**Chapter 4**

Second Law of Thermodynamics: Concept of Entropy

"The law that entropy always increases, holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation." Sir Arthur S Eddington

While the first law of thermodynamics defines a relation between work and heat, in terms of internal energy, the second law of thermodynamics provides an expression for the maximum amount of energy available for work. The thermodynamics functions, entropy and free energy, those arise from the second law of thermodynamics play pivotal role in all branches of pure and applied science (physics, chemistry, biology and materials science). In this chapter, we discuss the statements and consequences of the Second Law of Thermodynamics.

2.1 Second Law of Thermodynamics

The efficiency of Carnot cycle gives an indication that heat cannot be converted totally into work. However, there are many other cyclic machines consisting of different systems (not an ideal gas) and involved steps can be quite different from Carnot cycle. Is it possible for any of them to convert heat totally into work? After considering this question for many years, around1850 several scientists reached the conclusion that it is not possible and formulated the second law of thermodynamics as follows. There are two apparently different but actually equivalent statements of the second law.
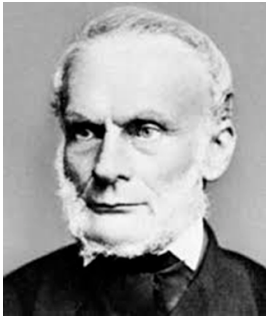
Rudolf Clausius (1822-1888), a German physicist, is a pioneer in thermodynamics. In 1850, he showed that there was a contradiction between Carnot's principle and the first law. This led him to propose the Second Law of thermodynamics. In 1865, he proposed the concept of entropy.
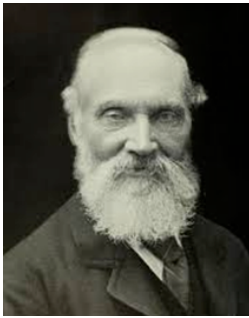
William Thomson (Lord Kelvin, 1824-1907), after whom the unit of absolute temperatures is named, first determined the correct value of absolute zero as approximately −273.15 Celsius (earlier estimated to be −267 Carnot). He formulated the Kelvin-Planck statement of Second law of thermodynamics

Max Planck (1858-1947), the founder of quantum theory, was deeply inspired by Clausius. His Ph. D. thesis (*On the second law of thermodynamics*, 1879) and his famous book, *Treatise on Thermodynamics* (1897) deeply influenced the development of the subject.

Second Law: Kelvin-Planck statement

"It is impossible for a cyclic machine to convert heat totally into work without producing change elsewhere in the universe."

Second Law: Clausius statement

"It is impossible for a cyclic machine to transfer heat from low temperature to high temperature without producing change elsewhere in the universe."

A third statement popularly referred to as the second law is given as:

"The entropy of the universe always increases as it evolves toward the thermodynamic equilibrium, a state with maximum entropy."

However, this popular statement should not be regarded as an original statement of the second law. We show below that this third statement is a corollary of the Clausius statement, and need not be included as a formal statement of the second law.

Equivalence of the two statements

We will now show that the two statements are equivalent.

a) We will first show that if Clausius statement is untrue then Kevin-Planck statement is also untrue. To prove this let us assume Clausius statement is untrue. Then one can transfer heat from low temperature to high temperature without causing any change elsewhere. . Then let the sink and the source in a cyclic machine (e.g. Carnot cycle) are connected by a conductor of heat. Then every time the machine gives out Q_2 heat to sink we can transfer it to the source.

Then the net amount of heat absorbed from source reservoir= Q_1-Q_2

and   the net amount of heat change at the sink = 0

Then whatever amount of heat (Q_1-Q_2) is absorbed from the source may be totally converted into work (since there is no heat loss to the sink) without producing any change elsewhere. This however violates Kelvin-Planck statement! Thus we have proved *that if Clausius statement is untrue then Kelvin-Planck statement is also untrue.*

Note, if Clausius statement is untrue, one can transfer heat from a refrigerator to a stove. This will keep the refrigerator perpetually cool and the stove perpetually hot without needing any external source of energy (e.g. electricity or gas). *Such an impossible machine (stove-*

refrigerator) is called a perpetual machine of the second kind. A lot of effort was made at one point of time to invent such a machine but none succeeded.

b) Let us now show that if Kelvin-Planck Statement is untrue than the Clausius statement is also untrue.

