

Chemical Thermodynamics-02

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1. Statement of 1st law of thermodynamics:

The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic processes, distinguishing two kinds of transfer of energy, as heat (Q) and as thermodynamic work (W) and relating them to a function of a body's state, called Internal energy (U).

The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed.

For a thermodynamic process without transfer of matter, the first law is often formulated

$$\Delta U = Q - W$$

Where, ΔU denotes the change in the internal energy of a closed system, Q denotes the quantity of energy supplied to the system as heat, and W denotes the amount of thermodynamic work done by the system on its surroundings.

An equivalent statement 1st law of thermodynamics is that perpetual motion machines of the first kind are impossible.

Heat and Work :- According to SI Convention heat absorbed by the system is regarded as the +ve quantity whereas the heat released by the system is regarded as the -ve quantity. We may spell q as the heat involved (in the system) during the transformation. The numerical value of q will imply ^{heat} either absorbed or released by the system. To be more specific -

Heat involved = 20 kJ (say)

∴ Heat absorbed = +20 kJ

and Heat released = -20 kJ

Again, heat involved = -20 kJ (say)
 \therefore Heat absorbed = -20 kJ
 and Heat released = $+20 \text{ kJ}$

According to SI Convention, the work is to take on the +ve quantity when it is done on the system whereas it is -ve quantity when work is done by the system. We may spell w as the work involved during the transformation. The numerical value of w will imply work done either on the system or by the system. To be more specific -

Work involved = 20 kJ
 \therefore work done on the system = $+20 \text{ kJ}$
 \rightarrow work done by the system = -20 kJ

Again work involved = -20 kJ
 \therefore work done on the system = -20 kJ
 \rightarrow work done by the system = $+20 \text{ kJ}$

According to new SI convention $+w$ is replaced by $-w$ \rightarrow vis-a-vis. Also, ^{implies} maximum, minimum greater than \rightarrow lesser than by +ve & -ve phrases respectively.

Energy and Internal energy :-

Energy: All systems possess some thing which can yield work and secondly, all different kind of energy are inter convertible. Energy should be defined as a property which can be transformed into or produced from work.

Internal Energy: A thermodynamic system in virtue of its very existence must possess a store of energy. This is sustained by common observations in diverse systems. Example:

- i) a liquid freeze into solid, yielding heat energy
- ii) Zn and CuSO_4 in a Daniell cell reacts producing electrical energy
- iii) Steam expands from higher to lower press. yielding work (mechanical energy).
- iv) yellow phosphorous (P) glows in oxygen (O_2) producing light.
- v) $\text{C} + \text{O} = \text{CO}$ and $\text{CO} + \text{O} = \text{CO}_2$ in both reactions produces heat energy etc.

Thus, it is believed that every system has with itself a quantity of energy. This energy is called internal energy and denoted by U.