Entropy change in a reversible process:-

Let us consider a reservior is in contact with a system and that heat Q is absorbed irreversibly by the reservior at temperature T. The reservior undergoes nondissipative changes determined entirely by the quantity of heat absorbed. Exactly the same changes in the reservior would occur if the same amount of heat Q were transferred reversibly. Hence, the entropy change of the reservior is Q/T. Therefore, whenever a reservior absorbs heat Q at the temperature T from any system during any kind of process, the entropy change of the reservior is Q/T.

Let us now consider a reversible process. The process will, in general, be accompanied by a flow of heat between a system and a set of reserviors ranging in temperature from T_i to T_f. During any infinitesimal portion of the process, an amount of heat dQ_R is transferred between the system and one of the reserviors at temperature T. If dQ_R is absorbed by the system, then

$$ds \text{ of the system} = + \frac{dQ_R}{T}$$

$$ds \text{ of the reservior} = - \frac{dQ_R}{T}$$

and the entropy change of the universe, which is the sum of these two changes, is zero. If dQ_R is rejected by the system, then

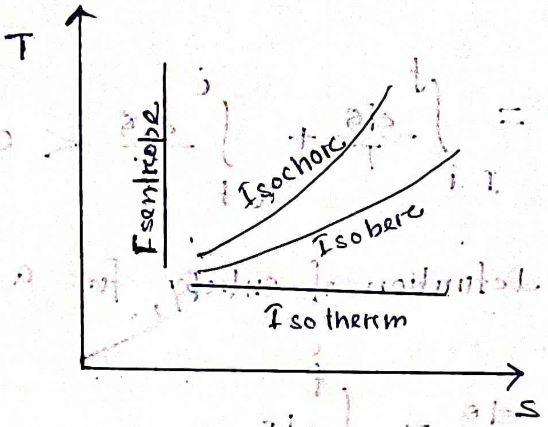
$$ds \text{ of the system} = - \frac{dQ_R}{T}$$

$$ds \text{ of the reservior} = + \frac{dQ_R}{T}$$

and the entropy change of the universe is again zero.

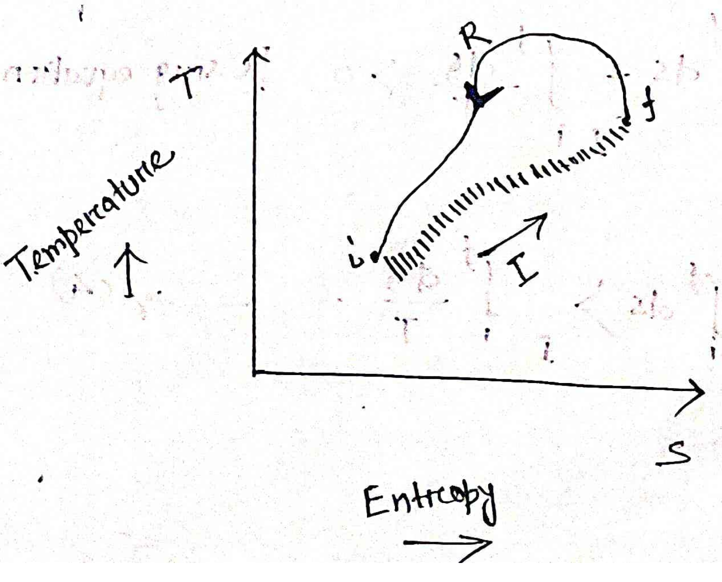
If no heat is transferred, then dQ_R is zero. Neither the system nor the reservoir will have an entropy change, and the entropy change of the universe is still zero. Since there is no infinitesimal entropy change of the universe for any infinitesimal portion of the reversible process, then there is no entropy change for all such portions. In general, the change of entropy of the universe is zero for a reversible process.

i.e; $\boxed{ds = 0}$ — for reversible process.



Entropy change in Irreversible process →

Let us consider a cycle in which a system begins in an initial equilibrium state i, passes during an irreversible process I to a final equilibrium state f, and then returns by a reversible process R to the initial state ~~I~~ i, as shown in figure.



