The Second Law: Entropy

A number of processes occur without any change in the energy ($\Delta U = 0 \; or \; \Delta H = 0$). There should be something more than energy that drives these changes. E.g. mixing of non-interacting gases. What is the spontaneous process?

Need for a state function

$$\delta q_{rev} = dU - \delta w_{rev} = C_V(T)dT + PdV = C_V(T)dT + \frac{nRT}{V}dV$$
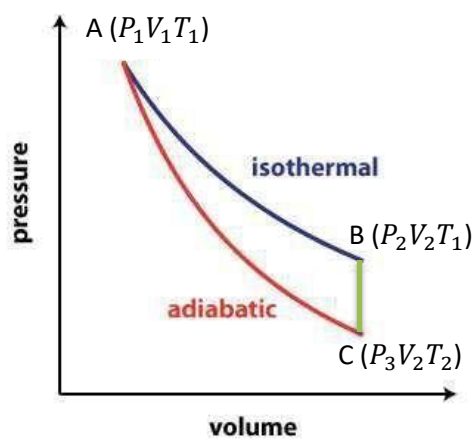
T depends on V. That is where the path dependence comes in the second term. Divide by T.

$$\frac{\delta q_{rev}}{T} = \frac{C_V(T)}{T}dT + \frac{nR}{V}dV$$

Now its exact and hence we can integrate it. Define $\boxed{dS = \delta q_{rev}/T}$

Entropy is a state function

Consider I.G.

$$\delta q_{rev,AB} = \frac{nRT_1}{V}dV \;\Rightarrow\; q_{rev,AB} = nRT_1 \ln\frac{V_2}{V_1}$$

$$\delta q_{rev,AC} = 0 \;\; \text{and} \;\; \delta q_{rev,CB} = C_V(T)dT$$

$$\Rightarrow q_{rev,AC+CB} = \int_{T_2}^{T_1} C_V(T)dT$$

where T_2 is given by, $\boxed{\text{See last lecture}}$

$$\int_{T_1}^{T_2} \frac{C_V(T)}{T}dT = -\int_{V_1}^{V_2} \frac{nR}{V}dV = -nR\ln\frac{V_2}{V_1}$$

Now, q differs for the two paths. What about $\Delta S = \int \frac{\delta q_{rev}}{T}$?

$$\Delta S_{AB} = \int_A^B \frac{\delta q_{revAB}}{T_1} = \int_{V_1}^{V_2} \frac{1}{T_1}\frac{nRT_1}{V}dV = nR\int_{V_1}^{V_2}\frac{dV}{V} = nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{AC} = \int_A^C \frac{\delta q_{rev,AC}}{T} = 0 \;\text{(adiabatic path)}$$

$$\Delta S_{CB} = \int_C^B \frac{\delta q_{rev,CB}}{T} = \int_{T_2}^{T_1} \frac{C_V(T)}{T}dT = nR\ln\frac{V_2}{V_1}$$

$\boxed{\begin{array}{l}\text{Using the}\\ \text{above equation}\end{array}}$

Same ΔS independent of the path. S is a state function!

Clausius Inequality

$$dU = \delta q + \delta w = \delta q_{rev} + \delta w_{rev}$$

$$\delta q_{rev} - \delta q = \underbrace{\delta w - \delta w_{rev}}_{\text{Always}} \geq 0 \therefore \delta q_{rev} \geq \delta q \therefore \frac{\delta q_{rev}}{T} \geq \frac{\delta q}{T}$$

Now, $dS = \frac{\delta q_{rev}}{T}$ So, $dS \geq \frac{\delta q}{T}$ For an isolated system, $dS \geq 0$. The entropy of the universe cannot decrease for a spontaneous process.
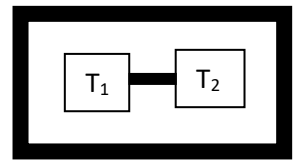
When the isolated system comes to equilibrium, no further change occurs $\rightarrow dS = 0$

Also, for a reversible process in an isolated system (as a rev. process maintains the system at equilibrium), $dS = 0$

For other systems (not isolated), heat can flow in or out and one can consider two parts – system and surrounding.

Entropy tells about the direction of heat flow.

initially $T_1 \neq T_2$

$$dS = dS_1 + dS_2 = \frac{\delta q_1}{T_1} + \frac{\delta q_2}{T_2} = \delta q_1 \frac{(T_2 - T_1)}{T_2 T_1} \because (\delta q_1 = -\delta q_2)$$

Now, $dS > 0$ for spontaneous change

If $T_2 > T_1 \Rightarrow \delta q_1 > 0$ whereas if $T_1 > T_2 \Rightarrow \delta q_1 < 0$ (heat flows from hot to cold object)

Entropy changes

Isothermal expansion: I.G. (see above)

$\Delta S_{sys} (1 \rightarrow 2) = nR \ln \frac{V_2}{V_1}$ for rev/irr processes

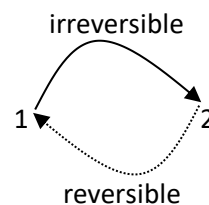$dq_{surr} = -dq$ Always

For a rev. process, $\Delta S_{surr} = \frac{q_{surr}}{T} = -\frac{q_{rev}}{T} = -nR \ln \frac{V_2}{V_1}$
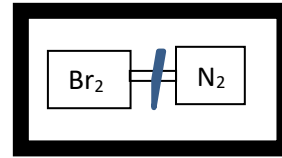
$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = 0 \text{ (reversible process)}$$

Free isothermal expansion ($\Delta U = 0$), $w = 0 \therefore q = 0$ $\Delta S_{surr} = 0$,

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = nR \ln \frac{V_2}{V_1} > 0 \text{ (irreversible process)}$$

irreversible

1 → 2

reversible

ΔS is the same! Calculate by constructing a reversible path!

