AVAILABILTY
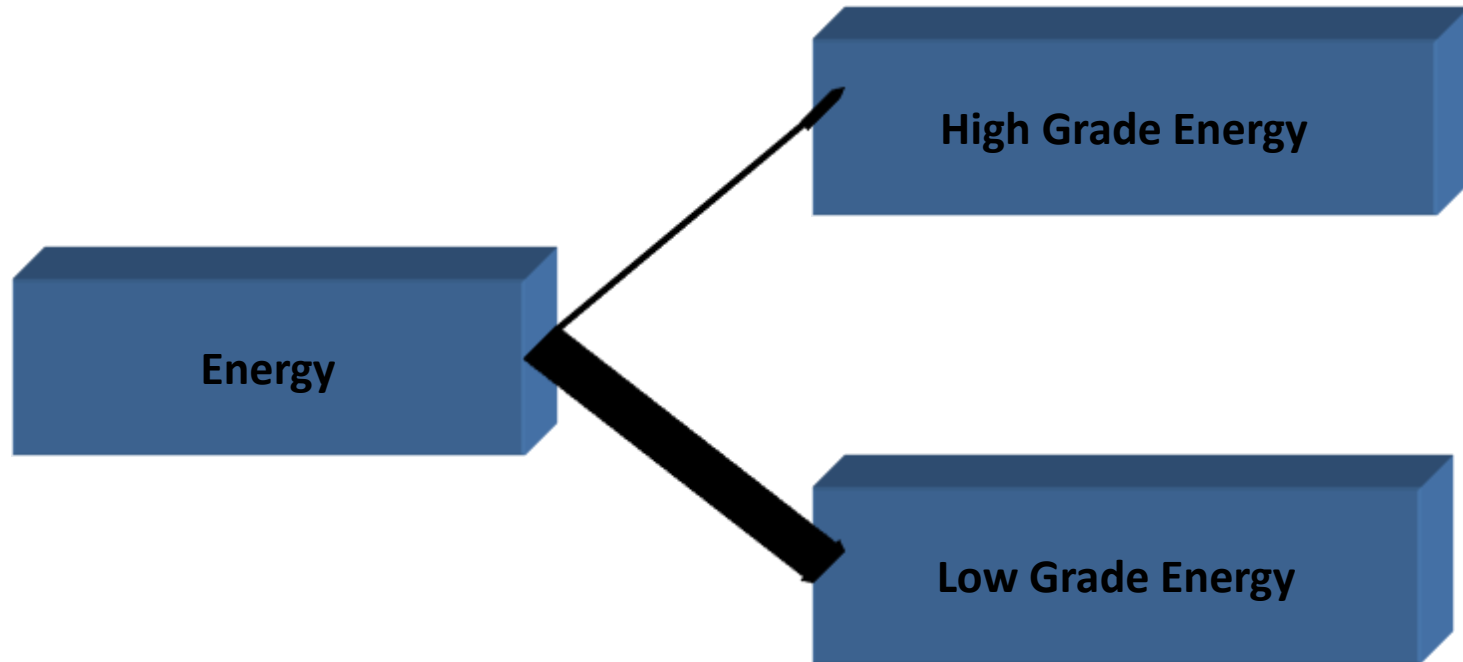
Sources of energy can be divided into two groups as shown below:

HIGH GRADE ENERGY

- Energy that can be completely transformed into work without any loss i.e. fully utilizable.
- Examples of high grade energy are:
1. Mechanical work
2. Electrical work
3. Water Power
4. Wind Power
5. Tidal Power

LOW GRADE ENERGY

• Energy of which only a certain portion can be converted into mechanical work is called low grade energy.

• Examples of Low grade energy are:

1. Heat or Thermal Energy
2. Heat derived from combustion of fossil fuels
3. Heat derived from nuclear fission or fusion.
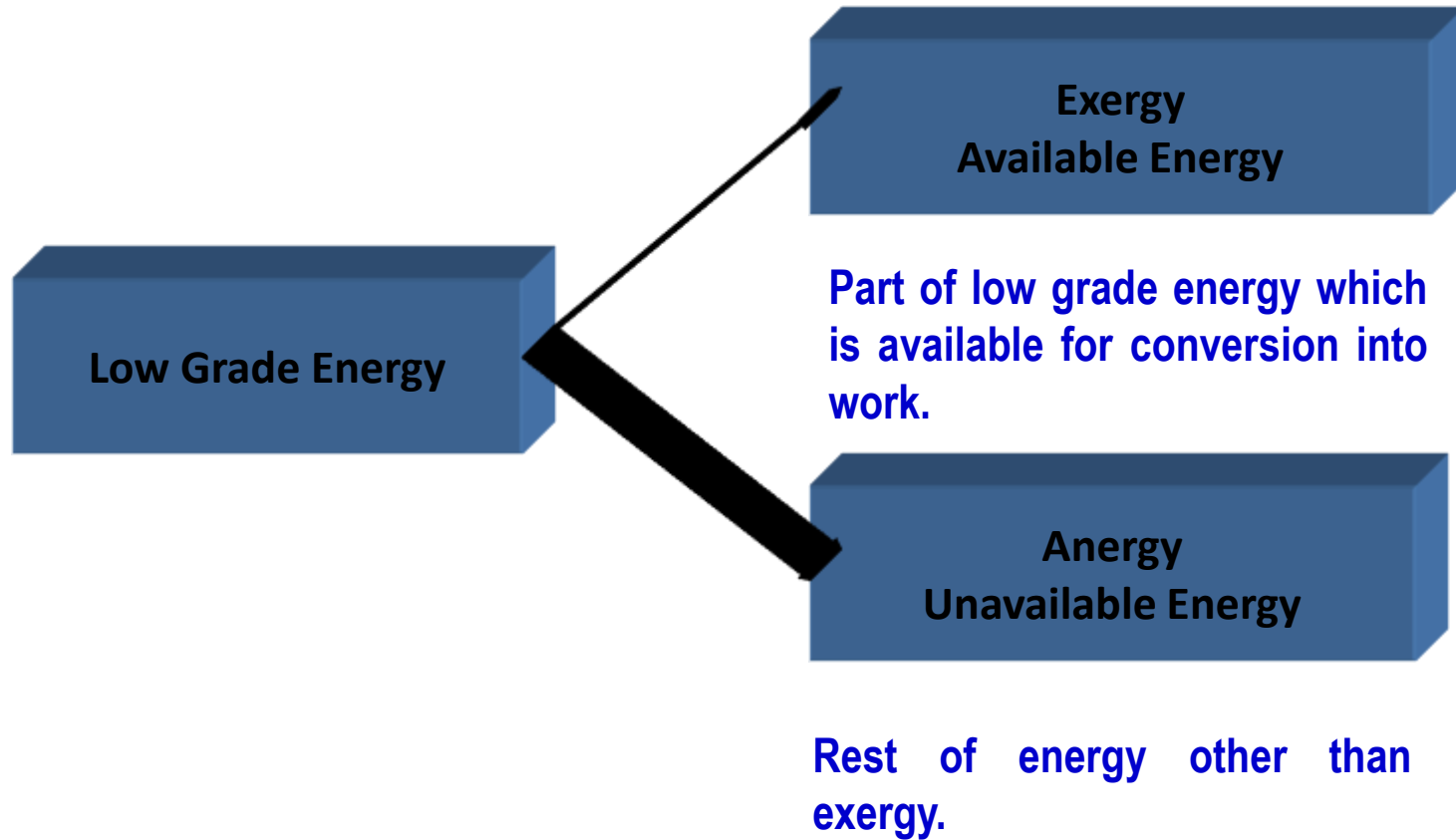
AVAILABLE ENERGY

