

# Thermodynamics : A review

The aim of thermodynamics is to establish a to deal with systems with “many-particle” (and hence “many degrees of freedom”). It is essential to recognise that new types of regularities arise when the number of particles ( $N$ ) is large. These can not be reduced to purely mechanical laws and they cease to have meaning for small number of particles (or degrees of freedom).

Thermodynamics deals with the macroscopic properties of a system, as a whole (as opposed to that of individual particles), of large number of particles. Any macroscopic system with  $N \gtrsim N_{Avogadro}$  is a thermodynamic system. The measurable parameters of the system are called thermodynamic parameters and a thermodynamic state is described by specifying the values of the required number of thermodynamic parameters. A macroscopic system has many degrees of freedom, only a few of which are measurable. Thermodynamics thus concerns itself with the relation between a small number of variables which are sufficient to describe the bulk behaviour of the system in question. Not all parameters are independent and the functional relationship among thermodynamic parameters in the equilibrium state is called the equation of state.

## Basic Definitions

- thermodynamic system : any macroscopic ( $N \gtrsim N_A$ ) system; could be (*isolated, closed (energy exchange), or open*)
- thermodynamic variables : measurable macroscopic quantities (extensive/intensive).
- thermodynamic limit :  $\lim_{N,V \rightarrow \infty} N/V = \text{constant}$   
(intensive variables should be system-size independent in this limit);
- internal energy - energy arising from causes entirely internal to the system (kinetic energy + energy of inter-particle interaction);
- thermodynamic state : uniquely and completely specified by a set of thermodynamic variables;
- thermodynamic equilibrium : a thermodynamic state *unchanging* over an interval time, of interest for a particular thermodynamic process (*mechanical, thermal, chemical*), \* this also defines, in comparison, the *infinitesimal time-interval*; \* a thermodynamic state usually means an equilibrium state;
- heat - energy absorbed or emitted if temperature changes without any work;
- heat reservoir - heat source/sink, maintains isothermal condition;
- thermodynamic engine : absorbs an amount of heat  $Q_2 > 0$  from reservoir at  $T_2$ , rejects an amount of heat  $Q_1 > 0$  to reservoir at  $T_1$  ( $T_2 > T_1$ ), performs an amount of work  $W > 0$ ;
- response functions : response of a system to external stimuli (eg. specific heat);
- equation of state : functional relationship between the thermodynamic parameters ( $f(P, V, T) = 0$ );
- thermodynamic transformation : change of state (quasi-static - slow, reversible - equilibrium maintained at every step, (isothermal/adiabatic); A thermodynamic process or transformation is any change in the state variables of the system. A spontaneous process is one that takes place without any change in the external constraints on the system, due simply to the internal dynamics of the system.

## Thermodynamic Laws

1. **Zeroth Law** - If two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.
2. **First Law** - The quantity  $dU$  defined by  $dU = dQ - dW$  is the same for all transformations from a specific initial state to a specific final state (Equivalence of work (mechanical energy) and heat).
3. **Second Law**  
*Kelvin's Statement* : There exists no thermodynamic transformation whose ‘sole’ effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely to work.  
*Clausius' Statement* : There exists no thermodynamic transformation whose ‘sole’ effect is to transfer a quantity of heat from a colder reservoir to a hotter reservoir.
4. **Third Law** - The entropy of a system at absolute zero is a universal constant, which may be taken to be zero. By providing for a zero-point, for every thermodynamic state a unique value of the entropy is ensured.

## Discussion : First Law

This implies that  $dU$  is exact and  $\int dU$  is independent of the path. (Convention :  $dU = \delta Q - \delta W$  and  $\delta W = PdV$ ). Thus we can define  $U$ , the internal energy, as a state function. The internal energy is defined to within an additive constant and a particular value corresponds to a chosen reference state. Also, from the definition  $dU$  is a perfect differential, a property not shared by  $\delta Q$  and  $\delta W$ .

