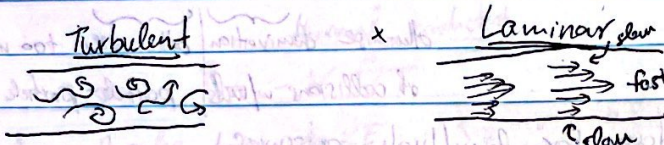


Transport and thermal diffusion

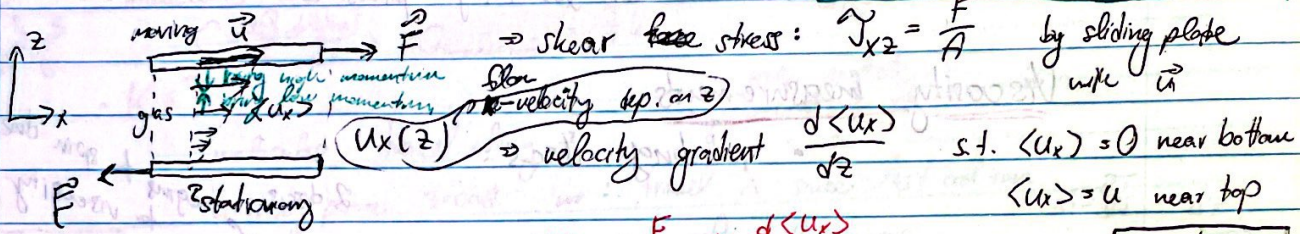
- Flows • non-equilibrium but steady state
- surroundings are time-dependent
- ↳ net moving ⇒ gradients, transport ↑

Transport properties in gases

① Viscosity = momentum transport : η = coeff. of viscosity
 [Pa.s] dynamic viscosity
 $= \left[\frac{N \cdot s}{m^2} \right]$



↳ ↑ η ⇒ further reach, easier to transfer momentum

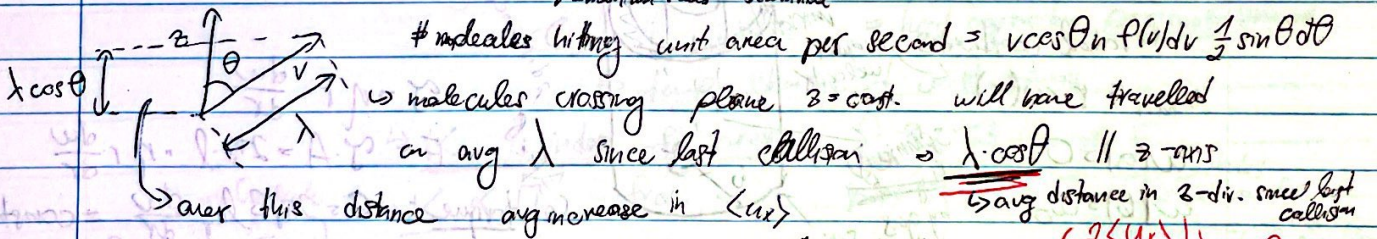


⇒ def. η : $\tau_{xz} = \frac{F}{A} = \eta \frac{d\langle u_x \rangle}{dz}$

• force = $\frac{dp}{dt}$ ⇒ momentum is transported through the fluid
 ⇒ transfer in -x direction

• τ_{xz} is equal to a flux of momentum (but ⊖ bc in opposite direction)

⇒ momentum flux $\Pi_{xz} = -\eta \frac{d\langle u_x \rangle}{dz}$



⇒ excess momentum in the x-direction = $-m \left(\frac{d\langle u_x \rangle}{dz} \right) \lambda \cos \theta$ per molecule

⇒ total x-momentum transported across unit area $\perp \hat{z}$ in unit time:

$\Pi_{xz} = \int_0^\pi \int_0^\pi v \cos \theta n f(v) dv \frac{1}{2} \sin \theta d\theta = \dots = \frac{1}{3} n m \lambda \langle v \rangle \left(\frac{d\langle u_x \rangle}{dz} \right)$

↳ particles can travel in both directions

$\eta = \frac{1}{3} n m \lambda \langle v \rangle$

$= \frac{1}{3} n m \lambda \sqrt{\frac{8k_B T}{\pi m}}$

$$\eta = \frac{1}{3} n m \lambda \langle v \rangle$$

η is indep. of pressure (and $n : \lambda \propto \frac{1}{n \sigma}$)
 \hookrightarrow cancels out

$\uparrow T \Rightarrow \downarrow \sigma$
 \Rightarrow particles appear smaller

$\hookrightarrow \eta \propto \sqrt{T}$ from $\langle v \rangle \propto \sqrt{T}$ \Rightarrow for gases: $\eta \uparrow$ with $\uparrow T$
 (vs. liquids: $\downarrow \eta$ w/ $\uparrow T$)

$$\eta = \frac{2}{3\pi d^2} \sqrt{\frac{mk_B T}{\pi}}$$

approximations for formula to hold: $L \gg \lambda \gg d$

size of container \gg molecular diameter
 otherwise domination of collisions w/ walls | otherwise too many particle-particle collisions

\hookrightarrow breaks down for low/high pressures

Viscosity measurements

rotating discs:

2 discs begins to spin due to viscosity of gas
 gas in between

fast spinning disc



see 9.4

more precisely \Rightarrow notice slightest movement of the disc

$$u_x(z) \rightarrow u_{tan}(r)$$

$u_{tan} = r \cdot \omega(r)$
 $\omega(a) = 0$
 $\omega(b) = \omega_0$



$$\tau = \eta r \frac{d\omega}{dr}$$

$$F = \tau \cdot A = 2\pi r \cdot l \cdot \eta r \frac{d\omega}{dr}$$

$$\tau \text{ torque: } G = 2\pi r^3 l \eta \frac{d\omega}{dr} = \text{const.}$$

\hookrightarrow equilibrium \Rightarrow

$$G \int_a^b \frac{1}{r^3} dr = 2\pi l \eta \int_0^{\omega_0} d\omega$$

$$\Rightarrow \frac{G}{2} \left(\frac{1}{a^2} - \frac{1}{b^2} \right) = 2\pi l \eta \omega_0$$

~~scribbles~~

$$\frac{du_{tan}}{dr} = \omega(r) + r \frac{d\omega}{dr}$$

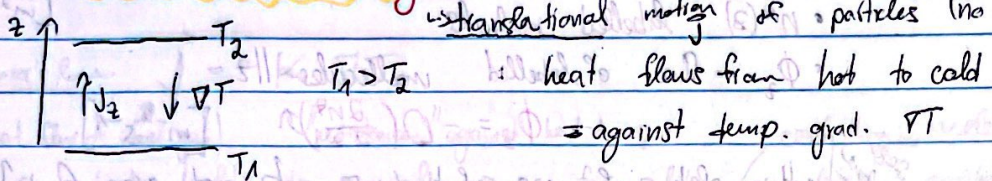
rigid system

$$\eta = \frac{G}{4\pi l \omega_0} \left(\frac{1}{a^2} - \frac{1}{b^2} \right)$$

$G = d\theta$
 torsion of pendulum \propto mass

$\frac{1}{2} k_B T$ per degree of freedom
 $U = \langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$

② Thermal conductivity = heat transport : K (③) ← $\{v_x, v_y, v_z\}$
 ↳ translational motion of particles (no rotation)



heat flux vector: \vec{J} - along direction of flow, mag. = heat energy flowing per unit time per unit area
 $J_z = -K \left(\frac{\partial T}{\partial z} \right)$ assuming const. gradient = steady state
 ↳ heat flows "downhill"

thermal conductivity

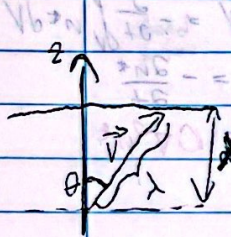
gen: $\vec{J} = -K \vec{\nabla} T$

monatomic real gas

• molecules has KE: $\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$ ↳ to increase T ↳ increase mean kinetic energy

$C = \frac{dQ}{dT} = \frac{d(\frac{3}{2} k_B T)}{dT} \Rightarrow C_{molecule} = \frac{3}{2} k_B$

• $K = ?$



- molecules travel along \hat{z} each particle transports E between collisions

- crossing plane z=const. \Rightarrow travel λ since last collision

$\Rightarrow \lambda \cos \theta$ || z-axis $\Delta T = \frac{\partial T}{\partial z} \cdot \Delta z$

\Rightarrow bring deficit of thermal E: $C_{molecule} \times \Delta T = C_{molecule} \frac{\partial T}{\partial z} \lambda \cos \theta$

\Rightarrow total thermal energy transported across unit area in unit time = heat flux

$J_z = \int_0^\pi \int_0^{2\pi} (-C_{molecule} \frac{\partial T}{\partial z} \lambda \cos \theta) v \cos \theta n f(v) \frac{1}{2} \sin \theta d\theta d\phi = -\frac{1}{3} n C_{molecule} \lambda \langle v \rangle \frac{\partial T}{\partial z}$

$\Rightarrow K = \frac{1}{3} C_v \lambda \langle v \rangle$

$\hookrightarrow C_v = n C_{molecule} =$ heat capacity per unit volume

↳ temp. change at const. volume

↳ K is indep. of pressure ($\lambda \propto \frac{1}{\sqrt{n\sigma}}$) and n

$C_v = n C_{molecule}$

$\hookrightarrow K \propto \sqrt{T}$ from $\langle v \rangle$, $K \propto \sqrt{m}$ ↳ heavy particles small K ↳ for thermal insulators, use heavy particles (A)

$\lambda = \frac{1}{\sqrt{n\sigma}}$
 $\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$

$K = \frac{2}{3\pi^{3/2}} C_{molecule} \left(\frac{k_B T}{\pi m} \right)^{1/2}$

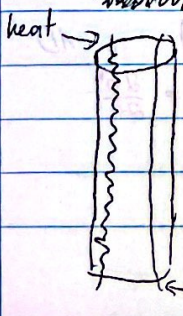
↳ to hold: $L \gg \lambda \gg d$

$\frac{K}{n} = \frac{C_{molecule}}{n} = C_v \Rightarrow K = C_v \eta$

Pirani (pressure meter)

↳ for $\downarrow p$ where $\lambda \sim L$ ↳ surroundings

$\Rightarrow K$ is depend. on R



• some heat lost but \rightarrow const.

