Chapter Two

The second law of thermodynamics

The differences between the two forms of energy, heat and work, provide some insight into the second law.

Work is readily transformed into other forms of energy: for example, into potential energy by elevation of a weight, into kinetic energy by acceleration of a mass, into electrical energy by operation of a generator. These processes can be made to approach a conversion efficiency of 100% by elimination of friction, a dissipative process that transforms work into heat. **Indeed, work is readily transformed completely into heat, as demonstrated by Joule's experiments.**

On the other hand, all efforts to devise a process for the continuous conversion of heat completely into work or into mechanical or electrical energy have failed.
Drawing further on our experience, we know that the flow of heat between two bodies always takes place from the hotter to the cooler body, and never in the reverse direction. This fact is of such significance that its restatement serves as an acceptable expression of the second law.

Statements of the Second Law:

Statement 1: No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by a system completely into work done by the system.

Kelvin-plank statement , it is impossible to construct an engine that operating continuously ; will produce to effect other than the transfer of heat from a single thermal reservoir at a uniform temperature and the performance of an equal amount of work.

Statement 2: No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

Clausius statement, it is impossible to construct a heat pump that operating continuously ,will produce no effect other than the transfer of heat from a lower temperature body to a higher temperature body.

There is no mathematical proof of the second law, the basis of this law is empirical. While work can be completely converted to the heat, heat cannot completely convert to the work. This is the basis of the second law: the heat to be converted to the work is done by a device called “***HEAT ENGINE***”.

Heat Engines

Heat engines, devices or machines that produce work from heat in a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically returns to its original state. In such a power plant the cycle (in its simplest form) consists of the following steps:

The word cyclic requires that the system be restored periodically to its original state.

- ➢ Liquid water at ambient temperature is pumped into a boiler at high pressure.
- ➢ Heat from a fuel (heat of combustion of a fossil fuel or heat from a nuclear reaction) is transferred in the boiler to the water, converting it to high-temperature steam at the boiler pressure.
- ➢ Energy is transferred as shaft work from the steam to the surroundings by a device such as a turbine, in which the steam expands to reduced pressure and temperature.
- ➢ Exhaust steam from the turbine is condensed by transfer of heat to the surroundings, producing liquid water for return to the boiler, thus completing the cycle.

