Unit 1: Laws of Thermodynamics

Dr Priya Hasan[1*]
[1]Department of Physics
Maulana Azad National Urdu University
Gachibowli, Hyderabad 500 032

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Abstract

Thermodynamic Description of system: Zeroth Law of thermodynamics and temperature. First law and internal energy, conversion of heat into work, Various Thermodynamical Processes, Applications of First Law: General Relation between C_P & C_V , Work Done during Isothermal and Adiabatic Processes, Compressibility & Expansion Coefficient, Reversible & irreversible processes, Second law & Entropy, Carnots cycle & theorem, Entropy changes in reversible & irreversible processes, Entropy-temperature diagrams, Third law of thermodynamics, Unattainability of absolute zero.

1 Thermodynamic Description of system

Thermodynamics is a branch of physics which deals with the transformation of thermal or heat energy into mechanical work or vice-versa. It deals with processes involving heat, work and internal energy. Thermodynamics is concerned with macroscopic behavior (P, V, T) rather than microscopic behavior of the system. Statistical Mechanics deals with the statistical study of the microscopic properties of the particles in a system like masses, positions and velocities.

Basic Terminology:

System: A definite quantity of matter bounded by some closed surface is known as a system. It is the part of the universe under investigation. The Surroundings is the part of the universe other than system, which can interact with it. A Boundary is anything which separates system from surrounding.

An Open System is a system which can exchange both energy and matter with its surroundings.

A Closed System is a system which permits passage of energy but not mass, across its boundary.

An Isolated system is a system which can neither exchange energy nor matter with its surroundings.

State variables are 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 are the 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.)

If the thermodynamic variables P, V, T are independent of time, i.e. they attain a steady state value, the system is said to be in Thermodynamic Equilibrium. For this we need: (i) Mechanical Equiibrium ($\Sigma F_i = 0$) (ii)Thermal Equilibrium (T=const) (iii) Chemical Equilibrium (μ=const)

Intensive properties are the properties of a system which do not depend on mass of the system i.e. Temperature, pressure, density, concentration. The Extensive properties are properties of a system which depend on mass of the system i.e. Volume, energy, enthalpy, entropy etc.

A Process is a path along which state of a system changes.

An Isothermal process is a process which takes place at constant temperature. An Isobaric process is a process which takes place at constant pressure. An Isochoric process is a process which takes place at constant volume. An Adiabatic process is a process during which transfer of heat cannot take place between system and surrounding.

Cyclic process are process in which system comes back to its initial state after undergoing series of changes. A Reversible process is a process during which the system always departs infinitesimally from the state of equilibrium i.e. its direction can be reversed at any moment.

Kinetic Energy is the energy possessed by the atoms or molecules by virtue of their motion is called kinetic energy.

*e-mail:priya.hasan@gmail.com, priyashasan@yahoo.com

Internal Energy (U):- Sum total of kinetic and potential energies of atoms/molecules constituting a system is called the internal energy of the system. (a) ΔU is taken as positive if the internal energy of the system increases. (b) ΔU is taken as negative if the internal energy of the system decreases.

Heat is the part of internal energy which is transferred from one body to another an account of the temperature difference. Work is said to be done when a force acting on a system displaces the body in its own direction.

$$dW = Fdx = PdV$$

$$W = P(V_f - V_i)$$

(a) If the gas expands, work is said to be done by the system. In this case $V_f > V_i$, therefore, W will be positive.

(b) If the gas is compressed, work is said to be done on the system. In this case $V_f < V_i$, therefore, work done is negative. Relation between joule and calorie:- 1 joule = 4.186 cal

Thermodynamic variables or parameters: The thermodynamic state of system can be determined by quantities like temperature (T), volume (V), pressure (P), internal energy (U) etc. These quantities are known as thermodynamic variables, or the parameters of the system.

Equation of state: A relation between the values of any of the three thermodynamic variables for the system, is called its equation of state.

Equation of state for an ideal gas is

$$PV = RT$$

Equilibrium of a system: A system is said to be in equilibrium if its macroscopic quantities do not change with time.

2 The zeroth law of thermodynamics

It states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other. Accordingly, thermal equilibrium between systems is a transitive relation.