•The maximum work output obtainable from a certain heat input in a cyclic heat engine is called available energy (A.E.).

•It is also called Exergy.

•In other words, Exergy can be quantified as the amount of work obtainable by bringing some matter to the state of thermodynamic equilibrium with common components of natural surroundings through reversible processes.

UNAVAILABLE ENERGY

•The minimum energy that has to be rejected to the sink as per Second law of Thermodynamics is called Unavailable Energy.

•It is also called Anergy.

•The portion of energy not available for conversion is called anergy.

•Mathematically;

Anergy = L.G.Energy – Exergy.

AVAILABILITY

- Useful work is available from a finite system as long as there exists positive pressure and temperature differential between system and surrounding.

- The process will terminate when the pressure and temperature of the system and surrounding are equal. This state is referred as dead state.

- Unless otherwise specified, the dead state temperature and pressure are considered as 298K and 1.01325 bar.

- Greater the deviation of the system from the dead state indicates greater availability.

AVAILABLITY
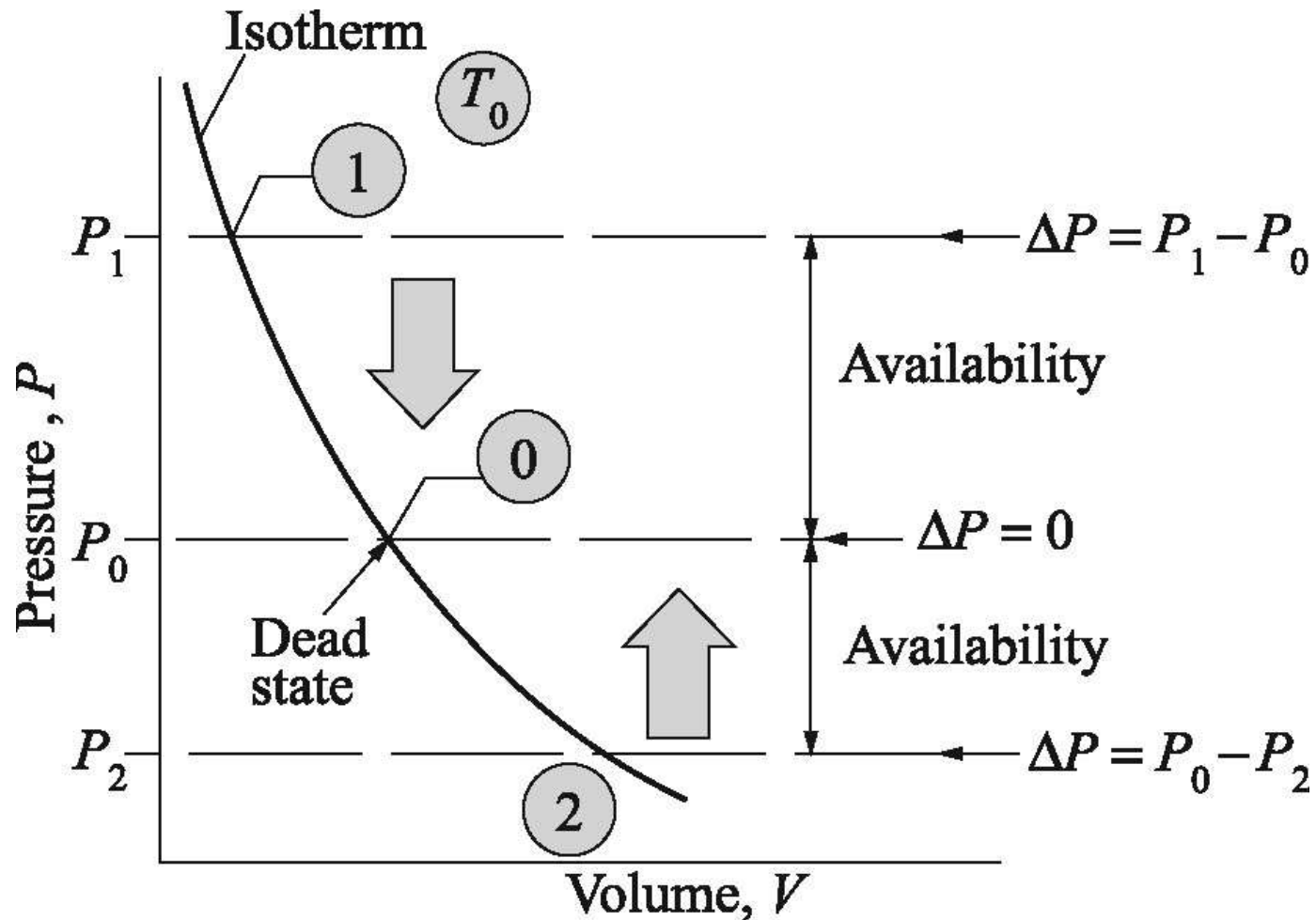
DEAD STATE

Dead state' refers to the state at which system and the environment are at mechanical, thermal and chemical equilibrium. Thus neither there can be any spontaneous change within the system or within the environment, nor any spontaneous interaction between the two. Dead state being a limiting state is also called 'restricted dead state'. At dead state the system is at same temperature and pressure as that of its' surroundings and shall have no kinetic energy or potential energy relative to surroundings. A system shall thus have zero exergy (availability) at dead state and yield maximum possible work only when it follows a reversible process from its' state to the state of its' surroundings (dead state).
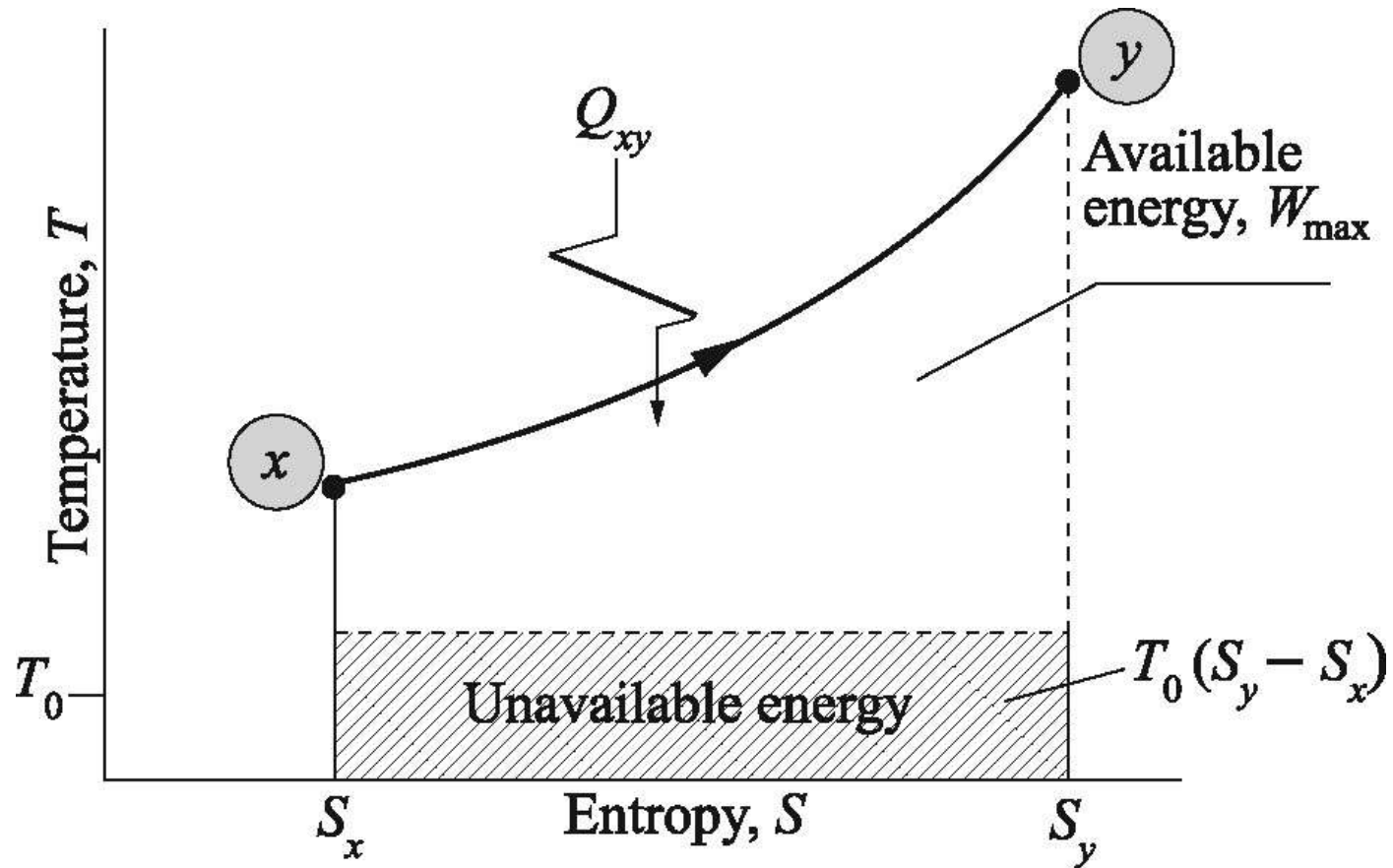
CLASSIFICATION OF EXERGY

Exergy as defined above is a measure of departure of the state of a system from that of environment.