From a mathematical perspective, the most important property of an exact differential is that its integral depends only on its end points, i.e. if  $F$  is an exact differential and  $i, f$  are arbitrary initial and final points of a path then,

$$\int_i^f F = F_f - F_i \quad (1)$$

or equivalently  $\oint F = 0$ . Clausius noted that at equilibrium  $\delta Q/T$  is an exact differential with these properties. In thermodynamics, variables with these properties are called state variables. At equilibrium, all thermodynamic variables are state variables. Hence, Taylor expansion exists in the form

$$dU = PdV - TdS = \frac{\partial U}{\partial V}_S dV - \frac{\partial U}{\partial S}_V dS, \quad (2)$$

with appropriate identification of  $P$  and  $T$ . Similarly, these relations can be written for  $S, V, N$  - all extensive variables. These are most appropriate for isolated system (microcanonical).

The first law is a manifestation of the law of conservation of energy.

## Heat capacities

$$C_X = \lim_{\delta T \rightarrow 0} \delta Q / \delta T|_X$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V, \quad (3)$$

$$C_P = \left( \frac{\partial(U + PV)}{\partial T} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P. \quad (4)$$

Note :  $C_P, C_V$  are extensive quantities.

Ideal Gas : An ideal gas in thermodynamics is defined to have the equation of state  $PV = Nk_B T$ . It can be shown from the considerations of kinetic theory of gases that for the molecules of an ideal gas the only interaction is an elastic collision between two molecules. Therefore the internal energy is simply the kinetic energy of the particles, and  $U$  depends only on  $T$ .

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT} \Rightarrow U = C_V T + \text{const.} \quad (5)$$

$$C_P - C_V = \left( \frac{\partial(U + PV)}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial(PV)}{\partial T} \right)_P = Nk_B. \quad (6)$$

## Discussion : Second Law

Equivalence of Kelvin's & Clausius' statements -

1. not K  $\Rightarrow$  not C : If 'not K' then  $Q$  extracted from reservoir  $T_1$  and converted into  $W$ . Now,  $W$  is converted to heat and given to  $T_2$  where  $T_2 > T_1$ . Hence, 'not C'.
2. not C  $\Rightarrow$  not K : If 'not C' then  $Q$  extracted from reservoir  $T_1$  and given to  $T_2$  where  $T_2 > T_1$ . Operate an engine between  $T_1$  and  $T_2$  such that it extracts  $Q$  from  $T_2$ , gives  $Q'$  to  $T_1$  and does work  $W$ . Effectively,  $Q - Q'$  is extracted from  $T_1$  and work  $W$  is done. Hence, 'not K'.

Carnot Engine : An engine working in a reversible way (isothermal-adiabatic-isothermal-adiabatic) absorbs an amount of heat  $Q_2$  from a reservoir at  $T_2$  and delivers  $Q_1$  to  $T_1$  performing an amount of work  $W$  where  $T_2 > T_1$ .

The efficiency of a Carnot engine is  $\eta = W/Q_2 = 1 - Q_1/Q_2$  where  $T_2 > T_1$ . If  $W > 0$  then  $Q_1, Q_2 > 0$  (if  $W > 0$ , assume  $Q_1 < 0$ ; this violates K and hence the assertion follows) and if  $W < 0$  then  $Q_1, Q_2 > 0$  (a refrigerator).

**Carnot's Theorem** - No engine operating between two temperatures is more efficient than a Carnot engine.

*Proof* - A Carnot engine,  $C$ , absorbs  $Q_2$  at  $T_2$  and delivers  $Q_1$  at  $T_1$  performing an amount of work  $W$ . Another engine,  $C'$ , absorbs  $Q'_2$  at  $T_2$  and delivers  $Q'_1$  at  $T_1$  performing an amount of work  $W'$ . If  $C$  operates  $N$ -times and  $C'$  operates in reverse for  $N'$ -times then for very large  $N, N'$  we can ensure  $Q_2/Q'_2 = N'/N$ . Now, the total work done is,

$$W = N'(Q'_1 - Q'_2) - N(Q_1 - Q_2) = N'Q'_1 - NQ_1, \quad (7)$$

which is equal to the total heat absorbed from the reservoir at  $T_1$ . This is contrary to second law if  $W > 0$ . Therefore,  $W \leq 0$  implying that  $\eta_c \geq \eta_{c'}$ .

**Absolute scale of temperature** - Since the efficiency of a Carnot engine operating between two reservoirs depends only on the temperatures of the reservoirs, temperature can be defined as  $T_1/T_2 = Q_1/Q_2 = 1 - \eta$ .

**Exercise** - Show that the ideal gas temperature  $T$  is identical with the temperature defined using the efficiency of a Carnot engine.

