Spontaneous Changes

Direction

Second Law:

Entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$

$dS \rightarrow$ change in entropy. Since work stimulates uniform motion in the atoms and heat random, the entropy (or randomness) is measured by the heat exchanged.

Definition: $dS = dq_{rev}/T$ (the rev in the subscript is very important)

For surroundings $dS = dq_{surr}/T_{surr}$ (surrounding is huge! T_{surr} is constant)

Statements of second law

Kelvin: It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it into work in the surroundings without at the same time transferring some heat to a cold reservoir.
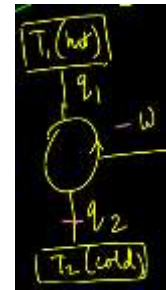
Clausius: It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir without at the same time converting some work into heat
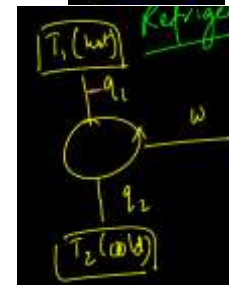
Entropy is a state function: $\oint dq_{rev}/T = 0$

1. For Carnot cycle with ideal gas
2. For any material
3. For any closed cycle

Carnot cycle: isothermal expansion, adiabatic expansion, isothermal compression, adiabatic compression

Adiabatic stages – no heat exchange $\rightarrow$ no change in S

Isothermal steps: $\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$

Isothermal expansion of an I.G.: $\Delta S = \frac{1}{T}\int_i^f dq_{rev} = \frac{q_{rev}}{T}$

$q_{rev} = -w_{rev} = nRT \ln\frac{V_f}{V_i}$, gives $\Delta S = nR \ln\frac{V_f}{V_i}$

So, $q_h = nRT_h \ln\frac{V_B}{V_A}, q_c = nRT_c \ln\frac{V_D}{V_C}$

For rev. ad. $V_A T_h^\alpha = V_D T_c^\alpha$ and $V_C T_c^\alpha = V_B T_h^\alpha \rightarrow V_A V_C T_h^\alpha T_c^\alpha = V_D V_B T_h^\alpha T_c^\alpha \rightarrow \frac{V_A}{V_B} = \frac{V_D}{V_C} \rightarrow q_c = nRT_c \ln\frac{V_D}{V_C} = nRT_c \ln\frac{V_A}{V_B} = -nRT_c \ln\frac{V_B}{V_A} \rightarrow$

$\frac{q_h}{q_c} = \frac{nRT_h \ln(V_B/V_A)}{-nRT_c \ln(V_B/V_A)} = -\frac{T_h}{T_c}$ (though proven here for an I.G., it is true for any material under rev. process)
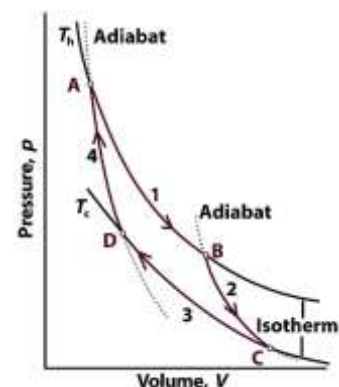
So, $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$ which gives, $\oint dS = 0$ (true for Carnot cycle, I.G.)

Now for any material,

Efficiency, $\epsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h} = \frac{q_h+q_c}{q_h} = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h}$

Connect two rev. engines, A and B in opposite configurations (one is engine, the other refrigerator). Suppose A is more efficient than B. This means A could drive engine B and in the process generate some extra work. Net result → work has been done, cold reservoir unchanged, hot reservoir lost some heat!! Impossible as per the second law. Therefore, all reversible engines must have the same efficiency.
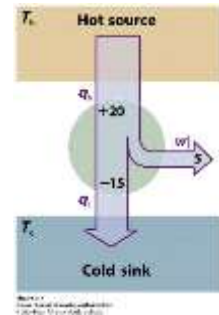
Third, for any cycle: Construct infinitesimal Carnot cycles → $\oint dS = 0$

Clausius Inequality

$$dU = dq + dw = dq_{rev} + dw_{rev}$$

$$dq_{rev} - dq = dw - dw_{rev} \geq 0 \therefore dq_{rev} \geq dq \therefore \frac{dq_{rev}}{T} \geq \frac{dq}{T}$$

Now, $dS = \frac{dq_{rev}}{T}$ So, $dS \geq \frac{dq}{T}$ For an isolated system, $dS \geq 0$. The entropy of the universe cannot decrease for a spontaneous process.
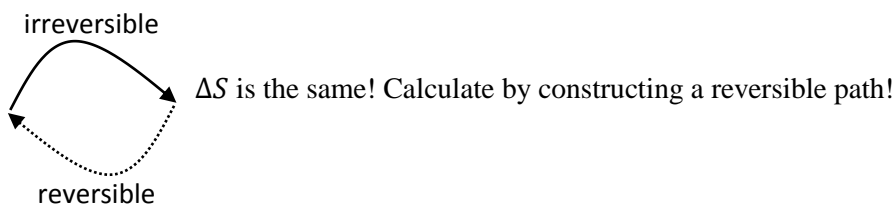
Entropy changes

(a) Isothermal expansion: I.G. (see above)

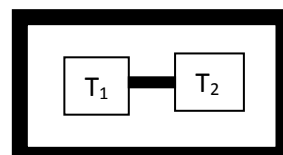$\Delta S = nR \ln \frac{V_f}{V_i}$ for rev/irr processes

$dq_{surr} = -dq$ Always

For a rev. process, $\Delta S_{surr} = \frac{q_{surr}}{T} = -\frac{q_{rev}}{T} = -nR \ln \frac{V_f}{V_i}$ So, $\Delta S_{tot} = 0$

Free isothermal expansion ($\Delta U = 0$), $w = 0 \therefore q = 0$ $\Delta S_{surr} = 0, \Delta S_{tot} = nR \ln \frac{V_f}{V_i} > 0$ (expected for irreversible processes).

irreversible

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

reversible

(b) connect 2 metal blocks
    initially $T_1 \neq T_2$

2

$$dS = dS_1 + dS_2 = \frac{dq_1}{T_1} + \frac{dq_2}{T_2} = dq_1 \frac{(T_2 - T_1)}{T_2 T_1} \quad \because (dq_1 = -dq_2)$$

Now, $dS > 0$ for spontaneous change

If $T_2 > T_1 \Rightarrow dq_1 > 0$ whereas if $T_1 > T_2 \Rightarrow dq_1 < 0$ (heat flows from hot to cold object)
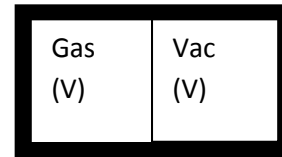
(c) Joule expansion with an I.G. (adiabatic)

1 mol gas $(V, T) \to$ 1 mol gas $(2V, T)$ → irr.

Compress back isothermally and reversibly, $\Delta S = -\Delta S_{comp}$

($q_{rev} \neq 0$. It need not be. The reversible path can be any.

It just needs to go back to the initial state.)

Gas	Vac
(V)	(V)

1 mol gas $(2V, T) \to$ 1 mol gas (V, T)

$$\Delta S_{comp} = \int \frac{dq_{rev}}{T} = -\int \frac{dw}{T} = \int_{2V}^{V} \frac{R dV}{V} = R \ln \frac{1}{2}$$

$$\therefore \Delta S = R \ln 2 > 0$$