• keep T const., some heat lost to molecules collisions

• generate heat at rate Q [W/m]; radial flux of heat $\equiv J_r = \frac{Q}{2\pi r L}$

$\Rightarrow Q = \int_0^L \int_a^R 2\pi r J_r = -2\pi r K \left(\frac{\partial T}{\partial r} \right)$

$Q \ln\left(\frac{R}{a}\right) = -2\pi K L (T_B - T_A)$ ↳ circumference of circle

$\Rightarrow K = \frac{Q \ln\left(\frac{R}{a}\right)}{2\pi L (T_B - T_A)}$

③ Diffusion = particle transport : D = coeff. of diffusion [m^2/s]

• $n^*(z)$ labelled molecules

• ϕ_z = flux of labelled molecules $\parallel z$

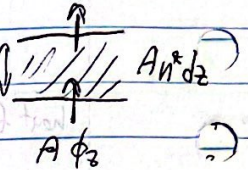
$$\phi_z = -D \left(\frac{\partial n^*}{\partial z} \right) \quad [m^{-2} s^{-1}]$$

$$A \left[\phi_z + \frac{\partial \phi_z}{\partial z} dz \right]$$

• thin slab of gas of thickness dz and area $A dz$

⇒ flux in: $A \phi_z$

⇒ flux out: $A \left(\phi_z + \frac{\partial \phi_z}{\partial z} dz \right)$



difference balanced by time-dep. changes in number of labelled particles in region

$\frac{2n^*(z)}{2z}$ explicitly contains surface numbers

$$\frac{1}{2} n v \cos \theta f(v) \sin \theta$$

$$\Rightarrow \frac{1}{2} v \cos \theta f(v) \sin \theta$$

no need to include n again because it's in $\frac{\partial n^*}{\partial z}$

$$\Rightarrow \frac{\partial}{\partial t} (n^* A dz) = -A \frac{\partial \phi_z}{\partial z} dz$$

$$\Rightarrow \frac{\partial n^*}{\partial t} = -\frac{\partial \phi_z}{\partial z} = D \frac{\partial^2 n^*}{\partial z^2}$$

diffusion equation

$$\oint \vec{\phi} \cdot d\vec{S} = -\frac{\partial}{\partial t} \int n^* dV$$

$$\nabla \cdot \vec{\phi} = -\frac{\partial n^*}{\partial t}$$

$$\Rightarrow \frac{\partial n^*}{\partial t} = D \nabla^2 n^*$$

the excess of molecules hitting unit area per second is:

$$\phi_z = \int_0^\infty \int \int v_x \cos \theta f(v) \frac{1}{2} \sin \theta \left(\frac{\partial n^*}{\partial z} \right) \cos \theta$$

$$= -\frac{4}{3} \lambda \langle v \rangle \frac{\partial n^*}{\partial z}$$

$$\Rightarrow D = \frac{1}{3} \lambda \langle v \rangle$$

$$\lambda \propto \rho^{-1}$$

$$\lambda \propto T^{3/2}$$

$$\rho = n k_B T, \langle v \rangle \propto T^{1/2}$$

$$\lambda \propto \eta$$

$$D = \frac{2}{3 \pi n d^2} \sqrt{\frac{k_B T}{m \pi}} = \frac{2}{3 \pi d^2} \frac{k_B T}{\rho} \sqrt{\frac{k_B T}{\pi m}}$$

diffusion of 2 types of molecules:

$$D_{12} = \frac{2}{3 \pi n \left[\frac{1}{2} (d_1 + d_2) \right]^2} \sqrt{\frac{k_B T (m_1 + m_2)}{\pi m_1 m_2}} = \frac{1}{\text{reduced mass}} = \frac{m_1 m_2}{m_1 + m_2}$$

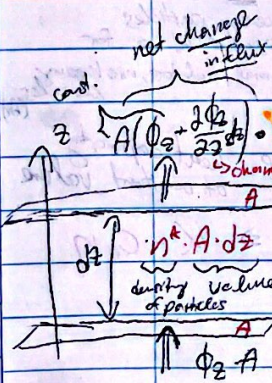
Time dependence - if gradients are time-dependent

$$-A \frac{\partial \phi_z}{\partial z} dz = \frac{\partial}{\partial t} (n^* A dz)$$

change in flux $\phi_z = -D \frac{\partial n^*}{\partial z}$ change of number of particles

$$\Rightarrow D \frac{\partial^2 n^*}{\partial z^2} = \frac{\partial n^*}{\partial t} \quad (A dz \text{ cancels out})$$

$$\text{or } 3D: \nabla^2 n^* = \frac{\partial n^*}{\partial t}$$



Thermal diffusion equation

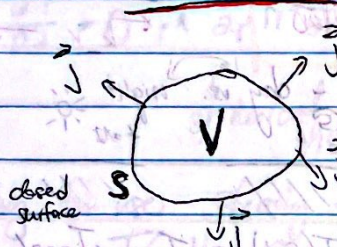
↳ Fourier's law $\vec{J} = -K \nabla T$

(heat flux of ideal gas) ↳ "resistance" against heat transport
 but holds in general ⇒ even for solids: ↳ conducting: ~ electron gas
 ↳ insulating: ~ phonon gas
 ↳ not real particles but model
 ↳ vibration of lattice

↳ Fick's law: $\vec{J} = -D \nabla n$

↳ "resistance" against particle transport - holds generally

Time-dependence?



flux = δE in the volume

$\vec{J} = -K \nabla T(x, y, z)$
 ↳ scalar field

$\vec{J}(x, y, z)$ ⇒ vector field

heat flow changes thermal energy in V

total heat flow through S: $\oint \vec{J} \cdot d\vec{S}$

↳ changes thermal energy in V: $C = \frac{dQ}{dT}$

assume at $T=0K \Rightarrow Q=0$

$\Rightarrow Q = CT$

↳ heat capacity per unit volume
 $C = \rho c$

continuity equation ⇒ total thermal energy in V: $\int CT dV$

↳ density
 ↳ specific heat capacity

$\oint \vec{J} \cdot d\vec{S} = -\frac{\partial}{\partial t} \int CT dV$

heat flow through S change in thermal energy

$\oint \vec{\nabla} \cdot \vec{J} dV = -\frac{\partial}{\partial t} \int CT dV$
 $\Rightarrow \vec{\nabla} \cdot \vec{J} = -C \frac{\partial T}{\partial t}$

$K \nabla^2 T = C \frac{\partial T}{\partial t}$ $T(x, y, z, t)$

generally true for all kinds of materials
 (bc Fourier's law holds generally)

Laplace operator ↳ $D = \frac{K}{C}$ = thermal diffusivity
 = constant

$\Rightarrow \nabla^2 T = \frac{\partial T}{\partial t}$



thermal diffusion in 1D : $\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2}$, $D = \frac{k}{c}$
 ↳ wave equation : $T(x,t) = A e^{i(kx - \omega t)}$

$\frac{\partial}{\partial t} (A e^{i(kx - \omega t)}) = D \frac{\partial^2}{\partial x^2} (A e^{i(kx - \omega t)})$
 $e^{ikx} = \cos x + i \sin x$ wavenumber $k = \frac{2\pi}{\lambda}$

$-i\omega A = D (-k^2) A$
 $i\omega = D k^2 \Rightarrow k^2 = \frac{i\omega}{D} \Rightarrow k = \pm \sqrt{\frac{i\omega}{D}} = \pm (1+i) \sqrt{\frac{\omega}{2D}}$

spatial part: $e^{ikx} = e^{\pm (1+i) \sqrt{\frac{\omega}{2D}} x} = e^{\pm (i-1) \sqrt{\frac{\omega}{2D}} x} \frac{1+i}{\sqrt{2}}$
 ↳ $k_+ \rightarrow \infty$ as $x \rightarrow \infty$
 ↳ $k_- \rightarrow \infty$ as $x \rightarrow -\infty$
 } converging sol. choose based on axis definition

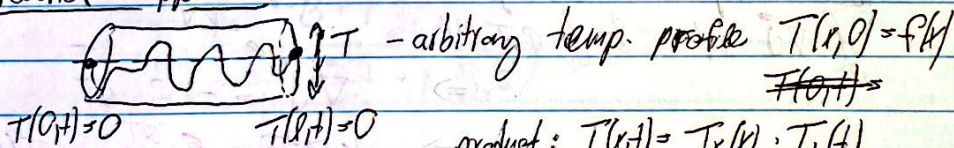
for (k_+) general sol: $T(x,t) = \int_{-\infty}^{\infty} A(\omega) e^{-i\omega t} e^{(i-1) \sqrt{\frac{\omega}{2D}} x} dx$
 ↳ $k_- \checkmark \rightarrow k_+ \checkmark$

for periodic heat development - day vs. night
 $x=0$ $t=0$ $t=1/2$ 


$T(x,t) = T_0 + \frac{\Delta T}{2} \left[e^{-i\omega t} e^{(i-1) \sqrt{\frac{\omega}{2D}} x} + e^{i\omega t} e^{(i-1) \sqrt{\frac{\omega}{2D}} x} \right]$
 ↳ as $\omega \rightarrow 0$ $T_0 + \Delta T \frac{e^{i\omega t} + e^{-i\omega t}}{2}$
 ↳ $A(0) = T_0$ $\left. \begin{array}{l} \text{freq. indep.} \\ \text{temp. (off-set)} \end{array} \right\} A(\omega) = \frac{\Delta T}{2}$

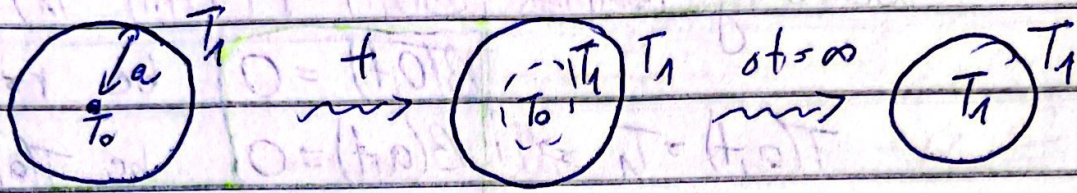
$T(x,t) = T_0 + \frac{\Delta T}{2} e^{-\sqrt{\frac{\omega}{2D}} x} \cos(\omega t - \sqrt{\frac{\omega}{2D}} x)$
 $= T_0 + \frac{\Delta T}{2} e^{-\frac{x}{\delta}} \cos(\omega t - \frac{x}{\delta})$
 $\delta = \sqrt{\frac{2D}{\omega}}$... skin depth
 ↳ describes the depth where change in T when is decreased to $\frac{1}{e} \approx 37\%$

Fourier's approach



product: $T(x,t) = T_x(x) \cdot T_t(t)$
 $\frac{D}{T_x(x)} \frac{\partial^2 T_x}{\partial x^2} = \frac{1}{T_t(t)} \frac{\partial T_t}{\partial t} = \text{const.}$
 $\Rightarrow \frac{\partial T_t}{\partial t} \propto T_t \Rightarrow T_t \propto e^{\pm t}$ \oplus diverges for $t > 0$
 $\frac{\partial^2 T_x}{\partial x^2} \propto T_x \Rightarrow T_x \propto \sin(\omega t)$
 $\Rightarrow T(x,t) = \sum_n D_n \sin(n\pi x) e^{-b^n t}$ ~ Fourier series
 ↳ x-dep.