**Clausius' Theorem** - In any cyclic transformation throughout which the temperature is defined,  $\oint \frac{dQ}{T} \leq 0$ .

*Proof* - Let us break the cycle into  $N$  infinitesimal steps such that an amount of heat  $\delta Q_i$  is absorbed at  $T_i$  in the  $i$ -th step. Also consider  $N$  Carnot engines operating the  $i$ -th thermodynamic state and a reservoir at  $T_0$  ( $> T_i$  for all  $i$ ). The Carnot engines absorb  $dQ_0^i$  from the reservoir at  $T_0$  and deposit  $dQ_i$  at  $T_i$ . Therefore,

$$\delta Q_0^i = T_0 \frac{dQ_i}{T_i}. \quad (8)$$

Therefore, in a complete cycle of all the Carnot engines and the original transformation the total heat absorbed from the reservoir at  $T_0$  is

$$\Sigma_i dQ_0^i = T_0 \Sigma_i \frac{dQ_i}{T_i}. \quad (9)$$

Since after a cycle, the system and the Carnot engines as a whole return to its initial status, the difference of the internal energy is zero. Therefore, the net result of this cyclic operation is to extract  $\Sigma_i Q_0^i$  from  $T_0$  and convert it entirely to work, in contradiction to the second law. This is not possible unless  $\Sigma_i Q_0^i \leq 0$ , and therefore  $\oint dQ/T \leq 0$ .

**Entropy** : A corollary of Clausius' theorem is the definition of entropy. Since, for a reversible process the entire cycle can be run in the reverse we obtain  $\oint dQ/T = 0$ . Therefore, for a reversible transformation  $\int dQ/T$  is independent of path. Therefore, we can define *entropy* as  $S(B) - S(A) = \int_A^B dQ/T$ . Hence, for infinitesimal, reversible transformations we can define  $dS = \delta Q/T$ , where  $S$  is a state function.

1. For any arbitrary transformation  $\int_A^B dQ/T \leq S(B) - S(A)$ , equality valid for reversible transformations.
2. Entropy is additive.
3. Entropy of a thermally isolated system never decreases.

Consequences of Second Law -

$$TdS = C_V dT + \left( \left( \frac{\partial U}{\partial V} \right)_T + P \right) dV, \quad (10)$$

$$TdS = C_P dT + \left( \left( \frac{\partial U}{\partial P} \right)_T + P \left( \frac{\partial V}{\partial P} \right)_T \right) dP. \quad (11)$$

Since,  $dS$  is an exact differential we can also write -

$$TdS = C_V dT + T \left( \frac{\partial P}{\partial T} \right)_V dV, \quad (12)$$

$$TdS = C_P dT - T \left( \frac{\partial V}{\partial T} \right)_P dP. \quad (13)$$

Defining,

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P, \text{ coeff. of thermal expansion} \quad (14)$$

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T, \text{ isothermal compressibility} \quad (15)$$

$$\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S, \text{ adiabatic compressibility} \quad (16)$$

we have the following relations,

$$TdS = C_V dT + \frac{\alpha T}{\kappa_T} dV, \quad (17)$$

$$TdS = C_P dT + \alpha TV dP \quad (18)$$

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T}, \quad (19)$$

$$C_P/C_V = \gamma = \frac{\partial V/\partial P|_T}{\partial V/\partial P|_S}, \text{ for adiabatic processes.} \quad (20)$$

$$C_V = \frac{TV\alpha^2\kappa_S}{(\kappa_T - \kappa_S)\kappa_T}, \quad (21)$$

$$C_P = \frac{TV\alpha^2}{\kappa_T - \kappa_S}. \quad (22)$$

Aside : Increase of entropy is the only law of physics that tells us that there is an arrow of time. All other laws of physics are time-symmetric.

### Discussion : Third Law

- Specific heats (defined thus -  $S(A) = \int_0^A C(T)dT/T$ ) must vanish at absolute zero.
- Coefficients of thermal expansion  $\alpha$  vanish at absolute zero.

