✓ If P is zero, then work done equal zero.(increase of gas expanding against a vacum).

✓ Units of work done by or on a gas are (liter. atmosphere).

1 L.atm = 101.3 J.

للتحويل من L.atm الى Joule نضرب القيمة المعطاه L.atm في 101.3

$$\Delta E = q + w = q - P\Delta V$$

Heat: The other component of internal energy.

- ❖ Like work, heat not a state function.
- ❖ It depends on how the process is carried out.

Note:

- ❖ Work and heat not a state function so can't write $\Delta q = q_f - q_i$ or $\Delta w = w_f - w_i$.
- ❖ Their value depend on the path of the process and vary accordingly.

Choose

1) Composition, volume and temperature are considered …….

A) State of a system
B) State function
C) Properties of system
D) both A and B

2) Which of the following is a state function? ……..

A) Volume
B) Pressure
C) Temperature
D) A,B,C

3) When state of a system changes, the system depends on …….

A) Initial value
B) Final value
C) Initial and final value
D) Process carried out

4) The first law of thermodynamics depends on ……

A) State of system
B) State function
C) Law of conservation of energy
D) initial and final value

5) Energy can be converted from one form to another but can't be created or destroyed expressed ……

A) Law of conservation of energy
B) Second law of thermodynamics
C) Third law of thermodynamics
D) both B and C

6) Energy is considered a ……., so change in energy can be expressed by……..

A) State function- $\Delta E=E_f - E_i$
B) State function- how change carried out
C) state function
D) None of them

7) Internal energy of the system consist of ……..

A) Kinetic energy
B) Potential energy
C) Nuclear energy
D) Both A and B

8) Consist of various types of molecular motion and the movement of electrons within molecules is ……

A) Potential energy
B) Kinetic energy
C) Solar energy
D) Nuclear energy

9) Formula of the first law of thermodynamics is ……

A) $\Delta E= q+w$
B) $\Delta E=E_f - E_i$
C) $\Delta E= E_{(product)} - E_{(reactant)}$
D) $\Delta E= q - w$

10) The change in internal energy of a system equal ……..

A) Heat change

C) The sum of heat exchange and work done by or on the system

B) Work done by or on the system

D) None of them

11) If energy gives off the reaction and work done by the system on the surroundings, the internal energy will …….

A) Increase

C) Decrease

B) Not change

D) infinity

12) If energy added to the system and work done on the system by the surroundings, energy will …….

A) Increase

C) Constant

B) Decrease

D) inifinity

13) Which of the following is true about first law of thermodynamics?.....

A) Depend on law of conservation of energy

C) Energy can be converted from one form to another but can't be destroyed or created

B) Can be expressed by formula: $\Delta E = q+w$

D) All of above

14) Unit of work done is …….

A) Liter. atmosphere
B) Atmosphere
C) Liter
D) Kelvin

15) In work done unit's joule equal ……..

A) 101.3 L.atm
B) L.atm/101.3
C) 1L.atm
D) L.atm/100

16) Force multiplied by distance equal ……..

A) Work
B) Energy
C) Heat
D) Temperature

17) Work done by a gas on the surroundings is …….

A) W=f.d
B) W=-PΔV
C) W=PΔV
D) W=P/ΔV

18) Work done and heat are ……

A) State function
B) Not a state function
C) Their depend on final initial magnitude
D) both B and C

19) For gas compression ……..

A) ΔV>0 C) ΔV=0

B) ΔV<0 D) ΔV= ∞

20) Work has a boarder mean that include ……

A) Mechanical work C) Electrical work

B) Surface work D) All of the above

21) For gas expansion ……

A) ΔV>0 C) ΔV=0

B) ΔV<0 D) ΔV= ∞

22) A certain gas expanding volume from 2.0L to 6.0L at constant temperature, calculate the work done by the gas if it expands:

A-against a vacuum .

B-against a constant pressure of 1.2 atm.

Solution:-

Initial volume=2L, final volume=6L

Therefore $\Delta V = V_f - V_i$ =6-2 =4L

A-against vacuum

Therefore P=0, so no work is done in the expansion.

W= -PΔV = -(0) (4)=zero

B-Against a constant pressure of 1.2 atm

P=1.2 atm W= -PΔV = -1.2 x 4

Therefore W= -4.8L.atm or W= -4.8L.atm x $\frac{101.3}{1L-atm}$ = -4.9 x10^2 J

23) A gas expands from 264 ml to 971 ml at constant temperature, calculate work done (in joules) by a gas if it expands:
A-against a vacuum.

B-against a constant pressure of 4.00 atm.

Solution:-

A-against a vacuum.

Since P=0 , Therefore work done=0

B-against constant pressure of 4.00 atm.

P=4.00 atm

$\Delta V = V_f - V_i$

=0.971-0.264

=0.707

W= -P.ΔV = -4.00*.707= -2.828 L.atm

= -286.4 J

24) The work done when gas is compressed in a cylinder 264 J during this process there is a heat transfer of 128 J from the gas to the surroundings; calculate energy change for this process.

Solution:-

ΔE = q + w

=-128+264=136 J