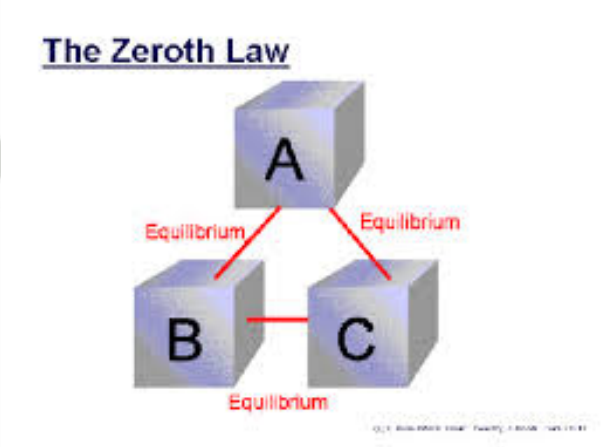

Figure 1: The zeroth law of thermodynamics

Two systems are said to be in the relation of thermal equilibrium if they are linked by a wall permeable only to heat and they do not change over time.

3 First law of thermodynamics

If the quantity of heat supplied to a system is capable of doing work, then the quantity of heat absorbed by the system is equal to the sum of the increase in the internal energy of the system, and the external work done by it.

$$dQ = dU + dW$$

Thermodynamic Process: A process by which one or more parameters of thermodynamic system undergo a change is called a thermodynamic process or a thermodynamic change. P-V diagram of isothermal, isobaric, isochoric and adiabatic process in a single figure.

(a) Isothermal process: The process in which change in pressure and volume takes place at a constant temperature, is called a isothermal change. It may be noted that in such a change total amount of heat of the system does not remain constant.

(b) Isobaric process: The process in which change in volume and temperature of a gas take place at a constant pressure is called an isobaric process.

(c) Isochoric process: The process in which changes in pressure and temperature take place in such a way that the volume of the system remains constant, is called isochoric process.

(d) Adiabatic process: The process in which change in pressure and volume and temperature takes place without any heat entering or leaving the system is called adiabatic change.

(e) Quasi-static process: The process in which change in any of the parameters take place at such a slow speed that the values of P,V, and T can be taken to be, practically, constant, is called a quasi-static process.

(f) Cyclic process: In a system in which the parameters acquire the original values, the process is called a cyclic process.

(g) Free expansion: Such an expansion in which no external work is done and the total internal energy of the system remains constant is called free expansion.

Application of first law of thermodynamics: (a) Cooling caused in adiabatic process:-

$$dT = PdV/C_v$$

(b) Melting:

$$dU = mL_f$$

(c) Boiling:

$$dU = mL_vP(V_f - V_i)$$

(d) Mayers formula:

$$C_p - Cv = R$$

3.1 Specific heat capacity of gases

Specific heat capacity of a substance is defined as the amount of heat required to raise the temperature of a unit mass of substance through 1^0C.

(a) Specific heat capacity at constant volume (C_v): Specific heat capacity at constant volume is defined as the amount of heat required to raise the temperature of 1 g of the gas through 1^0C keeping volume of the gas constant.

(b) Specific heat capacity at constant pressure (C_p):- Specific heat capacity, at constant pressure, is defined as the amount of heat required to raise the temperature of 1 g of gas through 1^0C keeping its pressure constant.

Difference between two specific heat capacities (Mayer's formula):

$$dQ = dU + dW$$

$$dQ = dU + PdV$$

$$C = dQ/T, C_v = (dQ/T)_V = (dU/T)_V$$

$$C_p = (dQ/T)_p$$

From Ideal Gas Equation:

$$PV = RT$$

At constant Pressure,

$$PdV = RdT$$

$$C_pdT = C_vdT + PdV$$

$$(C_p - C_v)dT = RdT$$

$$(C_p - C_v) = R$$

3.2 Adiabatic gas equation: PV^γ =constant

Adiabatic gas constant,$\gamma = C_p/C_v$

(a) Mono-atomic gas: $\gamma = 1.67$

(b) Diatomic gas: $\gamma = 1.4$

We know from the 1st law of thermodynamics

$$dQ = dU + dW$$

For an adiabatic process, we can say

$$dQ = 0$$

So,

$$dU + dW = 0 = dU + PdV$$

We know,

$$dU = C_v dT$$

For an ideal gas,

$$PV = RT$$

Or,

$$T = PV/R$$

$$dT = (PdV + VdP)/R$$

Putting in 2,we get,

$$dU = C_v R(PdV + VdP)$$

$$dP/P = dV/V\frac{(C_v + R)}{C_v}$$

or,

$$dP/P = dV/V^\gamma$$

(as $\gamma = C_p/C_v$

or,

$$\int dP/P = \gamma \int dV/V$$

or,

$$\mathrm{lnP} = \gamma \mathrm{lnV} + \mathrm{c}$$

or,

$$P + \gamma \mathrm{lnV} = \mathrm{k}$$

$$\mathrm{lnPV}^\gamma = \mathrm{k}$$

(a) Equation of adiabatic change in terms of T and V: $TV^{\gamma-1}$ = Constant

(b) Equation of adiabatic change in terms of P and T: $T^\gamma P^{1-\gamma}$ = Constant

4 Indicator Diagram

A plot between P and V is called an indicator diagram. The area bounded by the curve gives the work done by the system.

Comparison of slopes of an isothermal and adiabatic:

(a) Slope of isothermal:- $dP/dV = -P/V$

(b) Slope of adiabatic:- $dP/dV = -\gamma P/V$

(c) Adiabatic gas constant:- $\gamma = C_p/C_v$

As, $C_p > C_v$, So, $\gamma > 1$

This signifies that, slope of adiabatic curve is greater than that of isothermal.

Slope on PV diagram:- (a) For isobaric process: zero

(b) For isochoric process: infinite

Work done for isobaric process: $W = P(V_2 - V_1)$

Work done for isochoric process: W = 0

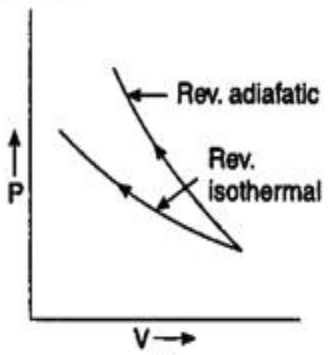

Figure 2: Reversible isothermal and adiabatic curve

4.1 Work done in isothermal and adiabatic processes

Work done in an isothermal process: Work done in isothermal expansion and compression:

$$dW = \int PdV$$

$$PV = RT, P = RT/V$$

$$\int dW = \int RT/VdV$$

$$W = 2.3026RTlog_{10}V_f/V_i$$

(isothermal expansion)

$$W = -2.3026RTlog_{10}V_f/V_i$$

(isothermal compression)

Work done during an adiabatic expansion:

$$dW = \int PdV$$

$$PV^\gamma = k, P = k/V^\gamma$$

$$\int dW = \int k/V^\gamma dV$$

$$W = \frac{k}{1-\gamma}(V_f^{1-\gamma} - V_i^{1-\gamma})$$

(isothermal expansion)

$$W = \frac{1}{1-\gamma}[P_2V_2 - P_1V_1] = \frac{R}{1-\gamma}[T_2 - T_1]$$

Work done in expansion from same initial state to same final volume:

$$W_{adiabatic} < W_{isothermal} < W_{isobaric}$$

Work done in compression from same initial state to same final volume:

$$W_{adiabatic} < W_{isothermal} < W_{isobaric}$$

4.2 Reversible processes

Reversible process: It is a process which can be made to proceed in the reverse direction by a very slight change in its conditions so that the system passes through the same states as in direct process, and at the conclusion of which the system and its surroundings acquire the initial conditions.

Example: All isothermal and adiabatic process when allowed to proceed slowly, are reversible, provided there is no loss of energy against any type of resistance. Friction, viscosity are other examples.

Irreversible process: A process which cannot be made to be reversed in opposite direction by reversing the controlling factor is called an irreversible process.

Example:

(a) work done against friction

(b) Joules heating effect

(c) Diffusion of gases into one another

(d) Magnetic hysteresis

5 Carnot Engine

Heat engine is a device used to convert heat into mechanical energy

(a) Work done,

$$W = Q_1 - Q_2$$

(b) Efficiency:- Efficiency η of an engine is defined as the fraction of total heat, supplied to the engine which is converted into work.

