Chemical Thermodynamics

Basic Terminology:

Terms	Explanation
System	Part of the universe under investigation.
Open System	A system which can exchange both energy and matter with its surroundings.
Closed System	A system which permits passage of energy but not mass, across its boundary.
Isolated system	A system which can neither exchange energy nor matter with its surrounding.
Surroundings	Part of the universe other than system, which can interact with it.
Boundary	Anything which separates system from surrounding.
State variables	The variables which are required to be defined in order to define state of any system *i.e.* pressure, volume, mass, temperature, surface area, etc.
State Functions	Property of system which depend only on the state of the system and not on the path. Example: Pressure, volume, temperature, internal energy, enthalpy, entropy etc.
Intensive properties	Properties of a system which do not depend on mass of the system *i.e.* temperature, pressure, density, concentration,
Extensive properties	Properties of a system which depend on mass of the system*i.e.* volume, energy, enthalpy, entropy etc.
Process	Path along which state of a system changes.
Isothermal process	Process which takes place at constant temperature
Isobaric process	Process which takes place at constant pressure
Isochoric process	Process which takes place at constant volume.
Adiabatic process	Process during which transfer of heat cannot take place between system and surrounding.
Cyclic process	Process in which system comes back to its initial state after undergoing series of changes.
Reversible process	Process during which the system always departs infinitesimally from the state of equilibrium *i.e.* its direction can be reversed at any moment.

Irriversible Process	This type of process is fast and gets completed in a single step. This process cannot be reversed. All the natural processes are of this type

Heat, energy and work:

Heat (Q):

- Energy is exchanged between system and surround in the form of heat when they are at different temperatures.
- Heat added to a system is given by a positive sign, whereas heat extracted from a system is given negative sign.
- It is an extensive property.
- It is not a state function.

Energy:

- It is the capacity for doing work.
- Energy is an extensive property.
- Unit : Joule.

Work (W):

- Work = Force × Displacement *i.e.* dW = Fdx
- Work done on the system is given by positive sigh while work done by the system is given negative sign.
- Mechanical Work or Pressure-Volume Work: work associated with change in volume of a system against an external pressure.
- Work done in reversible process: W=

$$\int_{V_1}^{V_2} PdV$$

$W = -2.303\ nRT \log v_2/v_1 = -2.303\ nRT \log p_1/p_2$

Wok done in isothermal reversible contraction of an ideal gas:

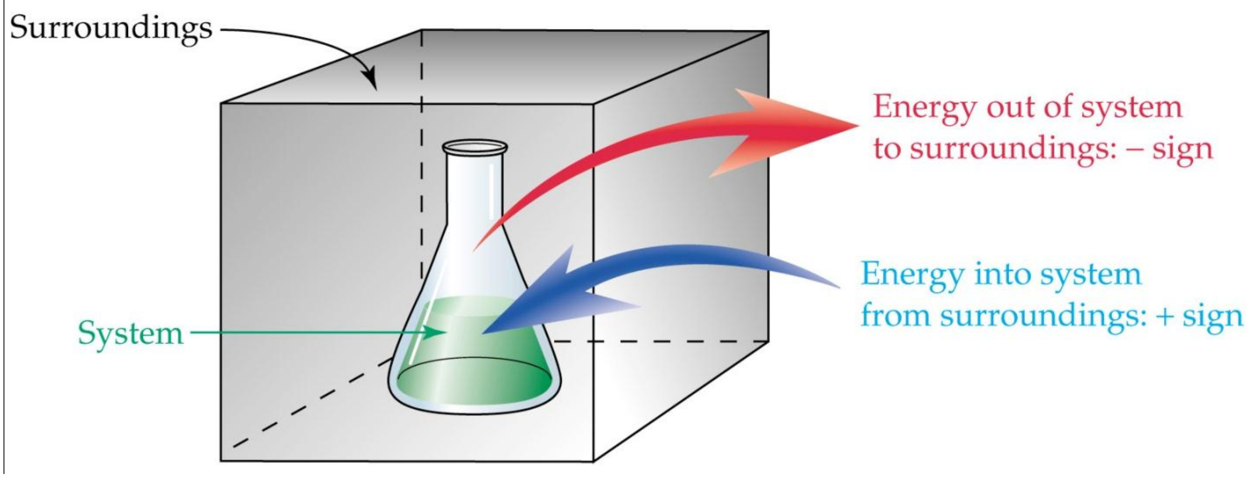
- ?$W = -2.303\ nRT \log v_2/v_1 = -2.303\ nRT \log p_1/p_2$
- Unit : Joule.

Internal Energy (E or U):

- Sum of all the possible types of energy present in the system.
- ΔE = heat change for a reaction taking place at constant temperature and volume.
- ΔE is a state function.
- It is an extensive property.

- Value of ΔE is -ve for exothermic reactions while it is +ve for endothermic reactions.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$



First Law of Thermodynamics:

*Energy can neither be created nor destroyed although it can be converted from one form to another.*Or

Energy of an isolated system is constant**.**

Mathematical Expression

Heat observed by the system = its internal energy + work done by the system. *i.e.* q = dE + w

For an infinitesimal process

dq = dE + dw

Where, q is the heat supplied to the system and w is the work done on the system.

For an ideal gas undergoing isothermal change ΔE =0.

so q= -w.

- **For an isolated system, d*q=0***

so, dE = - dw

Heat capacity:

Amount of heat required to rise temperature of the system by one degree.

C = q / dT

- **Specific heat capacity:** Heat required to raise the temperature of 1 g of a substance by one dgree.

C_s = Heat capacity / Mass in grams

- **Molar heat capacity**: Heat required to raise the temperature of 1 g of a substance by one dgree.

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C_m = Heat capacity / Molar mass.

- **Heat capacity of system at constant volume:**

$C_v = (dE/dT)_v$

- **Heat capacity of system at constant pressure:**

$C_p = (dE/dT)_p$

Bomb Calorimeter: