

Entropy

From 1st law of TD, $q = \Delta u + w$

For an infinitesimally small change, $dq = du + dw$

Consider only mechanical work is involved,

$$dq = du + p dv$$

$$\Rightarrow \frac{dq}{T} = \frac{du}{T} + \frac{p}{T} dv$$

$$\Rightarrow ds = \frac{c_v dT}{T} + \frac{R dv}{V}$$

$$\Rightarrow \int ds = c_v \int \frac{dT}{T} + R \int \frac{dv}{V}$$

$$\therefore \boxed{\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}} \quad \text{---} \rightarrow \textcircled{1}$$

$$= C_v \ln \frac{T_2}{T_1} + R \ln \frac{RT_2/P_2}{RT_1/P_1}$$

$$= C_v \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$= (C_v + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\therefore \boxed{\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}} \quad \text{---} \rightarrow \textcircled{2}$$

Entropy change in various physical process:-

① Reversible isothermal expansion of an ideal gas:-

At isothermal process, $T_1 = T_2$

$$\therefore \boxed{\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}}$$

For isothermal expansion, $V_2 > V_1 \therefore \Delta S = +ve$

" " Compression, $V_2 < V_1 \therefore \Delta S = -ve$

② Isochoric process:- Here, $V_1 = V_2$

$$\therefore \Delta S = C_v \ln \frac{T_2}{T_1}$$

For heating $T_2 > T_1, \therefore \Delta S > 0$

Cooling $T_2 < T_1, \therefore \Delta S < 0$

③ Isobaric process:- Here $P_1 = P_2$

$$\therefore \boxed{\Delta S = C_p \ln \frac{T_2}{T_1}}$$

④ Adiabatic process:-

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \rightarrow \text{①}$$

Now, we know, for reversible adiabatic expansion,

$$TV^{\gamma-1} = \text{Constant}$$

$$\therefore T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{V_1}{V_2}\right)^{R/C_v} \quad [\text{Since, } \gamma = \frac{C_p}{C_v}]$$

$$\therefore \ln \frac{T_2}{T_1} = \frac{R}{C_v} \ln \left(\frac{V_1}{V_2}\right)$$

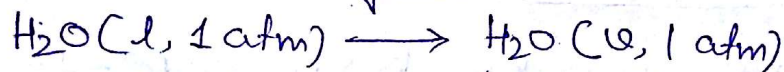
$$\Rightarrow C_v \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}$$

So, eqn ① becomes

$$\Delta S = R \ln \frac{V_1}{V_2} + R \ln \frac{V_2}{V_1} = 0$$

$\therefore \boxed{\Delta S = 0}$ for a diabatic reversible process.

⑤ Reversible phase change:-



$$\text{Now, } dS = \frac{dq_{\text{rev}}}{T}$$

$$\therefore \text{Here, } dS_{\text{vap}} = \frac{dH_{\text{vap}}}{T_b} \Rightarrow \int dS_{\text{vap}} = \int \frac{dH_{\text{vap}}}{T_b}$$

$$\text{So, } \boxed{\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}} = \frac{\Delta U + P\Delta U}{T_b} = +ve \quad [\text{Since, } \Delta U > 0]$$

$$\therefore \Delta S_{\text{vap}} = +ve$$

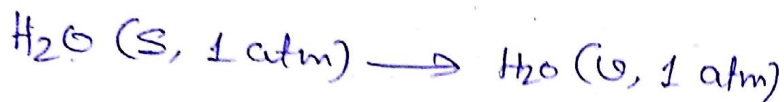
$$\therefore, S_{\text{vap}} - S_{\text{liq}} > 0 \Rightarrow \boxed{S_{\text{vap}} > S_{\text{liq}}}$$



$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} = \frac{\Delta U + P\Delta V}{T_{\text{fus}}} > 0$$

$$\Rightarrow \Delta S_{\text{fus}} > 0$$

$$\therefore S_{\text{liq}} - S_{\text{sol}} > 0 \Rightarrow \boxed{S_{\text{liq}} > S_{\text{sol}}}$$



