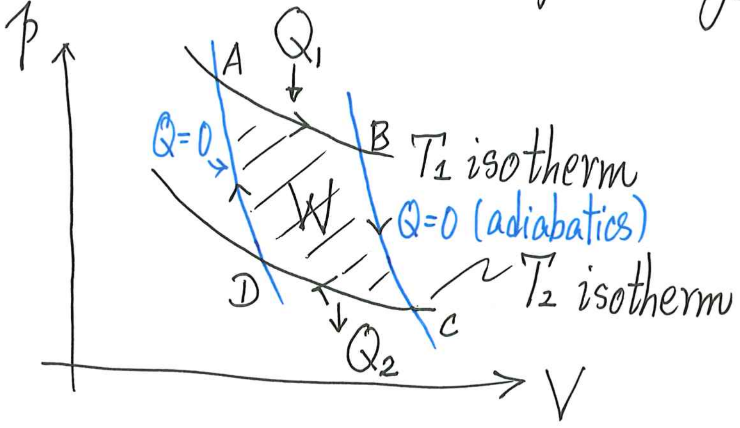
V. Entropy

- It is usually said that the 0th law is about temperature, the 1st law is about energy, and the 2nd law is about entropy (熵)
- How did $\underbrace{\text{entropy}}_{\text{a new state function}}$ emerge?

  In 1st law, there is a $đQ$ term, 2nd law and entropy are also about the $đQ$ term

A. Carnot Cycle hints at a new State function

Recall: Reversible, operating between two heat baths T_1 and T_2



$$\underbrace{A \to B \to C \to D \to A}$$

$\Delta U = 0$ (∵ U is a state function)

(Anything else?)

$$\text{Net heat into system} = \underbrace{Q_1 - \tilde{Q_2}}_{\neq 0\ (=W)}$$

$\underbrace{(Q_2 \text{ itself is +ve})}$ but it is rejected into bath 2

$W_{1\,\text{cycle}} \neq 0$

(So Work (1 cycle) CANNOT be a state function)

(So "Heat into system" in a cycle CANNOT be a state function)

But

$$\underbrace{\frac{Q_2}{Q_1} = \frac{T_2}{T_1}}_{\text{see Ch. IV}} \Rightarrow \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \Rightarrow \underset{A\to B}{\frac{Q_1}{T_1}} + \underset{\substack{B\to C\\(Q=0)}}{0} + \underset{C\to D}{\left(\frac{-Q_2}{T_2}\right)} + \underset{\substack{D\to A\\(Q=0)}}{0} = 0 \qquad (1)$$

[c.f. Δ(Something) $= 0$ in a cycle]

Let's analyze $$\underbrace{\frac{Q_1}{T_1}}_{(A\to B)} + \underbrace{0}_{(B\to C)} + \underbrace{\left(\frac{-Q_2}{T_2}\right)}_{(C\to D)} + 0 = 0 \quad (1)$$

Q_1 = heat into system in A→B

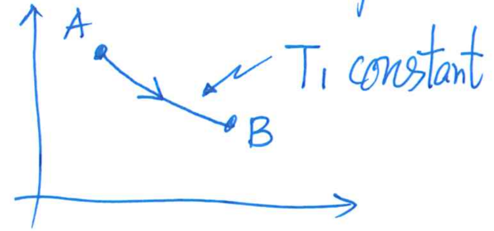
$(B\to C)$ adiabatic $(Q=0)$

$-Q_2$ is negative — heat taken out of system

T_1 is temperature of bath in principle during heat exchange

since reversible process

T_1 is also temperature of system



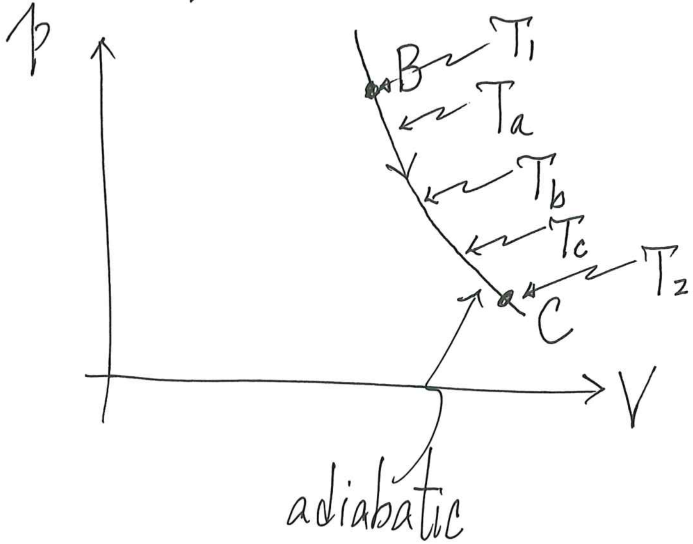
T_2 is temperature of bath during heat exchange

∵ reversible, T_2 is temperature of system

$$\frac{Q_1}{T_1} = \int_A^B \frac{dQ_{rev}}{T} ; \quad \underset{\text{(adiabatic)}}{\int_B^C \frac{dQ_{rev}}{T}} = 0 ; \quad \frac{-Q_2}{T_2} = \int_C^D \frac{dQ_{rev}}{T} ; \quad 0 = \underset{\text{(adiabatic)}}{\int_D^A \frac{dQ_{rev}}{T}}$$

$$\boxed{dQ_{rev} \rightarrow \text{emphasize reversible processes}}$$

Let's analyze the "0" from B → C



In each step from B → C,

$$\frac{\bar{d}Q_{rev}^{(adiabatic)}}{T_a} \;,\; \frac{\overset{=0}{\boxed{\bar{d}Q_{rev}^{(adiabatic)}}}}{T_b} \;,\; \ldots$$

$$\text{So, "0"} = \int_{\substack{B \\ (adiabatic)}}^{C} \frac{\bar{d}Q_{rev}}{T}$$