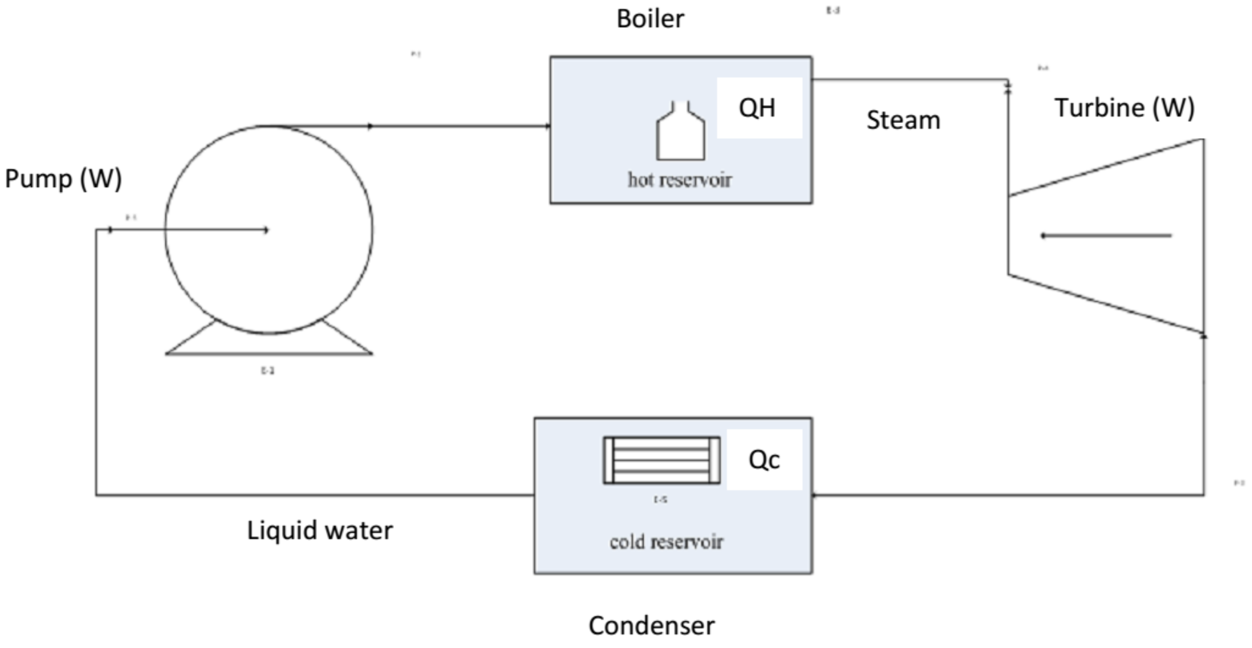

Figure (1) Steps of heat engine

Essential to all heat-engine cycles are absorption of heat into the system at a high temperature, rejection of heat to the surroundings at a lower temperature, and production of work. In the theoretical treatment of heat engines, the two temperature levels which characterize their operation are maintained by heat reservoirs, bodies imagined capable of absorbing or rejecting an infinite quantity of heat without temperature change.

In operation, the working fluid of a heat engine absorbs heat $|Q_H|$ from a hot reservoir, produces a net amount of work $|W|$, discards heat $|Q_C|$ to a cold reservoir, and returns to its initial state. The first law therefore reduces to:

$$|W| = |Q_H| - |Q_C|$$

The thermal efficiency of the engine is defined as: **η= net work output/heat absorbed**
With Eq. (1) this becomes:

$$\eta \equiv \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|}$$

Absolute-value signs are used to make the equations independent of the sign conventions for Q and W. For q to be unity (100% thermal efficiency), $|Q_C|$ must be zero. No engine has ever been built for which this is true; some heat is always rejected to the cold reservoir

Diagrammatically the principle of heat engines is shown in figure:

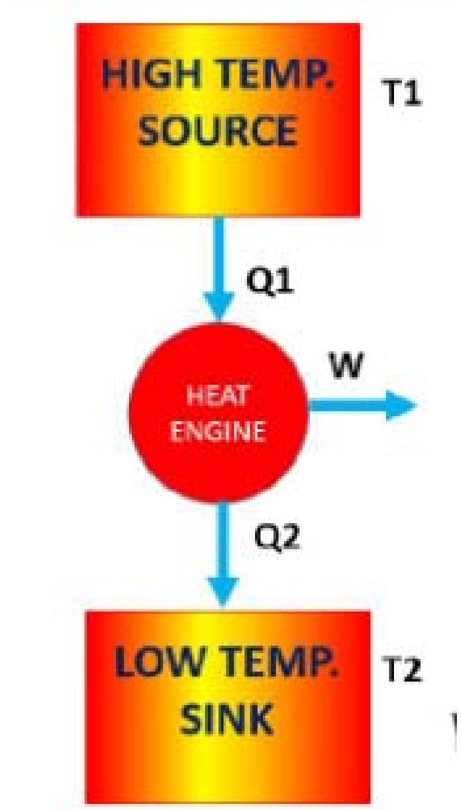

Figure (2): Principle of heat engine

Where : $\mathbf{Q_1 = Q_H}$ $\mathbf{Q_2 = Q_C}$ $\mathbf{W = W_{NET}}$

Heat pump: The actual meaning of heat pump is also thermodynamic system which operating in a cycle removes heat from the low temperature body to high temperature body by the application of external energy in the form of work on the pump.

