Thermodynamics

- Zeroth Law of Thermodynamics states that 'two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other'.
- The Zeroth Law clearly suggests that when twosystems A and B, are in thermal equilibrium,there must be a physical quantity that has thesame value for both. This thermodynamicvariable whose value is equal for two systems inthermal equilibrium is called temperature (T).
- Internal energy of a system is the sum of kinetic energies and potential energies of themolecular constituents of the system. It does not include the over-all kinetic energy ofthe system. Heat and work are two modes of energy transfer to the system. Heat is theenergy transfer arising due to temperature difference between the system and thesurroundings. Work is energy transfer brought about by other means, such as movingthe piston of a cylinder containing the gas, by raising or lowering some weight connectedto it.

- The first law of thermodynamics is the general law of conservation of energy applied toany system in which energy transfer from or to the surroundings (through heat andwork) is taken into account. It states that

  $\Delta Q = \Delta U + \Delta W$

  where ΔQ is the heat supplied to the system, ΔW is the work done by the system and ΔU is the change in internal energy of the system.
- The specific heat capacity of a substance is defined by

  $s = (1/m)\,(\Delta Q/\Delta T)$

  where m is the mass of the substance and ΔQ is the heat required to change its temperature by ΔT.

  The molar specific heat capacity of a substance is defined by

  $C = (1/\mu)(Q/T)$

  where μ is the number of moles of the substance. For a solid, the law of equipartition of energy gives

  $C = 3R$

  which generally agrees with experiment at ordinary temperatures.

For an ideal gas, the molar specific heat capacities at constant pressure and volumesatisfy the relation

$C_p - C_v = R$

where R is the universal gas constant.

- Equilibrium states of a thermodynamic system are described by state variables. Thevalue of a state variable depends only on the particular state, not on the path used toarrive at that state. Examples of state variables are pressure (P), volume (V), temperature(T), and mass (m). Heat and work are not state variables. An Equation of State (likethe ideal gas equation $PV = \mu RT$) is a relation connecting different state variables.

- A quasi-static process is an infinitely slow process such that the system remains inthermal and mechanical equilibrium with the surroundings throughout. In aquasi-static process, the pressure and temperature of the environment can differ fromthose of the system only infinitesimally.

- In an isothermal expansion of an ideal gas from volume V_1 to V_2 at temperature T theheat absorbed (Q) equals the work done (W) by the gas, each given by

$Q = W = \mu R T \ln(V2/ V1)$

- In an adiabatic process of an ideal gas

  PV^{γ}= constant

- Heat engine is a device in which a system undergoes a cyclic process resulting inconversion of heat into work. If Q1 is the heat absorbed from the source, Q2 is the heatreleased to the sink, and the work output in one cycle is W, the efficiency η of the engineis:

  $\eta = 1 - (Q2/Q1)$

- In a refrigerator or a heat pump, the system extracts heat *Q*2 from the cold reservoir andreleases *Q*1 amount of heat to the hot reservoir, with work *W* done on the system. Theco-efficient of performance of a refrigerator is given by$\alpha = Q2/W = Q2/(Q1 - Q2)$

- The second law of thermodynamics disallows some processes consistent with the First Law of Thermodynamics.

  Kelvin-Planck statement

  No process is possible whose sole result is the absorption of heat from a reservoir andcomplete conversion of the heat into work.

Clausius statement

No process is possible whose sole result is the transfer of heat from a colder object to ahotter object.

Put simply, the Second Law implies that no heat engine can have efficiency η equal to1 or no refrigerator can have co-efficient of performance α equal to infinity.

A process is reversible if it can be reversed such that both the system and the surroundingsreturn to their original states, with no other change anywhere else in the universe.

Spontaneous processes of nature are irreversible. The idealised reversible process is aquasi-static process with no dissipative factors such as friction, viscosity, etc.

- Carnot engine is a reversible engine operating between two temperatures $T1$ (source) and$T2$ (sink). The Carnot cycle consists of two isothermal processes connected by twoadiabatic processes. The efficiency of a Carnot engine is given by

$\eta = 1 - (T2/T1)$

No engine operating between two temperatures can have efficiency greater than that of the Carnot engine.

- If $Q > 0$, heat is added to the system

  If $Q < 0$, heat is removed to the system

  If $W > 0$, Work is done by the system

  If $W < 0$, Work is done on the system

Sample Examples