Since entropy is a state function, its closed integral is always zero.

$$\oint ds = \int_{I\,i}^{f} ds + \int_{R\,f}^{i} ds = 0 \longrightarrow (1)$$

Since for a irreversible process,

$$\oint_{I} \frac{dq}{T} < 0$$

$$\therefore \oint_{I} \frac{dq}{T} = \int_{I\,i}^{f} \frac{dq}{T} + \int_{R\,f}^{i} \frac{dq}{T} < 0. \longrightarrow (2)$$

From the definition of entropy, for a reversible process we have,

$$\int_{R\,f}^{i} \frac{dq}{T} = \int_{R\,f}^{i} ds. \longrightarrow (3)$$

Now, substracting equation (2) from equation (1) we get,

$$\int_{I\,i}^{f} ds + \int_{R\,f}^{i} ds - \int_{I\,i}^{f} \frac{dq}{T} - \int_{R\,f}^{i} \frac{dq}{T} > 0.$$

or, $\int_{I\,i}^{f} ds - \int_{I\,i}^{f} \frac{dq}{T} > 0$ [Using equation (3)]

or, $\int_{I\,i}^{f} ds > \int_{I\,i}^{f} \frac{dq}{T}. \longrightarrow (4)$

which means that the change of entropy during an irreversible process is greater than the integral of the heat divided by the temperature of the auxiliary reserviors.

For small changes in state, equation (4) can be written as,

$$ds_I > \left(\frac{dQ}{T}\right)_I$$

In general we have,

$$\boxed{ds \geq \frac{dQ}{T}}$$

Where the equality applies to reversible processes and the inequality applies to irreversible processes.

Thermodynamic Potentials:→

As we know, the internal energy (U) of a system is a function of state, which means that a system undergoes the same change in U when we move it from one equilibrium state to anothere, irrespective of routes. This makes U a very useful quantity, though not a uniquely useful quantity. In fact we can make a number of othere functions of state, simply by adding to U various othere combinations of the function of state P, V, T and S in such a way as to give the resulting quantity the dimensions of energy. These new functions of state are called thermodynamic potentials and of which three of them are extremely useful namely, Enthalpy (H), Helmhotz function (F) and Gibbs function (G). Let us now review some properties concerning internal energy (U), first.

Internal Energy:→

Changes in internal energy of a system is given by the first law of thermodynamics as

$$du = Tds - PdV \longrightarrow (1)$$

The natural variables to describe U are S and V, since changes in U are due to changes in S and/or V. Hence we can write $U = U(S, V)$. Moreover if S and V are held constant for the system, then,

$$dU = 0. \longrightarrow (2)$$

ie, U is also constant under these conditions.

From equation (1) we can ~~write~~ calculate temp^r as,

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

and similarly pressure can be expressed as,

$$P = -\left(\frac{\partial U}{\partial V}\right)_S$$

For isochoric process i.e., where, V is constant, we can write,

$$dU = T\,dS$$

and for reversible isochoric processes,

By definition, $\left(\frac{dQ}{dT}\right)_V = C_V$

$$dU = dQ_R = C_V\,dT$$

and hence

$$\Delta U = \int_{T_1}^{T_2} C_V\,dT$$

This is only true for the system held at constant volume.

Enthalpy :→

Enthalpy, H is defined as,

$$H = U + PV$$

$$\text{or,} \quad dH = dU + P\,dV + V\,dP$$

$$\therefore \text{ or,} \quad dH = T\,dS - P\,dV + P\,dV + V\,dP \quad [\text{Using eqn } \cancel{\text{from}}\ (1)]$$

$$= T\,dS + V\,dP \longrightarrow (2)$$

The natural variables for H are thus S and P, and we have that $H = H(S, P)$

∴ For an isobaric process, where P is constant

$$dH = T\,dS.$$

and for a reversible isobaric process,

$$dH = đQ_R = C_p\,dT$$

By definition, $\left(\frac{đQ}{dT}\right)_p = C_p$.