Eq. (1) means $\sum\limits_{\substack{i=A\to B,\, B\to C,\, C\to D,\, D\to A \\ \text{(paths in 1 cycle)}}} \frac{Q_i}{T_i} = 0$ (2) (reversible cycle)

∴ Take the quantity $\frac{Q_i}{T_i}$ around a cycle $[A \xrightarrow{\text{back to}} A]$, the quantity does not change ⇒ a state function emerges

Interpreting processes in reversible cycle as many infinitesimal changes,

$$\oint \frac{\text{đ}Q_{\text{rev}}}{T} = 0 \qquad (3)$$

(reversible cycle)

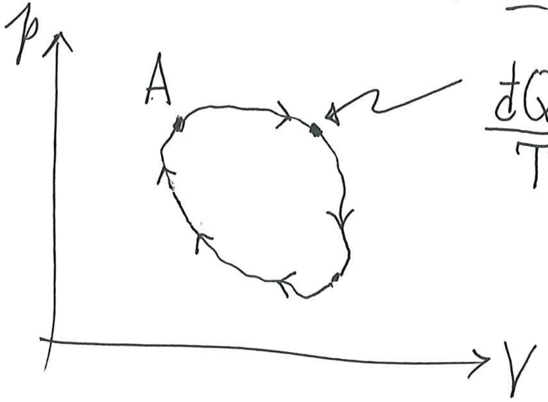
$\oint$ means over a cycle

- This is part of the Clausius Theorem (the "equality" of his inequality)
- It applies to reversible cycle.
- It leads us to define Entropy.

Remarks

- Carnot cycle involves two baths (two temperatures) only
- In Eq.(3), the analysis led us[†] to a result applicable to general reversible cycles

$\underbrace{\text{reversible cycles}}_{\text{Could involve many temperatures along the cycle}}$



$\frac{\bar{d}Q_{\text{rev}}}{T}$ involved

$$\underbrace{\oint}_{\text{add up bits of contributions in reversible cycle}} \frac{\bar{d}Q_{\text{rev}}}{T} = \overset{\text{no change}}{0}$$

[†] A formal treatment is cumbersome. The result, of course, is Eq.(3). Here we argued for Eq.(3) based on the Carnot cycle, for simplicity.

B. Entropy (Entropy Change)

Define a new variable, entropy S, by

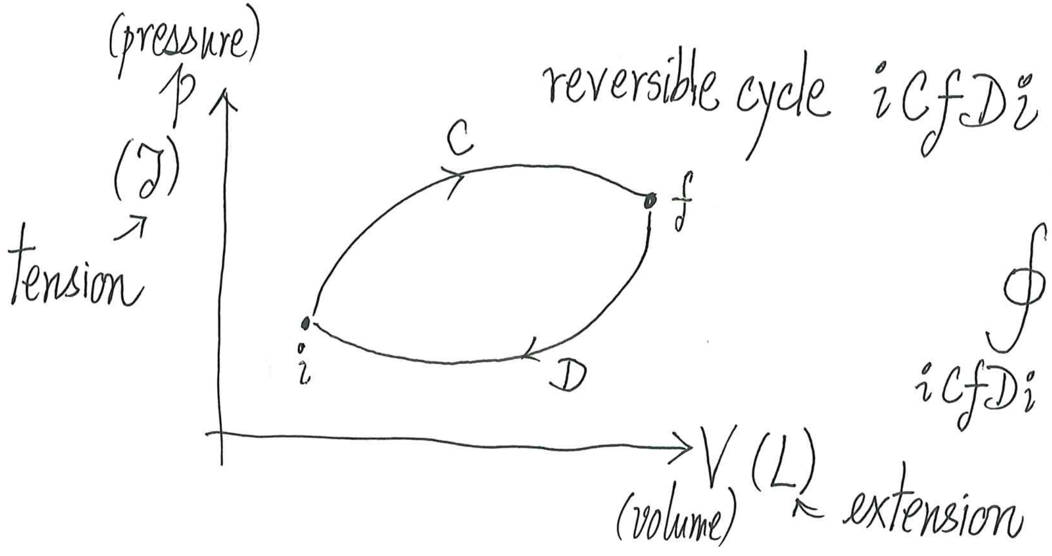
$$\boxed{\begin{array}{c} dS = \dfrac{\text{đ}Q_{rev}}{T} \qquad (4) \\ \text{for an infinitesimal reversible change} \end{array}}$$

(sometimes simply $dS = \frac{\text{đ}Q}{T}$)

(here, we stress that "reversible change" is involved, so $\frac{\text{đ}Q_{rev}}{T}$)

For a finite reversible change

$$\Delta S = \underset{\substack{\nearrow \\ \text{reversible path}}}{\int_i^f} \frac{\text{đ}Q_{rev}}{T} \qquad (5)$$



reversible cycle iCfDi formed by reversible paths iCf and fDi

$$\oint_{iCfDi} \frac{đQ_{rev}}{T} \underset{\text{Clausius theorem}}{=} 0 = \oint_{iCfDi} dS \quad \leftarrow \text{definition Eq.(4)}$$

$$0 = \oint_{iCfDi} dS = \int_{\substack{iCf \\ (\text{reversible})}} dS + \int_{\substack{fDi \\ (\text{reversible})}} dS \Rightarrow \underset{(\text{along } iCf)}{\int_i^f dS} = -\underset{(\text{along } fDi)}{\int_f^i dS} = \underset{(\text{along } iDf)}{\int_i^f dS}$$

∵ reversible

$$\therefore \underset{(\text{along } iCf)}{\int_i^f dS} = \underset{(\text{along } iDf)}{\int_i^f dS} = \underset{(\text{any reversible path from } i \text{ to } f)}{\int_i^f dS} \quad (\text{this integral is PATH Independent})$$

different reversible paths from i to f

$$= S_f - S_i \quad (\text{depends only on endpoints})$$

∴ <u>S (entropy)</u> <u>is a State function</u>

$\therefore$ Eq.(5) for a finite reversible change becomes

$$\Delta S = S_f - S_i = \int_i^f \frac{\text{đ}Q_{rev}}{T} \quad (5)$$

(any reversible path)

c.f. The hill S is really there.