★ Cooking of Spherical Chicken



$t=0$

$$\frac{\partial T}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \neq 0$$

not steady-state

↓ spherical symmetry

↳ try to use steady-state solution:

$$T(r,t) = A + \frac{B(r,t)}{r} \quad ; \quad A = T_1$$

$$\Rightarrow B(r,t) = r [T(r,t) - T_1]$$

$$\left\{ \begin{array}{l} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial B}{\partial t} \\ \frac{\partial T}{\partial r} = -\frac{B}{r^2} + \frac{1}{r} \frac{\partial B}{\partial r} \end{array} \right.$$

↳ into radial eq.

$$\frac{1}{r} \frac{\partial B}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \left(-\frac{B}{r^2} + \frac{1}{r} \frac{\partial B}{\partial r} \right) \right)$$

$$\frac{\partial B}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(-B + r \frac{\partial B}{\partial r} \right)$$

$$\frac{\partial B}{\partial t} = D \frac{1}{r} \left(-\frac{\partial B}{\partial r} + \frac{\partial B}{\partial r} + r \frac{\partial^2 B}{\partial r^2} \right)$$

$$\frac{\partial B}{\partial t} = D \frac{1}{r} \left(r \frac{\partial^2 B}{\partial r^2} \right)$$

$$\Rightarrow \boxed{\frac{\partial B}{\partial t} = D \frac{\partial^2 B}{\partial r^2}}$$

1-D thermal diffusion equation

↳ we know how to solve

Fourier's approach:

boundary conditions: $B(r,t) = r(T(r,t) - T_1)$

$$B(0,t) = 0 \quad \text{bc } r=0$$

$$T(a,t) = T_1 \Rightarrow B(a,t) = 0 \quad \text{bc } T(a,t) = T_1$$

$$\text{and } B(r,0) = r(T_0 - T_1)$$

try: $B(r,t) = \sin(kr)e^{-i\omega t}$

$$\Rightarrow i\omega = Dk^2$$

$$B(0,t) = B(a,t) = 0 \Rightarrow \sin(ka) = 0$$

$$ka = n\pi$$

$$k = \frac{n\pi}{a}$$

$$\Rightarrow i\omega = D\left(\frac{n\pi}{a}\right)^2$$

$$\Rightarrow B(r,t) = \sum_n A_n \sin\left(\frac{n\pi r}{a}\right) e^{-D\left(\frac{n\pi}{a}\right)^2 t}$$

from $B(r,0) = r(T_0 - T_1) \Rightarrow 1$ at $t=0$

$$\Rightarrow \sum_n A_n \sin\left(\frac{n\pi r}{a}\right) = r(T_0 - T_1)$$

Fourier series for $f \Rightarrow A_n = \frac{2a}{n\pi} (T_1 - T_0) (-1)^n$

$$\Rightarrow T(r,t) = T_1 + \frac{2a}{\pi} (T_1 - T_0) \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \frac{1}{r} \sin\left(\frac{n\pi}{a} r\right) e^{-D\left(\frac{n\pi}{a}\right)^2 t}$$

we are interested in center $\Rightarrow r \rightarrow 0 \Rightarrow \sin(r) \approx r$

$$\Rightarrow T \approx T_1 + \frac{2a}{\pi} (T_1 - T_0) \frac{n\pi}{a} \frac{r}{r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} e^{-D\left(\frac{n\pi}{a}\right)^2 t}$$

$$\Rightarrow T(r,t) \underset{r \rightarrow 0}{\approx} T_1 + 2(T_1 - T_0) \sum_{n=1}^{\infty} (-1)^n e^{-D\left(\frac{n\pi}{a}\right)^2 t}$$

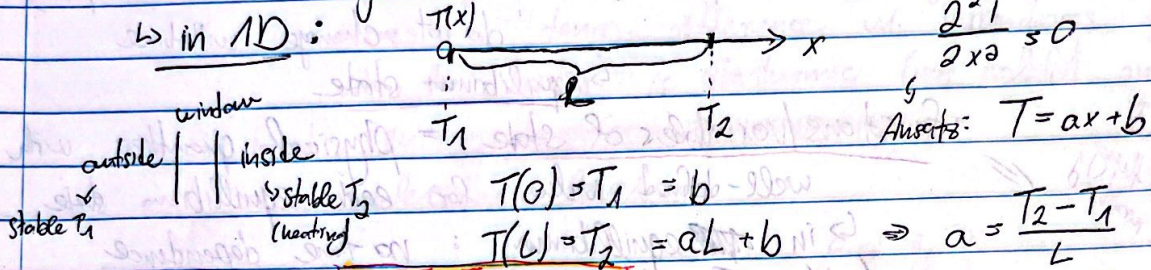
\hookrightarrow for long $t \approx \left(\geq \frac{a^2}{D\pi^2}\right) \Rightarrow$ only $n=1$ matters (is not negligible)

$$T(0,t) \approx T_1 - 2(T_1 - T_0) e^{-D\left(\frac{\pi}{a}\right)^2 t} \quad \text{for } t \gg \frac{a^2}{D\pi^2}$$

Steady state: $\frac{\partial T}{\partial t} = 0 \Rightarrow \frac{\partial^2 T}{\partial x^2} = 0 \propto \nabla^2 T = 0$

↳ system doesn't change with time anymore

↳ in 1D:



↳ $T = \frac{T_2 - T_1}{L} x + T_1$

• heat flux

$J_x = -\kappa \frac{\partial T}{\partial x} = -\left(\frac{\kappa}{L}\right) (T_2 - T_1)$

↳ energy loss through window

↳ per unit area: $J = [W \cdot m^{-2}] = [m^{-2} \cdot s^{-1} \cdot K]$

↳ Spherical symmetry $\nabla^2 T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin^2 \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2}$

↳ if system is spherically symmetric
 ⇒ no ϕ, θ dependence

⇒ simplify to: $\frac{1}{r^2} \frac{\partial T}{\partial r} = \nabla^2 T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right)$

★ Steady state in radial

$\frac{\partial T}{\partial t} = 0 \Rightarrow \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = 0$

⇒ $T = \text{const. in } r = A$

$\frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = 0 \Rightarrow r^2 \frac{\partial T}{\partial r} = \text{const.} \Rightarrow T = \frac{B}{r}$

⇒ $T(r) = A + \frac{B}{r}$

Heat equation with source

earlier: $\nabla \cdot \vec{J} = -C \frac{\partial T}{\partial t} \Rightarrow \vec{J} = -K \nabla T$

now: $\nabla \cdot \vec{J} = -C \frac{\partial T}{\partial t} + H$

↳ heat production rate $[W \cdot m^{-3}]$

$-K \nabla^2 T = -C \frac{\partial T}{\partial t} + H$

↳ ⊕ heating
 ↳ ⊖ cooling

$\frac{\partial T}{\partial t} = 0 \Rightarrow \nabla^2 T = -\frac{H}{C}$

1st Law

~~Thermodynamics~~ Energy

• thermal equilibrium: macroscopic observables (p, T) do not change with time

↳ equilibrium state

• functions/variables of state = physical quantities with well-defined value for each equilibrium state

↳ in ~~state~~ equilibrium: no time dependence

✓ V, p, T, U

✗ position of concrete particle, total work done on system, heat put into system

↳ state described by $\vec{x} = (x_1, x_2, \dots)$

↳ function of state: $f(\vec{x})$

$$\Delta f = \int_{\vec{x}_i}^{\vec{x}_f} df = f(\vec{x}_f) - f(\vec{x}_i)$$

↳ path indep.

total differential:

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots + \frac{\partial f}{\partial x_n} dx_n$$

exact differential.

↳ only depends on endpoints

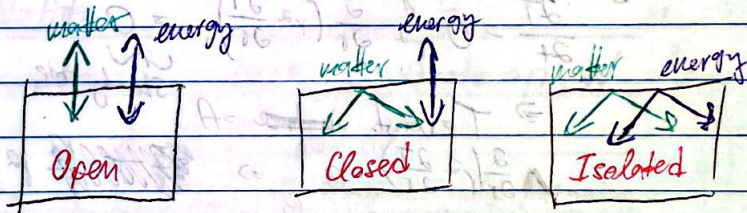
vs. inexact differential - not function of state

• extensive - depends on system size (U, V, m)

• intensive - indep. of size (T, p, ρ)

functions of state

System S:



but indicate the constant variable

↳ bc equations of state, relating the variables

$$Vp = nRT \Rightarrow p \text{ depends on } V \text{ and } T$$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

What is work?

$$W = \vec{F} \cdot \vec{s}$$

$$\Rightarrow dW = \vec{F} \cdot d\vec{s}$$

What is energy?

$E =$ capacity to do work

⇒ when work is done on isolated system

⇒ the system's capacity to do work increases

≡ energy

⇒ when system does work, its energy is reduced

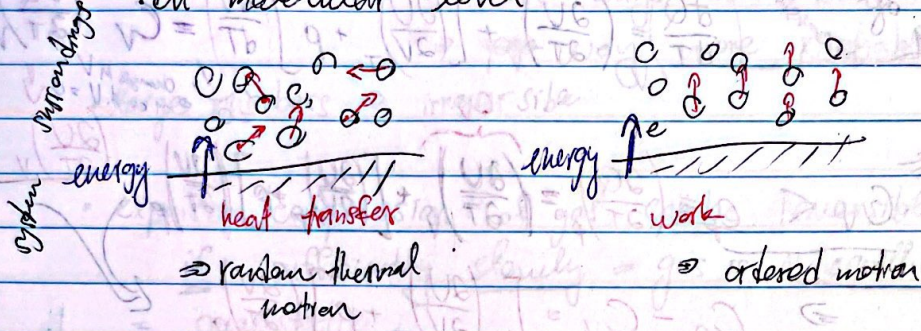
⇒ can do less work

What is heat?

- can change the energy of a system, when there's a temp. difference w/ surroundings and when the border is diathermic (not isolated system)

↳ heat = energy transfer = process

• on molecular level



First law of thermodynamic:

Energy is conserved and heat and work are both forms of energy.

- system has internal energy U = sum of energy of all internal degrees of freedom of the system
↳ function of state

↳ can be changed by heat (Q) or work (W)

↳ not functions of state

↳ concern the manner in which energy is delivered

↳ after delivery, we don't know anything about

$$\Delta U = \Delta Q + \Delta W$$

ΔQ : heat supplied to system
 ΔW : work done on system

⊕ for adding to system

⊖ for taking from system

- for thermally isolated ($\Delta Q = 0$) $\Rightarrow \Delta U = \Delta W$

$$dU = \delta Q + \delta W$$

↳ inexact differentials

$$\delta W = F dx \text{ for wire}$$

$$= pA dx = -p dV$$

↳ compressing gas

$$\delta W = -p dV$$

↳ when system is compressed \Rightarrow positive work is done $\Rightarrow U$ increases

Heat capacity $U = U(V, T)$ exact differential

Heat capacity
 $U = U(V, T)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dU = \delta Q + \delta W = \delta Q - p dV \Rightarrow \delta Q = dU + p dV$$

assuming only expansion work

generally for const. V

$$\left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{dT}\right)_V = C_V \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

change in V at const. V = 0

$C_p \Rightarrow$ expanding
 \Rightarrow need to also do work on surroundings while heating up

$$C_V < C_p \equiv \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

$\left(\frac{\partial U}{\partial T}\right)_V = C_V$ JK⁻¹ mol⁻¹

$$\Rightarrow C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

$$c_v = \frac{C_V}{M}, \quad c_p = \frac{C_p}{M}$$

adiabatic index $\gamma = \frac{C_p}{C_V}$

$$dU = C_V dT$$

★ monoatomic gas: $U = \frac{3}{2} RT$ per mole \Rightarrow only function of T

for ideal gas $\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$

$pV = RT$ for $n=1$
 $\Rightarrow V = \frac{RT}{p}$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$$

$$\Rightarrow C_p - C_V = [0 + p] \frac{R}{p} = R \text{ per mole}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} R \text{ per mole}$$

$R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$

$U = \frac{3}{2} RT$
 $C_p = C_V + R = \frac{5}{2} R \text{ per mole}$

★ for diatomic ideal gas (O_2, H_2, \dots)
 $\cdot C_V$ is temp. dep. \Rightarrow able to rotate, vibrate

$C_V = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow dU = C_V dT$ at const. V

$\Delta U = \int_{T_1}^{T_2} C_V dT = C_V (T_2 - T_1)$ if C_V is not (too) temperature dep.

ans

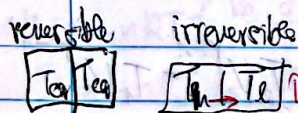
Isothermal & adiabatic processes

- assuming expansions are reversible

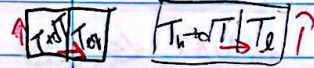
Reversibility of processes

- in nature after energy \rightarrow heat \rightarrow dissipated into the environment \rightarrow many more ways than in environment than in system \rightarrow way more probable
- large numbers \Rightarrow irreversible
- expansion/compression of gas can be reversible if sufficiently slowly = gas is in equilibrium whole time = quasistatic