$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}}} = \frac{\Delta U + P\Delta V}{T_{\text{sub}}} > 0$$

$$\therefore \boxed{S_{\text{vap}} > S_{\text{sol}}}$$

Entropy change of the total universe:-

(A) Reversible process:-

(i) Isothermal process:-

$$\Delta S_{\text{sys}} = R \ln \frac{V_2}{V_1} = \int \frac{dq_{\text{rev}}}{T}$$

$$\Delta S_{\text{sur}} = - \int \frac{dq_{\text{rev}}}{T} = - R \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

(ii) Isochoric process:- $\Delta S_{\text{sys}} = C_v \ln \frac{T_2}{T_1}$

$$\Delta S_{\text{sur}} = -C_v \ln \frac{T_2}{T_1}$$

$$\therefore \Delta S_{\text{total}} = 0$$

(iii) Isobaric process:- $\Delta S_{\text{sys}} = C_p \ln \frac{T_2}{T_1}$

$$\Delta S_{\text{sur}} = -C_p \ln \frac{T_2}{T_1}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

(iv) Adiabatic process:- since, in adiabatic process $q = 0$
 $\therefore \Delta S_{\text{sur}} = 0$

$$\text{Now, } \Delta S_{\text{sys}} = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} = 0$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

Conclusion:- Total entropy change of the universe is zero for a reversible process.

Ir-reversible process:-

Isothermal process:-

(a) Free expansion:- The gas expands against zero external pressure from V_1 to V_2 at temp. T without any exchange of heat, i.e., $dq_{\text{actual}} = 0$

$$\therefore \Delta S_{\text{sur}} = 0$$

$$\Delta S_{\text{sys}} = R \ln \frac{V_2}{V_1}$$

$$\therefore \boxed{\Delta S_{\text{total}} = R \ln \frac{V_2}{V_1} > 0}$$

(b) Intermediate expansion:-

$$\Delta S_{\text{sys}} = R \ln \frac{V_2}{V_1} = \frac{q_{\text{rev}}}{T} = \frac{w_{\text{rev}}}{T}$$

Now, expansion is done against a constant pressure.

$$\text{Thw, } q_{\text{irr}} = w_{\text{irr}} = -P_{\text{opp}}(V_2 - V_1)$$

$$\therefore \Delta S_{\text{sur}} = -\frac{q_{\text{irr}}}{T} = -\frac{w_{\text{irr}}}{T}$$

$$\text{Hence, } \Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = \frac{w_{\text{rev}}}{T} - \frac{w_{\text{irr}}}{T}$$

$$= +ve \quad [w_{\text{rev}} > w_{\text{irr}}]$$

Adiabatic process:- Here, $\Delta S_{\text{sur}} = 0$

$$\begin{aligned} \Delta S_{\text{sys}} &= C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \\ &= +C_v \ln \frac{T_2}{T_1} - C_v \ln \frac{T_2}{T_1} \end{aligned}$$

Now, we know, $w_{\text{rev}} > w_{\text{irr}}$ and $\boxed{w = -\Delta U}$ (for adiabatic)

Hence, $\Delta U_{irr} > \Delta U_{rev}$

$$\text{or, } C_v(T_2' - T_1) > C_v(T_2 - T_1)$$

$$\text{or, } \boxed{T_2' > T_1}$$

Hence ~~ΔS_{system}~~ $C_v \ln \frac{T_2'}{T_1} > C_v \ln \frac{T_2}{T_1}$

Thus, $\Delta S_{sys} > 0$

$\therefore \Delta S_{total} = \Delta S_{sys} + \Delta S_{sur}$
 $= +ve$

Math :- 258, 249, 267, 156 (1)



$$\Delta S = \frac{\Delta H_{fu}}{T_{fu}} = \frac{\Delta U + P \Delta V}{T_{fu}} > 0$$

$$\Delta V = 0$$

$$\therefore \boxed{S_{liq} - S_{sol} > 0}$$

$$\boxed{S_{liq} > S_{sol}}$$

⑧

Problem on Entropy :-

156 156. 249 (VVZ)
258 268
Tookay

Free energy

164, 212, 213, 217, 219
249 222, 228, 230, 234
263, 265, 267.

Why does 1 mole of water at $0^\circ C$ have greater entropy than one mole of ice at $0^\circ C$.