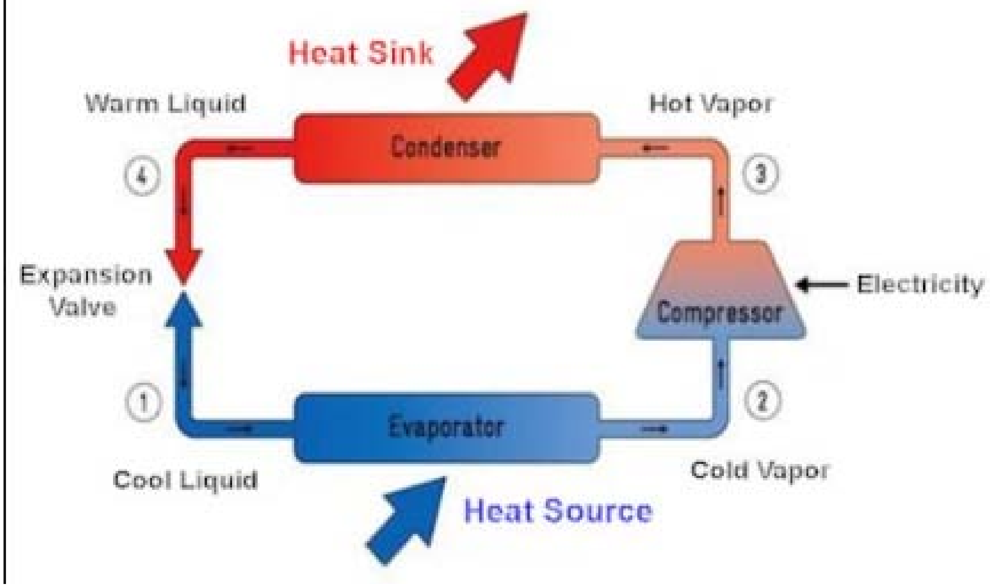

Figure (3) :Steps of heat pump

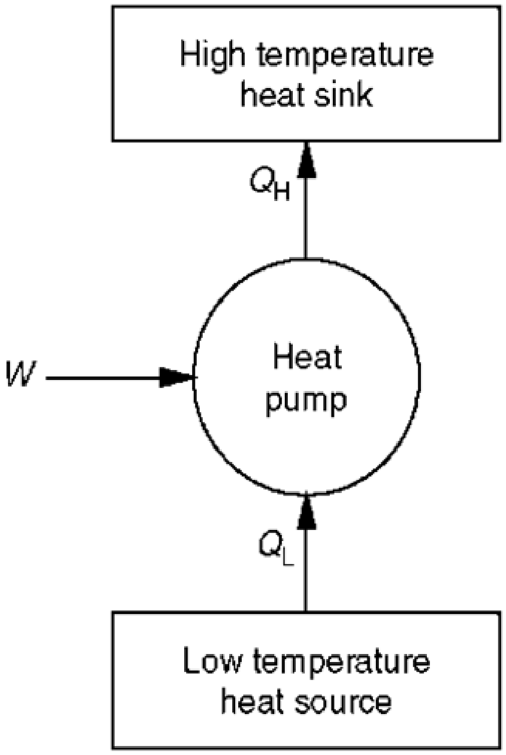

Figure (4): Energy flow of heat pump

The perfopmance of ***heat pump*** is indicated by C.O.P. defined as :

$$\boldsymbol{C.O.P.= \frac{energy\ out}{energy\ in}}$$

$$\boldsymbol{C.O.P.= \frac{QH}{Wnet.}}$$

$$\boldsymbol{C.O.P.= \frac{|Q_H|}{|Q_H| - |Q_C|}}$$

The Carnot Cycle (Carnot engine)

If a thermal efficiency of 100% is not possible for heat engines, what then determines the upper limit? One would certainly expect the thermal efficiency of a heat engine to depend on the degree of reversibility of its operation. Indeed, a heat engine operating in a completely reversible manner is very special, and is called a Carnot engine. The characteristics of such an ideal engine were first described by N. L. S. Carnot in 1824. The four steps that make up a Carnot cycle are performed in the following order:

Step 1: A system at the temperature of a cold reservoir Tc undergoes a reversible adiabatic process that causes its temperature to rise to that of a hot reservoir at T_H.

Step 2: The system maintains contact with the hot reservoir at T_H, and undergoes a reversible isothermal process during which heat $|Q_H|$ is absorbed from the hot reservoir.

Step 3: The system undergoes a reversible adiabatic process in the opposite direction of step 1 that brings its temperature back to that of the cold reservoir at Tc.

Step 4: The system maintains contact with the reservoir at Tc, and undergoes a reversible isothermal process in the opposite direction of step 2 that returns it to its initial state with rejection of heat $|Q_C|$ to the cold reservoir.

That means two adiabatic reversible processes and two isothermal processes

Since a Carnot engine is reversible, it may be operated in reverse; the Carnot cycle is then transverse in the opposite direction, and it becomes a reversible refrigeration cycle for which the quantities | Q_H |, | Q_C | and | W | are the same as for the engine cycle but are reversed in direction.

