Thermo Review 2022

System - part of universe we care about. Bath - rest, or surrounding area in contact

1st law $dE = đq + đw$

Energy is conserved

$đq > 0$ or $đw > 0$, system energy goes up

(heat in, work done on)

Isolated system (microcanonical)

$đq = 0$, $đw = 0$

E is conserved

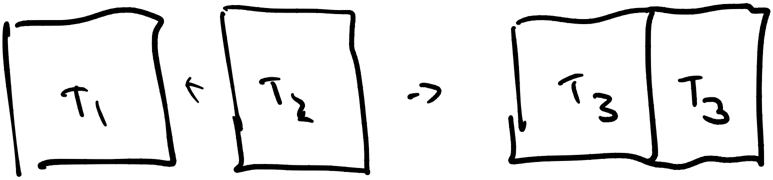
whole universe is isolated system

State of system : $d + 2$ variables

such as N, V, E (isolated)

Still sort of isolated

2 systems in thermal contact
Heat flows until temperature equal, high to low



$C = d\mathcal{E}/dt$, $q = C\,\Delta T$

$T_f - T_i^1$ $\quad$ $T_f - T_i^2$

final temp? $n_1 C_1 \Delta T_1 = -n_2 C_2 \Delta T_2$

During this process <u>entropy</u> is maximized

$dS = dq^{rev}/T$

$\mathcal{E}$ & S are state functions,
any path, even non reversible, has same ΔS, $\Delta\mathcal{E}$ from $a \to b$, $\Delta\mathcal{E} = 0$, $\Delta S = 0$ for cycle

<u>Second law</u> No heat from hot -> cold, not all heat can be converted to work

$dS > 0$ for spontaneous process

$dS = 0$ for reversible process

Non isolated (or isolated)

$$dS = dS_{\text{produced}} + dS_{\text{exchange}}$$

$$= dS_{\text{prod}} + \text{đ}q/T$$

rev, $dS_{\text{prod}} = 0$, $dS = \text{đ}q_{\text{rev}}/T$

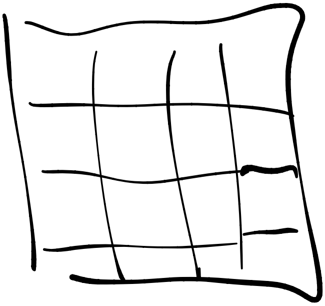
Irrev, $dS_{\text{prod}} > 0 \Rightarrow dS > \text{đ}q_{\text{rev}}/T$

Universe $dS \geq \text{đ}q/T \geq 0$

If fixed E:

$S = k_B \ln W$, W is # of states

Eg



N_ℓ = volume

lattice gas w/ overlap, no overlap

$W = \binom{N_\ell}{M}$ $\quad N_\ell^{M}$

$\ln N! \approx N \ln N - N$

Also, A/B mixing model

Compare

↙ good way to compare, or divide

$$k_B \ln\left(\frac{N_L!}{m!(N_L-m)!}\right) - k_B \ln\left(N_L^{m}\right)$$

$$= k_B\Big[N_L \ln N_L - \cancel{N_L} - m\ln m + \cancel{m} - (N_L-m)\ln(N_L-m) + \cancel{N_L} - \cancel{m}$$
$$- m \ln N_L\Big]$$

$$= k_B\Big[(N_L-m)\ln(N_L) \underbrace{- (N_L-m)\ln(N_L-m)}_{\approx 0} - m\ln m\Big]$$

< 0 so no overlap, more states

Showed entropy was maximized @ $\frac{1}{2}$ filled for first model

$\partial S/\partial m = 0$ @ $m = N_L/2$ and $\frac{\partial^2 S}{\partial m^2} \geq 0$

Other states

N, V, T

isothmal

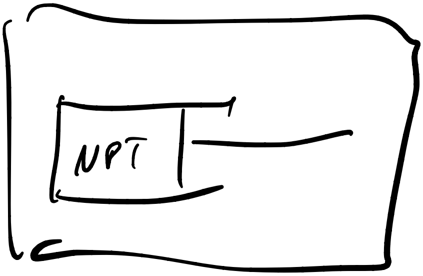
isochoric

(canonical)

NPT

isothermal

isobaric



now can do pV work

$dw = -PdV$

Change of state, add heat, do work to change state. Change properties of bath

When heat system

@ const V

$$dE = dq = C_v dT$$

$$\Delta E = C_v \Delta T$$

@ const P

$$dE = C_p dT - P dV$$

so $C_p = \dfrac{dE + PdV}{dT} = \left(\dfrac{\partial H}{\partial T}\right)_P$

where $H = E + PV$

Cr

Ideal gas!

