Thermo Review 2024

"System", part of the universe

Everything else - bath, surroundings

System:

1st law $\quad dE_{sys} = \overset{\text{in}}{dq} + \overset{\text{on}}{dw}$

Isolated system: $\quad$ [N, V, E are const]

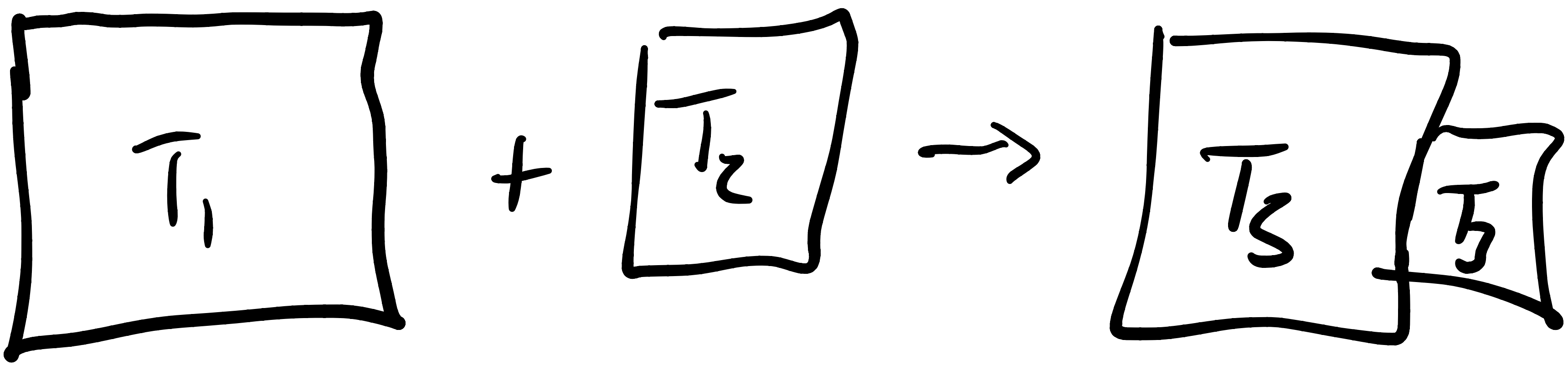
$dq = 0, \; dw = 0 \quad E$ is conserved

State of the system [# + 2 variables]