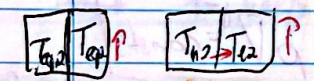
f doesn't start in equil. \Rightarrow irreversible



\rightarrow almost in completely unchanging static equilibrium
 \rightarrow heat can still be absorbed/emitted and be reversible (but no friction!)



irreversible: non-zero change made to system \Rightarrow not equilibrium
 reversible: infinitesimally small changes



\rightarrow possible to run in reverse

$$dW = -pdV$$

$$\Delta W = \int_{V_1}^{V_2} -pdV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$\Delta T = 0$ Isothermal expansion of ideal gas

$$dU = C_V dT \Rightarrow \Delta U = 0 \Rightarrow dU = 0$$

$$\Rightarrow dW = -dQ$$

for reversible, $-pdV$

\Rightarrow expansion of 1 mole from V_1 to V_2 at const. T:

$$\Delta Q = \int dQ = - \int dW = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \Delta Q = RT \ln\left(\frac{V_2}{V_1}\right)$$

expansion: $V_2 > V_1 \Rightarrow \Delta Q > 0, \Delta U = 0$

$\uparrow U = \downarrow p$ = energy density

$\delta Q = 0$

Adiabatic expansion of an ideal gas

- adiathermal = "without flow of heat"
- system w/ adiaathermal walls = thermally isolated
- adiabatic = adiathermal & reversible

$\delta Q = 0 \Rightarrow dU = \delta W$

$C_V dT = p dV = -\frac{RT}{V} dV$

$\Rightarrow \int_{T_1}^{T_2} C_V dT = -R \int_{V_1}^{V_2} \frac{dV}{V}$

$\Rightarrow \ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_V} \ln\left(\frac{V_2}{V_1}\right)$

$C_p = C_V + R$

$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$

$\Rightarrow -\frac{R}{C_V} = 1 - \gamma$

$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_V}}\right)$

$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma} \Rightarrow \frac{T_2}{T_1} \frac{V_2^{\gamma-1}}{V_1^{\gamma-1}} = 1 \Rightarrow T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$

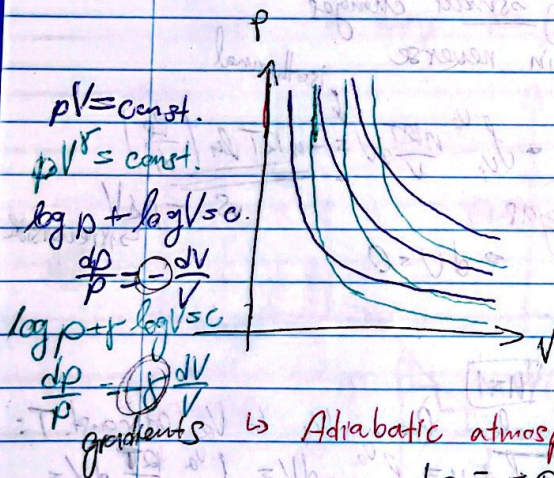
$\Rightarrow TV^{\gamma-1} = \text{const.}$

$pV^\gamma T \Rightarrow p \propto \frac{1}{V} \propto V^{-1}$

$TV^{\gamma-1} = T \frac{V^\gamma}{V} = \left(\frac{p}{V}\right) V^\gamma$

$\Rightarrow pV^\gamma = \text{const.}$

$V \propto \frac{1}{p} \Rightarrow p \left(\frac{1}{p}\right)^\gamma = \text{const.} = T^\gamma p^{1-\gamma} = \text{const.}$



isotherms & adiabats → adiabats have steeper gradient than isotherms everywhere

Adiabatic atmosphere

$dp = -\rho g dz$ = additional pressure due to thickness dz

$\rho = \frac{m}{V} = \frac{m}{k_B T}$ mass of atmosphere w/ density ρ

$\Rightarrow \frac{dp}{dz} = -\frac{g m \rho}{k_B T} \Rightarrow T \frac{dp}{p} = -\frac{m g}{k_B} dz$ isolated

• suppose each parcel of air doesn't exchange heat with surroundings
 ⇒ rising parcel of air expands adiabatically

$T^\gamma p^{1-\gamma} = \text{const}$

$(1-\gamma) \frac{dp}{p} + \gamma \frac{dT}{T} = 0$

$T \frac{dp}{p} = -\gamma dT \frac{1}{1-\gamma}$

$-\gamma \frac{dT}{dz} = -\frac{m g}{k_B} (1-\gamma)$

$\left(\frac{dT}{dz}\right) = -\frac{m g}{k_B} \left(\frac{\gamma-1}{\gamma}\right)$

$R = \frac{N_A k_B}{C_p}$

$\frac{dT}{dz} = -\frac{m g N_A}{C_p}$

$\Rightarrow \frac{dT}{dz} = -\frac{M g}{C_p}$

adiabatic lapse rate

* Reversible vs. Irreversible

$$n = 1 \text{ mol}$$

$$T = 20^\circ\text{C}$$

$$V_i = 10 \text{ l} = 10 \text{ dm}^3$$

$$V_f = 30 \text{ l} = 30 \text{ dm}^3$$

$$pV = nRT$$

• irreversible: $p_{\text{ex}} = p_{\text{e}}$

$$p_{\text{e}} V_{\text{e}} = nRT$$

$$p_{\text{e}} = \frac{nRT}{V_{\text{e}}} = 0.9 \text{ bar}$$

$$\Delta W_s = p_{\text{ex}} (V_{\text{e}} - V_i) = \underline{\underline{-1.62 \text{ kJ}}}$$

gas does work

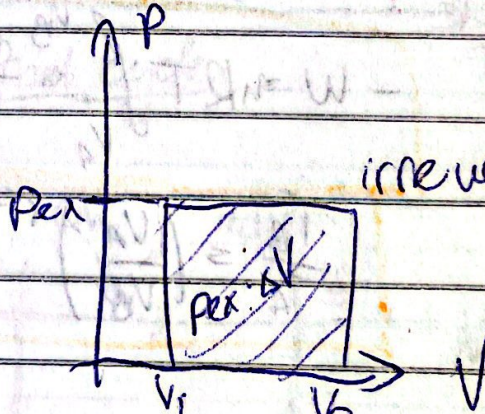
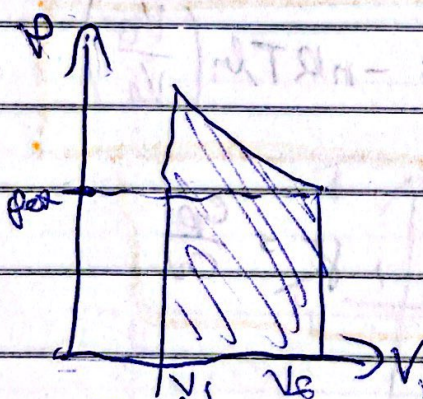
• reversible

$$\Delta W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} =$$

$$= -nRT \ln\left(\frac{V_f}{V_i}\right) =$$

$$= -1.8 \cdot 8.314 \ln(3) = \underline{\underline{-2.68 \text{ kJ}}}$$

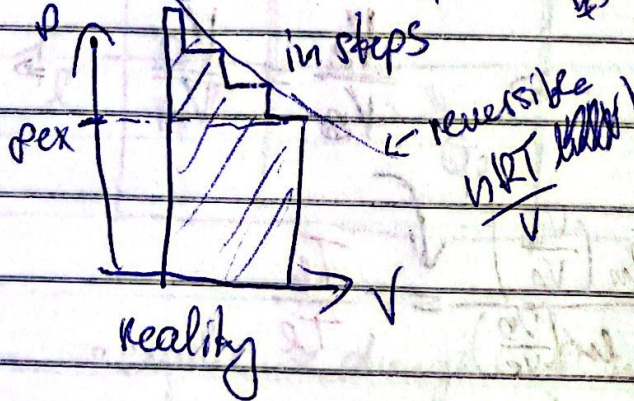
$\Delta W_{\text{rev}} \Rightarrow \Delta W_{\text{irr}}$ but we need to provide heat to keep temperature const.



ideal reversible

in steps

$t \rightarrow \infty$



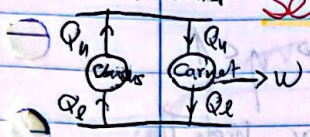
reversible $\frac{nRT}{V}$

2nd Law of Thermodynamics

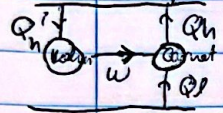
Heat engines and second law

statement about direction of heat flow when approaching equilibrium

Clausius violator



Kelvin violator



Second law of Thermodynamics

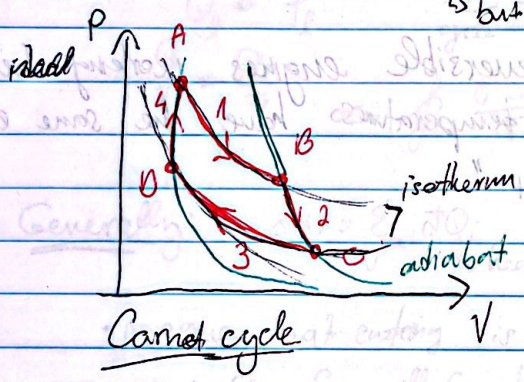
Clausius': "No process is possible whose sole result is the transfer of heat from colder to hotter body."

Kelvin's: "No process is possible whose sole result is the complete conversion of heat into work."

$Q_h' = W$

The Carnot engine

heat engine: converting heat into work (or reverse) cycle
 ↳ but never 100% efficient

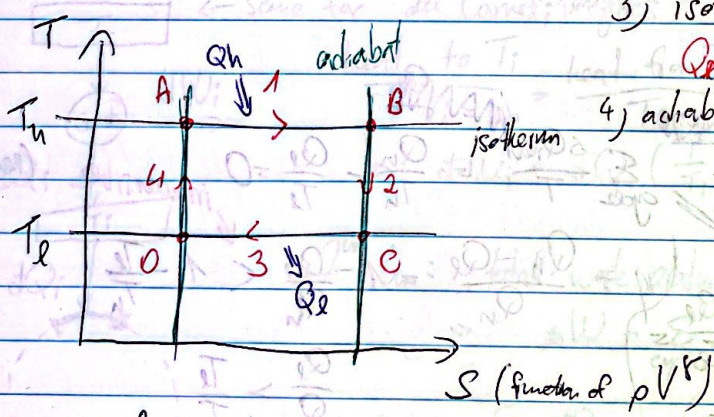


1) isothermal expansion at T_h with ΔQ_h
 $-W = Q_h = RT_h \int_{V_A}^{V_B} \frac{dV}{V} = RT_h \ln \frac{V_B}{V_A}$
 ↳ taking heat & doing work

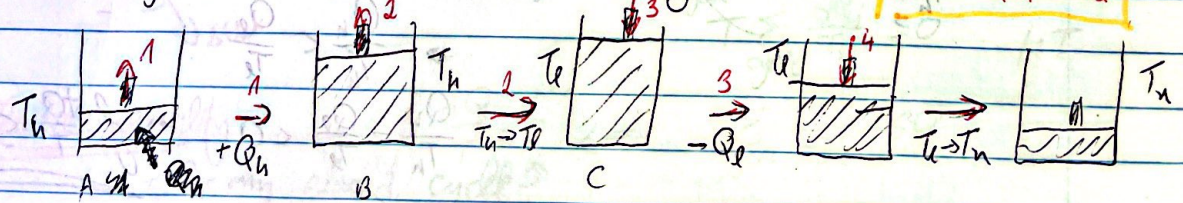
2) adiabatic expansion $\Delta Q = 0, T_h \rightarrow T_c$
 $\frac{T_h}{T_c} = \left(\frac{V_c}{V_b}\right)^{\gamma-1}$
 ↳ continues to do work but no new Φ