Meaning:

- S is a state function: Given state, S_{state} has a value[+]
- Given initial i and final f states, there is $\underbrace{\text{a certain } \Delta S}_{\text{doesn't matter how you go from } i \text{ to } f}$
- But if you want to use $\int_i^f \frac{\text{đ}Q}{T}$ to evaluate that "ΔS", then be careful! You must do the calculation along a reversible path (your choice), and $\int_i^f \frac{\text{đ}Q_{rev}}{T}$ stresses this point. "T" is the temperature during the heat exchange $\text{đ}Q_{rev}$ takes place.

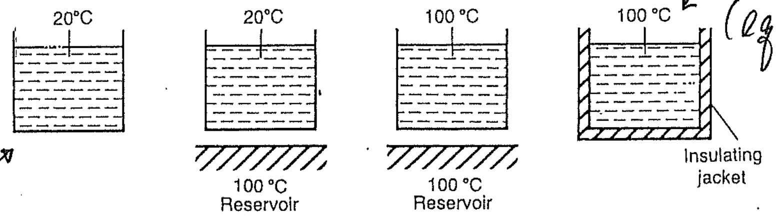
[+] Up to a constant, because only ΔS is defined via Eq.(5).

Illustration: Example taken from "Thermal Physics" by Finn $\Delta S = \int_i^f \frac{đQ_{rev}}{T}$ eq. (5.3) in text

An example of a calculation of an entropy change

So that we may see how entropy changes are calculated, let us determine the entropy change of a beaker of water when it is heated at atmospheric pressure between room temperature, at 20 °C, and 100 °C by placing it on a reservoir at 100 °C. When the water reaches 100 °C, the beaker is removed from the reservoir and placed in an insulating jacket. This process is shown in Fig. 5.3. Heat passes from the reservoir into the water and it might seem that a simple application of equation [5.3] would suffice. However this equation applies to a *reversible* process, while the actual process here is *irreversible* because of the inherent finite temperature differences.

Question →



initial (equilibrium)

final (equilibrium)

A beaker of water is heated irreversibly and isobarically between 20 °C and 100 °C in this process.

[So there is a $\Delta S = S_f - S_i$]

We resort again to the argument encountered in section 2.4. As the water is initially and finally in equilibrium states, with well-defined entropies, the entropy change for this process is also well defined. We can then *imagine any convenient reversible process* that takes the system between the same two end points and calculate, using equation [5.3], the entropy change for this imaginary process. *This entropy change is then the same as that occurring in the actual irreversible process.*

One simple reversible heating process between the end points could be effected by bringing up a whole series of reservoirs between 20 °C and 100 °C, keeping the pressure constant, so that the water passes through a series of equilibrium states. This imaginary process is shown in Fig. 5.4.

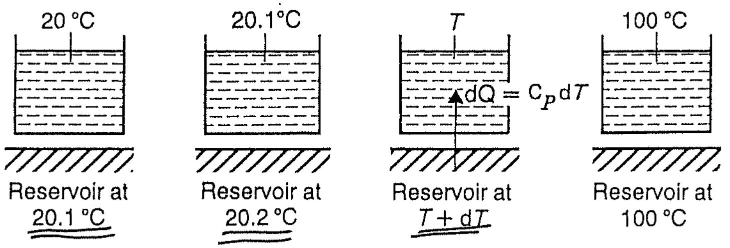


Fig. 5.4 The same beaker of water is heated reversibly and isobarically between 20 °C and 100 °C in this imaginary process.

But need to construct a convenient reversible path to use $\int_i^f \frac{đQ_{rev}}{T}$ for ΔS

When the water is at T and it is heated to $T + \mathrm{d}T$ by the reservoir at $T + \mathrm{d}T$, the heat entering the water reversibly is

$$đQ_R = C_P \,\mathrm{d}T$$

where C_P is the heat capacity at constant pressure of the water. Hence the entropy change of the water is

$$\mathrm{d}S = \frac{C_P \mathrm{d}T}{T}$$

or

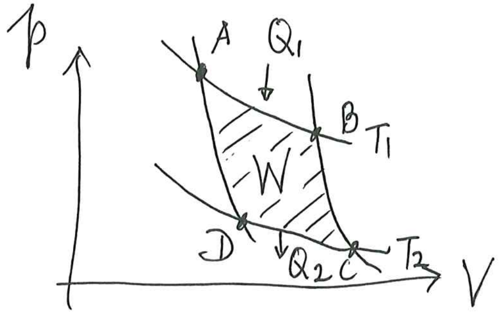
$$\Delta S = C_P \int_{T_i}^{T_f} \frac{\mathrm{d}T}{T} = C_P \ln\left\{\frac{T_f}{T_i}\right\} \qquad [5.5]$$

If we have 1 kg of water with $C_P = 4.2$ kJ K^{-1} and remembering that the T in equation [5.3] is the thermodynamic temperature,

$$\Delta S = 4.2 \times 10^3 \ln\left\{\frac{373}{293}\right\} = 1.01 \times 10^3 \text{ J K}^{-1}$$

Any other reversible path would give, of course, the same answer, but this path is probably the most convenient.