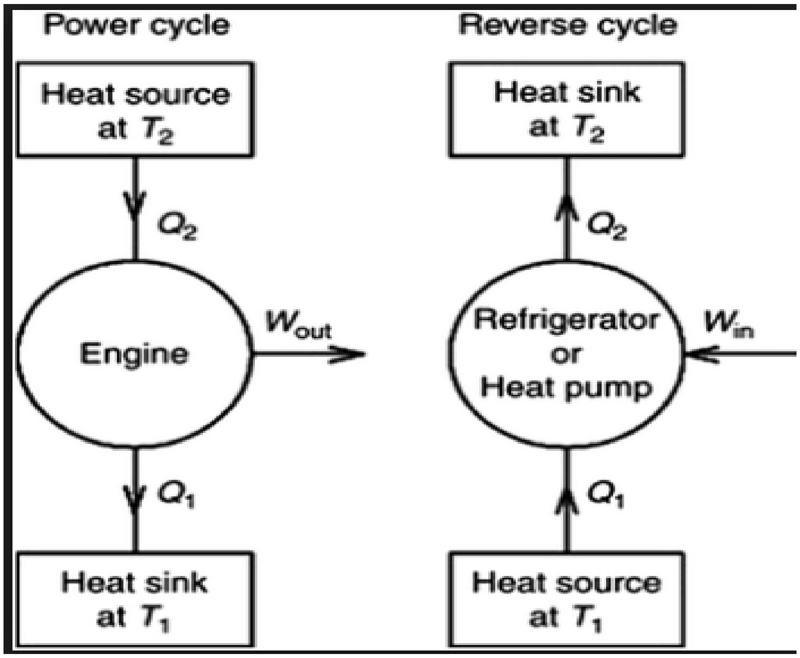

Figure (5): Operation of a Carnot cycle

For two given reserviors no engine can have a higher thermal efficiency than a Carnot engine.

Carnot cycle for ideal gas:

Ideal-Gas Temperature Scale; Carnot's Equations

The cycle traversed by an ideal gas serving as the working fluid in a Carnot engine is shown by a PV diagram in Fig. (6). It consists of four reversible steps:

a $\longrightarrow$ b Adiabatic compression until the temperature rises from Tc to TH.
b $\longrightarrow$ c Isothermal expansion to arbitrary point c with absorption of heat $|QH|$.
c $\longrightarrow$ d Adiabatic expansion until the temperature decreases to Tc .
d $\longrightarrow$ a Isothermal compression to the initial state with rejection of heat $|Qc|$.