$$\therefore \quad \Delta H = \int_{T_1}^{T_2} C_p\,dT$$

This shows that for reversible isobaric processes the enthalpy represents the heat absorbed by the system. If for any process with constant S and P, we have that

$$dH = 0,$$

∴ From equation (2), the tempr and volm can be calculated as,

$$T = \left(\frac{\partial H}{\partial S}\right)_P$$

and $$V = \left(\frac{\partial H}{\partial P}\right)_S$$

∴ Both U and H suffer from the drawback that one of their natural variables is the entropy S, which is not a very easy parameter to vary in a lab. It would be more convenient if we could substitute that for the temperature T, which is of course a much easier parameter to vary in a lab. This is accomplished with Helmholtz and Gibbs functions.

Helmholtz function (F) :→ or (A)

Helmholtz function is given by,

$$F = U - TS$$

hence, $dF = dU - TdS - SdT$

$= TdS - PdV - TdS - SdT$ (using equn (1))

or, $dF = -SdT - PdV \longrightarrow (3)$

This implies that, the natural variables for F ~~and V~~ are V and T and we can therefore write,

$$F = F(T, V).$$

Now, for an isothermal process (constant T), we can write from equ^n (3),

$$dF = -P\,dV$$

and hence, $\Delta F = -\int_{V_1}^{V_2} P\,dV$

Hence a positive change in F represents reversible work done on the system by the surroundings, while a negative change in F represents reveresible work done on the surroundings by the system.

From equation (3), we can ~~write,~~ calculate entropy & pres^r as,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

And the pressure P as,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

If T and V are constants, we have $dF = 0$, and F is a constant.

Gibbs function (G): →

The Gibbs function is defined as,

$$G = H - TS$$

hence, $dG = dH - TdS - SdT$

$$= TdS + VdP - TdS - SdT \quad |\text{using equ}^n\ (2)|$$

$$= VdP - SdT \longrightarrow (4)$$

Hence the natural variable of G are T and P. Hence we can write $G = G(T, P)$.

Having T and P as natural variables in particularly convenient as T and P are the easiest quantities to measure or to control. of T and P are constant, $dG = 0$. Hence G is conserved in any isothermal isobaric process.

From equation(4),

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

So the $\overset{S}{\text{vol}^m}$ and the $\overset{V}{\text{~~entropy~~}}$ may then be calculated as

and $$V = \left(\frac{\partial G}{\partial P}\right)_T.$$

Gibbs function is extremely important in chemistry, since chemical reactions begins and end at the same equilibrium atm p and ambient T.

Function of state	Differentials	Natural Variables	First derivatives
Internal Energy, U	$dU = TdS - PdV$	$U = U(S,V)$	$T = \left(\frac{\partial U}{\partial S}\right)_V$, $P = -\left(\frac{\partial U}{\partial V}\right)_S$
Enthalpy $H = U + PV$	$dH = TdS + VdP$	$H = H(S,P)$	$T = \left(\frac{\partial H}{\partial S}\right)_P$, $V = \left(\frac{\partial H}{\partial P}\right)_S$
Helmholtz Function $F = U - TS$	$dF = -SdT - PdV$	$F = F(T,V)$	$S = -\left(\frac{\partial F}{\partial T}\right)_V$, $P = -\left(\frac{\partial F}{\partial V}\right)_T$
Gibbs function $G = H - TS$	$dG = -SdT + VdP$	$G = G(T,P)$	$S = -\left(\frac{\partial G}{\partial T}\right)_P$, $V = \left(\frac{\partial G}{\partial P}\right)_T$

$$\begin{tikzcd}
U \arrow[r, "-TS"] \arrow[d, "+PV"'] & F = U - TS \arrow[d, "+PV"] \\
H = U + PV \arrow[r, "-TS"'] & G = U + PV - TS
\end{tikzcd}$$

$F = U - TS$

$G = U + PV - TS$

or

$G = H - TS$