Let us operate a machine in the reverse direction. Instead of absorbing Q_1 heat from source, doing W amount of work and releasing Q_2 heat to sink, let the machine absorbs Q_2 heat from sink and some external agency does W amount of work on the system. Note, *work can be totally converted into heat without violating any law*. Thus let this W work be fully converted into heat. Then the system would transfer $Q_1=W+Q_2$, heat to the hot source. This is equivalent to transferring Q_2 amount of heat from the cold sink (at temperature T_2) to the hot source (temperature $T_1>T_2$), without causing any change elsewhere!. This violates Clausius statement.

Thus if Kelvin-Planck Statement is untrue than the Clausius statement is also untrue.


2.2 Carnot Theorems

First Theorem: *All reversible engines have same efficiency.*

Proof: Let us consider two reversible machines operate between a heat source reservoir at temperature T_1 and a sink reservoir at temperature T_2. Let their size be so adjusted that both release Q_2 amount of heat to the sink. Let the first and the second machine absorbs Q_1 and Q_1' heat from the source reservoir, respectively. Then the efficiencies of the first and second machines are given ,respectively, by

$$\varepsilon_1 = 1- Q_2 / Q_1 \qquad\qquad (2.1)$$

$$\varepsilon_2 = 1- Q_2 / Q_1' \qquad\qquad (2.2)$$

Q_1 may be less than, greater than or equal to Q_1'.

Source

T_1

Q_1

W

Q_2

Sink

T_2
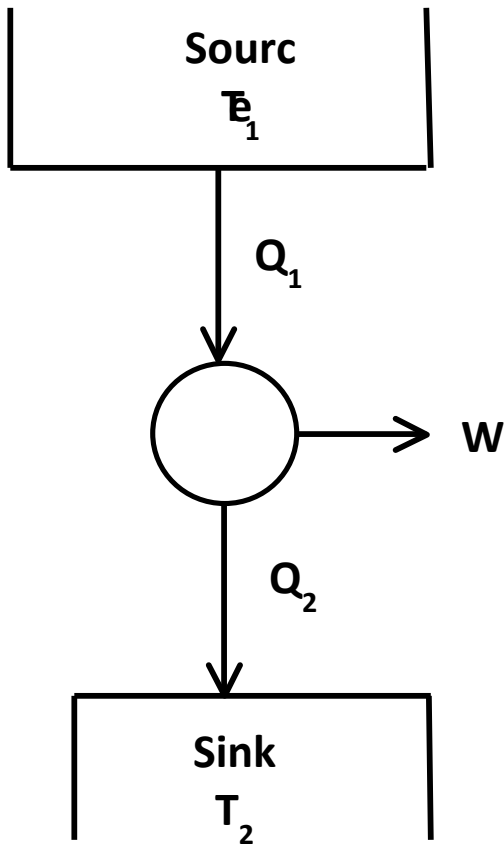
Since the machines are reversible let us assume that the second machine operates in the reverse mode i.e. it takes Q_2 from sink and give Q_1' to the source. In this case, there is no change of heat content in the sink.

The net amount of heat absorbed from source $= Q_1 - Q_1'$ (2.3)

If $Q_1 - Q_1' > 0$, i.e. the difference is positive, then the composite machine which absorbs $Q_1 - Q_1'$ heat from source would convert it totally into work, as there is no loss to the sink. This will violate the second law.

Therefore, $Q_1 - Q_1'$ can not be positive i.e. Q_1 cannot be greater than Q_1'.

If $Q_1 - Q_1'$ is less than zero, let us operate the first machine in the reverse mode it would absorb Q_2 from sink while the second machine would release Q_2 to the sink. Then net heat change at source is $Q_1' - Q_1$. If $Q_1' - Q_1$ is positive that will violate second law. So Q_1' cannot be greater than Q_1, i.e., Q_1 cannot be less than Q_1'.