$$\eta = W/Q_1 = [Q_1 - Q_2]/Q_1 = 1 - [Q_2/Q_1]$$

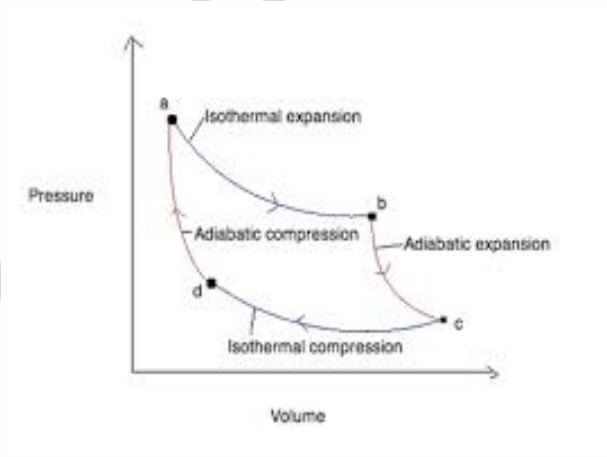

Figure 3: Carnot Engine

Carnot engine is a reverse cycle made of the following processes:

(a) First (isothermal expansion):-

$$W_1 = 2.3026RT_1\log_{10}\mathrm{V}_2/\mathrm{V}_1$$

(b) Second (adiabatic expansion):-

$$W_2 = \frac{R}{1-\gamma}[T_1 - T_2]$$

(c) Third (isothermal compression):-

$$W_3 = 2.3026RT_2\log_{10}\mathrm{V}_3/\mathrm{V}_4$$

(d) Fourth (adiabatic compression):-

$$W_4 = \frac{R}{1-\gamma}[T_2 - T_1]$$

(e) Total work done in one cycle,

$$W = W_1 + W_2 + W_3 + W_4 = R(T_1 - T_2)\ln(\mathrm{V}_2/\mathrm{V}_1)$$

Efficiency of Carnot engine:- Efficiency η of an engine is defined as the ratio between useful heat (heat converted into work) to the total heat supplied to the engine.

$$Q_1 = RT_1 \ln(V_2/V_1)$$

$$\eta = W/Q_1 = W/Q_1 = 1 - [Q_2/Q_1]$$
$$= \frac{R(T_1 - T_2)\ln(V_2/V_1)}{R(T_1)\ln(V_2/V_1)} = 1 - T_2/T_1$$

6 Carnot Theorem

Carnot Theorem states that no engine can be more efficient than a reversible engine working between the same two temperatures.

OR

All reversible engines working between the same two temperatures have the same efficiency, whatever may be the working substance.

7 Second law of thermodynamics

(a) Clausius statement:- Heat cannot flow from a cold body to a hot body without the performance of work by some external agency.

(b) Kelvins statement:- It is impossible to obtain a continuous supply of energy by cooling a body below the coldest of its surroundings.

(c) Plancks statement:- It is impossible to extract heat from a single body and convert the whole of it into work.

Refrigerator:- It is a device which is used to keep bodies at a temperature lower than that of surroundings. Coefficient of performance (β):- Coefficient of performance of a refrigerator is defined as the amount of heat removed per unit work done on the machine. β = Heat removed/work done $= Q_2/W = Q_2/[Q_1 - Q_2] = T_2/[T_1 - T_2]$

Coefficient of performance of a refrigerator is not a constant quantity since it depends upon the temperature of body from which the heat is removed.

For a perfect refrigerator, $W = 0$ or $Q_1 = Q - 2$ or $\beta = \infty$

8 Kelvin Scale of Temperature

Temperature measurements are based on the properties of substances like, expansion of Mercury, increase in volume or pressure of a gas, variation of resistance, thermo emf, etc. Kelvin wanted an absolute temperature scale independent of the working substance. So he based it on the Carnot engine. Let Q_1 be he amount of heat absorbed by a reversible hear engine at temperature T_1 and Q_2 be the amount rejected at T_2 on this scale.

We know that the efficiency of Carnot Engine is only a function of the temperature of the source and sink.

$$\eta = 1 - [Q_2/Q_1] = f(T_1, T_2)$$

$$Q_2/Q_1 = 1 - f(T_1, T_2)$$

$$Q_1/Q_2 = \frac{1}{1 - f(T_1, T_2)} = F(T_1, T_2)$$

Consider another reversible hear engine absorbing Q_2 at temperature T_2 and rejecting Q_3 at T_3.

$$Q_2/Q_3 = F(T_2, T_3)$$

For a reversible engine between T_1 & T_2, where $T_1 > T_3$

$$Q_1/Q_3 = F(T_1, T_3)$$

$$Q_1/Q_2 \times Q_2/Q_3 = F(T_1, T_2) \times F(T_2, T_3)$$
$$= Q_1/Q_3 = F(T_1, T_3)$$