$$PV = nRT$$

$R = 0.08206 \dfrac{L\,atm}{K\,mol}$

8.314 J/K mol

(mono)

$$E = \frac{3}{2} nRT$$

$C_v = 3/2\, nR$

$C_p = 5/2\, nR$ $\qquad C_p > C_v$

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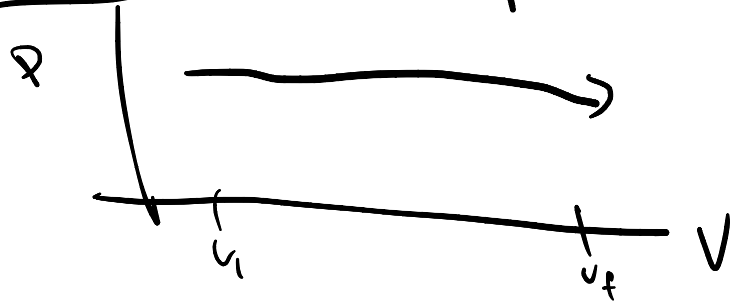
change state of ideal gas reversibly

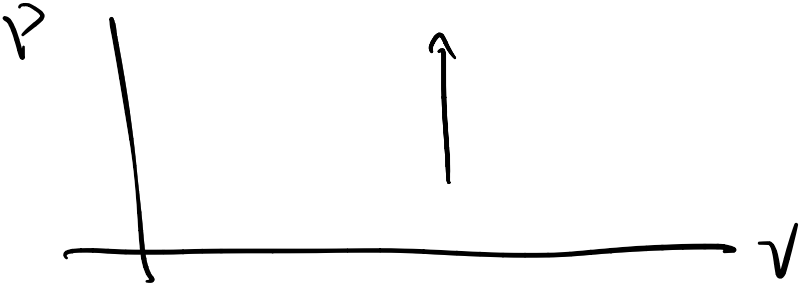
<u>scenario</u> 1 Const pressure expansion/comp



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

$W = -P\Delta V$

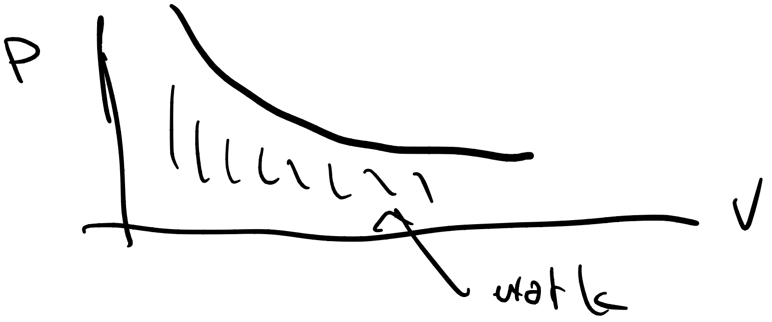
Scenario2 heat @ const V
pressure up



$W = -P\Delta V = 0$

$\Delta E = C_v \Delta T$

Scenario3 const T, isothermal



$$P = \left(\frac{nR}{V}\right) T$$

$$W = -\int_{V_1}^{V_2} \frac{nR}{V} T\, dV = -nRT \ln\left(V_f / V_i\right)$$

$d\mathcal{E} = 0$ (ideal gas)

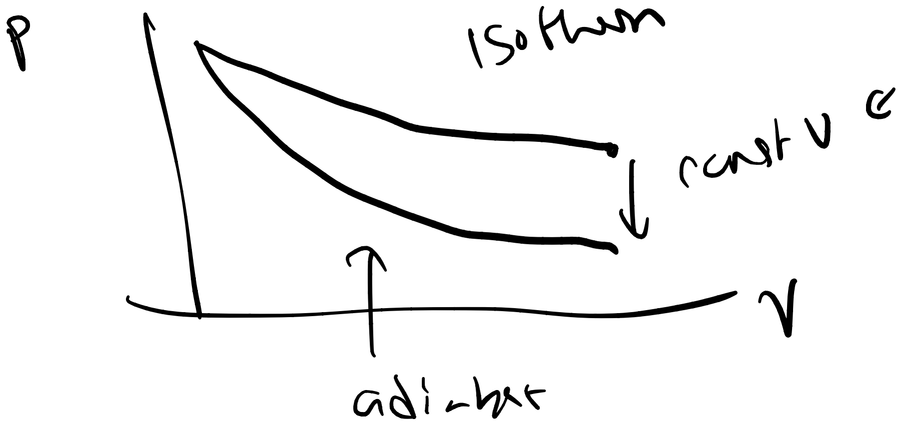
so $q = -w = nRT\ln(V_f/V_i)$

$\Delta S = nR\ln(V_f/V_i)$ [showed w/ lattice gas]