An appreciation of $\sum_i \frac{Q_i}{T_i} = 0$ (reversible cycle) or $\oint \frac{đQ_{rev}}{T} = 0$



$$Q_1 \neq 0,\quad Q_2 \neq 0,\quad \underbrace{\overset{\text{(bigger)}}{Q_1} > \overset{\text{(smaller)}}{Q_2}}\ ,\quad \underbrace{Q_1 - Q_2 = W}_{1^{st}\text{ law}} \quad \text{in 1 cycle}$$

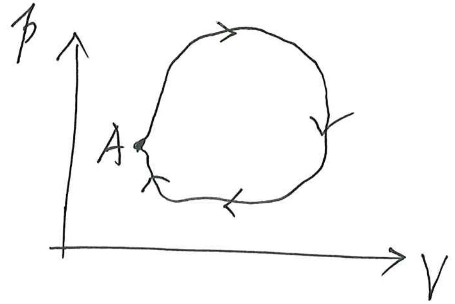
$$\overset{\text{(bigger)}}{T_1} > \overset{\text{(smaller)}}{T_2}$$

Q itself is NOT function of state

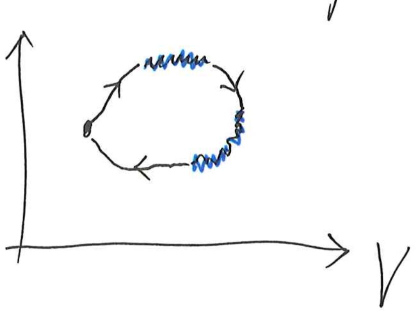
$$\text{But}\left(\frac{Q_1 \leftarrow \text{bigger}}{T_1 \leftarrow \text{higher temp}} \quad \text{along } A \to B\right) = \left(\frac{Q_2 \leftarrow \text{smaller}}{T_2 \leftarrow \text{lower temp}} \quad \text{along } C \to D\right)$$

C. The Clausius Theorem

We have $\oint_{\substack{\text{reversible}\\ \text{cycle}}} \frac{\text{đ}Q_{\text{rev}}}{T} = 0$ for reversible cycle



Question: Cycle with some part(s) being irreversible processes



"〰" ← irreversible processes

$\underbrace{\text{(involve states NOT in equilibrium)}}_{\text{Can't draw on indicator diagram}}$

For every bit, there is đQ involved and the heat exchange is carried out by an external source at some temperature T (for a reversible bit, T is also temperature of system), the question is about the property of $\oint_{\text{cycle (any)}} \frac{\text{đ}Q}{T}$

The Clausius Theorem

saw argument for this part

$$\boxed{\oint_{\substack{\text{cycle}\\ \text{(any)}}} \frac{\text{đ}Q}{T} \leqslant 0 \qquad \text{with} \quad \oint_{\substack{\text{reversible}\\ \text{cycle}}} \frac{\text{đ}Q_{rev}}{T} = 0 \quad \text{for reversible cycle}} \qquad (6)$$

T is (in general) is the temperature of the source supplying the heat đQ

Meaning

$$\oint_{\substack{\text{cycle with part(s)}\\ \text{being irreversible}}} \frac{\text{đ}Q}{T} < 0$$

(one-sided)

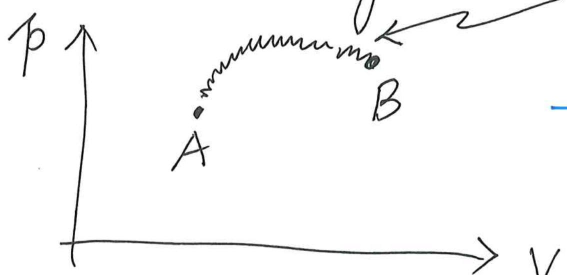
distinguishes naturally occuring & not occuring phenomena

- Take this in
- Let's not worry about how[+] to get this "< 0" result for the moment
- Let's see the consequence
- Remember the "< 0" result

[+] Simply put, if it were $\oint \frac{\text{đ}Q}{T} > 0$, 2nd law will be violated.

D. Entropy change in irreversible changes

- What is the question?



involve (some) irreversible processes
(NOT all intermediate states are equilibrium states)
thus, can't draw path on indicator diagram

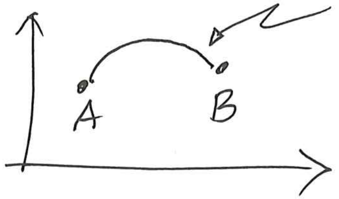
But $\Delta S = S_B - S_A$ (∵ S is state function)

There is some $\text{đ}Q$ involved in the process, and heat exchange is done at temp T of the external source [system may not have well-defined temp.]

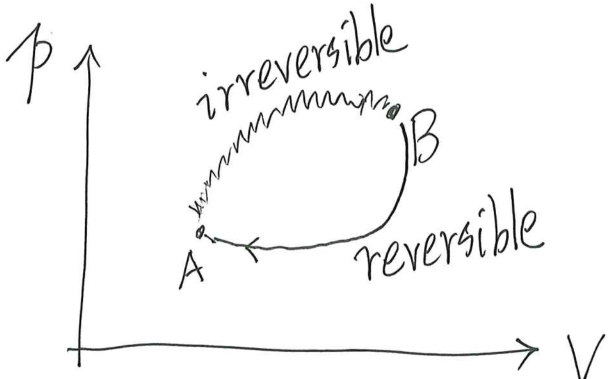
$$\Delta S \qquad\qquad \frac{\text{đ}Q}{T}$$

$$\boxed{\text{Are they related? If yes, how?}}$$

Know: $dS = \frac{\text{đ}Q_{rev}}{T}$ if



reversible path



irreversible cycle

Use Clausius Theorem

$$\oint_{\text{cycle}} \frac{đQ}{T_0} < 0$$

(Use T_0 to stress that it is <u>generally</u> not the system's temp, except for the reverible path)

$$\int_{A\,(\text{irrev})}^{B} \frac{đQ}{T_0} + \int_{B\,(\text{reversible})}^{A} \frac{đQ_{rev}}{T} < 0 \Rightarrow \int_{A\,(\text{irrev})}^{B} \frac{đQ}{T_0} < -\int_{B}^{A} \frac{đQ_{rev}}{T} = \int_{A}^{B} \frac{đQ_{rev}}{T} = S_B - S_A$$

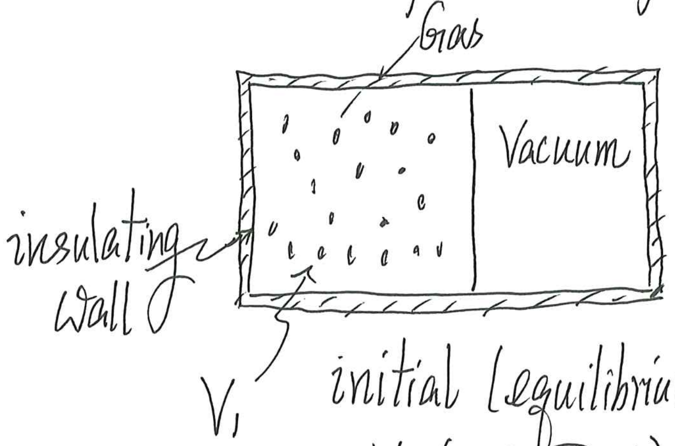
$$\therefore \boxed{S_B - S_A = \Delta S > \int_{A\,\text{irreversible}}^{B} \frac{đQ}{T_0}} \qquad (7)$$

This is the relation.