In summary, Q_1 cannot be neither less nor greater than Q_1'. Thus the only possibility is

$$Q_1 = Q_1' \qquad\qquad (2.4)$$

From 2.1 and 2.2, $\varepsilon_1 = \varepsilon_2$ (2.5)

Thus both the reversible machines must have the same efficiency. Note, since all reversible machines must have the same efficiency, we may assume their efficiency is same as that of the Carnot cycle. Therefore, we can write

Efficiency of any reversible engine, $\varepsilon_{rev} = 1 - Q_2 / Q_1 = 1 - T_2 / T_1$ (2.6)

Second Theorem: *Efficiency of a reversible engine is greater than that of an irreversible machine.*

Proof: Let us consider two machines operating between a source reservoir of temperature T_1 and a sink reservoir of temperature T_2. Let their size be so adjusted that both release Q_2 amount of heat to the sink. Let the first and the second machine absorbs Q_1 and Q_1' heat from the source reservoir. Also let the first machine is reversible while the second one is irreversible. Then the efficiencies of the reversible and irreversible machines are respectively,

$$\varepsilon_{rev} = 1 - Q_2 / Q_1 \qquad\qquad (2.7)$$

$$\varepsilon_{irrev} = 1 - Q_2 / Q_1' \qquad\qquad (2.8)$$

Q_1' may be less than, greater than or equal to Q_1'. Since the first machine is reversible let us assume that it operates in the reverse mode i.e. it takes Q_2 from sink and give Q_1 to the source. In this case, there is no heat change at the sink.

The net amount of heat absorbed from source = $Q_1' - Q_1$ (2.9)

If $Q_1' - Q_1 > 0$,   i.e. positive, then the composite machine which absorbs $Q_1 - Q_1'$ heat from source would convert it totally into work because there is no loss to the sink ! This will violate the second law. So, Q_1' cannot be greater than Q_1.

Again Q_1' cannot be equal to Q_1 because that would imply the effect of an irreversible machine is completely negated by a reversible machine.

Eliminating these two possibilities, Q_1' must be less than Q_1. Then from (2.7) and (2.8)

$$\varepsilon_{rev} > \varepsilon_{irrev} \qquad (2.9)$$

Hence from (2.8) and (2.9)

$\varepsilon_{irrev} = 1 - Q_{2,\,irrev} / Q_{1,\,irrev} < 1 - T_2 / T_1$

$$\text{Or,} \quad Q_{2,\,irrev} / Q_{1,\,irrev} < T_2 / T_1 \quad (2.10)$$

2.3 Clausius and the concept of entropy:

For a reversible machine, equation (69) may rewritten as

$Q_2 / Q_1 = T_2 / T_1$

Or, $(Q_1 / T_1) + (-Q_2 / T_2) = 0$ (2.11)

Note, $-Q_2$ denotes the heat absorbed by the sink reservoir. Thus we can say that for any reversible cycle, sum of heat absorbed divided by temperature is zero.

Thus for a reversible cycle, Cyclic integral $dQ_{rev} / T = 0$ (2.12)

Equation (2.12) prompted Rudolf Clausius (1822–1888) to propose in 1865 that dQ_{rev}/T represents a new property of state. He called it entropy (S) and defined entropy as

$$dS = dQ_{rev}/T \qquad (2.13)$$

2.4 Entropy is a state function (Saha-Srivastava, p. 245)

This can be proved in the following way. The efficiency of a reversible heat engine operating between heat baths at temperatures T_1 and T_2, with Q_1 is the heat absorbed at T_1 and Q_2 as the heat released at T_2 (the same notation as employed above and throughout this chapter) is given by two alternative expressions

$$\varepsilon = 1 + \frac{Q_2}{Q_1}, and,$$

$$\varepsilon = 1 - \frac{T_2}{T_1}.$$

We can eliminate efficiency ε from above equations to obtain

$$\frac{Q_2}{Q_1} + \frac{T_2}{T_1} = 0$$

This can be rearranged to obtain

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Since an engine is a cyclic process, we can write the above as

$$\oint \frac{dQ_{rev}}{T} = 0$$

Thus, the above equation satisfied the condition of a state function that the sum over a cycle that brings the engine to its initial state must be zero, the quotient $\dfrac{dQ_{rev}}{T}$ is a state function, and called

the entropy function, $\frac{dQ_{rev}}{T}$ is the change in entropy when dQ_{rev} quantity of heat is absorbed at

temperature T

$$dS = \frac{dQ_{rev}}{T}$$

The above proof that entropy is a state function can be made more general by following the same

procedure used above where a second engine is added to the first engine, and then look for a

contradiction to the second law.