Even though both the heat capacities and the coefficient of the thermal expansion vanish at absolute zero, experimentally it is seen that the ratio  $V\alpha/C_P$  remains finite as  $T \rightarrow 0$ . This implies that a system can not be cooled to absolute zero by a finite change of the thermodynamic parameters (for example, since  $\left(\frac{\partial P}{\partial T}\right)_{V(T \rightarrow 0)} \rightarrow 0$ , it can be seen that as  $T \rightarrow 0$  to obtain a finite  $dT$ ,  $dP$  should become unbounded). On the other hand, the second law of thermodynamics implies that if a system is at absolute zero there is no way to heat it to a higher temperature ( $\delta Q = TdS = 0$  at  $T = 0$  for any reversible transformation, meaning at  $T = 0$  all processes are adiabatic. No reversible way to heat a system which is at  $T = 0$ , hence no Carnot engine (therefore, no other engine) with the lower reservoir at absolute zero.). Combining these two, we arrive at the implication that the temperature of absolute zero is thermodynamically unattainable.

### Axiomatic Postulates

1. There exist particular states of any system which, macroscopically speaking, can be completely characterized by a set of extensive parameters including its internal energy  $U$ . These are the equilibrium states.
2. There exists a function of the extensive parameters, the entropy  $S$ , which is defined for all equilibrium states, with the following properties -
  - $S$  is continuous and differentiable, and is monotonically increasing function of  $U$  when all other extensive variables are held constant.
  - The entropy of a composite system is additive over the constituent subsystems.  $S$  is itself extensive.
3. If a state is not in equilibrium, its entropy will be less than the entropy of the equilibrium state with the same values for all extensive variables. Left to itself at the fixed values of the extensive parameters, the non-equilibrium state will gain entropy and try to attain the equilibrium state.

## Gibbs-Duhem Relation

Consider an isolated system, completely described by the extensive thermodynamics variables  $S, V, N$ , with internal energy  $U$  given by  $U = E(S, V, N)$ . If we now consider  $m$  copies of this system combined together, then the extensive quantities would add and for the new system we shall have,

$$S_m, V_m, N_m \equiv mS, mV, mN. \quad (23)$$

Moreover, now  $U_m = U(mS, mV, mN)$  implying

$$\mathbf{U}(m\mathbf{S}, m\mathbf{V}, m\mathbf{N}) = m\mathbf{U}(\mathbf{S}, \mathbf{V}, \mathbf{N}), \quad (24)$$

that is,  $U$  is a homogeneous function of first order.

Such homogeneous functions have certain special properties which can be seen as follows. Consider a function  $f(x_i)$  ( $i = 1, \dots, N$ ) such that

$$f(u_i) = mf(x_i), \quad (25)$$

when  $u_i = mx_i$  for all values of  $i$ . On the other hand,

$$\begin{aligned} \frac{\partial f(u_i)}{\partial m} &= \sum_{i=1}^N \frac{\partial f}{\partial u_i} \cdot \frac{\partial u_i}{\partial m} \\ &= \sum_{i=1}^N \frac{\partial f}{\partial x_i} \cdot x_i \\ &= mf(x_i). \end{aligned} \quad (26)$$

Therefore, for  $m = 1$

$$mf(x_i) = \sum_{i=1}^N \frac{\partial f}{\partial x_i} \cdot x_i. \quad (27)$$

Applying this to  $U(S, V, N)$  we find that,

$$U(S, V, N) = T.S - P.V + \mu.N. \quad (28)$$

Recalling the well known thermodynamic relation  $dU = TdS - PdV + \mu dN$ , we obtain

$$\mathbf{SdT} - \mathbf{VdP} + \mathbf{Nd}\mu = \mathbf{0}, \quad (29)$$

implying that it is impossible to vary all the intensive variables freely. This relation is known as the **Gibbs-Duhem** relation and distinguishes the intensive variables from the extensive variables, which can vary independently of each other.

## Intensive Variables

$$U = U(S, V, N) \rightarrow dU = T dS - P dV + \mu dN,$$

where,

$$T = \left( \frac{\partial U}{\partial S} \right)_{V,N} \quad (30)$$

$$P = - \left( \frac{\partial U}{\partial V} \right)_{S,N} \quad (31)$$

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{V,S} \quad (32)$$

$T, P, \mu$  are intrinsic quantities of the system.

$U$  is defined in terms of the extensive variables. It can be shown that if  $U$  is defined in terms of intensive variables, say  $U = U(T, V, N)$  then there would exist an infinite number of functions  $A(T, V, N) = U - TS$  that can lead to the same  $U(T, V, N)$  giving rise to the same physics.