3) isothermal compression at $T_c, \Delta Q_c$
 $Q_c = -RT_c \int_{V_B}^{V_A} \frac{dV}{V} = -RT_c \ln \left(\frac{V_A}{V_B}\right)$
 ↳ released

4) adiabatic compression $\Delta Q = 0, T_c \rightarrow T_h$
 $\frac{T_c}{T_h} = \left(\frac{V_A}{V_B}\right)^{\gamma-1}$



cycle \Rightarrow change of internal energy = 0 \Rightarrow $W = Q_h - Q_c$

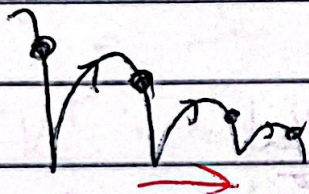
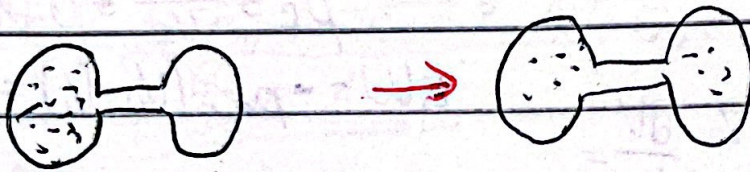


Spontaneity



spontaneously equalibrate
but not backwards

◦ spontaneity defines the arrow of time



the ball cannot take heat
from ground to jump higher,
only loose it

Remember :

$$-W = nRT \int_{V_A}^{V_B} \frac{dV}{V} = -nRT \ln\left(\frac{V_B}{V_A}\right)$$

$$\frac{T_B}{T_A} = \left(\frac{V_A}{V_B}\right)^{\gamma-1}, \quad \gamma = \frac{C_p}{C_v}$$

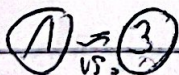
Carnot engine



\Rightarrow

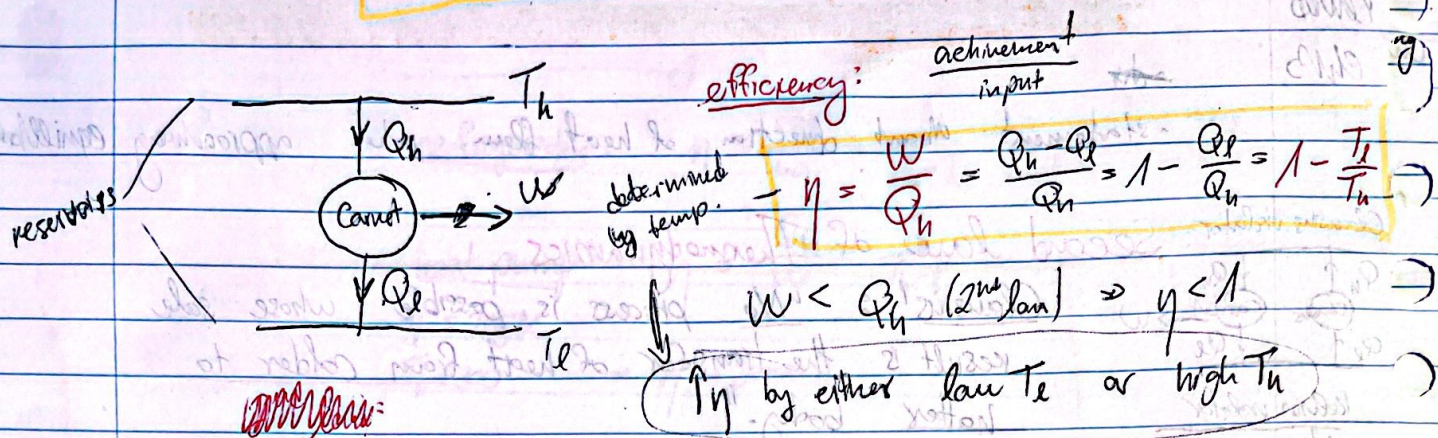
$$\frac{V_c}{V_B} = \frac{V_D}{V_A}$$

$$\Rightarrow \frac{V_B}{V_A} = \frac{V_c}{V_D}$$



$$\frac{Q_h}{Q_c} = \frac{RT_h \ln\left(\frac{V_B}{V_A}\right)}{-RT_c \ln\left(\frac{V_D}{V_c}\right)} = \frac{T_h}{T_c}$$

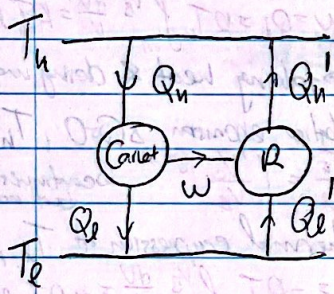
! learn to draw p-V diagram



Carnot's theorem ~ 2nd law

"Of all heat engines working between two given temperatures, none is more efficient than a Carnot engine."

↳ "All reversible engines working between two temperatures have the same efficiency"



Integral form:

$$\oint \frac{\delta Q_{rev}}{T} = \int_1^2 \frac{\delta Q_h}{T_h} - \int_2^1 \frac{\delta Q_c}{T_c} = \frac{Q_h}{T_h} - \frac{Q_c}{T_c} = 0$$

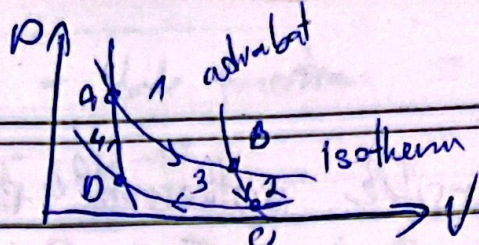
$\eta = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} < 1 - \frac{T_c}{T_h}$ (irreversible) (reversible =)

$\frac{Q_c}{Q_h} > \frac{T_c}{T_h}$

$\Rightarrow \frac{Q_h}{T_h} < \frac{Q_c}{T_c}$

$\frac{Q_h}{T_h} - \frac{Q_c}{T_c} < 0 \Rightarrow \oint \frac{\delta Q}{T} \leq 0$

Carnot cycle



① Isotherm $T = \text{const.}$, gas does work, abs. ΔQ_H

For ideal gas: $\Delta U = 0$
 $\Rightarrow -\Delta W_1 = RT_H \ln \frac{V_B}{V_A} = \Delta Q_H \Rightarrow \Delta S = \frac{\Delta Q_H}{T_H}$

② Adiabatic - isentropic $\Delta Q = 0$

$\Rightarrow \Delta W = \Delta U$
 $\Rightarrow \Delta W_2 = C_V(T_H - T_L) = \frac{3}{2}R(T_H - T_L), \Delta S = 0$

③ reversible isothermal compression, surroundings do work

$-\Delta W_3 = RT_L \ln \left(\frac{V_D}{V_C} \right) = Q_L \Rightarrow \Delta S = \frac{\Delta Q_L}{T_L}$

④ isentropic, $\Delta Q = 0$

$\Delta W_4 = C_V(T_L - T_H) = \frac{3}{2}R, \Delta S = 0$

n	w	Q	ΔU	ΔS
1	$-RT_H \ln \left(\frac{V_B}{V_A} \right)$	$RT_H \ln \left(\frac{V_B}{V_A} \right)$	0	$\frac{Q_H}{T_H}$
2	$C_V(T_H - T_L)$	0	$C_V(T_H - T_L)$	0
3	$-RT_L \ln \left(\frac{V_D}{V_C} \right)$	$RT_L \ln \left(\frac{V_D}{V_C} \right)$	0	$\frac{Q_L}{T_L}$
4	$C_V(T_L - T_H)$	0	$C_V(T_L - T_H)$	0

Backwards heat engines

$$T_0 = 200K, T_1 = 300K \Rightarrow \eta = 200\%$$

\Rightarrow input 1kW \Rightarrow coal using 2kW

• refrigerator: $\eta = \frac{Q_c}{W} = \frac{T_c}{T_h - T_c} > 1 \Rightarrow \frac{\text{useful output: } Q_c}{\text{input: work}}$

• heat pump: $\eta = \frac{Q_h}{W} = \frac{T_h}{T_h - T_c} > 1 \Rightarrow \frac{\text{useful output: } Q_h}{\text{input: } W}$

$T_c = 200K$
 $T_h = 300$
 $\Rightarrow \eta = 2000\%$

Clausius' Theorem

• heat is not conserved in Carnot cycle

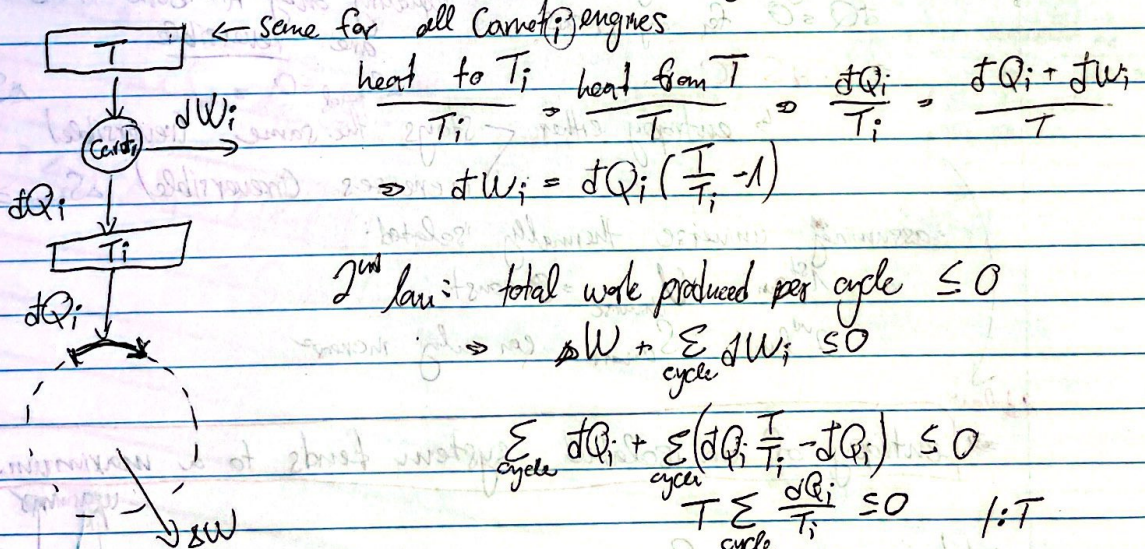
Carnot: $\frac{Q_h}{T_h} = \frac{Q_c}{T_c} \Rightarrow \sum_{\text{cycle}} \frac{\delta Q_{rev}}{T} = \frac{Q_h}{T_h} + \frac{(-Q_c)}{T_c} = 0$

heat entering system at each point

$\frac{Q_h}{T_h} = \frac{Q_c}{T_c}$ or $\oint \frac{\delta Q_{rev}}{T} = 0$ \rightarrow path-independent

Generally: $\delta W = \sum_{\text{cycles}} \delta Q_i$ \rightarrow heat entering system at T_i

