Example : System in contact with reservoir.

Heat is added reversibly to a system with heat capacity C increases temp from $T_A \to T_B$., $dQ = CdT$

$$(\Delta S)_{system} = C \int_{T_A}^{T_B} \frac{dT}{T} = C \ln \left(\frac{T_B}{T_A} \right)$$

$\downarrow$
iso increases

$(\Delta S)_{reservoir} = ?$

$$(\Delta S)_{reservoir} = \frac{Q_{reservoir}}{T_B} = \frac{-C(T_B - T_A)}{T_B}$$

$$= -C \left(1 - \frac{T_A}{T_B} \right)$$

Entropy change of universe

$$= (\Delta S)_{system} + (\Delta S)_{res}$$

$$\approx C \left[\ln\left(\frac{T_B}{T_A}\right) + \frac{T_A}{T_B} - 1 \right] \qquad \text{Let} \quad x = \frac{T_A}{T_B}$$
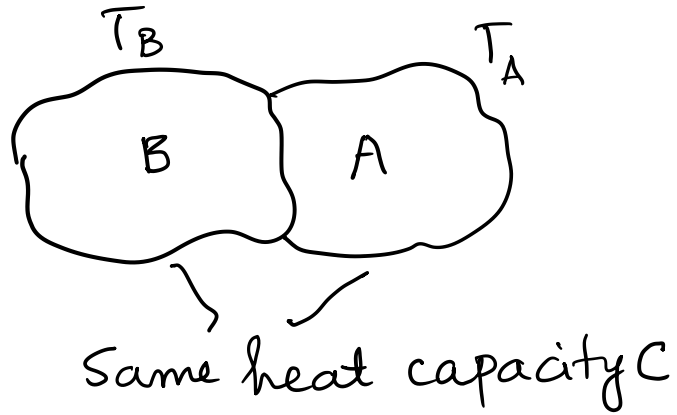
$$\Delta S = C \left[\ln x - 1 + x \right]$$

$f(x) = x - 1 - \ln x$, has a single minimum at $x = 1$

$$f(x) \geqslant f(1) \geqslant 0$$

$$\boxed{\Delta S \geqslant 0}$$

Heat transfer by conduction

T_B

T_A

B   A

Same heat capacity C

$T_B > T_A$

Heat flows from $B \rightarrow A$

equilibrium temp T_c.

Heat lost by B = $C(T_B - T_c) > 0$

Heat gained by A = $C(T_c - T_A) > 0$

$$T_c - T_A = T_B - T_c \quad \leadsto \text{ heat lost = heat gained}$$

$$\boxed{T_c = \frac{1}{2}(T_A + T_B)}$$

$$\Delta S_A = \int_{T_A}^{T_C} \frac{dQ}{T} = C \int_{T_A}^{T_C} \frac{dT}{T} = C \ln\left(\frac{T_C}{T_A}\right) > 0$$
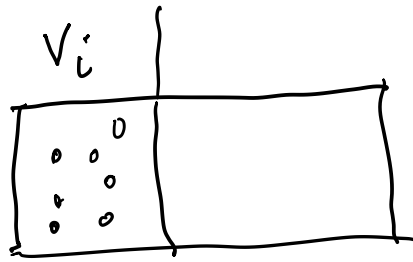
$$\Delta S_B = \int_{T_B}^{T_C} \frac{dQ}{T} = C \ln\left(\frac{T_C}{T_B}\right) < 0$$
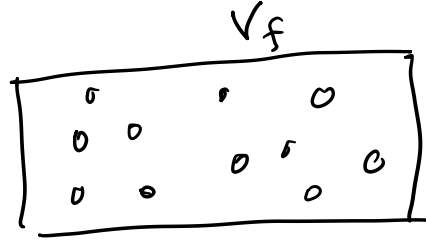
$$(\Delta S)_{Total} = (\Delta S)_A + (\Delta S)_B$$

$$= C \ln\left(\frac{T_C^2}{T_A T_B}\right) \qquad 0 \qquad T_C = \frac{1}{2}(T_A + T_B)$$