## Intensive Variables : Entropic Formulation

$$S = S(U, V, N), \rightarrow T dS = dU + P dV - \mu dN,$$

where,

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N} \quad (33)$$

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{U,N} \quad (34)$$

$$\frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{V,U} \quad (35)$$

$T, P, \mu$  are intrinsic quantities of the system.

## Thermodynamic Potentials

However,  $U, V, S, N$  may not be the most natural variables to describe all systems. For example, a system at constant temperature ( $T$  constant, hence  $U$  is not), or one undergoing particle exchange with its environment ( $N$  is not constant,  $\mu$  is) - by its nature require certain intensive variables in its description. Such systems are typically connected to external reservoirs, and the effect of the reservoirs need to be taken into account for correct thermodynamic description of such systems.

It needs to be noted that the intensive and the extensive variables come in conjugate pairs. Typically, an intensive variable is obtained by differentiating the appropriate thermodynamic potential with respect to the corresponding extensive variable. For example, we obtain the intensive variable temperature as  $T = \partial U / \partial S|_{V,N}$  and so on.

In classical mechanics, the Lagrangian description of a system can be transformed to an equivalent Hamiltonian description through the following Legendre transformation -

$$L(q, \dot{q}) \rightarrow H(p, q) = pq - L(q, \dot{q}), \quad (36)$$

where  $p \equiv \partial L / \partial \dot{q}$ . Similar Legendre transformations can be performed to obtain other thermodynamic potentials from  $U$ . For example, if we consider  $U(V, S, N)$  and perform a Legendre transformation with respect to  $S$  we obtain the following.

$$U(V, S, N) \rightarrow U(V, S, N) - S \left( \frac{\partial U}{\partial S} \right)_{V,N} = U(V, S, N) - S.T = A(V, T, N). \quad (37)$$

$A(V, T, N)$ , the Helmholtz free energy, is indeed the correct potential to use while considering equilibrium states under isothermal conditions; because an equilibrium state is given by either of the following two - maximum entropy or minimum (appropriate) energy.

Some of the most useful thermodynamic potentials are -

$$U, \text{ internal energy} \quad (38)$$

$$H = U + PV, \text{ enthalpy} \quad (39)$$

$$A = U - TS, \text{ Helmholtz free energy} \quad (40)$$

$$G = U - TS + PV, \text{ Gibbs potential} \quad (41)$$

giving, for infinitesimal, reversible transformations -

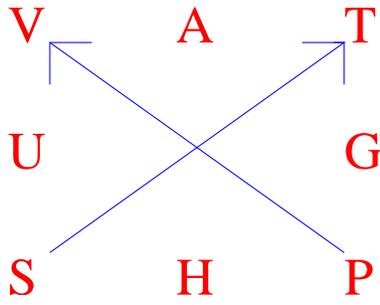
$$dU = TdS - PdV, \quad (42)$$

$$dH = TdS + VdP, \quad (43)$$

$$dA = -SdT - PdV, \quad (44)$$

$$dG = -SdT + VdP. \quad (45)$$

1. Condition of adiabaticity (thermal isolation) :  $dS \geq 0$
2. Adiabatic, Isochoric (thermally, mechanically isolated) :  $dU \leq 0$
3. Adiabatic, Isobaric (thermally isolated, constant pressure) :  $dH \geq 0$
4. Isothermal, Isochoric (in contact with heat bath, mechanically isolated) :  $dA \leq 0$
5. Isothermal, Isobaric (in contact with heat bath, constant pressure) :  $dG \leq 0$



**Maxwell relations -**

$$T = \left(\frac{\partial U}{\partial S}\right)_V, P = -\left(\frac{\partial U}{\partial V}\right)_S; \tag{46}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P, V = \left(\frac{\partial H}{\partial P}\right)_S; \tag{47}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_V, P = -\left(\frac{\partial A}{\partial V}\right)_T; \tag{48}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, P = \left(\frac{\partial G}{\partial P}\right)_T. \tag{49}$$

**Relativistic Systems :**

In case of relativistic systems, appropriate thermodynamic quantities need to be modified to include the rest mass energy of the relevant particles, as follows -

$$U \rightarrow U + mc^2N, \tag{50}$$

$$\mu \rightarrow \mu + mc^2, \tag{51}$$

and so on.