2.5 Total entropy change in a reversible process:

Let a system goes from state A to B by a reversible process (path II) in which the system absorbs

dQ_{rev} heat from the surrounding (source) at a temperature T.

Obviously, entropy change of system, $dS_{system} = dQ_{rev}/T$ (2.14)

Note, since dQ_{rev} flows from surrounding to system,

        Heat absorbed by surrounding $= - dQ_{rev}$

As a result, entropy change of surrounding, $dS_{surrounding} = -dQ_{rev}/T$ (2.15)

Combining (2.14) and (2.15),

   In this case, total entropy change, of the universe for a reversible process,

      $dS_{tot} = dS_{system} + dS_{surrounding} = dQ_{rev}/T - dQ_{rev}/T = 0$ (2.16)

Thus, we have an important result that *the total entropy change of the universe during a*

reversible process is zero.

2.6 **Irreversible process**

Let us now consider that a system goes from state A to state B in an irreversible process (path I)

B by absorbing dQ_{irrev} heat from the surrounding (source) at a temperature T. Let the same

system also goes from state A to B also by a reversible process (path II) in which the system absorbs dQ_{rev} heat from the surrounding (source) at a temperature T.

Obviously, $dS_{system}= S_B-S_A= dQ_{rev}/T$ (2.17)

Let us now reverse the reversible path II so that the system now absorbs $-dQ_{rev}$ in the reverse process. In this cycle (path I plus reverse of path II),

The total heat absorbed by the system$= dQ_{irrev}-dQ_{rev}$ (2.18)

Now $dQ_{irrev}-dQ_{rev}\neq0$, because that would mean that the effect of irreversible path is compensated by a reversible path.

Again, $dQ_{irrev}-dQ_{rev}$ can not be positive (>0) because that would imply that in this cycle there is a net absorption of heat which must have been totally converted to work. This will violate second law.

Then the only alternative is, $dQ_{irrev}-dQ_{rev}<0$

Or, $dQ_{irrev} - TdS_{system} <0$

Or, $dS_{system} > dQ_{irrev}/T$ (2.19)

2.7 Clausius inequality:

Combining Equations (2.16) and (2.19) we can write that

$dS_{system} \geq dQ/T$ (2.20)

The relation (2.20) is known as Clausius Inequality where the equality corresponds to a reversible process and the greater than sign applies for irreversible process. Clausius Inequality plays a highly important role in the subsequent developments of thermodynamics. As we show

later, this inequality, under appropriate conditions, give rise to statements about stability of systems through changes in free energy of the system.

The Clausius Inequality, has been, from the time of its inception, has also been subject of countless discussions as it seem to provide a direction of change, the oft quoted "arrow of time", as discussed below.

2.8 Entropy Change of the Universe

As the system goes from state A to state B in an irreversible process B, let dQ heat from the surrounding (source) at a temperature T. Now, the surrounding is such a big reservoir that there is no difference in heat absorbed in reversible of irreversible process. Thus for the surrounding for both reversible and irreversible process

$$dS_{surrounding} = -dQ/T \qquad (2.21)$$

Substituting this in (82) we can write, $\qquad dS_{system} \geq -dS_{surrounding}$

Thus, for an irreversible process, $dS_{system} + dS_{surrounding} \geq 0$

Thus, the total entropy change of the universe,

$$dS_{system} + dS_{surrounding} \geq 0 \qquad\qquad (2.22)$$

In (84) the equality corresponds to a reversible process while the greater than sign applies for irreversible process. In the universe always some irreversible processes occur. Thus one can say that *entropy of the universe is continuously increasing*. Thus this statement is a corollary to the second law.

2.9 Entropy is a measure of unavailable energy

Let in a Carnot cycle, system absorbs Q heat from the source (high temperature reservoir) at a temperature T_1 and gives heat to the sink (low temperature reservoir) at T_0. Then from the definition of efficiency of Carnot cycle.