For state at Temperature T and environment at temperature T0 the difference (T ~ T0) shall decide the value of exergy i.e. greater the difference, the greater shall be exergy value. This exergy can be of basically two types i.e. chemical exergy and thermomechanical exergy. Thermomechanical exergy can be further classified as physical, kinetic and potential exergy. Physical exergy is the work obtainable by taking the substance by reversible physical processes from its initial states pressure 'p' and temperature 'T ' to the state determined by the temperature and pressure of environment. Kinetic exergy is equal to the kinetic energy, when the velocity is considered relative to the surface of the earth. Potential exergy is equal to the potential energy when it is evaluated with respect to the average level of the surface of the earth in the locality of the process under consideration.

Chemical exergy refers to the work that can be obtained by taking a substance state at environmental pressure and temperature to the state of thermodynamic equilibrium with environment and bring system to restricted dead state.

AVAILABLE ENRGY OF HEAT SOURCE

AVAILABLE ENERGY OF HEAT SOURCE

- Available energy = Maximum work output = W_{max}

- Unavailable energy = $Q_{xy} - W_{max}$

    Where Q_{xy} is the heat received by the heat engine to execute x-y.

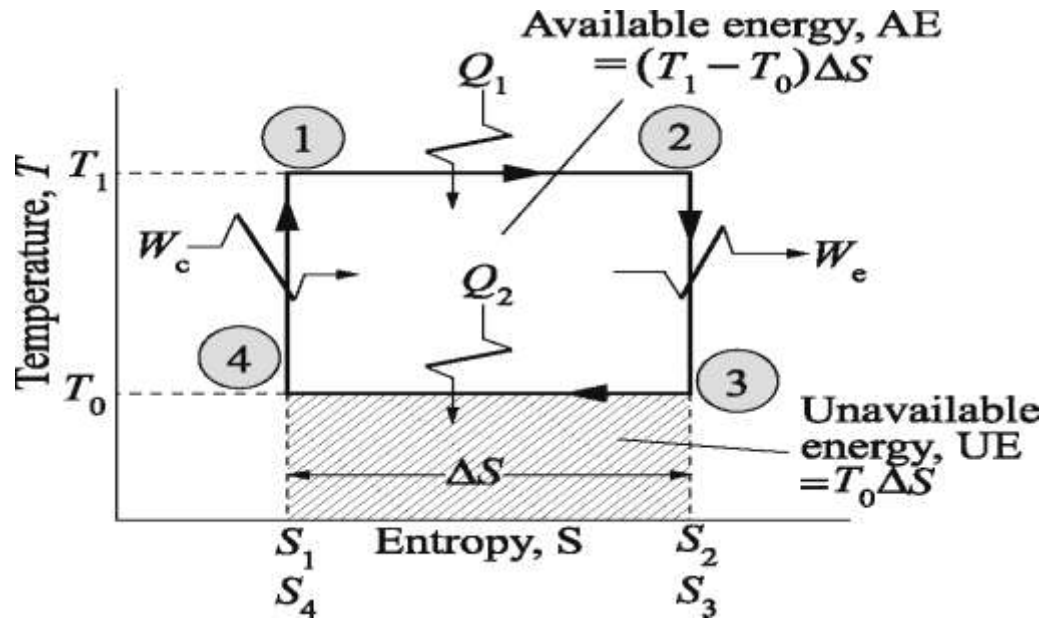$$\int_x^y \delta W_{max} = \int_x^y \delta Q_{xy} - \int_x^y \frac{T_0}{T_1} \delta Q_{xy}$$

or

$$W_{max} = Q_{xy} - T_0(S_y - S_x)$$

$$= Q_{xy} - T_0 \Delta S$$

$$UE = Q_{xy} - W_{max} = T_0 \Delta S$$

where $(S_y - S_x)$ is the change in entropy of the system.

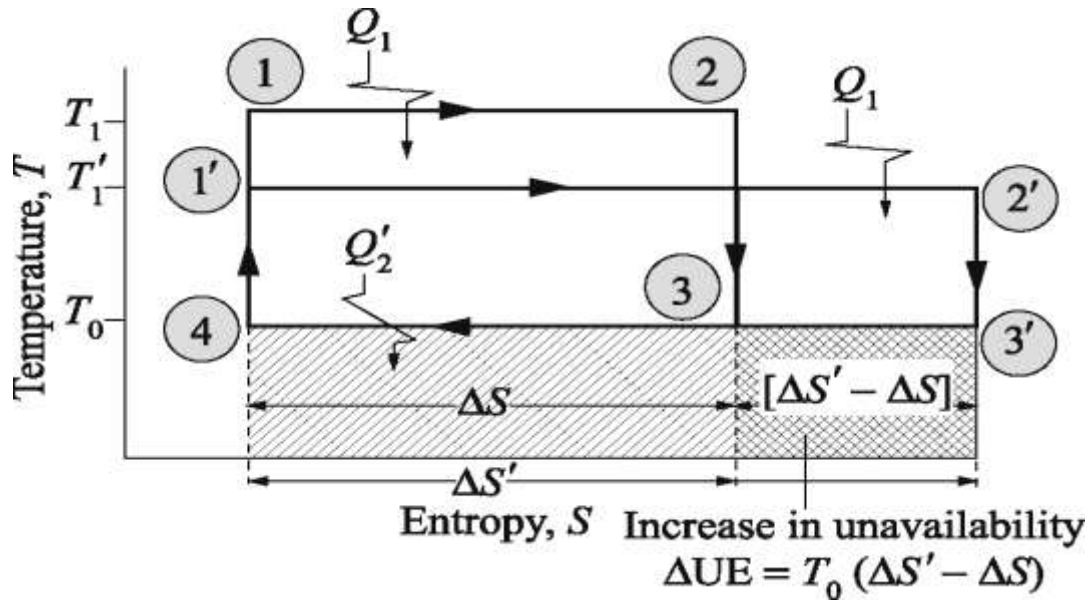# Decrease in Available Energy due to Finite Temperature Difference

$$AE = W_{max} = (T_1 - T_0)\Delta S$$

$$= \text{Area } 1\text{-}2\text{-}3\text{-}4\text{-}1$$

$$UE = \text{Area below } 3\text{-}4$$

$$= T_0 \Delta S$$

Increase in unavailability
$$\Delta UE = T_0(\Delta S' - \Delta S)$$

$$AE' = W'_{max} = Q_1 - Q_2' = (T_1' - T_0)\Delta S$$

$$\Delta S' > \Delta S$$

$$\therefore Q_2' > Q_2 \quad \Rightarrow W_{max}' > W_{max}$$

$$W_{max} - W_{max}' = T_0(\Delta S' - \Delta S) = \text{Decrease in availability}$$

CONCLUSIONS:

• Whenever a heat is transferred through a finite temperature difference , there is always a loss of available energy.