• imagine heat entering is supplied by Carnot engine



Clausius inequality

$\oint \frac{\delta Q}{T} \leq 0 \Leftrightarrow \sum_{\text{cycles}} \frac{dQ_i}{dT_i} \leq 0$

- for any closed cycle
- equality holds for a reversible cycle

Qn 4

Entropy

$$\oint \frac{\delta Q_{rev}}{T} = 0 \Rightarrow \int_A^B \frac{\delta Q_{rev}}{T} \text{ is path indep.}$$

$\Rightarrow \frac{\delta Q_{rev}}{T}$ is exact differ. = state function \equiv entropy

$$dS = \frac{\delta Q_{rev}}{T} \quad [J \cdot K^{-1}]$$

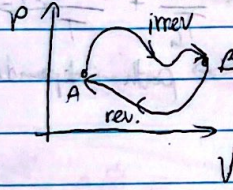
$$\Delta S(B) - S(A) = \int_A^B \frac{\delta Q_{rev}}{T} \quad \text{only for reversible}$$

• for adiabatic = reversible adiabatic process: $\delta Q_{rev} = 0$

\Rightarrow no change in entropy \equiv isentropic $\Delta S = 0$

• if change in entropy: $\oint \frac{\delta Q}{T} \neq 0 \Rightarrow$ irreversible

Irreversible change



$\oint \frac{\delta Q}{T} \leq 0$ by Clausius Thm

$$\int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q_{rev}}{T} \leq 0$$

$$\int_A^B \frac{\delta Q}{T} \leq \int_A^B \frac{\delta Q_{rev}}{T} \rightarrow \text{entropy}$$

$$\frac{\delta Q}{T} \leq \frac{\delta Q_{rev}}{T} = dS \rightarrow \text{state function} \Rightarrow \text{path-indep.}$$

• for thermally isolated system:

$$\delta Q = 0 \text{ for any process}$$

$$\Rightarrow \Delta S \geq 0$$

equality only if both $A \rightarrow B$ and $B \rightarrow A$ are reversible

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

\hookrightarrow entropy either stays the same (reversible)

increases (irreversible) $\Delta S_{total} > 0$

• assuming universe thermally isolated:

1st law: $U_{universe} = \text{const.}$

2nd law: $S_{universe}$ can only increase

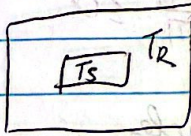
2nd law

\Rightarrow entropy of an isolated system tends to a maximum. $\Delta S_{reservoir}$

* Universe

$$\Delta Q_{res} \rightarrow \text{sys}$$

$$T_R = \text{const.} = T_f$$

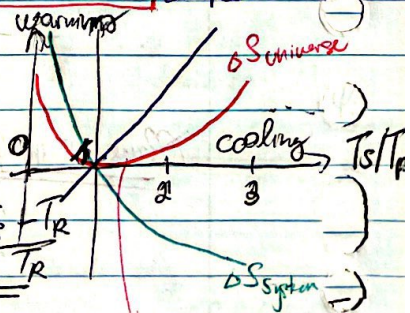


$$\Delta Q = C_V (T_R - T_s)$$

$$\Delta S_R = \int \frac{\delta Q}{T} = \frac{1}{T_R} \int \delta Q = \frac{-\Delta Q_R}{T_R} = C \frac{T_s - T_R}{T_R}$$

$$T_s = \text{changing: } \Delta S_s = \int_{T_s}^{T_R} \frac{C dT}{T} = C \ln\left(\frac{T_R}{T_s}\right)$$

$$\Rightarrow \Delta S_{total} = \Delta S_R + \Delta S_s = C \left[\ln\left(\frac{T_R}{T_s}\right) + \frac{T_s - T_R}{T_R} \right]$$



always increase of entropy of universe (regardless of heating or cooling)

Entropy

reversible isothermal expansion

$$V_i \Rightarrow V_f$$

$$T = \text{const.}$$

$$\Delta S = \int_{V_i}^{V_f} \frac{dQ_{\text{rev}}}{T}$$

• ideal gas, $T = \text{const.} \Rightarrow \Delta U = \text{const.}$

• isothermal \Rightarrow heat must flow into system during expansion

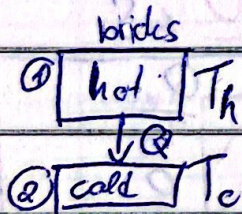
$$-\Delta Q_{\text{rev}} = \Delta W_{\text{rev}} = -pdV$$

$$\Delta W_{\text{rev}} = -\int_{V_i}^{V_f} pdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right) = -\Delta Q_{\text{rev}}$$

$$\underline{\underline{\Delta S}} = \frac{\Delta Q_{\text{rev}}}{T} = \frac{nRT \ln\left(\frac{V_f}{V_i}\right)}{T} = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln\left(\frac{P_i}{P_f}\right)$$

$P_i V_i = P_f V_f$

ΔS for heat flow



$$\Delta S_1 = \int_{T_h}^{T_f} \frac{dQ}{T}, \quad dQ = C dT$$

$$\Delta S_1 = \int_{T_h}^{T_f} \frac{C dT}{T} = C \ln\left(\frac{T_f}{T_h}\right)$$
$$\Delta S_2 = \int_{T_c}^{T_f} \frac{dQ}{T} = \int_{T_c}^{T_f} \frac{C dT}{T} = C \ln\left(\frac{T_f}{T_c}\right)$$

$$\Delta S = \Delta S_1 + \Delta S_2 = C \left[\ln\left(\frac{T_f}{T_h}\right) + \ln\left(\frac{T_f}{T_c}\right) \right] =$$
$$= C \ln\left(\frac{T_f^2}{T_h T_c}\right) \geq 0$$

1st law combined with 2nd law

$$\hookrightarrow dU = \delta Q + \delta W$$

↳ for reversible: $\delta Q = T dS$

$$\delta W = -pdV$$

$$\Rightarrow dU = TdS - pdV$$

only expansion work

Fundamental eq. of Thermodynamics

↳ all state functions, all exact differentials \Rightarrow path-indep.

\Rightarrow holds for irreversible too!

$\delta Q \leq TdS$ and $\delta W \geq -pdV \Rightarrow$ exactly cancel out

$$U(S, V)$$

natural variables, extensive

vs. p, T - intensive \sim forces

exact diff.

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

$= T$ $= -p$

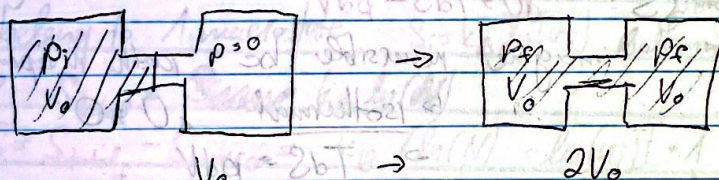
$$T = \left(\frac{\partial U}{\partial S}\right)_V$$

$p = -\left(\frac{\partial U}{\partial V}\right)_S$

def. of temp.!
thermodynamical

$$\Rightarrow \frac{p}{T} = -\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V = \left(\frac{\partial S}{\partial V}\right)_U$$

Joule expansion / male



thermally isolated $\Rightarrow \Delta U = 0$
 $\Delta W = 0$
 $\Delta T = 0$
 $T_f = T_i$

Sudden change \hookrightarrow suddenly open tap \Rightarrow irreversible non-equilibrium

$$p_i V_0 = nRT_i$$

$$p_f (2V_0) = nRT_f = nRT_i$$

$$p_i V_0 = 2p_f V_0$$

$$\Rightarrow p_f = \frac{p_i}{2}$$

For reversible: $\Delta S = \int_i^f dS = \int_{V_0}^{2V_0} \frac{pdV}{T} = \int_{V_0}^{2V_0} \frac{R dV}{V} = R \ln(2)$

but $S =$ function of state \Rightarrow same for any process

↳ to go back \rightarrow only by using work - best if reversible

$$\Delta W = \int_{2V_0}^{V_0} pdV = - \int_{V_0}^{2V_0} \frac{nRT}{V} dV = RT \ln(2) = T \Delta S_{\text{gas}}$$

\Rightarrow increase of entropy $\Delta S = \frac{\Delta W}{T}$

Statistical basis for entropy

2-state system of N particles
 $\Rightarrow \Omega = 2^N$

$$dU = TdS - pdV$$

two definitions of temp.

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

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

$$\text{and } \frac{1}{k_B T} = \frac{d \ln \Omega}{dE} = \frac{d \ln \Omega}{dU}$$

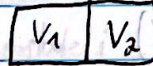
$$\Rightarrow S = k_B \ln(2^N) = N k_B \ln(2)$$

$$S = k_B \ln(\Omega)$$

\hookrightarrow number of microstates associated w/ macrostate

$$1.38 \cdot 10^{-23} \text{ J/K}$$

The entropy of mixing



$$V = V_1 + V_2$$

two gases in separate vessels

with volumes $V_1 = xV$ and $V_2 = (1-x)V$

at the same p , same T

$$x = \frac{V_1}{V}$$

$$p = \frac{N}{V} k_B T$$

$$\Rightarrow \frac{N}{V} = \frac{p}{k_B T} = \text{same}$$

$$\Rightarrow \underline{N_1 = Nx}, \quad \underline{N_2 = (1-x)N}$$

\Rightarrow open tap \Rightarrow gases spontaneously mix

\Rightarrow increasing entropy = entropy of mixing

\hookrightarrow to find ΔS : $dU = TdS - pdV$

- imagine reversible bc path independent

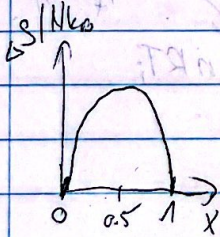
\hookrightarrow isothermal $\Delta U = 0$

$$\Rightarrow TdS = pdV$$

$$dS = \frac{p}{T} dV = \frac{Nk_B}{V} dV$$

$$\Rightarrow \Delta S = x N k_B \int_{xV}^V \frac{dV_1}{V_1} + (1-x) N k_B \int_{(1-x)V}^V \frac{dV_2}{V_2}$$

$$\Rightarrow \Delta S = -Nk_B (x \ln x + (1-x) \ln(1-x))$$



\hookrightarrow no entropy increase when $x=0$ and $x=1$

largest at $x = \frac{1}{2} \Rightarrow \Delta S = Nk_B \ln(2)$ - Jules exp.

\hookrightarrow each molecule 1 extra microstate per molecule

(same # molecules of 1 and 2 for $x = \frac{1}{2}$)

$$\Rightarrow \ln \Omega \rightarrow \ln 2^N \Omega \Rightarrow Nk_B \ln(2)$$

\Rightarrow distinguishability matters!

\hookrightarrow if mixing same things \Rightarrow no change

Entropy and probability

N : # equally likely microstates

n_i : # microstates per macrostate i

$$\sum_i n_i = N$$

probability $P_i = \frac{n_i}{N}$ to observe macrostate i

$$\sum_i P_i = \sum_i \frac{n_i}{N} = \frac{1}{N} \cdot N = 1 \quad \checkmark$$

$$S_{\text{total}} = S + S_{\text{micro}}$$

entropy due to macrostates

entropy due to microstates within a macrostate

S_{micro} for each microstate

Macrostates depend on arbitrary def.