$W = Q_1 (1-T_0/T_1)$ (2.23)

Evidently, a part of the total heat absorbed from source (Q) is not converted into work. This is known as unavailable energy.

Thus unavailable energy, $W_{unavail} = Q - W = QT_0/T_1$ (2.24)

Let, the source transfers an identical amount of heat Q to another reservoir of temperature (T_x) where $T_1 > T_x > T_0$. Let us consider, a Carnot cycle operates between T_x and T_0. For this cycle, in analogy to equation (2.24), the unavailable energy,

$W_{unavail}' = QT_0/T_x$ (2.25)

Since, $T_1 > T_x$, $W_{unavail}' > W_{unavail}$. Subtracting (2.24) from (2.25), the increase in amount of unavailable energy because of transfer of heat Q from reservoir of temperature T_1 to reservoir of temperature T_x is

$\Delta W_{unavail} = T_0 (Q/T_x - Q/T_1)$ (2.26)

The increase of entropy for transfer of heat Q from reservoir of temperature T_1 to reservoir of temperature T_x is given by

$\Delta S = (Q/T_x - Q/T_1)$ (2.27)

From (2.26) and (2.27)

Increase in unavailable energy $= T_0 \Delta S$ (2.28)

Evidently, the higher is increase in entropy the more is the amount of unavailable energy. Thus *Entropy is a measure of unavailable energy.*

2.10 Entropy change of an ideal gas: reversible process

From equation (3) $dE=dQ-dW=dQ-P_{ext}\,dV$

For an ideal gas, $dE=C_V dT$

For a reversible process, $dQ=TdS$ and $P_{ext}=P_{int}=P=RT/V$ (for one mole)

Thus $CvdT=TdS-(RT/V)\,dV$

Thus $dS=(Cv/T)\,dT+(R/V)\,dV$

Integrating between (V_1, T_1) and (V_2, T_2)

$$\Delta S=C_V \ln (T_2/T_1) + R \ln (V_2/V_1) \qquad\qquad (2.25)$$

Problem: Draw S versus T curve for the Carnot Cycle.

2.11 Entropy change of other processes

a) Entropy Change during vaporization at boiling point: Trouton's rule

Let us consider evaporation of a liquid at the boiling point. If L_{vap} denotes the latent heat of vaporization per mole and T_B, the boiling point in absolute scale, under one atmosphere (1 atm) pressure the entropy change during this process

$$\Delta S_{vap} = L_{vap}/T_B \qquad\qquad (2.26)$$

The quantity given by equation (2.26), is called standard molar entropy of vaporization at boiling point It is observed for a large number of liquids, the standard molar entropy of vaporization at boiling point, given by equation (2.26), is approximately same (around 85 J K^{-1} M^{-1}). This empirical rule is called Trouton's Rule.

Problem: Given that the boiling point of water and liquid bromine 100^0 C and 59.2^0C, respectively, calculate latent heat of vaporization of water and liquid bromine.

b) Entropy change of a solid under constant pressure

Let us consider a solid being heated from T_1 to T_2 at constant pressure

$\Delta S_P = \int dQ_P / T = \int C_P dT/T = C_P \ln (T_2/T_1)$ (2.27)

In equation (89) we have assumed that the C_P is constant.

In general, for a wide range of temperature C_P is given by

$C_P = b + cT$ (2.28)

Near absolute zero (0^0K or -273^0 C) C_P is found to be proportional to T^3. This is known as *Deby extrapolation*.

Thus for temperatures between 0^0 K at T′, $C_P = aT^3$ (2.29)

Combining (2.27-29) for a solid below its melting point

$\Delta S_P = \int aT^2 dT + \int bdT + \int cdT$

Or $S (T) - S (0) = (a/3) T'^3 + b \ln (T/T') + c (T-T')$ (2.30)

Problem: Consider one mole of a solid at its melting point (T_m). Calculate entropy change of melting and subsequent heating of the liquid under constant pressure up to a temperature, $T < T_B$ (boiling point).