↑ types of species

Eg N, V, E

N, V, T



heat flows

$q_1 = -q_2$

$q_i = n C_i \Delta T_i$

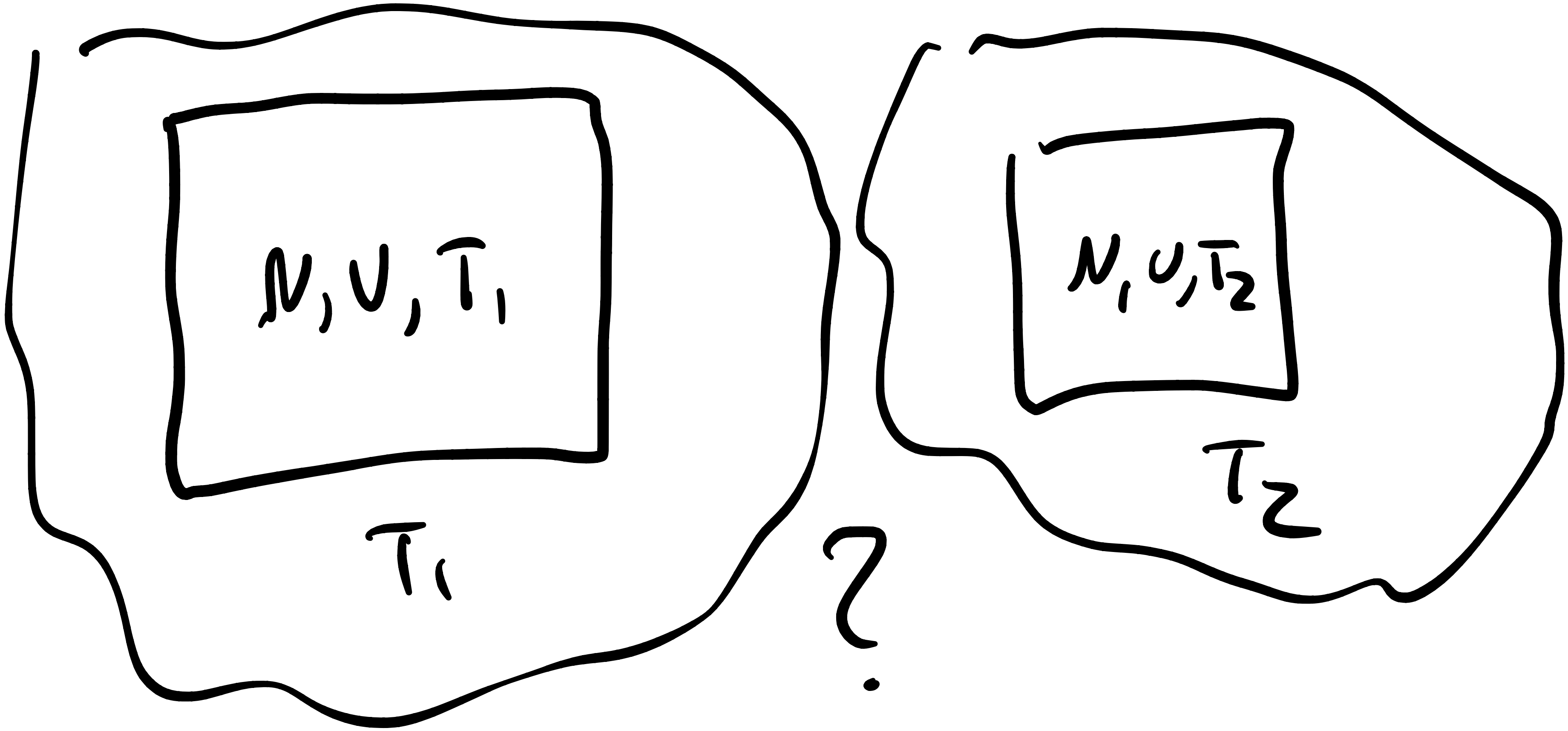
$q = \int n \underbrace{C\,dT}_{dq}$ ← C could depend on T

Spontaneous process, entropy of systems was maximized

$$dS = dq^{rev}/T$$

E & S are state function

q, w are not state functions (depend "path")



N, V, T1
T1
?
N, V, T2
T2

Second law

heat flows from "hot" to "cold"

true on average "in expectation"

$dS > 0$ for a spontaneous process

$dS = 0$ for a reversible process

$$dS = dS_{produced} + \underbrace{dS_{exchanged}}_{dq/T}$$

$=0$

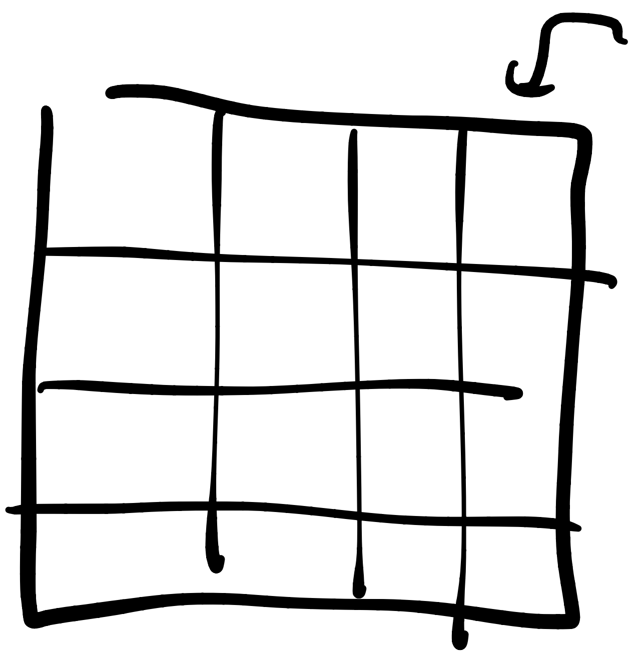
reversible

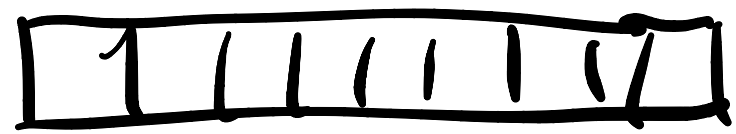
$$dS_{universe} \geq dq^{rev}/T \geq 0$$

for fixed $\mathcal{E}$, $S = k_B \ln \underbrace{\Omega(\mathcal{E})}$

\# <u>micro</u> states

arrangements





ideal:

N^M

excluded volume

$\binom{N}{M}$ no 2 particles on same spot excluded volume: $N(N-1)(N-2)\cdots(N-m)$

$$\frac{N!}{(N-m)!}$$

also $m!$ to shuffle indistiguishable

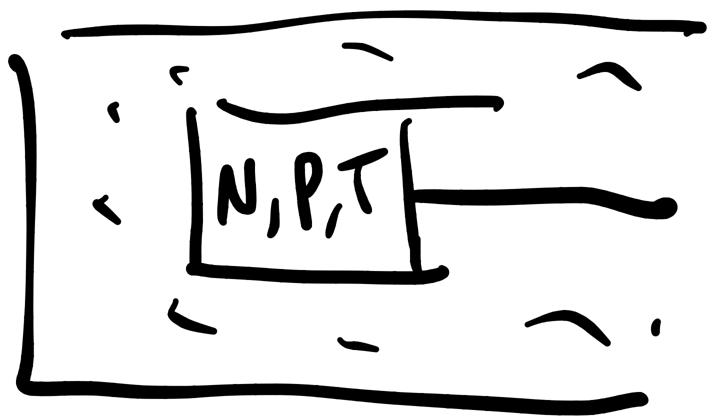
indisting: $$\frac{N!}{(N-m)!\,m!} = \binom{N}{m}$$ binomial coef.

$$\frac{N!}{m_1!\,m_2!\,m_3!\cdots m_i!}$$ multinomial coefficent

Sterling's approx

$$\ln(N!) = N \ln N - N$$

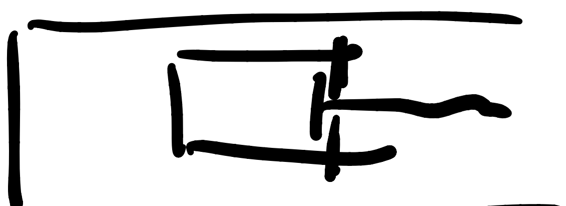
other "ensembles"



← Port

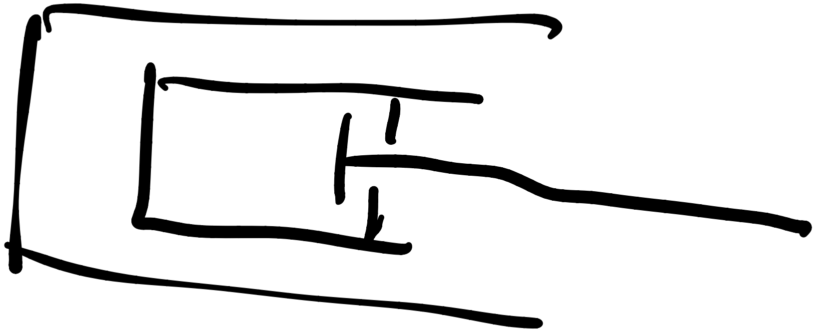
Spontaneous process

$G \downarrow$



N, V, T

change V



N, V, T

change V, do work

$$dW = -PdV$$

at const V

$$dE = C_V dT$$

$$C_P = \frac{dE + PdV}{dT}$$

at const P

$$dE = C_P dT - PdV$$

$$= \frac{dH}{dT}$$

$$H = E + PV$$

Ideal gas:

$$PV = nRT$$

$$P = \rho RT$$

$R = 0.08206 \frac{\text{l atm}}{\text{K mol}}$

$R = 8.314 \frac{\text{J}}{\text{K mol}}$

monatomic

$$\mathcal{E} = \underbrace{\tfrac{3}{2} nRT}_{\text{kinetic energy avg}}$$

$$C = \frac{d\mathcal{E}}{dT} = AR$$

$\frac{3}{2}n, \frac{5}{2}n$ etc

$$C_p = R + C_V \qquad C_p > C_V$$

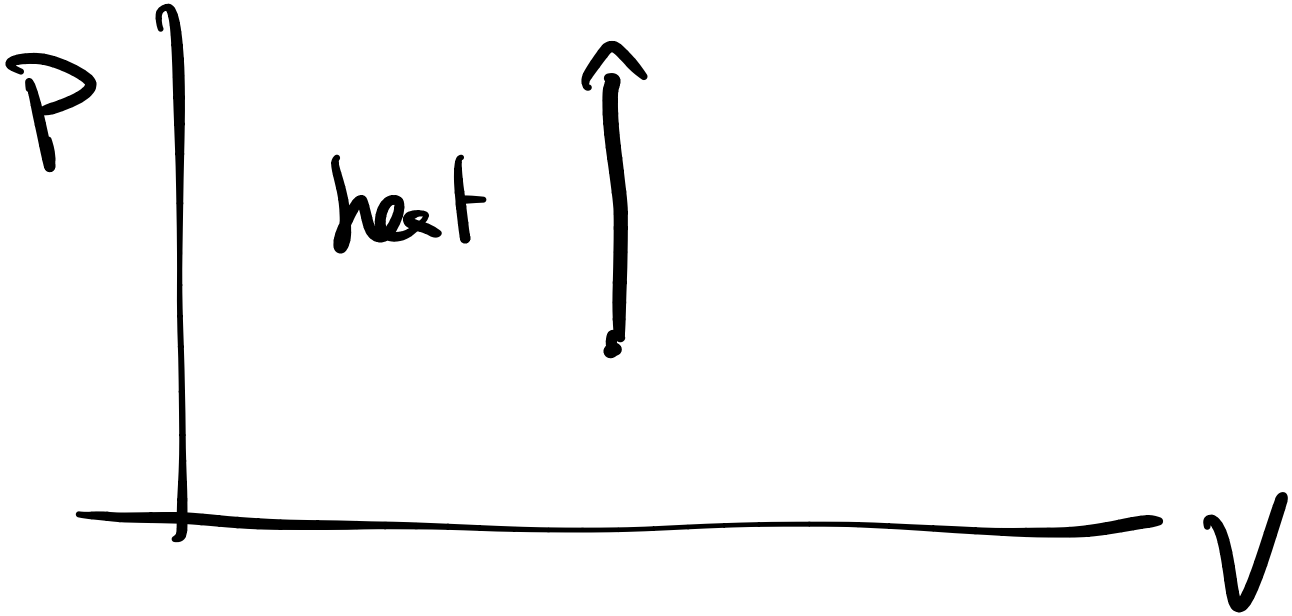
Change states of an ideal gas

const pressure, change V

$\Delta E = C_p \Delta T - P\Delta V$

$W = -P\Delta V$

#2 heat @ const V



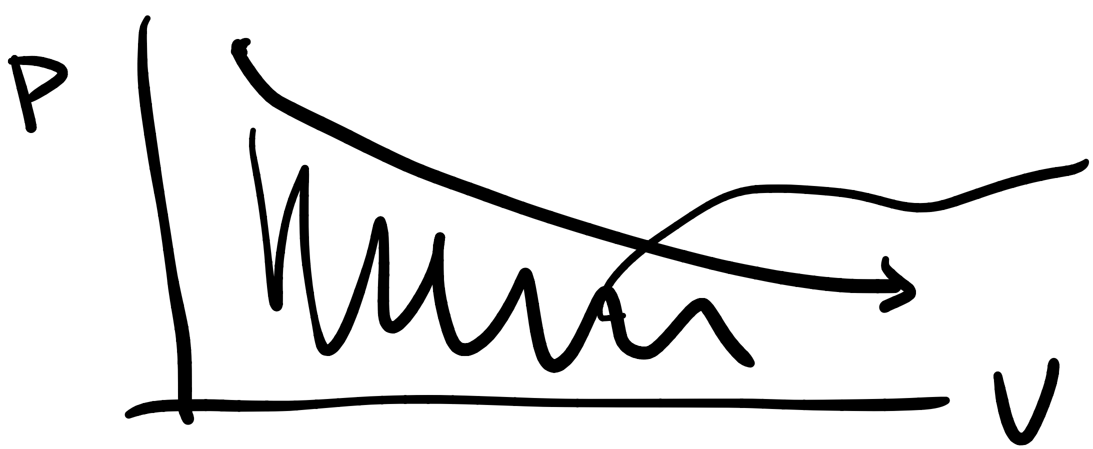
$$w = -P\Delta V = 0$$

$$\Delta E = \underbrace{C_v \Delta T}_{\text{heat in}}$$

#3 const T, isothermal

$$dE = 0$$

$$dq = -dw$$



$$w = -\int P\,dV$$

$$= -nRT \int \frac{1}{V}\,dV$$

$$= -nRT \ln(V_2/V_1)$$

$$\Delta S = \int \frac{dq}{T} = nR\ln(V_2/V_1)$$

#4 adiabatic expansion

$$dq = 0$$

$$dE = dw = -P\,dV$$

$$= -\frac{nRT(V)}{V}\,dV$$

$$T_2 = T_1 \left(V_1/V_2\right)^{nR/C_V}$$

$$P_2 = P_1 \left(V_1/V_2\right)^{\frac{nR}{C_V}+1}$$

$$\epsilon = w_{done}/q_{in}$$

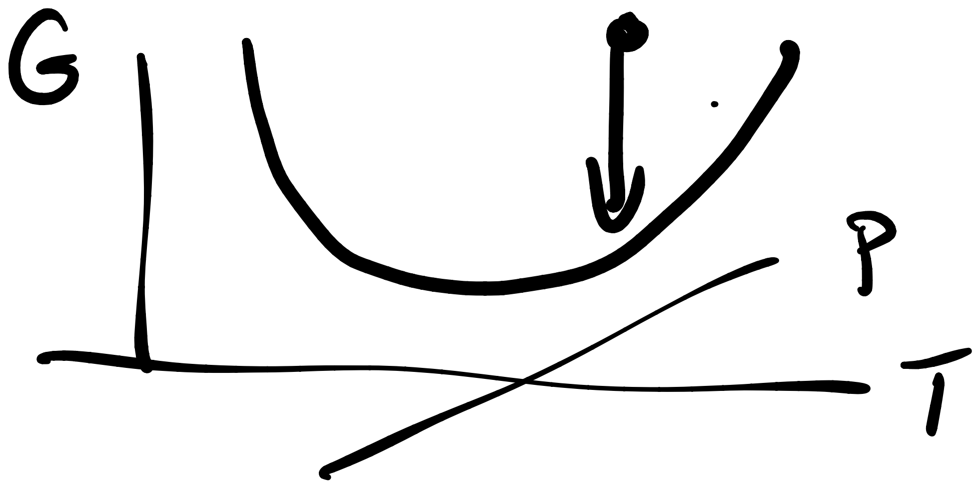
Thermodynamic potential
something minimized for a particular state