<u>Meaning</u>: You can calculate RHS alright, but it is <u>NOT</u> ΔS and it is less than ΔS

[e.g. even $đQ = 0$, irreversible process could have $\Delta S > 0$]
(free expansion of gas)

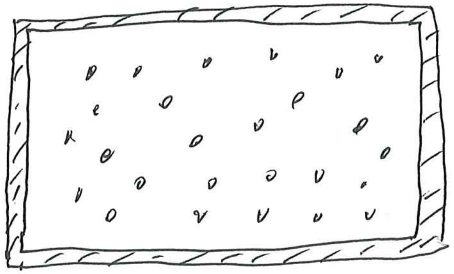
Free expansion of an ideal gas: $\text{đ}Q = 0$ but $\Delta S \neq 0$ example



Take Partition Away $\longrightarrow$

and wait!

[in between, go through states out of equilibrium]



initial (equilibrium)
V_1 (LHS Part), T_1

S_1

final (equilibrium)
V_2 (whole box), T_2

S_2

[Note: $\xrightarrow{\text{this way}}$ Naturally occurring $\underbrace{\underset{\text{by themselves}}{\xleftarrow{\text{gas back to } V_1}} \ \underline{\text{NOT}} \text{ happening}}_{\text{must } \underline{\text{have been}} \text{ banned by 2nd law}}$]

[irreversible!]

$\Delta S = S_2 - S_1$ is there!

But $W = 0$ (no work done against the vacuum)
$Q = 0$ [insulating walls]
$\Rightarrow \Delta U = 0 \Rightarrow U_1 = U_2 \Rightarrow T_1 = T_2$ (ideal gas)

- It is wrong to say $\Delta S = 0$ because $\text{đ}Q = 0$ (so $\frac{\text{đ}Q}{T} = 0$) in every bit of the expansion! Here, the process is irreversible.
- To relate $\underbrace{\Delta S}_{\text{it is there}}$ to $\frac{\text{đ}Q}{T}$, it is $\int_1^2 \frac{\text{đ}Q_{rev}}{T}$ (reversible path) for $\underbrace{\text{a reversible path}}_{\text{Pick a convenient reversible path}}$

[forget about the actual free expansion process]

Since T is kept constant,
isothermal (reversible) expansion is convenient!

We did Q going from V_1 to V_2 (Ch. III):

$$Q = RT\ln\left(\frac{V_2}{V_1}\right) \quad [1 \text{ mole}]$$

OR

$$Q = nRT\ln\left(\frac{V_2}{V_1}\right) = NkT\ln\left(\frac{V_2}{V_1}\right) \quad [n \text{ moles}, N \text{ atoms}]$$

$$\frac{Q}{T}(\text{from } 1 \rightarrow 2 \text{ states}) = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore \boxed{\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)} \qquad (8)$$

(ideal gas free expansion)

The result also illustrates for an irreversible process,

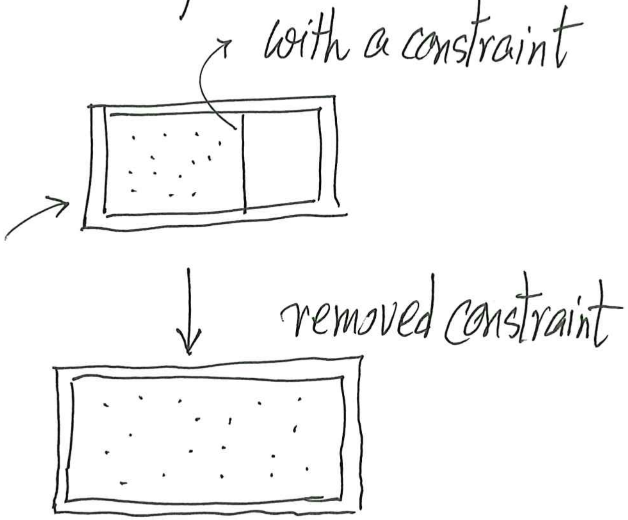
$$\Delta S \left(= nR \ln\left(\underbrace{\frac{V_2}{V_1}}\right)\right) > \int \frac{\text{đ}Q}{T} \left(= 0 \right)$$

in this example

$$V_2 > V_1$$

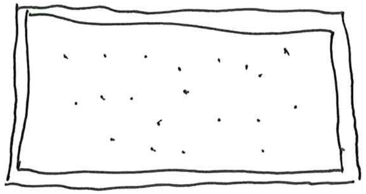
$$\ln\left(\frac{V_2}{V_1}\right) > 0$$

Remark: Here, also see that for an isolated system



$$\Delta S > 0$$

and at the end as



becomes equilibrium

S is a maximum.