Mixing of two ideal gases

$$\Delta S_{N_2} = -n_{N_2} R \ln \frac{V_{N_2}}{V_{N_2} + V_{Br_2}} \quad \text{and} \quad \Delta S_{Br_2} = -n_{Br_2} R \ln \frac{V_{Br_2}}{V_{N_2} + V_{Br_2}}$$

I.G. : $V \propto n$

$$\Delta S = -n_{N_2} R \ln \frac{V_{N_2}}{V_{N_2} + V_{Br_2}} - n_{Br_2} R \ln \frac{V_{Br_2}}{V_{N_2} + V_{Br_2}} = -n_{N_2} R \ln \frac{n_{N_2}}{n_{N_2} + n_{Br_2}} - n_{Br_2} R \ln \frac{n_{Br_2}}{n_{N_2} + n_{Br_2}}$$

Divide both sides by $n_{tot} = n_{N_2} + N_{Br_2}$ and use mole fraction $y_i = n_i/n_{tot}$

$$\Delta_{mix}\bar{S}/R = -y_{N_2} \ln y_{N_2} - y_{Br_2} \ln y_{Br_2} > 0$$

Statistical considerations

Consider an ensemble of $\mathcal{A}$ isolated systems – Energy E, Volume V, Number of particles N.

The various $\mathcal{A}$ systems are distinguishable. a_1 systems are in state 1, a_2 systems in state 2 …

Number of ways of such an arrangement

$$W(a_1, a_2, \dots) = \frac{\mathcal{A}!}{a_1! \, a_2! \dots} = \frac{\mathcal{A}!}{\prod_j a_j!}$$

Totally ordered system is where all the $\mathcal{A}$ systems are in the same state. E.g.

$$a_1 = \mathcal{A}, a_2 = 0, a_3 = \dots = 0$$

$$\Rightarrow W = 1$$

Totally disordered state would be when all $a_j's$ are equal.

So W is a quantitative measure of disorder. It is therefore proportional to entropy.

$$\boxed{S = k_B \ln W}$$

The logarithmic function arises because you want the entropies of two systems to be additive. Since, $W_{AB} = W_A W_B$, using the log function, $\ln W_{AB} = \ln W_A + \ln W_B$. This ensures that we can write $S_{AB} = S_A + S_B$.

Entropy and Probability

The entropy of the ensemble is

$$S = k_B \ln W = k_B \ln\left(\frac{\mathcal{A}!}{\prod_j a_j!}\right)$$

$$= k_B \ln \mathcal{A}! - k_B \sum_j \ln a_j !$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \mathcal{A} - k_B \sum_j a_j \ln a_j + k_B \sum_j a_j$$

(Here we used the Stirling's approximation: $\ln N! = N \ln N - N$)

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \mathcal{A} - k_B \sum_j a_j \ln a_j + k_B \mathcal{A}$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \sum_j a_j \ln a_j$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \sum_j p_j \mathcal{A} \ln(p_j \mathcal{A}) \quad \left(\text{we know } p_j = \frac{a_j}{\mathcal{A}}\right)$$

$$= k_B \mathcal{A} \ln \mathcal{A} - k_B \sum_j p_j \mathcal{A} \ln p_j - k_B \sum_j p_j \mathcal{A} \ln \mathcal{A}$$

$$S_{ensemble} = -k_B \sum_j p_j \mathcal{A} \ln p_j$$

$$\boxed{S_{system} = S_{ensemble}/\mathcal{A} = -k_B \sum_j p_j \ln p_j}$$

If all probabilities except one are zero, the entropy goes to zero – a perfectly ordered system. It can be shown that the entropy is maximum when all $p_j's$ are equal – maximum disorder.

Entropy and Partition Function

$$S_{sys} = -k_B \sum_j p_j \ln p_j = -k_B \sum_j \frac{e^{-\beta E_j}}{Q} \ln \frac{e^{-\beta E_j}}{Q}$$

$$= -k_B \sum_j \frac{e^{-\beta E_j}}{Q} (-\beta E_j - \ln Q) = \beta k_B \sum_j \frac{E_j e^{-\beta E_j}}{Q} + \frac{k_B \ln Q}{Q} \sum_j e^{-\beta E_j}$$

$$= \frac{U}{T} + k_B \ln Q = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q$$

Molecular and Classical equivalence

$$S = -k_B \sum_j p_j \ln p_j$$

$$dS = -k_B \sum_j (dp_j + \ln p_j \, dp_j)$$

Now, $\Sigma dp_j = 0 \because \Sigma p_j = 1$

$$\therefore \ dS = -k_B \sum_j \ln p_j \, dp_j = -k_B \sum_j \ln \frac{e^{-\beta E_j}}{Q} dp_j = -k_B \sum_j (-\beta E_j - \ln Q) dp_j$$

Since $\ln Q \, \Sigma dp_j = 0$

$$dS = \beta k_B \sum_j E_j(N,V) dp_j(N,V,\beta)$$

The summed up term is the average heat exchanged reversibly.

<div style="border:1px solid">See last lecture</div>

So,

$$dS = \beta k_B q_{rev} \text{ and classically } dS = \frac{q_{rev}}{T}$$

Equate the two and get $\beta = 1/k_B T$