• Greater the temp. difference, the more is the net increase in entropy and therefore, loss of available energy.

• The available energy of a system at higher temperature is more than at lower temperature and decreases progressively as temp. falls.

• Quality of energy of a fluid at higher temp. is superior to that at lower temperature.

QUALITY OF ENERGY
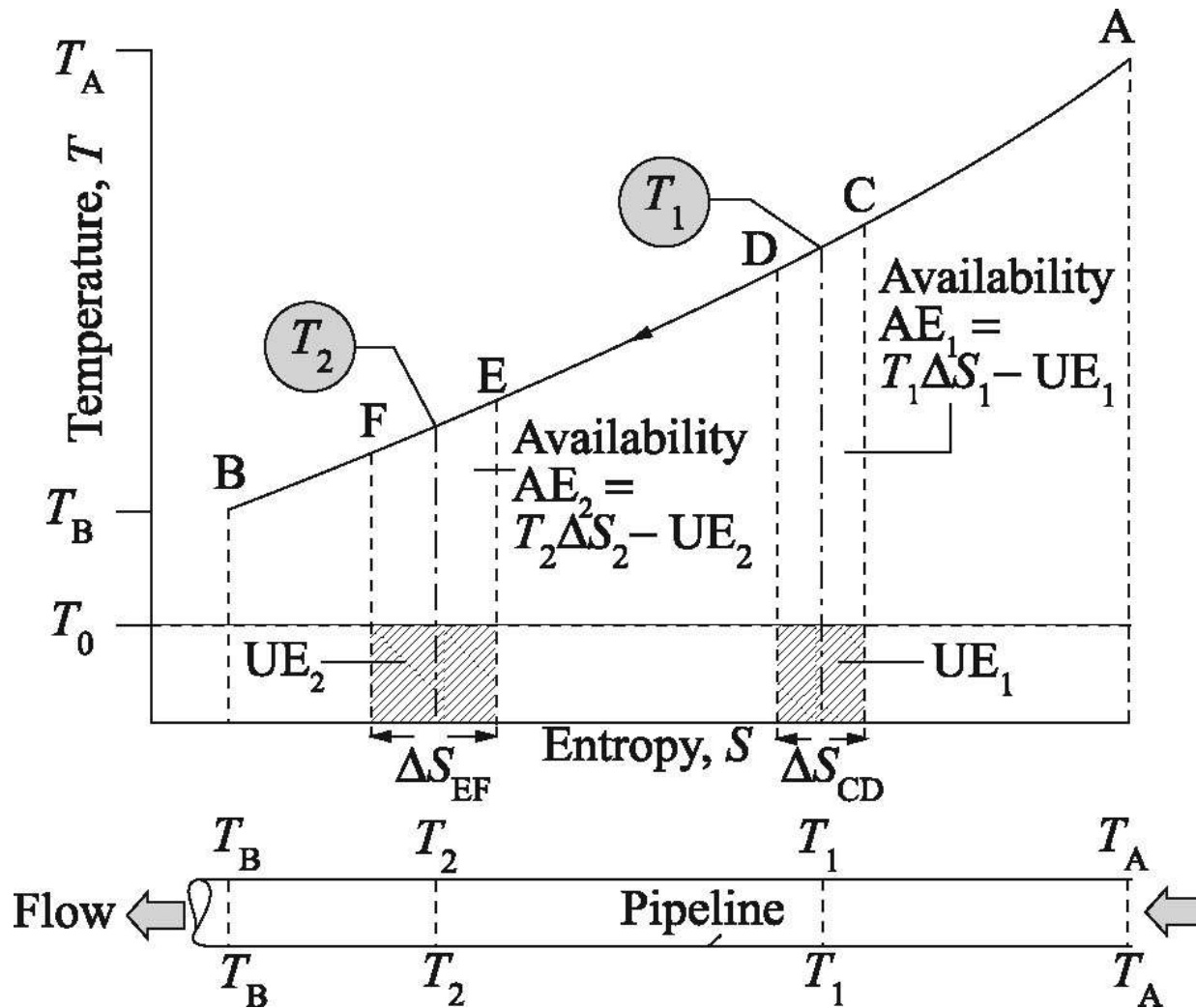
- **During cooling from C to D, the heat lost,**

$$Q = T_1 \Delta S_{CD}$$

- **Loss of availability of Q at T1 is,**

$$W_{CD,irr} = Q - T_0 \Delta S_{CD}$$
$$= (T_1 - T_0)\Delta S_{CD}$$

- **If same heat is lost during cooling from E to F, then,**

$$Q = T_2 \Delta S_{EF}$$

- **Loss of availability of Q at T2,**

$$W_{EF,irr} = Q - T_0 \Delta S_{EF} = (T_2 - T_0)\Delta S_{EF}$$
$$\text{Since, } T_1 > T_2, \quad \Delta S_{CD} < \Delta S_{EF}$$
$$\therefore \ W_{CD,irr} > W_{EF,irr}$$

- **Quality of energy at a high temperature is more than that if the heat source were at a low temperature** .

LAW OF DEGRADATION OF ENERGY

- When heat is transferred from system to surroundings, its temperature decreases and hence quality of energy deteriorates.