(idea will be used / further illustrated in statistical mechanics)

Summary.

$$\underbrace{\frac{\text{đ}Q_{rev}}{T} \underset{\uparrow\,\text{def.}}{=} dS \quad ; \quad \frac{\text{đ}Q}{T} < dS \ (\text{irreversible})}$$

Put together

$$\boxed{dS \geqslant \frac{\text{đ}Q}{T} \qquad \text{for any infinitesimal change with the equal sign works for reversible change}} \qquad (9)$$

E. Principle of Increasing Entropy for a thermally isolated system

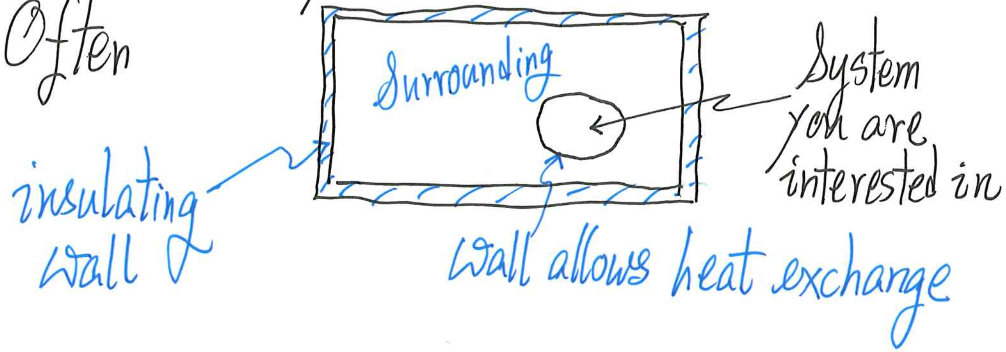
$$dS \geq \frac{\text{đ}Q}{T}$$ "=" sign for reversible change

For a thermally isolated system $\text{đ}Q = 0$

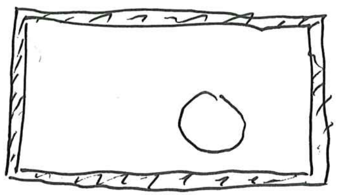
$$\therefore (dS)_{\text{thermally isolated}} \geq 0 \qquad (10)$$

For finite change $\Delta S = S_{\text{final}} - S_{\text{initial}} \geq 0$ (thermally isolated)

- Note "thermally isolated" condition
- Often



$\Delta S \geq 0$ applies to



(including the "surrounding")

$\Delta S \geq 0$ (thermally isolated)

↳ one-sided (meaning $\Delta S > 0$ process (thermally isolated)) will occur

[$\Delta S < 0$ banned]

$$\boxed{\text{For a thermally isolated system, } S \text{ evolves (increases) so that } S \to \underline{\text{maximum}} \text{ (}\underline{\text{approaches}}\text{ }\underline{\text{equilibrium}}\text{)}}$$

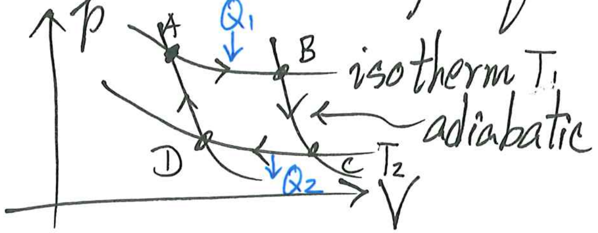
↑

This is useful in Statistical Mechanics.

F. Carnot cycle in Entropy-Temperature diagram

Previously, we only know P, V (T related by equation of state)

so Carnot cycle is

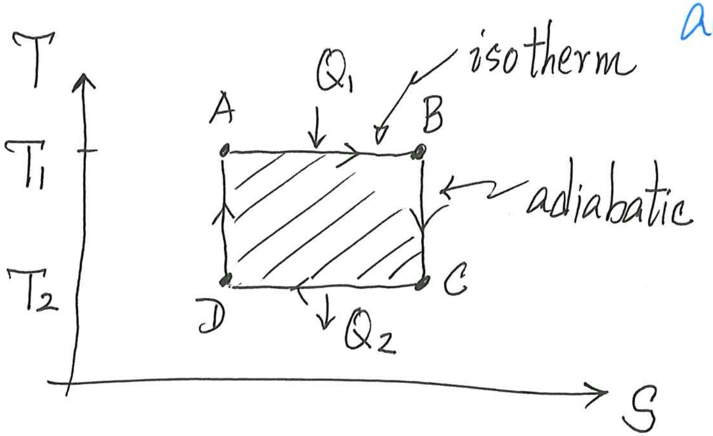


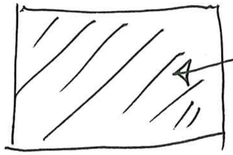
[reversible]

Equally well to use S-T

isotherms: constant T ⇒ lines ⊥ to T-axis

adiabatics: $dQ_{rev}=0$ ⇒ constant S ⇒ lines ⊥ to S-axis





Area = Net heat absorbed in a Carnot Cycle

$$\oint_{\text{cycle (reversible)}} T\,dS$$

G. Central (Fundamental) Equation of Thermodynamics : A Magical Moment

Let's put 1st law and 2nd law together

both reversible and irreversible processes

$$dU = \text{đ}Q + \text{đ}W$$ (1st law, always true, just balancing energies)

$$\text{đ}W = -p\,dV$$ (reversible infinitesimal processes)

$$\frac{dQ_{rev}}{T} = dS$$ (reversible infinitesimal processes)

$$\boxed{\begin{aligned} &\therefore\quad dU = T\,dS - p\,dV \quad \text{(reversible infinitesimal processes)} \\ &\text{OR}\quad T\,dS = dU + p\,dV \\ &\text{OR}\quad dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV \end{aligned}}$$

The magical moment

$$\underset{\uparrow}{dU} = \underset{\uparrow}{T}\,\underset{\uparrow}{dS} - \underset{\uparrow}{p}\,\underset{\uparrow}{dV}$$

They are all state functions, i.e. take on definite values given an equilibrium state

Meaning: Given two nearby equilibrium states

U, T, S, p, V (one point) $U+dU, T+dT, S+dS, p+dp, V+dV$ (another point)

$\boxed{\text{The quantities are related by } dU = TdS - pdV \quad \text{thermodynamics}}$

Regardless how the system is taken from one point to the other!