**External Fields :**

In presence of external fields (electromagnetic, gravitational etc.) the internal energy needs to be modified to incorporate for those, like -

$$dU = TdS - PdV + \mu dN - \mathbf{B} \cdot d\mathbf{M} + \mathbf{E} \cdot d\mathbf{P}, \tag{52}$$

where  $\mathbf{B}$  and  $\mathbf{E}$  are the external magnetic and electric fields with  $\mathbf{M}$  and  $\mathbf{P}$  denoting the total magnetic dipole moment and the total electric dipole moment.

**Limitations of Thermodynamics**

Thermodynamics works well, starting from a known fundamental relation (equation of state) describing the system. However, there is no way to determine this fundamental relation within the premises of thermodynamics. Statistical Mechanics provides for the formalism to derive this macroscopic fundamental relation from the behaviour of the microscopic constituent particles.

**Application : Black Hole Thermodynamics**

Theoretically, a black hole is a solution of Einstein's equation for a point mass  $M$ . However, the basic physical idea behind a black hole may be understood by considering the escape velocity from a gravitationally bound object of mass  $M$  and radius  $R$ . The escape velocity, at the surface of such an object is given by

$$V_{\text{esc}} = \left(\frac{2GM}{R}\right)^{1/2}. \tag{53}$$

Evidently, this purely Newtonian non-relativistic calculation breaks down for  $2GM/R > c^2$  or for  $R < R_G$  where  $R_g = 2GM/c^2$ . A black hole may be thought of as an object whose actual radius is smaller than its gravitational radius,  $R_G$  from which nothing, not even light, can escape. However, there is no restriction on matter (or radiation) falling through the radius  $R_G$  into the black hole.

Astrophysically, three classes of BHs are of interest -

- Stellar mass BH - They have masses  $\sim 10 - 100 M_\odot$  and are thought to be formed in supernova explosions.
- Supermassive BH - These collapsed star clusters are understood to be present in the centres of active galaxies (accretion onto these power the extremely energetic phenomena associated with quasars and AGNs) and the masses range from  $\sim 10^6 M_\odot$  for the central black hole in the Milky Way to  $> 10^9 M_\odot$  for some quasars.
- Mini BH - These are objects that could have formed in the early Universe. There is no direct evidence for the existence of mini BH.

Since  $M$  increases as  $r^3$  at fixed density, one can have a BH at any density. For a solar mass, the critical density is a little above nuclear density. In fact, a neutron star of mass  $1.4M_\odot$  has a radius of about 10 KM and a Schwarzschild radius of about 3 KM, so it is rather close to the Schwarzschild limit. A black hole formed from a billion stars in a galactic center can initially have an average density lower than that of ordinary matter. Of course the stars will collapse together, and eventually reach much higher (in fact infinite) density.

Is an elementary particle a black hole? No! Its Compton wavelength is much greater than its Schwarzschild radius. For a proton,  $\lambda/R_G \approx 10^{39}$ . When the Compton wavelength of a particle is of the order of  $R_G$  we have -

$$\lambda_C = \frac{\hbar}{Mc} \sim \frac{GM}{c^2} \quad (54)$$

or

$$M = \left( \frac{\hbar c}{G} \right)^{\frac{1}{2}}, \quad (55)$$

where this is the Planck Mass ( $M_P$ ). Therefore, we have the following -

$$M_P = \left( \frac{\hbar c}{G} \right)^{\frac{1}{2}} \sim 10^{-5} \text{ gm} \quad (56)$$

$$E_P = \left( \frac{\hbar c^5}{G} \right)^{\frac{1}{2}} \sim 10^{19} \text{ GeV} \quad (57)$$

$$\ell_P = \left( \frac{\hbar G}{c^3} \right)^{\frac{1}{2}} \sim 10^{-33} \text{ cm}. \quad (58)$$

There are certain problems with the thermodynamics of such a classical black hole. One of the problems is associated with the change in entropy when material falls into a black hole. If a black hole does not have any entropy then the entropy associated with the infalling material is lost to the rest of the Universe, contradicting the second law of thermodynamics ( $dS \geq 0$ ). (Here we need to think of entropy as a measure of the configuration space or the information content of the system under consideration.) Moreover, a classical black hole absorbs radiation but does not emit any. These problems are overcome by assigning a temperature and an entropy to a black hole, such that they are in conformity with thermodynamical laws.