This is only possible if there is no term with T_2 such that

$$F(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2}, F(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

$$F(T_1, T_2) \times F(T_2, T_3) = \frac{\phi(T_1)}{\phi(T_2} \times \frac{\phi(T_2)}{\phi(T_3)}$$

$$= \frac{\phi(T_1)}{\phi(T_3)} = F(T_1, T_3)$$

$$Q_1/Q_2 = \frac{\phi(T_1)}{\phi(T_2)}$$

The thermodynamic or Kelvin scale is that scale, the ratio of any two temperature is the same as the ratio of the heats absorbed and rejected by a reversible Carnot Engine operating between the two temperatures.

8.1 Scales

$$\eta = 1 - T_2/T_1$$

Absolute Zero is when $T_2 = 0$, $\eta = 1$. It is the temperature of the sink of a reversible engine which converts all heat into work. This is impossible by the 2 nd law of thermodynamics.

Ice point and steam point are measured in terms of water and divided into 100 equal parts to give the Celsius scale.

$$Q_{100}/Q_0 = \frac{T_0 + 100}{T_0}$$

Negative scale implies $\eta > 1$, which is impossible.

9 Entropy

The thermal property of a body which remains constant in an adiabatic process is called entropy. Consider a grid of isothermal and adiabatic processes then

$$Q_1/Q_2 = T_1/T_2, Q_1/T_1 = Q_2/T2$$

According to the Clausius equality, for a closed homogeneous system, in which only reversible processes take place,

$$\frac{\delta Q}{T} = 0$$

With T being the uniform temperature of the closed system and δQ the incremental reversible transfer of heat energy into that system.

That means the line integral

$$\int_L \frac{\delta Q}{T}$$

is path independent.

So we can define a state function S, called entropy, which satisfies

$$\mathrm{d}S = \frac{\delta Q}{T}$$

In statistical mechanics, entropy is an extensive property of a thermodynamic system. Boltzmann explained the entropy as a measure of the number of possible microscopic configurations Ω of the individual atoms and molecules of the system (microstates) which comply with the macroscopic state (macrostate) of the system. Boltzmann then went on to show that $S = k\ln\Omega$ was equal to the thermodynamic entropy. The factor k has since been known as Boltzmann's constant. Hence an increase in entropy implies an increase in the number of microstates or the level of disorder.

10 Entropy and Second Law of Thermodynamics

The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time. The total entropy of a system and its surroundings can remain constant in ideal cases where the system is in thermodynamic equilibrium, or is undergoing a (fictive) reversible process. In an irreversible process, entropy always increases, so the change in entropy is positive. The total entropy of the universe is continually increasing.

Clausius statement:

Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

Heat cannot spontaneously flow from cold regions to hot regions without external work being performed on the system, which is evident from ordinary experience of refrigeration, for example. In a refrigerator, heat flows from cold to hot, but only when forced by an external agent, the refrigeration system.

Kelvin statement:

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.[32] Equivalence of the Clausius and the Kelvin statements:

Derive Kelvin Statement from Clausius Statement:

Suppose there is an engine violating the Kelvin statement: i.e., one that drains heat and converts it completely into work in a cyclic fashion without any other result. Now pair it with a reversed Carnot engine as shown by the figure. The net and sole effect of this newly created engine consisting of the two engines mentioned is transferring heat $\Delta Q = Q\left(\frac{1}{\eta - 1}\right)$ from the cooler reservoir to the hotter one, which violates the Clausius statement. (This is a consequence of the first law of thermodynamics, as for the total system's energy to remain the same, Input + Output $= 0 \implies Q + \frac{Q}{\eta} = -Q_c$, so therefore $Q_c = Q\left(\frac{1}{\eta} - 1\right)$. Thus a violation of the Kelvin statement implies a violation of the Clausius statement, i.e. the Clausius statement implies the Kelvin statement. We can prove in a similar manner that the Kelvin statement implies the Clausius statement, and hence the two are equivalent.