$dU = TdS - pdV$ (always true! Good for reversible and irreversible processes)

$$\boxed{dU = TdS - pdV \quad \text{OR} \quad TdS = dU + pdV} \quad \text{(always true)} \qquad (11)$$

Central (Fundamental) Equation of Thermodynamics

(The most important equation)

Remarks

- It is an identity (meaning: always true). Results derived from it are generally true.
- There may be other energy terms, e.g.

$$dU = TdS - pdV + \underbrace{\mu dN}_{\text{exchange of matter}} \quad \text{OR} \quad \boxed{TdS = dU + pdV - \mu dN} \qquad (12)$$

this is the equation connecting to Stat. Mech.

- For irreversible processes, while $dU = TdS - pdV$, it is not saying that "TdS" is $\text{đ}Q$ and $-pdV = \text{đ}W$ separately.

Take $\underset{\substack{\uparrow \\ \text{state function}}}{dS} = \frac{1}{T}\,dU + \frac{p}{T}\,dV$

Think partial derivatives, $S(U,V)$ [nice surface]

$$\therefore\ dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

thus

$$\boxed{\begin{aligned} \left(\frac{\partial S}{\partial U}\right)_V &= \frac{1}{T} \\ \left(\frac{\partial S}{\partial V}\right)_U &= \frac{p}{T} \end{aligned}} \quad (13)$$

(a way to define T from $\overbrace{S(U,V)}^{\text{this will be the 1st quantity to evaluate in stat. mech}}$)

Sense: $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$

→ "low temp" refers to rapid increase in S when U increases

→ "high temp" refers to little increase in S when U increases

H. Entropy of Classical Ideal Gas (from Thermodynamics[+])

$$T\,dS = dU + p\,dV$$

$$U_{\text{ideal gas}} = U(T) \text{ only}, \qquad C_V = \left(\frac{\text{đ}Q_{rev}}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} \quad (\because U(T)\text{ only})$$

$$\therefore\ dS = \frac{1}{T}C_V\,dT + \frac{p}{T}\,dV = \frac{3}{2}Nk\frac{dT}{T} + Nk\frac{dV}{V} \quad (\text{monatomic})$$

$$S = \frac{3}{2}Nk\ln T + Nk\ln V + S_0 \leftarrow \text{a constant}$$

$$= Nk\ln\left(T^{3/2}V\right) + S_0 \quad (14) \quad (\text{Done!})$$

[+] Statistical Mechanics can be applied to obtain $S(U,V)$ for an ideal gas.

To illustrate some properties further, let's absorb S_0 into

$$S = Nk\ln\left[\frac{T^{3/2}V}{C'(N)}\right] = Nk\ln\left[\frac{U^{3/2}V}{N^{3/2}C''(N)}\right] \qquad U=\frac{3}{2}NkT$$

constant not depending on T and V (could depend on N)

- S is an extensive quantity $\Rightarrow \underbrace{U\to\lambda U,\ V\to\lambda V,\ N\to\lambda N}_{S\to\lambda S}$ (scale system by λ)

$$\lambda Nk\ln\left[\frac{U^{3/2}}{N^{3/2}}\frac{V}{C''(N)}\right] \underset{?}{=} (\lambda N)k\ln\left[\frac{(\lambda U)^{3/2}}{(\lambda N)^{3/2}}\frac{\lambda V}{C''(\lambda N)}\right]$$

True if $C''(N) = cN$

another constant (doesn't depend on T, V, N)

$$\therefore S = Nk\ln\left[\left(\frac{U}{N}\right)^{3/2}\left(\frac{V}{N}\right)\frac{1}{c}\right] \quad \text{from thermodynamics} \qquad (15)$$

Remarks

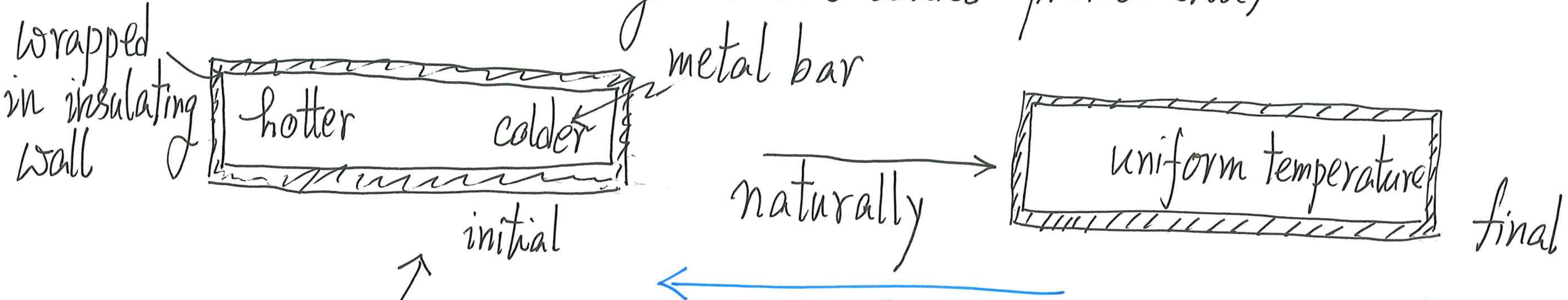
- Prefactor "Nk" [extensive, right unit for S]
- $\frac{U}{N} = \underbrace{\text{internal energy per particle}}_{\text{intensive}} \left(\frac{3}{2}kT\right)$; $\underbrace{\frac{V}{N} = \text{volume per particle}}_{\frac{N}{V} = \underbrace{\text{number density}}_{\text{intensive}}}$.
- Now we see $S(U, V, N)$

  try $\underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{\frac{1}{T}}$, $\underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{\frac{p}{T}}$, $\underbrace{\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{-\frac{\mu}{T}}$ (Central equation of thermodynamics)

  and see what shows up.