The resolution actually comes from the proposition of Hawking radiation. Stephen Hawking argued that a black hole can radiate when quantum effects are taken into account. According to the theory of Quantum Electrodynamics there exist fluctuations in a vacuum in which virtual pairs of electrons and positrons are created and destroyed over timescale of  $\delta t$  such that  $\delta t \delta E \sim \hbar$ , where  $\delta E \sim 2mc^2$ ,  $m$  being the mass of the particle/anti-particle. It is known that these virtual pairs can become real pairs in presence of electro-magnetic fields. Hawking argued that this is also the case in presence of a gravitational field. The electron and the positron are created very close to each other but not exactly at the same point. For pairs created near  $R = R_G$  it is possible for one particle to be created at  $R < R_G$  (don't ask me how!) and the other at  $R > R_G$ . The former is trapped and falls into the black hole while the latter escapes. Hawking radiation consists of such escaping electrons and positrons.

If Hawking radiation exists then it becomes possible to assign a temperature to a black hole such that it is in equilibrium between emission and absorption at this temperature. On dimensional grounds, this temperature must be such that the *wavelength*,

$\hbar c/k_B T$ , of thermal radiation at this temperature is of order of  $R_G$  (the only length-scale of the problem). The numerical value is determined by a more detailed argument and is given by

$$T = \frac{\hbar c^3}{8\pi k_B G} M^{-1} \simeq 10^{-7} \left( \frac{M}{M_\odot} \right)^{-1} K. \quad (59)$$

The area of a black hole is taken to be,

$$A = 4\pi R_G^2 = \frac{16\pi G^2 M^2}{c^4}. \quad (60)$$

Now, the area of a black hole never decreases. Thus if the entropy of a black hole is defined to be proportional to its area,  $dS \geq 0$  is satisfied. Then entropy is determined by noting that a change in its mass by  $dM$  implies a change in its energy by  $d(Mc^2)$  and equating this change to the amount of heat. Thus we have,

$$TdS = d(Mc^2) \quad (61)$$

$$dS = \frac{8\pi k_B G}{\hbar c} M dM$$

$$S = \frac{4\pi G k_B}{\hbar c} M^2 \simeq 10^{61} \left( \frac{M}{M_\odot} \right)^2 \quad (62)$$

$$= \left( \frac{k_B c^3}{4\hbar G} \right) A \quad (63)$$

For a supermassive or a stellar mass black hole, the temperature is exceedingly small (of no practical interest) and the entropy is exceedingly large. The temperature of a BH is so small that it cannot be in thermal equilibrium with BB radiation at any temperature of practical interest. The entropy of a BH is very large and it increases when the BH accretes matter (thereby increasing  $M$ ). This suggests that in practice supermassive and stellar mass BHs are very far from thermodynamic equilibrium with their surroundings.

[ *Historical Development* : Starting from theorems proved by Stephen Hawking, Jacob Bekenstein conjectured that the black-hole entropy was proportional to the area of its event horizon divided by the Planck area. In 1973 Bekenstein suggested  $(1/2 \cdot \ln 2)/4\pi$  as the constant of proportionality, asserting that if the constant was not exactly this, it must be very close to it. The next year, in 1974, Hawking showed that black holes emit thermal Hawking radiation corresponding to a certain temperature (Hawking temperature). Using the thermodynamic relationship between energy, temperature and entropy, Hawking was able to confirm Bekenstein's conjecture and fix the constant of proportionality at  $1/4$ . Therefore, we have

$$S_{\text{BH}} = \frac{k_B A}{4\ell_p^2} = \left( \frac{k_B c^3}{4\hbar G} \right) A, \quad (64)$$

where  $A (= 4\pi R_G^2)$  is the area of the event horizon, and  $\ell_p = \sqrt{G\hbar/c^3}$  is the Planck length. This is often referred to as the Bekenstein-Hawking formula. The subscript BH either stands for "black hole" or "Bekenstein-Hawking".]

## Laws of BH Mechanics

The four laws of black-hole mechanics, analogous to the laws of thermodynamics, were discovered by Brandon Carter, Stephen Hawking, and James Bardeen.

**The zeroth law** : The horizon has constant surface gravity for a stationary black hole.

This is analogous to the zeroth law of thermodynamics, which states that the temperature is constant throughout a body in thermal equilibrium. It suggests that the surface gravity is analogous to temperature. T constant for thermal equilibrium for a normal system is analogous to  $\kappa$  constant over the horizon of a stationary black hole.