- This degradation is more when heat is transferred at a higher temperature than at a lower temperature.

- Quantum of energy loss may be same, but quality – wise the loss of available energy is different.

- Energy is always conserved quantity – wise (Inferred from first law)

- Energy always degrades quality – wise (affixed by second law)

AVAILABILITY OF A NON FLOW / CLOSED SYSTEM

Consider a piston cylinder arrangement in which the fluid at P_1 V_1 T_1 expands reversibly to the environmental state with parameter p_o V_o T_o. The following energy interaction take place:

• The fluid expands and expansion work W_{exp} is obtained. From the principle of energy conservation

• $\delta Q = \delta W + dU$ we get,

$$-Q = W_{exp} + U_o - U_1$$

The heat interaction is negative as it leaves the system

$$W_{exp} = U_1 - U_o - Q$$

• $_v$ The heat Q rejected by the piston cylinder assembly may be made to run reversible heat engine . The output from the reversible engine equals

• $\qquad W_{eng} = Q[1-T_o/T_1] = Q - To(S_1-S_o)$

• The sum of total W_{exp} and W_{eng} gives maximum work obtainable from the arrangement

$$W_{max} = U_1 - U_o - To(S_1 - S_o)$$

As we know the piston expands hence doing positive amount of work on surroundings which is equal to

$$W_{surr} = p_o(V_o - V_1)$$

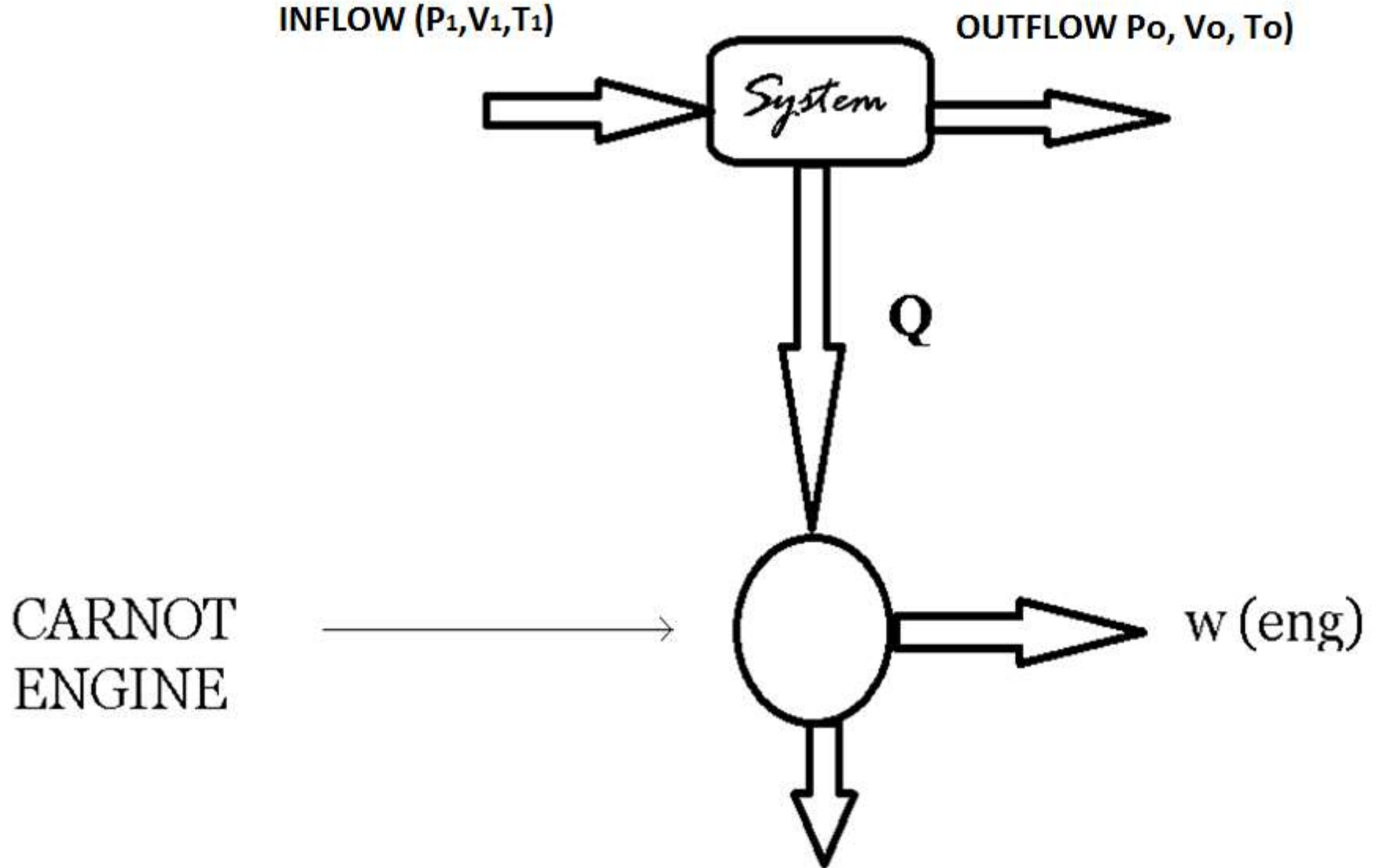Maximum work available or useful work

$$W_{net} = W_{max} - W_{surr}$$
$$= (U_1 + P_oV_1 - T_oS_1) - (U_o + P_oV_o - T_oS_o)$$
$$= A_1 - A_o$$

Where $A = (U + P_oV - T_oS)$ is known as non flow availability function. It is composite property of system and surroundings.

Availability of a Steady Flow Equation

The properties of fluid changes when flowing through the system.