Scenario 4 adiabatic expansion

$$d\mathcal{E} = dw = -\frac{nRT(V)}{V}\,dV$$

energy decreases



Result $\frac{C_v}{T} dT = -\frac{nR \cdot T}{V} dV$

gives $T_f = T_i \left(V_i / V_f \right)^{nR/C_v}$

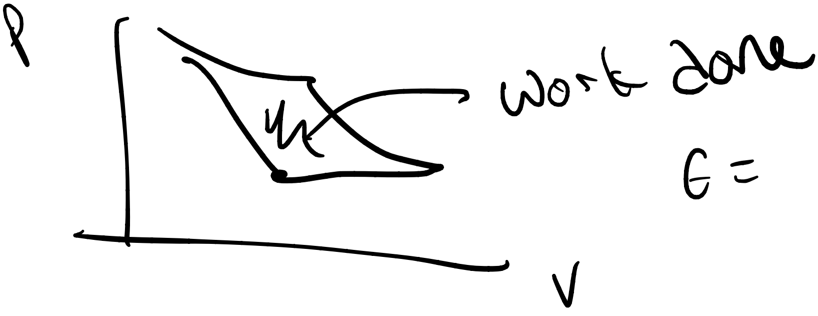
$P_f / P_i = \left(V_i / V_f \right)^{\frac{nR}{C_v} + 1}$

$\uparrow$

$C_p / C_v = \gamma$

5/3 for monatomic

Engine, cycle of PV changes that produces work



$\epsilon = \frac{W_{done}}{q_{in}}$

Thermodynamic pot

For isolated system, $dS \geq 0$ for spontaneous process

$dS \geq dq/T$,

$d\mathcal{E} = dq + dw$

$\leq TdS - PdV$ if S, V const $\mathcal{E}$ always decreases

Consider $G = \mathcal{E} - TS + PV$

$dG = d\mathcal{E} - TdS + SdT + PdV - VdP$

$\leq SdT - VdP$, so const T, P G always goes down

$A = \mathcal{E} - TS$

$dA = d\mathcal{E} - TdS - SdT$

$\leq -PdV - SdT$, const V, T, Helmholtz is key microstates

for a particular state N, V, T
~~N~~ N P, T, etc

there are many molecular configurations possible. these have some likelihood

for NVE, $p_i = 1/W$

NPT $p_i = e^{-\beta E}/Q$,

$$Q = \sum_{i=1}^{W} e^{-\beta E_i}$$, partition function

if we know Q, can calculate A, S
other thermo properties

$E = -\partial \ln Q/\partial \beta$ $A = -k_B T \ln Q$

Free energy controls chemical reactions, or mixing processes

if now have n_1, n_2, P, T

Where n_1, n_2 are # moles in each phase, or of two components

$\mu_i = \left(\frac{\partial G}{\partial n_i}\right) = \bar{G}_i$ contribution of that thing to chemical pot

Go from high to low chemical pot during reaction

So if μ ice > μ water
ice will melt

μ is a func of the NpT

$\mu^\alpha = \mu^\beta$ at phase eq

-Can control μ w/ changing eg P
and we talked about how
this changes transition temp

In mixture, can be non ideal. Near extremes

$P_{vap} = \chi K_H$ henry

$P_{vap} = \chi P_0$ raoult

Kinetics

$P(\varepsilon) \propto e^{-\beta \varepsilon}$

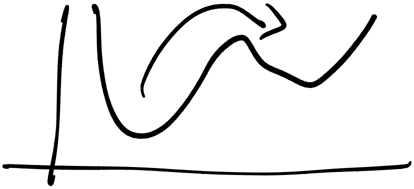
$P(vel\ x,y,z) \propto e^{-\beta \frac{1}{2} m v^2}$

$P(speed) \propto s^2 e^{-\beta/2\, m s^2}$

most probable, avg, rms speed
all depend on m & T

higher T, faster, more
energy for reaction

$k_{rxn} \propto e^{-E_A/k_BT}$



reaction mechanism

$v = k[A]^a[B]^b$ etc

elem

$aA + bB \Rightarrow C$

$r = k[A]^a[B]^b$

determine by initial rates or relaxation

for $A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B$

$k_{rxn} = k_f + k_b$

for 1st order

$$[A](t) = [A]_0 e^{-kt} \qquad t_{1/2} = \ln 2 / k$$

get half life

2nd order

$$1/[A] = kt + \frac{1}{[A]_0}$$

so $t_{1/2} = 1/[A]_0 k$