10.1 Entropy in Irreversible Processes

Consider an irreversible cycle where Q_1 is absorbed at T_1 and Q_2 is rejected at T_2. In the case of Carnot Engine, the efficiency of an irreversible process is always lesser than that of a reversible process.

$$/eta = 1 - Q_2/Q_1 < 1 - T_2/T_1$$

$$Q_2/Q_1 > T_2/T_1$$

$$Q_2/T_2 - Q_1/T_1 > 0$$

The Entropy always increases in all irreversible processes.

11 Temperature-Entropy diagram of Carnot Cycle

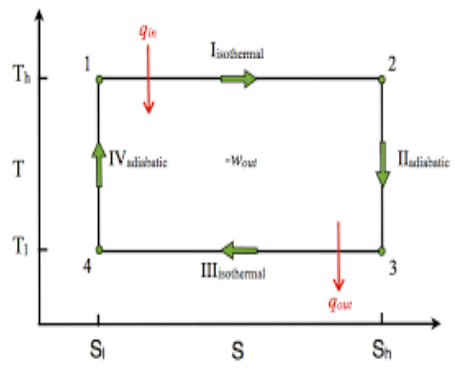

Figure 4: Temperature-Entropy diagram of Carnot Cycle

A temperature-entropy diagram, or T-S diagram, is used in thermodynamics to visualize changes to temperature and specific entropy during a thermodynamic process or cycle. It is a useful and common tool, particularly

because it helps to visualize the heat transfer during a process. For reversible (ideal) processes, the area under the Ts curve of a process is the heat transferred to the system during that process.

The entropy change is S_1 to S_2,

$$(S_1 - S_2)T_1 = Q_1$$

From 3 to 4:

$$T_2(S_2 - S_1)$$

Available energy is

$$Q_1 - Q_2$$

Efficiency

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_2} = 1 - T2/T_1$$

12 Entropy of a Perfect Gas

The term entropy refers to the energy that is unavailable for the conversion into work. From thermodynamics second law, Change in entropy,

$$dS = dQ/T$$

Here, change in heat is dQ and constant temperature is T. From thermodynamics first law,

$$dU = dQ - PdV$$

$$dU = TdS - PdV$$

$$C_v dT = TdS - PdV$$

$$dS = C_v dT/T + P/TdV/V$$

Equation for ideal gas is given by $PV = RT$, then the above equation becomes

$$dS = C_v dT/T + RdV/V$$

In event of free expansion process occurring adiabatically, the volume increases without a considerable decrease in temperature, which causes the entropy to increase.

$$\Delta S = \int C_v dT/T + R \int dV/V$$

Modify the above equation for an ideal gas that undergoes adiabatic expansion with constant specific heats

$$\Delta S = C_v \mathrm{ln(T_2/T_1)} + \mathrm{Rln(V_2/V_1)}$$

The above equation evaluates the Entropy change for an ideal gas with constant specific heats.

12.1 Change in Entropy when ice changes to steam

Ice to water:

$$\Delta S_1 = mL_1/T_1$$

Heating of water

$$\Delta S_2 = \int dQ/T = \int \frac{mCdT}{T} = mC \ \mathrm{lnT_2/T_1}$$

Water to steam

$$\Delta S_3 = mL_2/T_2$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= mL_1/T_1 + = mC\mathrm{lnT_2/T_1} + \mathrm{mL_2/T_2}$$

12.2 Change in Entropy in free expansion

Suppose there are two parts in an insulated chamber, one filled with ideal gas and other is complete vaccum, separated by a partition. Now if partition is removed then gas will rush in other part to fill the whole chamber.

In this case there is no heat flow. But that does not determine whether there is a change in entropy. Entropy is a state function - it is the integral of dQ/T between the beginning and end states over the reversible path between those two states. Here you have the case of a gas with initial thermodynamic state $(P, V, T) = (P_0, V_0, T_0)$ and final state $(P_0/2, 2V_0, T_0)$. The reversible path between these two states is an isothermal, quasi-static expansion. In such an expansion, work is done: $PdV \neq 0$. Since dU = 0 (constant T), an incremental expansion requires heat flow dQ = PdV. Over the entire expansion:

$$\Delta S = \int dQ/T = \in tPdV/T = \int nRTdV/VT = nR \int dV/V = nR\ln(\mathrm{V_f}/\mathrm{V_i})$$

13 The third law of thermodynamics

The third law of thermodynamics is stated as follows, regarding the properties of closed systems in thermodynamic equilibrium: The entropy of a system approaches a constant value as its temperature approaches absolute zero.