2.12 Entropy is measure of disorder in a system

Let us consider that a system consists of N number of molecules which are distributed among energy levels ε_1, ε_2, ε_3 … such that n_1, n_2, n_3, … molecules are in energy levels ε_1, ε_2, and so on, respectively. When the number of molecules N and the number of energy levels both are large, one can achieve this distribution in a large number of ways. The total number of such arrangements or complexions are called thermodynamic probability, Ω. Obviously, Ω is given by,

$$\Omega = {}^{N}C_{n1} \, {}^{N-n1}C_{n2} \, {}^{N-n1-n2}C_{n3} \ldots$$

$$= (N!)/(n_1!)(n_2!)(n_3!)(n_4!) \qquad\qquad (2.31)$$

Since, N is an exceedingly large number of the order of Aavogadro Number and the populations of individual energy levels (n_1, n_2….) are very small, Ω, is a very large number. Ω is measure of disorder of the system. Entropy is related to Ω by the equation,

$$S = k \ln \Omega \qquad\qquad (2.32)$$

From (2.32) the greater is disorder in the system, the larger is Ω and the higher is entropy. Thus

Entropy is measure of disorder in a system.

Special Topics

1. Entropy and concept of negative temperature

Since $TdS = dQ_{rev} = dE + PdV$

At constant volume $TdS_V = dE_V$

Thus $(\partial S/\partial E)_V = 1/T$ (2. Xy)

If there are infinite energy levels, with increase in E, Ω increases and hence entropy, S (=k ln Ω) increases. Thus T is always positive from (2.xy).

However, for a system with finite levels (a two level system figure 2) Ω decreases with increase in E. In such a case, one can achieve a negative temperature. Population inversion in lasers is another example of formal negative temperature (to be discussed in chapter ??).

2. Cryogenics: Cooling to very low temperature

Using Joule-Thomson expansion (below inversion temperature) one can liquefy all gases. Liquid helium has a temperature 4 K. If liquid helium is evaporated by pumping one can go below 4K. However, at temperature below ?? helium becomes superfluid and produces a fountain like creeping over the container. This makes further cooling difficult. We will now discuss some novel methods of achieving very low temperature as low as mK (10^{-3} K) and nK (10^{-9} K) range.

2.1 Adiabatic Demagnetization

In paramagnetic substances with unpaired electron, each unpaired electron act as a tiny magnet of spin $\pm$ 1/2. The -1/2 spin (β state) and + ½ spin (α state) correspond to different orientations. In the absence of magnetic field, the two spin states have equal energy and will be equally populated (state A). As a result there will no net magnetization and the disorder (or entropy) of the system will be high. In the presence of a magnetic field, the state with -1/2 spin (β spin) is of lower energy and hence, more of the electrons would have β spin (state B). Thus there will be a net magnetization. As shown in fig 2, during magnetization from A to B net magnetic energy of the system (E_M) decreases and the system releases a lot of energy as heat. This heat is absorbed

by liquid helium surrounding the system so that the temperature is kept at 4 K. Thus the magnetization process is isothermal.

Once the system reaches state B, the liquid helium is pumped out so that the system is now thermally insulated. Now the external magnetic is slowly and reversible reduced to zero. This is an adiabatic process. In this case, when the magnetic field is zero, the overall magnetic energy of the system increases. The increase in magnetic energy because of adiabatic demagnetization causes a decrease in thermal energy and hence, in temperature.

 The disorder or entropy will be lower than that in absence of magnetic field.

Since at low temperature (near 4 K) the entropy is given by T^3 law let us assume the entropy in absence of magnetic field is aT^3 and that in the presence of magnetic field as bT^3. Evidently, $a>b$. From the S against T curve the system first goes isothermally from A to B. B to C is a reversible adiabatic process in which dS=0 but temperature drops. Thus if the temperature at B and C are T and T′, respectively,

T′ = (b/a) $^{1/3}$T

Thus in each cycle the temperature drops. By repeating the cycle n the temperature drops enormously by a factor of $(a/b)^{n/3}$.

A typical sample for adiabatic demagnetization is Gadolinium (III) ion with many (seven) f-electrons with parallel spin. If instead of electron spin one can make use of nuclear spin. One achieve better cooling and lower temperature in the case of nuclear spin.