→ e.g. all microstates

belong to 1 macrostate

$$S_{\text{micro}} = \sum_i P_i \cdot S_i$$

entropy of microstates in macrostate i

$$S_i = k_B \ln(n_i) \quad \text{Boltzmann}$$

$$S_{\text{total}} = k_B \ln(N)$$

$$S = S_{\text{total}} - S_{\text{micro}} = k_B [\ln(N) - \sum_i P_i \ln(n_i)]$$

$$= k_B [\sum_i P_i \ln(N) - \sum_i P_i \ln(n_i)]$$

$$= k_B \sum_i P_i \ln\left(\frac{N}{n_i}\right)$$

$$= \frac{1}{P_i} \Rightarrow \ln\left(\frac{1}{P_i}\right) = -\ln(P_i)$$

$$S = -k_B \sum_i P_i \ln(P_i)$$

probabilistic expression for entropy

= Gibbs entropy, more general

↳ within 1 macrostate = Boltzmann can be used $k_B \ln(\Omega)$

but for multiple microstates: $S_{\text{total}} = S + S_{\text{micro}}$

Information Theory - conceptually 15.1, 15.2

The information content Q of a statement is defined by: $Q = -k \cdot \log P$

if we use \log_2 and $k=1$ | \downarrow positive const. | \downarrow Probability of statement
 \Rightarrow in [bits]

if used \ln and $k=k_B$ - thermodynamics

Average information content:

$$S = \langle Q \rangle = \sum_i Q_i P_i = -k \sum_i P_i \log P_i$$

= Shannon Entropy

set of statements of i | information of i | probability of statement i

\hookrightarrow how much information we gain on average by measuring quantity
 \sim how much uncertainty we have about quantity before measurement

Shannon's noiseless channel coding theorem

compression: turn $\{x_1, x_2, \dots, x_n\}$ into a string of length nR - smaller R = better compress. compression factor

if we have a source with entropy S and if $R > S$, $\Rightarrow \exists$ reliable compression scheme of R ;

if $R < S$, any compression scheme of R won't be reliable

random bits = incompressible

if #0 \gg #1 \Rightarrow encoding rate: $00 \rightarrow 10$, $01 \rightarrow 110$, $10 \rightarrow 11$, $11 \rightarrow 1110$

Quantum information

probability \Rightarrow density matrix - describes statistical state of quantum system

system is state $|\psi_i\rangle$ w/ prob. P_i

$$\rho = \sum_i P_i |\psi_i\rangle \langle \psi_i|$$

if $P_j \neq 0$ and $P_{i \neq j} = 0 \Rightarrow$ pure state: $\rho = |\psi_j\rangle \langle \psi_j|$, otherwise: mixed state

$\text{Tr} = \text{trace}$

$$\langle \hat{A} \rangle = \text{Tr}(\hat{A} \rho) \quad \text{and} \quad \text{Tr}(\rho) = 1 \Leftrightarrow \sum_i P_i = 1$$

system in thermal eq. at temp. T , $P_i \propto e^{-\beta E_i}$, where E_i is eval of \hat{H}

\Rightarrow thermal density matrix $\rho_{th} = \sum_i e^{-\beta E_i} |\psi_i\rangle \langle \psi_i| = \exp(-\beta \hat{H})$

only works if same $P_i \rightarrow k_B \ln(2) = k_B \sum_{i=1}^5 \frac{1}{5} \ln(5) = k_B \sum_{i=1}^5 \ln(5) = k_B \ln(5)$

* 5 macrostates : $S = k_B \ln(5)$

each macrostate has 3 microstates :

$S_{\text{micro}} = k_B \ln(3)$

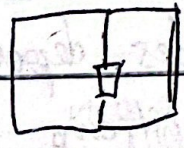
$\Rightarrow S_{\text{total}} = S_{\text{micro}} + S_{\text{macro}} = k_B \ln(5) + k_B \ln(3) = \underline{k_B \ln(15)}$

$S = -k_B \sum_{i=1}^5 \left(\frac{1}{5} \ln\left(\frac{1}{5}\right) \right) = k_B \sum_{i=1}^5 \left(\frac{1}{5} \ln(5) \right) = \underline{k_B \ln(5)}$

works for any probability ratios

Maxwell's Demon

• gas equally split in two sides of a box



• observe and only

let $\frac{1}{2}$ particles through one-side

\Rightarrow decreasing entropy w/o increasing anywhere?! ~~breaks~~

\Rightarrow paradox - breaks 2nd law

\Rightarrow solution : demon must store information, when this is erased \Rightarrow entropy of universe increase

* to make space for more information

• for quantum: information $\sim -k \log p$

$k=1 \Rightarrow \text{avg info} = \langle -\log p \rangle$

\Rightarrow von Neumann entropy $S(\rho) = -\text{Tr}(\rho \log \rho)$
 $\Rightarrow S(\rho) = -\sum p_i \log p_i \sim \text{Shannon}$

• classically: sequences of "0", "1" evals of ρ
 \Rightarrow break down to yes/no questions

• quantum: qubits - two-level quantum system
 - represent by LC of "0" and "1"

$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle, |\alpha|^2 + |\beta|^2 = 1$

- entanglement = 2

cannot be described by a pure state \Leftrightarrow quantum info contains entangled
 \Rightarrow entropy is important
 \hookrightarrow quantifies degree of mixing

superposition: e.g. $\frac{|01\rangle + |10\rangle}{\sqrt{2}}$
 measurement of first bit forces the second bit

Conditional and joint probabilities

probability that A occurs, given B happened $P(A|B)$
 probability of both A and B occurring $P(A \cap B)$
 $P(A \cap B) = P(A|B) \cdot P(B) = P(B|A) \cdot P(A)$

$P(A|B)$

\hookrightarrow if independent: $P(A|B) = P(A)$

$\Rightarrow P(A \cap B) = P(A) \cdot P(B)$

• mutually exclusive events: $\sum P(A_i) = 1$

$\Rightarrow P(X) = \sum P(X|A_i) \cdot P(A_i)$

Bayes' theorem:

$P(A|B) = \frac{P(B|A) \cdot P(A)}{P(B)}$

prior probability (no knowledge about B)

posterior probability

Thermodynamics potentials [J]

$$+pV \downarrow \frac{U}{H} \frac{F}{G} \rightarrow -TS$$

$$H = U + pV$$

$$F = U - TS$$

$$G = U + pV - TS$$

U : $dU = TdS - pdV \rightarrow U = U(S, V)$

natural variables - U changes unless S or V changes

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

$$p = -\left(\frac{\partial U}{\partial V}\right)_S$$

(const. V) for isochoric: $dU = TdS$

reversible $\rightarrow dU = dQ_{rev} = C_V dT \Rightarrow \Delta U = \int_{T_1}^{T_2} C_V dT$

Enthalpy H

work required to make room for the system

$$H = U + pV \Rightarrow H = H(p, S)$$

all state functions

$$dH = dU + pdV + Vdp = TdS - pdV + pdV + Vdp = TdS + Vdp$$

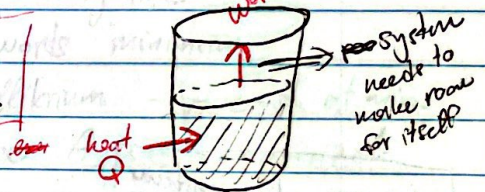
(const. p) for isobaric: $dH = TdS$

for reversible isobaric: $dH = dQ_{rev} = C_p dT \Rightarrow \Delta H = \int_{T_1}^{T_2} C_p dT$

\hookrightarrow Enthalpy = heat absorbed by system

$$T = \left(\frac{\partial H}{\partial S}\right)_p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S$$



Helmholtz function F

$$F = U - TS$$

$$dF = TdS - pdV - TdS - SdT = -pdV - SdT$$

$$\Rightarrow F = F(T, V)$$

(const. T) for isothermic: $dF = -pdV$

$$\Rightarrow \Delta F = -\int_{V_1}^{V_2} pdV$$

\hookrightarrow positive change in F = reversible work done on the system

\hookrightarrow max. amount of work we can get from system at const. temp

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Gibbs function G

$$G = H - TS = U + pV - TS$$

$$dG = TdS + Vdp - TdS - SdT = Vdp - SdT$$

$$\Rightarrow G = G(p, T)$$

G is conserved by isothermal isobaric process const. T, p

$$S = - \left(\frac{\partial G}{\partial T} \right)_p$$

$$V = \left(\frac{\partial G}{\partial p} \right)_T$$

Constraints

• free energy = amount of available useful work a system can provide

★ fixed V , fixed T

dQ enters system \Rightarrow entropy of surroundings changes

$$dS_0 = -dQ/T$$

\Rightarrow entropy of system $dS = -dS_0 = +dQ/T$

$$TdS \equiv dQ = dU - dW$$

$$dW = dU - TdS$$

$dW < 0$ when system is doing work

$$T = \text{const.} \Rightarrow F = d(U - TS)$$

$$dW \equiv dF$$

\rightarrow gives limitation of how much work the system can do (both negative)

• for reversible $dW = dF$

\Rightarrow added work \Rightarrow increase of Helmholtz free energy

• extracting work \Rightarrow at least as big drop in F

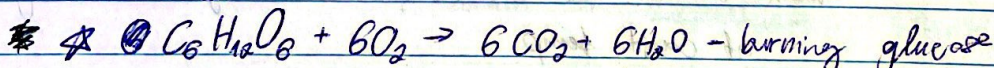
$(dW \leq 0) \Rightarrow$ drop in $F \Rightarrow$ equality for reversible

• if mechanically isolated \Rightarrow no work can be done

$$\Rightarrow dF \leq 0$$

\rightarrow nearing equilibrium \rightarrow lowering F

\rightarrow equilibrium reached at min. F



$\Delta U = -2808 \text{ kJ mol}^{-1}$: exothermic \rightarrow heat flows out of the system

$$\Delta S \approx 182.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

but still entropy of system increases

$$\Delta F = \Delta U - T\Delta S = -2808 \cdot 10^3 - 300 \cdot 182.4 =$$

bc more moles produced

$$= -2862 \text{ kJ mol}^{-1}$$

(7 \rightarrow 12) $\Delta n \approx 1.7$

more particles

38

\Rightarrow more work to use (free energy) because of increase of entropy although decrease of heat

• generally: system in contact w/ surroundings at p_0, T_0

• δQ enters $\Rightarrow T_0 dS \geq \delta Q$

$$\delta Q = dU - \delta W - (-p_0 dV)$$

↑ mechanical work added to system
 ↓ work done by surrounds due to volume change

$$\delta W = dU + p_0 dV - T_0 dS$$

$$U + p_0 V - T_0 S = A = \text{availability}$$

$p_0, T_0 = \text{const.}$: $dA = dU + p_0 dV - T_0 dS$

$$\delta W \geq \delta A$$

↳ changes in availability provide free energy "available" to do work

↳ if mechanically isolated system: $dA \leq 0$

↳ changes in A are negative

⇒ tend towards minimum

↳ once reached equilibrium - A const. at min.