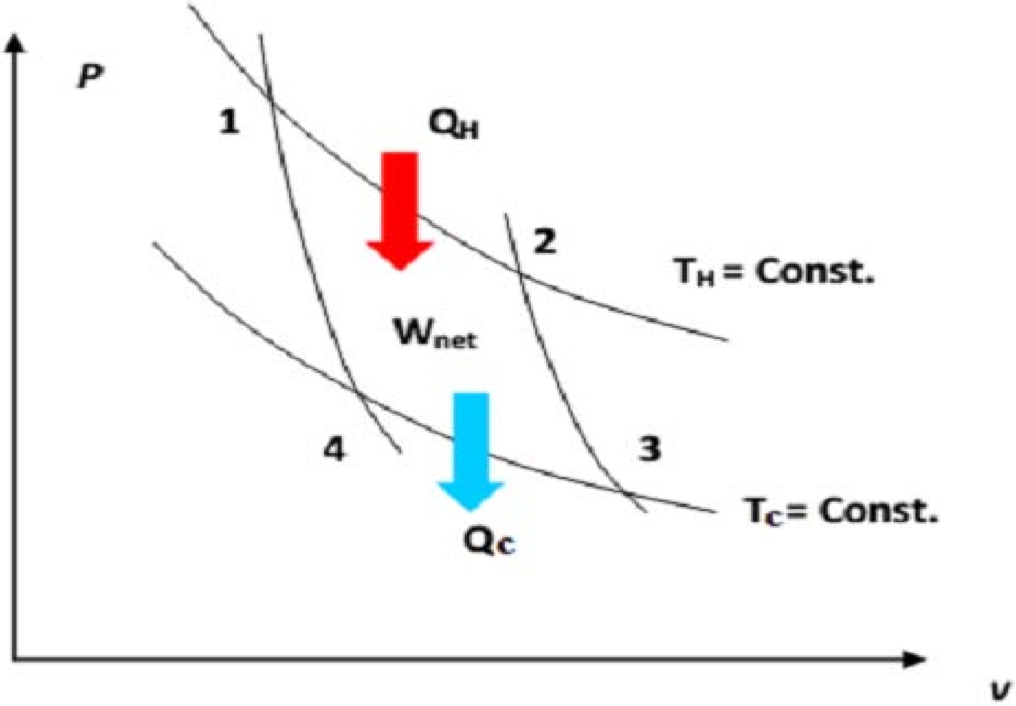

Figure (7): PV diagram showing Carnot cycle for an ideal gas

For any reversible process with an ideal gas the system, the first law is given by:

$$\Delta U = Q - W$$

$$d\,Q = cv\,.\,dT + P.\,dV$$

For the isothermal steps b ⟶ c

With $P = \frac{R\,.T_H}{V}$, after integrated eq. above:

$$|Q_H| = RT_H \ln \frac{V_c}{V_b}$$

Similarly, for the isothermal step d ⟶ a with $P = \frac{R\,.T_C}{V}$

$$|Q_C| = RT_C \ln \frac{V_d}{V_a}$$

Therefore,

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}\,\frac{\ln(V_c/V_b)}{\ln(V_d/V_a)}$$

For an adiabatic process Eq.1, with dQ=0 becomes, P=RT/v

$$-\frac{C_V}{R}\frac{dT}{T} = \frac{dV}{V}$$

For step $a \rightarrow$ b and c $\rightarrow$ d, integration gives:

$$\int_{T_C}^{T_H} \frac{C_V}{R}\frac{dT}{T} = \ln\frac{V_a}{V_b} \qquad \text{and} \qquad \int_{T_C}^{T_H} \frac{C_V}{R}\frac{dT}{T} = \ln\frac{V_d}{V_c}$$

Because of the left sides of these two equations are the same,

$$\ln\frac{V_a}{V_b} = \ln\frac{V_d}{V_c} \qquad \text{or} \qquad \ln\frac{V_c}{V_b} = \ln\frac{V_d}{V_a}$$

Equation becomes now:

$$\boxed{\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}}$$

Substitution of Eq. (for Carnot cycle ;ideal gas) into Eq. (for efficiency) gives:

$$\boxed{\eta \equiv \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}}$$

There are some terms when you see or hear it directly remember the Carnot engine like:

1. **Ideal**
2. **Theoretical**
3. **Reversible**
4. **Maximum work**

5. Maximum temperature.

Examples:

Entropy:

It is the most important thermodynamic property, which serves as measure of the unavailability or degradation of energy. A thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system.

The entropy of a system is affected only by the nature of the matter under consideration and the state in which it exists. And it is not affect by the external position of the body or its motion relative to other bodies.

- The entropy of the system is increased by the addition of heat through any mechanism or from source.
- The increase in entropy accompanying the addition of a given amount of heat to a system with lowering the temperature at which the heat is added. And its lead to a great degradation of energy than at a higher temperature.
- In addition , in order to complete the definition of entropy, the nature of the process should also be specified. The change in entropy ***(a state function)*** is dependent only on the initial and final states and **not on the path**.
- The amount of heat transferred to measure the increase in entropy through the term **(Q / T)** is the degradation of higher forms of energy into heat, which is possible only in a reversible process. Therefore be measured as **(Q_R / T) ,** where **Q_R** is the heat transferred when the process is occurring reversible.

Equation for a Carnot engine may be written:

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}$$

If the heat quantities refer to working fluid in the engine (rather than to the heat reservoirs), the numerical value of QH is positive and that of Qc is negative. The equivalent equation written without absolute-value signs is therefore

$$\frac{Q_H}{T_H} = \frac{-Q_C}{T_C}$$

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

Each Carnot cycle has its own pair of isotherms T_H and T_c and associated heat quantities Q_H and Q_C. When the adiabatic curves are so closely spaced that the isothermal steps are infinitesimal, the heat quantities become dQ_H and dQ_c, and Eq. for each Carnot cycle is written:

$$\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0$$

In this equation T_H and Tc, absolute temperatures of the working fluid of the Carnot engines, are also the temperatures traversed by the working fluid of the arbitrary cycle. Summation of all quantities dQ/ T for the Carnot engines leads to the integral:

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

where the circle in the integral sign signifies integration over the arbitrary cycle, and the subscript "rev" indicates that the cycle is reversible. Thus the quantities Q_{rev}/T sum to zero for the arbitrary cycle, exhibiting the characteristic of a property. The property is called entropy, and its differential changes are:

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

Where : $\mathbf{S^t}$ is the total (rather than molar) entropy of the system. Alternatively,

$$\boxed{dQ_{\text{rev}} = T\,dS^t}$$

If a process is **reversible** and **adiabatic**, $\mathbf{dQ_{rev} = 0}$; $\mathbf{dS^t = 0}$. Thus the entropy of a system is constant during a reversible adiabatic process, and the process is said to be isentropic.

The change in entropy of any system undergoing a finite reversible process is:

$$\Delta S^t = \int \frac{dQ_{rev}}{T}$$

Integration is not carried out for the irreversible path. Since entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.

- **The mathematical statement of the second law is that every process proceeds in such a direction the total entropy changes ΔS^t associated with it is always positive, the process is possible.**

$$\boxed{\Delta S_{total} \geq 0}$$

This mathematical statement of the second law affirms that every process proceeds in such a direction that the total entropy change associated with it is positive, the limiting value of zero being attained only by a reversible process. No process is possible for which the total entropy decreases.

Entropy Changes of an Ideal Gas:

For one mole or a unit mass of fluid undergoing a mechanically reversible process in a closed system, the first law, becomes:

$$dU = dQ_{rev} - P\,dV$$

Differentiation of the defining equation for enthalpy**, H = U + P V**, yields:

$$dH = dU + P\,dV + V\,dP$$

Eliminating **dU** gives:

$$dH = dQ_{rev} - P\,dV + P\,dV + V\,dP$$

or

$$dQ_{rev} = dH - V\,dP$$

For an ideal gas, **dH = Cp^{ig} .dT** and **V = RT/ P**. With these substitutions and then division by T,

$$\frac{dQ_{rev}}{T} = C_P^{ig}\frac{dT}{T} - R\frac{dP}{P}$$

this becomes:

$$dS = C_P^{ig}\frac{dT}{T} - R\frac{dP}{P}$$

$$\frac{dS}{R} = \frac{C_P^{ig}}{R}\frac{dT}{T} - d\ln P$$

Where : **S** is the molar entropy of an ideal gas. Integration from an initial state at conditions T_o and P_o to a final state at conditions T and P gives:

$$\boxed{\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R}\frac{dT}{T} - \ln\frac{P}{P_0}}$$

$$\langle C_P^{ig}\rangle_S = \frac{\int_{T_0}^{T} C_P^{ig}\,dT/T}{\ln(T/T_0)}$$

$$\int_{T_0}^{T} C_P^{ig}\frac{dT}{T} = \langle C_P^{ig}\rangle_S \ln\frac{T}{T_0}$$

$$\boxed{\frac{\Delta S}{R} = \frac{\langle C_P^{ig}\rangle_S}{R}\ln\frac{T}{T_0} - \ln\frac{P}{P_0}}$$

Although derived for a mechanically reversible process, this equation relates properties only, and is independent of the process causing the change of state. It is therefore a general equation for the calculation of entropy changes of an ideal gas.

$$\boldsymbol{Cp_{ms}^{ig} = A + B.T_{lm} + T_{am}.T_{lm}.[C + \frac{D}{(T_1 . T_2)^2}]}$$

$$\boldsymbol{T_{am} = \frac{T_1 + T_2}{2}}$$

$$\boldsymbol{T_{lm} = \frac{T_{2-}\ T_1}{ln\,(T_2 - T_1)}}$$

Liquid Entropy:

Consider unit mass of a liquid which will ultimately be raised to unit mass of vapor at constant pressure. For the unit mass of liquid,

$$\mathbf{dQ = cp_L\ .\ dT}$$

where: $\mathbf{cp_L}$ is specific heat capacity of the liquid at constant pressure.

Dividing eq. throughout by $\mathbf{T}$,then,

$$\mathbf{dQ/T = cp_L\ .\ dT/T}$$

Since $\mathbf{dS=dQ/T}$

$$\mathbf{dS= cp_L\ .\ dT/T}$$

Integrating this equation from initial state to final state:

$$[S_2 - S_1] = cp_L \, .\ln (T_2/T_1)$$

Example:

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