I. $\underline{\Delta S \geq 0}$ (thermally isolated) and $\Delta S > 0$ in irreversible process

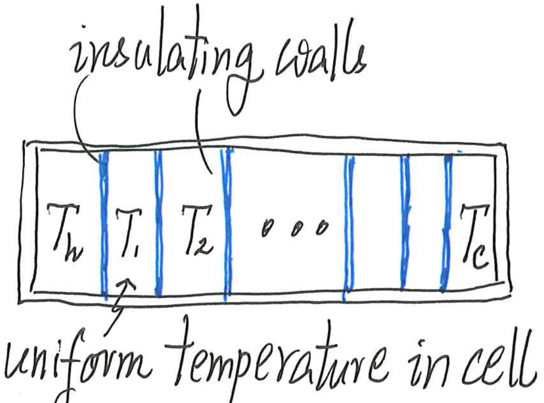
one-sided (distinguish one-sided phenomena)



Won't happen (use 2nd law to ban it)
(observation)

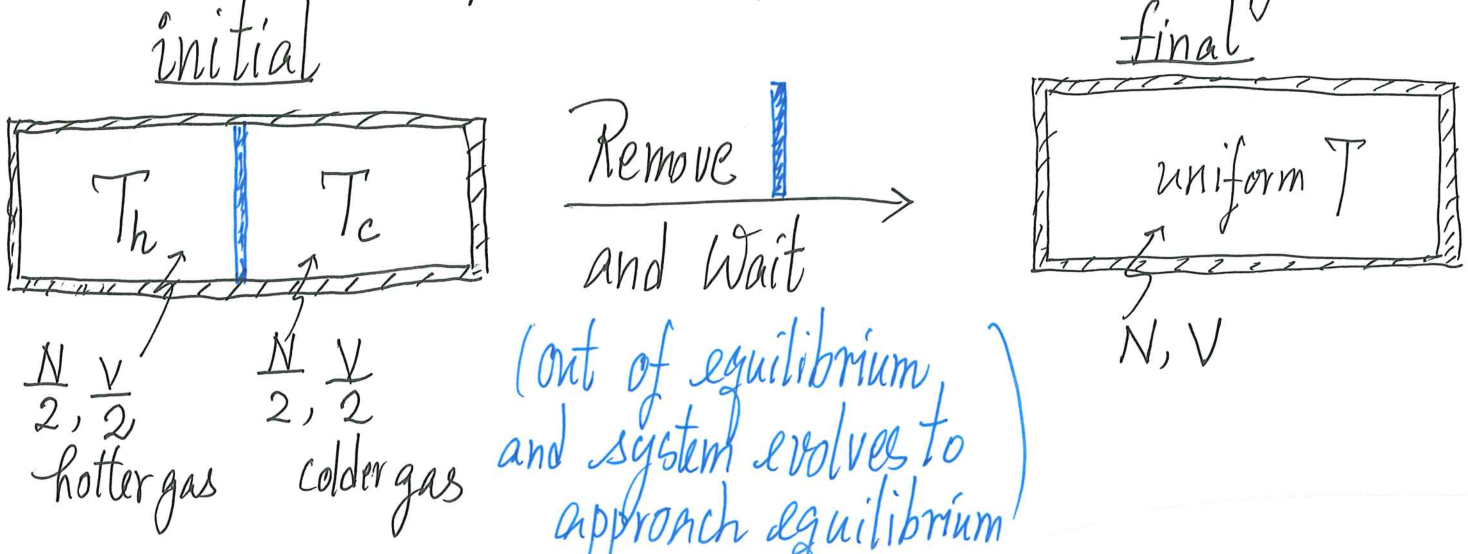
In principle, this is **NOT** a equilibrium state,
what do we meant by S_i?

Practically, consider "initial state" as



then we can talk about S_i!

To illustrate the point, simply consider ideal gases



(out of equilibrium, and system evolves to approach equilibrium) [one-sided]

By this device, the initial state becomes an equilibrium state

$$S_{\text{initial}} = \frac{N}{2} k \ln\left[\frac{T_h^{3/2}}{c}\left(\frac{V}{N}\right)\right] + \frac{N}{2} k \ln\left[\frac{T_c^{3/2}}{c}\frac{V}{N}\right]$$

$$= Nk \ln\left[\left(\frac{V}{N}\right)\frac{1}{c}\right] + \frac{N}{2} k \frac{3}{2} \ln\left[T_h \cdot T_c\right]$$

The final state is an equilibrium state

$$S_{\text{final}} = Nk \ln\left[\frac{\left(\frac{T_c+T_h}{2}\right)^{3/2}}{c}\frac{V}{N}\right]$$

$$= Nk \ln\left[\frac{V}{Nc}\right] + Nk \frac{3}{2} \ln\left[\left(\frac{T_c+T_h}{2}\right)\right]$$

Note that : $\left(\frac{T_c + T_h}{2}\right) > \sqrt{T_c \cdot T_h}$

$$(\because \ (T_h - T_c)^2 = T_h^2 + T_c^2 - 2T_hT_c = T_h^2 + 2T_hT_c + T_c^2 - 4T_hT_c$$
$$= (T_h + T_c)^2 - 4T_hT_c > 0$$
$$\Rightarrow \ \frac{T_h + T_c}{2} > \sqrt{T_hT_c}$$

$$\therefore \ S_f - S_i = Nk\frac{3}{2}\left\{\ln\left[\left(\frac{T_c + T_h}{2}\right)\right] - \ln\sqrt{T_cT_h}\right\} > 0$$ (explicit example)

(i) $\Delta S > 0$ in this naturally occuring irreversible process

(ii) the device of viewing an out-of-equilibrium state initially as an equilibrium state is often used to illustrate the point of $\Delta S > 0$ for naturally occuring processes [out of equilibrium towards equilibrium]

(iii) $S \rightarrow$ maximum when system becomes equilibrium

Summary

- $TdS = dU + pdV - \mu dN$ (identity)
- $dS > \frac{\bar{d}Q}{T}$ (one-sided, from 2nd law, for $\overbrace{\text{banning things}}^{\text{those not observed}}$ from happening)
- $S(U, V, N)$ and its derivatives
- Results from Central equation are generally true
- $dU = TdS - pdV + \mu dN$ will give useful results
- Legendre Transform from $U \rightarrow H, F, G$ and other useful results