INFLOW (P_1, V_1, T_1)

OUTFLOW Po, Vo, To)

System

Q

CARNOT
ENGINE

w (eng)

AVAILABILITY OF A STEADY FLOW EQUATION

For previous system, Steady Flow Equation may be written as:

$$U_1 + p_1 V_1 + (c_1^2)/2 + gz_1 - Q = U_o + p_o V_o + (c_o^2)/2 + gz_o + W_s$$

Where, U = internal energy,

v = specific volume,

h = specific enthalpy,

p = pressure,

c = velocity,

z = location.

Neglecting potential and kinetic energy changes,

$$U_1 + p_1 V_1 - Q = U_o + p_o V_o + W_s$$
$$H_1 - Q = H_o + W_s$$

shaft work, $W_s = (H_1 - H_o) - Q$

The heat rejected by the system may be made to run this reversible heat engine. The output from this engine equals:

$$W_{eng} = Q[1 - T_o/T_1] = Q - T_o(S_1 - S_o)$$

$$W_{net} = W_s + W_{eng} = (H_1 - T_o S_1) - (H_o - T_o S_o)$$
$$= B_1 - B_o$$

Where, $B = (H - T_o S)$ is known as **Steady flow availability function.** It is a composite property of a system and surroundings too . It is also known as, **Darrieus function and the Keenam function.**

HELMHOLTZ AND GIBBS FUNCTION

Consider a closed system which is initially and finally at the temperature of environment around it and exchanges heat only with atmosphere. Then

$$\delta Q = \delta W + dU$$
$$\delta Q = TdS$$

Hence for a non- flow reversible process;
$$W_{max} = (U_1 - T_o S_1) - (U_o - T_o S_o)$$
Replacing To by T_1 or T_2

$$W_{max} = (U_1 - T_1 S_1) - (U_2 - T_2 S_2)$$
$$= A_1 - A_2$$

The term U- TS is called **Helmholtz Function.**

CONCLUSIONS

•Helmholtz function is defined as the difference between the internal energy and the product of temperature and entropy .

•Thus if a closed system is taken from one state to another state at same temperature while exchanging heat only with the surrounding atmosphere at that temperature ($T_1=T_2=T_0$), the maximum work of the process is equal to the *decrease in Helmholtz function of the system.*

•Its useful is only restricted to non flow processes only.

GIBB'S FUNCTION

In case of flow processes, flow work at entry P1V1 is supplies from the surroundings to the system while at exit point flow work P_2V_2 is supplies by the system to the surroundings.

$$W_{max} = U_1 - U_2 + T_o(S_2 - S_1) - (P_2V_2 - P_1V_1)$$

Where To can be replaced by T1 or T2 as the processes at constant temp. of surroundings

$$W_{max} = (U_1 + P_1V_1 - T_1S_1) - (U_2 + P_2V_2 - T_2S_2)$$

$$W_{max} = (H_1 - T_1S_1) - (H_2 - T_2S_2)$$

$$= G_1 - G_2$$

The term H −TS is called Gibb's function.

CONCLUSIONS

•Gibb's function is defined as the difference between enthalpy and product of entropy and temperature.

•Thus if a substance enters and leaves a steady flow system at the temp. of surrounding atmosphere and exchanges heat only with the atmosphere, the maximum work that can be produced is equal to decrease in Gibb's function.

•The changes of both Helmholtz and Gibb's function are called free energy i.e. energy that is free to be converted to work.

EFFECTIVENESS

Effectiveness represents the fraction of maximum useful work $(w)_{max}$ actually utilized and is expressed as the ratio of useful work W_u to the maximum useful work $(W_u)_{max}$. During cooling or expansion process , the work produced is at the expense of loss of availability of the system , the work produced increases the availability of the environment which is objective

$\varepsilon = W_u /(W_u)_{max}$
 =gain of availability of environment/ loss of availability of system

All of the work performed by a system W_{exp} is not available for delivery , a certain portion of it has to be spent in pushing out the atmosphere . The work done on the atmosphere equals $p_o dv$ where p_o is the atmospheric pressure and dv is the change in volume

$$W_u = W_{exp} - W_{surr}$$
$$= W_{exp} - P_o dV$$

Likewise , maximum useful work

$$(W_u)_{max} = W_{max} - P_o dV$$

In steady flow system, there is no change in the volume of system i.e. no work is done on the atmosphere.

$$(W_u)_{max} = W_{max} \text{ in steady flow }.$$

CONCLUSION

- For a reversible process, $(W_u)_{max} = W_{u\,m}$ and thus effectiveness is **unity.**

- for a heating or compression process
$$= \text{loss of availability of system/gain of availability of environment.}$$

IRREVERSIBILITY

•It is amount of increase in anergy.
•Irreversibility denotes the loss of work due to the fact that all real processes are irreversible and is defined as difference between the maximum work output from the system and the expansion work.

$$I = [(U_1 - T_oS_1) - (U_2 - T_oS_2)] - [-Q - (U_2 - U_1)]$$
$$= T_o(S_2 - S_1) + Q$$

Change in entropy of environment due to addition of heat Q at constant atmospheric temp. T_o .
$$dS_{surr} = Q/ T_o$$
$$Q = T_o \, dS_{surr}$$
Q is negative for the system and positive for the surroundings.

Similarly for steady flow processes,

$$I = [(h_1 - T_o S_1) - (h_2 - T_o S_2)] - [(h_1 - h_2) - Q]$$
$$= T_o(S_2 - S_1) + Q$$
$$= T_o \, dS_{sys} + T_o \, dS_{surr}$$
$$= T_o \, dS_{net}$$
$$= T_o \, dS_{univ}$$

the same expressions for irreversibility applies to both flow and non flow processes and it prescribes that irreversibility equlas the product of temp. of surroundings and the entropy production. The quantity $T_o \, dS_{univ}$ also represents an increase in anergy.