free energy minimized

[microcanonical $-S$]

$$dG \leq SdT - VdP$$

$$dG \leq 0 \quad \text{for const } T, P$$



$$dA \leq -PdV - SdT$$

helmholz free energy — potential for const V, T

$$A = -k_B T \ln Z(N, V, T)$$

$\quad = E - TS$

Free energy of mixing, phase transitions

$\mu_i = G/n_i$ $\left(\frac{dG}{\partial n_i}\right)$

thing go from high μ to low μ

Microstates system - arrangements

const $\mathcal{E}$ $\quad P(X_i) = \frac{1}{\Omega}$

N, V, T $\quad P_i = e^{-\varepsilon_i / k_B T} / Z$

$$Z = \sum_{i=1}^{n\,\text{states}} e^{-\varepsilon_i / k_B T}$$

$1/k_B T \equiv \beta$

$\langle \mathcal{E} \rangle = -\partial \ln Z / \partial \beta$ $\quad A = -k_B T \ln Z$

Kinetics

@ Eq, things are moving

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B \qquad @ \text{ eq}$$

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f}{k_b}$$

"detailed balance"

$$\text{rate} = \frac{1}{\nu_A}\frac{d[A]}{dt}$$

ν's are negative if "on left"

rate of reactions, barrer heigh

$$k \propto e^{-\varepsilon^*/k_B T}$$

$$\Delta \bar{G}^\circ = -RT \ln K_{eq}$$

$$K_{eq} = e^{-\Delta G / RT}$$

$$P_R / P_{ref}$$