⇒ equilibrium only once A was minimized

• Thermally Isolated at const. V

→ no heat enter → no work done → $dU = 0$

$$\Rightarrow dA = -T_0 dS \Rightarrow dA \leq 0 \Rightarrow \underline{dS \geq 0}$$

⇒ equilibrium at maximal S

• const. V, const. T

$$\Rightarrow dA = dU - T_0 dS \leq 0, \text{ fixed } T \Rightarrow dT = 0 \text{ and}$$

$$dF = dU - T_0 dS - SdT = dU - T_0 dS \Rightarrow \underline{dA = dF \leq 0}$$

⇒ equilibrium at minimal F

• const. p, const. T

$$\Rightarrow dA = dU - T_0 dS + p_0 dV \leq 0$$

$$G = H - TS$$

$$dG = dU + p_0 dV + V dp - T_0 dS - SdT = dU - T_0 dS + p_0 dV$$

$$\Rightarrow \underline{dA = dG \leq 0}$$

⇒ equilibrium at minimal G

Maxwell relations

• if differential is exact \Rightarrow ^{demonstrates} differentials in any order

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial F}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial F}{\partial y}\right)_x\right)_y$$

all exact

$$\downarrow dU = TdS - pdV$$

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S\right)_V \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial p}{\partial S}\right)_V$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp = TdS - pdV + pdV + Vdp = TdS + Vdp$$

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

$$\left(\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial S}\right)_p\right)_S = \left(\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial p}\right)_S\right)_p \Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$F = U - TS \rightarrow dF = -pdV - SdT$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right)_V\right)_T \Rightarrow -p = \left(\frac{\partial F}{\partial V}\right)_T, \quad -S = \left(\frac{\partial F}{\partial T}\right)_V$$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$G = H - TS \Rightarrow dG = TdV + Vdp - SdT \Rightarrow V = \left(\frac{\partial G}{\partial p}\right)_T, \quad -S = \left(\frac{\partial G}{\partial T}\right)_p$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p}\right)_T\right)_p = \left(\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T}\right)_p\right)_T \Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

easy to measure

\Rightarrow learn about entropy

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

not an exam only 17.2 - there can be any type of work
 any work can be used in thermodynamics

Surface tension of liquid



$dW = \gamma dA$
 surface tension γ vs. pressure

- ① relationship p and r
- $dW = F dx = +p dV$ work done on liquid
- work needed to change surface area of a droplet:

$dW = \gamma dA$, $A = \text{Surface area}$
 \rightarrow change in surface area

• equilibrium: $\gamma dA = p dV$

related: $V \rightarrow$ droplet $\sim A$
 $V = \frac{4}{3}\pi r^3 \Rightarrow dV = \frac{4}{3}\pi [(r+dr)^3 - r^3] = \frac{4\pi}{3} [3r^2 dr + 3r(dr)^2 + (dr)^3]$
 $A = 4\pi r^2 \Rightarrow dA = 4\pi [(r+dr)^2 - r^2] = 4\pi [2r dr + (dr)^2]$
 $dA \approx 4\pi \cdot 2r dr = 8\pi r dr$

$dV = A dr = 4\pi r^2 dr$
 $\gamma \cdot 8\pi r dr = p \cdot 4\pi r^2 dr$

$2\gamma = pr \Rightarrow \rho = \frac{2\gamma}{r}$ const. depending on material

- inside: all bonds same in all directions \Rightarrow cancel out
- surface: missing bonds on surface \Rightarrow net attractive force inwards \perp surface

• how to decrease γ ?

- mix with other things - e.g. soap
- increase T

$dU = T dS - p dV = T dS + \gamma dA$

• only interested in droplet

isothermal $\left(\frac{dU}{dA}\right)_T = T \left(\frac{dS}{dA}\right)_T + \gamma$ change in internal energy when surface changes

Helmholtz free en. $dF = -SdT + \gamma dA$ Maxwell $\Rightarrow \left(\frac{\partial}{\partial A}(-S)\right)_T = \left(\frac{\partial}{\partial T}\gamma\right)_A = \left(\frac{\partial \gamma}{\partial T}\right)_A$
 $-\left(\frac{\partial S}{\partial A}\right)_T = \left(\frac{\partial \gamma}{\partial T}\right)_A$

$\left(\frac{\partial U}{\partial A}\right)_T = -T \left(\frac{\partial \gamma}{\partial T}\right)_A + \gamma$

change in internal energy $\Delta Q = T \Delta S = -T \Delta S + \left(\frac{\partial \gamma}{\partial T}\right)_A \Delta A > 0$
 heat work - against surface tension
 \rightarrow increase of $r \Rightarrow$ increase of entropy
 $< 0 \Rightarrow$ γ with T

$\gamma \rightarrow \uparrow S$
 creating surface costs energy and produces entropy

Third Law - mostly conceptually

measuring entropy? C_p vs. T graph at const. p

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

$$\Rightarrow S = \int_{T_0}^T \frac{C_p}{T} dT$$

but! constants of integration !!

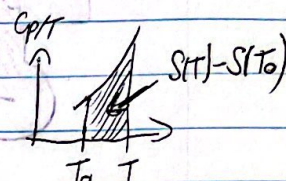
$$S(T) = S(T_0) + \int_{T_0}^T \frac{C_p}{T} dT$$

only changes entropy are measurable ...

$\Delta H < \begin{cases} > 0 \text{ for endothermic} \\ < 0 \text{ for exothermic} \end{cases}$

we expect $\Delta G = \Delta H - T\Delta S \Rightarrow$ as $T \rightarrow 0$, $\Delta G \rightarrow \Delta H$ and $\Delta S \rightarrow 0$

asymptotical approach (from measurements)



Nernst's third law: Near absolute 0, all reactions

$\Delta S \rightarrow 0$ for $T \rightarrow 0$ (for crystals) take place with no change in entropy.
 is a system in internal equilibrium perfectly ordered

for perfect crystals

$$S = k \ln(\Omega) = k \ln(1) = 0$$

$$S = 0 \Leftrightarrow \Omega = 1$$

\hookrightarrow at abs. 0, System at ground state. non-degenerate

Planck's third law: The entropy of all systems is the same at absolute 0 and may be taken to be 0.
 in equilibrium $\Rightarrow S \rightarrow 0$ at $T \rightarrow 0$ for perfectly ordered

Simon's third law: The contribution to the entropy of a system by each aspect of the system which is in internal thermodynamic equilibrium tends to 0 as $T \rightarrow 0$.
 parts in equilibrium
 ~~ignores for all parts~~
 but don't care about nuclear properties when dealing with atomic

$$S = 0 \text{ at } T = 0$$

cooling crystal \Rightarrow extract energy from lattice \Rightarrow drop in entropy but nuclear spin will retain entropy to lower temp.

then the more macro properties \Rightarrow additive entropies (electrons, nuclear spins, nucleons, ...)

residual entropy - even for perfectly ordered crystals \Rightarrow nuclear spins might be disordered - perfectly order spins \Rightarrow disordered nucleons ... etc.

\hookrightarrow assume substance not perfect crystal at $T=0 \Rightarrow$ different microstates

Energy & phase transitions

- use H

$$H = U + pV$$

$$dH = dQ + Vdp$$

$$\Delta H = \Delta Q \text{ for const. } p$$

- at transition temperature for a given phase transition (T_{trs}) both phases are in equilibrium

• heat transfer is reversible:

$$\Delta S_{trs} = \frac{\Delta Q_{rev}}{T_{trs}} = \frac{\Delta H_{trs}}{T_{trs}}$$

- putting Q into system but T doesn't change (only phase changes) $\rightarrow S$ changes

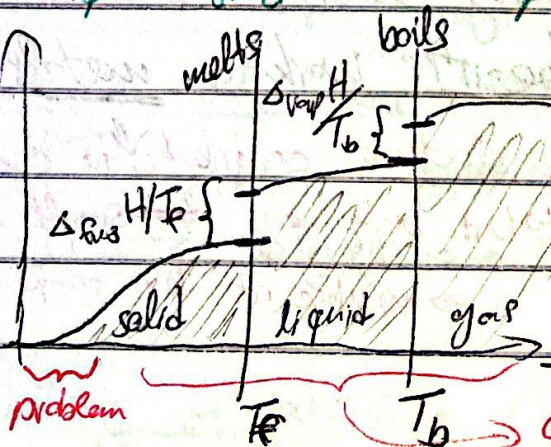
Measuring entropy

- abs. (molar) entropy of system at $T =$

= Σ all heating terms and phase transitions

$$S_m(T) = S(0) + \int_0^{T_f} C_{p,m}(s, T) \frac{dT}{T} + \frac{\Delta_{fus} H}{T_f} + \int_{T_f}^{T_b} C_{p,m}(l, T) \frac{dT}{T} + \frac{\Delta_{vap} H}{T_b} + \int_{T_b}^T C_{p,m}(g, T) \frac{dT}{T}$$

heating from 0 to freezing temp. heating from freezing to boiling
 liquid solid vapourisation/gas



can be measured using calorimeters

- solids - very different specific heat cap.
- but similar molar heat cap.

↳ law of Dulong - Petit (empirical)

$$C_{M} \approx 3R \quad (\text{vs. ideal gas: } C_V = \frac{3}{2}R)$$

at room temp.

↳ $\frac{1}{2}$ per deg. freedom

Why $3R$ for solid?

- gas: only kinetic energy

↳ 3 ways to store energy (movement in 3 directions)

- solid: atoms connected by springs

↳ $\frac{1}{2}R$ per mode (deg freedom) again

but ^{here} oscillation: in every direction

2 modes - kinetic and potential energy

but Dulong - Petit breaks down at low temp.

↳ derived from Maxwell-Boltzmann statistics

↳ at low temp. = quantum nature relevant

⇒ Bose-Einstein statistics must be used

• at low T ⇒ Debye approx. $C_{M} \propto T^3$ using extrapolation

- vibrating lattice excitations in solid vs photons in box

↳ but doesn't work for metals (only for semicond. / nonconductive)

free electrons contribute to C

e^- frozen for at low temp.

↳ but only very ~~small~~ small amount

⇒ visible at low temp.

- heat capacities tend to 0 as $T \rightarrow 0$

$$C = T \left(\frac{\partial S}{\partial T} \right) = \frac{\partial S}{\partial \ln(T)} \xrightarrow{T \rightarrow 0} 0$$

↳ disagrees w/ $C = \frac{R}{2}$ per mole per degree of freedom

- thermal expansion stops (at $T=0$)

$$\left(\frac{\partial S}{\partial p} \right)_T \xrightarrow[S \rightarrow 0]{as T \rightarrow 0} 0 \text{ as } T \rightarrow 0 \quad \text{isobaric expansivity}$$

by Maxwell relation: $\left(\frac{\partial S}{\partial p} \right)_T = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow 0 \Rightarrow \beta_p \rightarrow 0$

- no gas remains ideal as $T \rightarrow 0$

* $C_p - C_v = R$ per mole

but as $T \rightarrow 0$: $C_p, C_v \rightarrow 0 \Rightarrow C_p - C_v \rightarrow 0$

* $S = C_v \ln T + R \ln V + \text{const.}$ for ideal gas

but as $T \rightarrow 0 \Rightarrow S \rightarrow -\infty \neq 0$

↳ weak interactions between gas molecules become important

- Curie's law breaks down for low T

$\chi \propto \frac{1}{T} \Rightarrow \chi \rightarrow \infty$ as $T \rightarrow 0$

but: $\left(\frac{\partial S}{\partial B} \right)_T \rightarrow 0$ hence $\left(\frac{\partial S}{\partial B} \right)_T = \left(\frac{\partial m}{\partial T} \right)_B = \frac{VB}{M_0} \left(\frac{\partial \chi}{\partial T} \right)_B \rightarrow 0$

↳ contradiction

↳ derived from independent magnetic moments (also dep.)

~~↳~~ χ only depends on applied B and T

$\chi \rightarrow \infty$ when thermal fluctuations are removed

but other mag. moments also have effect

↳ at $\uparrow T \rightarrow$ micro indep. $\therefore E_{\text{therm}} = k_B T \Rightarrow$ interaction E

$\downarrow T \rightarrow$ interactions are important

- unattainability of absolute 0

It is impossible to cool to $T=0$ in a finite # of steps

- asymptotical approach $T \rightarrow 0K$

- reservoir cannot be at $T=0$ and serve as reservoir at the same time