**The first law** : For perturbations of stationary black holes, the change of energy is related to change of area, angular momentum, and electric charge by

$$dU = \frac{\kappa}{8\pi} dA + \Omega dJ + \Phi dQ, \quad (65)$$

where  $U$  is the energy,  $\kappa (= c^4/GM)$  is the surface gravity,  $A$  is the horizon area,  $\Omega$  is the angular velocity,  $J$  is the angular momentum,  $\Phi$  is the electrostatic potential and  $Q$  is the electric charge.

Analogously, the first law of thermodynamics is a statement of energy conservation, which contains on its right side the term  $TdS$ .

**The second law :** The horizon area is, assuming the weak energy condition, a non-decreasing function of time:

$$\frac{dA}{dt} \geq 0. \quad (66)$$

This "law" was superseded by Hawking's discovery that black holes radiate, which causes both the black hole's mass and the area of its horizon to decrease over time.

The second law is the statement of Hawking's area theorem. Analogously, the second law of thermodynamics states that the change in entropy in an isolated system will be greater than or equal to zero for a spontaneous process, suggesting a link between entropy and the area of a black-hole horizon. However, this version violates the second law of thermodynamics by matter losing (its) entropy as it falls in, giving a decrease in entropy. However, generalizing the second law as the sum of black-hole entropy and outside entropy, shows that the second law of thermodynamics is not violated in a system including the universe beyond the horizon.

**The third law :** It is not possible to form a black hole with vanishing surface gravity.  $\kappa = 0$  is not possible to achieve.

Extremal black holes have vanishing surface gravity. Stating that  $\kappa$  cannot go to zero is analogous to the third law of thermodynamics, which states that the entropy of a system at absolute zero is a well defined constant. This is because a system at zero temperature exists in its ground state. Furthermore,  $\delta S$  will reach zero at zero temperature, but  $S$  itself will also reach zero, at least for perfect crystalline substances. No experimentally verified violations of the laws of thermodynamics are known.

The power radiated in Hawking radiation can be estimated from the standard formula for the power radiated by a black body.

$$\frac{dE}{dt} \propto AT^4 \propto \frac{16\pi G^2}{c^4} M^2 \left( \frac{\hbar c^3}{8\pi k_B G} \right)^4 M^{-4} \propto \frac{\hbar^4 c^8}{4^5 \pi^3 k_B^4 G^2} M^{-2}. \quad (67)$$

Thus Hawking radiation increases with decreasing mass of the Black Hole. The emission of the radiation causes the mass to decrease, with power equal to  $-c^2 dM/dt$ . Thus Hawking radiation causes a Black Hole to radiate away its mass, so that the mass decreases at a rate  $dM/dt \propto -M^2$ . Therefore, we have, remembering that the proportionality constant is the Stefan-Boltzmann constant  $\sigma \propto k_B^4/\hbar^3 c^2$

$$\frac{dM}{dt} \propto \frac{\hbar c^4}{G^2} M^{-2}. \quad (68)$$

On integrating this expression one finds that the mass reduces to zero in a finite time, which is defined as,

$$\tau \sim \frac{G^2 M^3}{\hbar c^4} \sim 10^{10} \left( \frac{M}{10^{15} \text{ gm}} \right)^3 \text{ year}. \quad (69)$$

It follows that Black Hole masses less than about  $10^{15}$  gm evaporate due to Hawking radiation in less than the age of the Universe. An evaporating Black Hole would give an intense burst of high energy radiation. There is no convincing evidence that this predicted phenomenon has been observed, implying a restriction on the properties of mini black holes that might have been created in the Big Bang.

Further Readings : (compiled by Shreejit Jadhav & Anusree)

1. Black Holes: Thermodynamics, Information and Firewalls, Robert Mann  
<http://www.springer.com/in/book/9783319144955>
2. Introductory Lectures on Black Hole Thermodynamics, Ted Jacobson  
<http://www.physics.umd.edu/grt/taj/776b/lectures.pdf>
3. Black Holes and Entropy, Jacob D. Bekenstein  
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4. The Thermodynamics of Black Holes, Robert M. Wald  
<https://link.springer.com/article/10.12942/lrr-2001-6>
5. Hawking Radiation and Black Hole Thermodynamics, Don N. Page  
<https://arxiv.org/abs/hep-th/0409024>