Entropy change in adiabatic free expansion
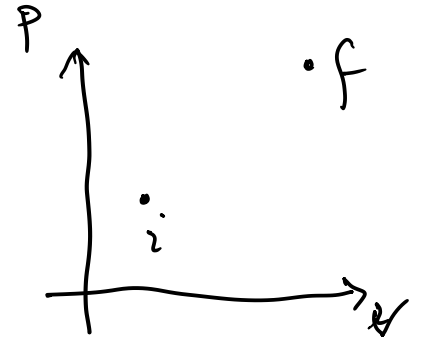

$$\Delta Q = 0$$
$$\Delta W = 0$$
$$T_i = T_f$$

$$\Delta S = \left(\int_i^f \frac{dQ}{T} \right)_{reversible \ path}$$

since entropy in a state fn. one can use any reversible path connecting $i \rightarrow f$ to calculate it

$\hookrightarrow$ use isothermal quasistatic reversible expansion

$$(T_i, V_i) \longrightarrow (V_f, T_i)$$

$$\Delta S = \int_{V_i}^{V_f} \frac{dQ}{T} = \int_{V_i}^{V_f} \frac{p\,dV}{T} = nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$(\Delta S) = nR \ln \frac{V_f}{V_i} > 0$$

adiabatic
Free expansion

entropy change of universe $\rightarrow (\Delta S)_{surrounding} = 0$

$$(\Delta S)_{universe} = (\Delta S)_{system}$$

Entropy of an ideal gas

$$dQ = C_v dT + p dV$$

$$= C_v dT + \frac{nRT}{V} dV$$

$$dS = \frac{dQ}{T}$$

$$dS = C_v \frac{dT}{T} + nR \frac{dV}{V}$$

ref. State P_0, V_0, T_0

entropy S_0

$$\boxed{S = S_0 + C_v \ln\left(\frac{T}{T_0}\right) + nR \ln\left(\frac{V}{V_0}\right)}$$

$$C_p = C_v + nR$$

or

$$= S_0 + C_p \ln\left(\frac{T}{T_0}\right) - nR \ln\left(\frac{P}{P_0}\right)$$

$$C_v = \alpha n R \qquad \alpha = \frac{3}{2} \text{ for monatomic}$$

$$\frac{5}{2} \text{ for diatomic}$$

$$S = S_0 + \alpha n R \ln\left(\frac{T}{T_0}\right) + n R \ln\left(\frac{V}{V_0}\right)$$

$$\boxed{S = S_0 + n R \ln\left[\left(\frac{T}{T_0}\right)^{\alpha}\left(\frac{V}{V_0}\right)\right]}$$

Entropy and degradation of energy

Q delivered to a heat engine from a reservoir at temp T_1. If T_0 is the temp of the coolest reservoir at hand then

$$W_1 = Q\left(1 - \frac{T_0}{T_1}\right) \implies \text{max work extractible from engine}$$

Suppos instead of immediatdly converting to work, I decide to transfer Q to a cooler reservoir at some temp T_2 (say by means of a metal bar). Now if I pass it on to the engine

$$W_2 = Q\left(1 - \frac{T_0}{T_2}\right) \implies \text{max work extractible} \quad W_2 < W_1$$

after heat transferred to cooler res, capable of doing less work

Although energy has been conserved in transfer to cooler reservoir, its capacity to do work has decreased.

$\Rightarrow$ degradation of energy

$$E_{degraded} = W_1 - W_2 = Q T_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

overall change in entropy

at T_1 $\qquad \Delta S_1 = -\frac{Q}{T_1}$

at T_2 $\qquad \Delta S_2 = \frac{Q}{T_2}$

$$E_{degraded} = T_0 \Delta S$$

$\Delta S = \Delta S_1 + \Delta S_2$

$\qquad = Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) > 0$

irreversible.