Third law of **Thermodynamics /NERNST LAW**
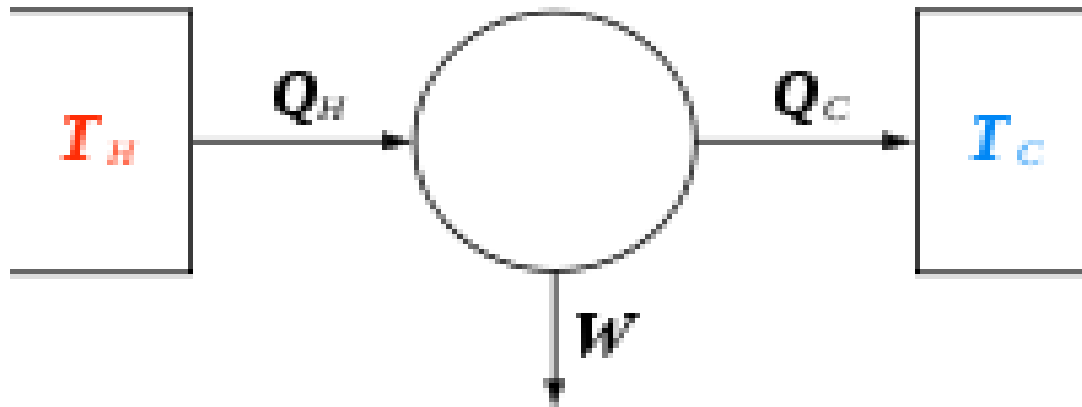
The classical Carnot heat engine

The **third law of thermodynamics** is sometimes stated as follows:

- The entropy of a perfect crystal at <u>absolute zero</u> is exactly equal to zero.

- At zero <u>kelvin</u> the system must be in a state with the minimum possible <u>energy</u>, and this statement of the third law holds true if the perfect crystal has only one minimum energy state. Entropy is related to the number of possible microstates, and with only one microstate available at zero kelvin, the entropy is exactly zero.

- A more general form of the third law applies to systems such as <u>glasses</u> that may have more than one minimum energy state.

Mathematical formulation

Consider a closed system in internal equilibrium. As the system is in equilibrium there are no irreversible processes so the entropy production is zero.

$$\delta S = \frac{\delta Q}{T}.$$

The temperature rise δT due to the heat δQ is determined by the heat capacity $C(T,X)$ according to

$$\delta Q = C(T, X)\delta T.$$

The parameter X is a symbolic notation for all parameters (such as pressure, magnetic field, liquid/solid fraction, etc.) which are kept constant during the heat supply. Combining r

$$\delta S = \frac{C(T, X)\delta T}{T}. \qquad \text{(2)}$$

Integration of Eq.(3) from a reference temperature T_0 to an arbitrary temperature T gives the entropy at temperature T

$$S(T, X) = S(T_0, X) + \int_{T_0}^{T} \frac{C(T', X)}{T'} dT'.$$

in the limit $T_0 \to 0$ the integral in Eq.(4) is finite. So that we may take $T_0 = 0$ and write

$$S(0, X) = S(0).$$

2. the value of $S(0,X)$ is independent of X. In mathematical form

$$S(T, X) = S(0, X) + \int_{0}^{T} \frac{C(T', X)}{T'} dT'.$$

So Eq.(5) can be further simplified to

$$S(T, X) = S(0) + \int_0^T \frac{C(T', X)}{T'} dT'.$$

Equation (6) can also be formulated as

$$\lim_{T \to 0} \left(\frac{\partial S(T, X)}{\partial X} \right)_T = 0.$$

at absolute zero all isothermal processes are isentropic. Eq.(8) is the mathematical formulation of the third law.
as one is free to chose the zero of the entropy it is convenient to take

$$S(0) = 0$$

so that Eq.(7) reduces to the final form

$$S(T, X) = \int_0^T \frac{C(T', X)}{T'} dT'.$$

The physical meaning of Eq.(9) is deeper than just a convenient selection of the zero of the entropy. It is due to the perfect order at zero kelvin as explained before.
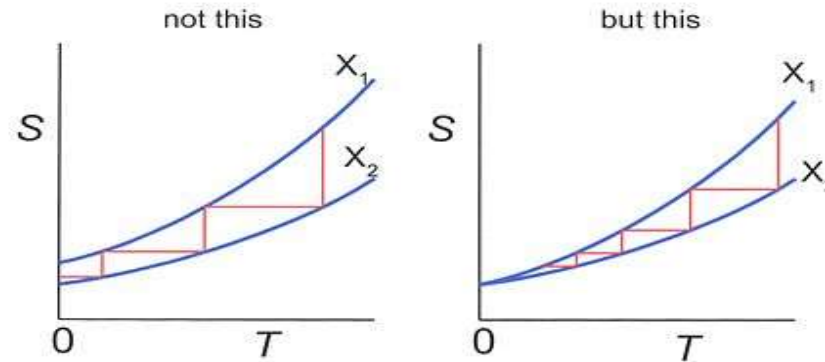
Consequences of the third law

Fig.1 Left side: Absolute zero can be reached in a finite number of steps if $S(0,X_1) \neq S(0, X_2)$. Right: An infinite number of steps is needed since $S(0,X_1) = S(0,X_2)$.

Can absolute zero be obtained?

- The third law is equivalent to the statement that
- "It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to zero temperature in a finite number of finite operations". The reason that T=0 cannot be reached according to the third law is explained as follows: Suppose that the temperature of a substance can be reduced in an isentropic process by changing the parameter X from X_2 to X_1. One can think of a multistage nuclear demagnetization setup where a magnetic field is switched on and off in a controlled way. [If there would be an entropy difference at absolute zero T=0 could be reached in a finite number of steps. However, at T=0 there is no entropy difference so an infinite number of steps would be needed. The process is illustrated in Fig