Thermodynamics Class : State of a system, 0th law and equation of state

Thermodynamics ⇒ macroscopic properties. (5.62) undergrad level course!

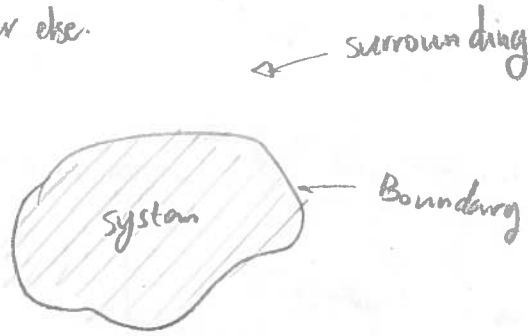
Thermo → heat, dynamics → motion

4 laws:
- 0th law : T : common sense
- 1th law : U : you can break even.
- 2nd law : S : " " " " out of law.
- 3rd law : numerical value to : you cannot go to 0 °k.

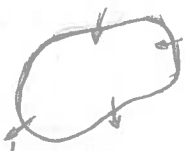
Definitions: system → Surroundings → Boundary

system → can be every thing

Surroundings → whatever else.



system
- open : mass & energy can flow through boundary
- close : no mass but energy can flow through boundary
- isolated : no mass & energy can go out of system.



Describe the system: P, T, V, n, m

- n → mass.
- m → molar.

component
- water + ice : H_2O
- Latte : many milk, ...

Equilibrium : These variables are constant throughout time & space.

properties
- Extensive: $V, m, \ldots$
- Intensive: $T, \bar{V} = \frac{V}{n}$.

$\bar{V}$ → molar volume.

State variables ⇒ Equilibrium

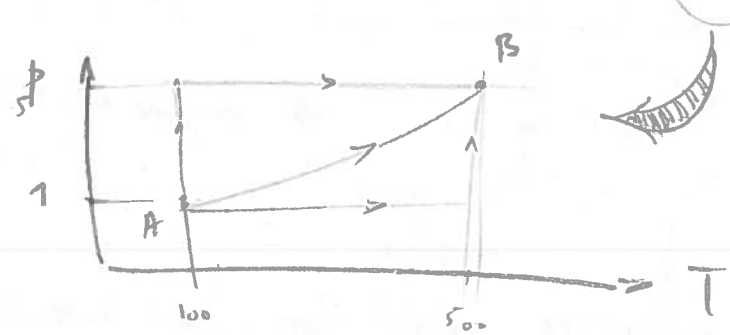
↳ they don't care about history.

⇒ one-component → n, 2 Intensive variables ⇒ get all infor

$\underbrace{3\ H_2(g, 1\,bar, 100\,^\circ C)}_{1^{st}\ Equ\ A}$ = $\underbrace{3\ H_2(g, 5\,bar, 500\,^\circ C)}_{2nd\ Equ\ B}$

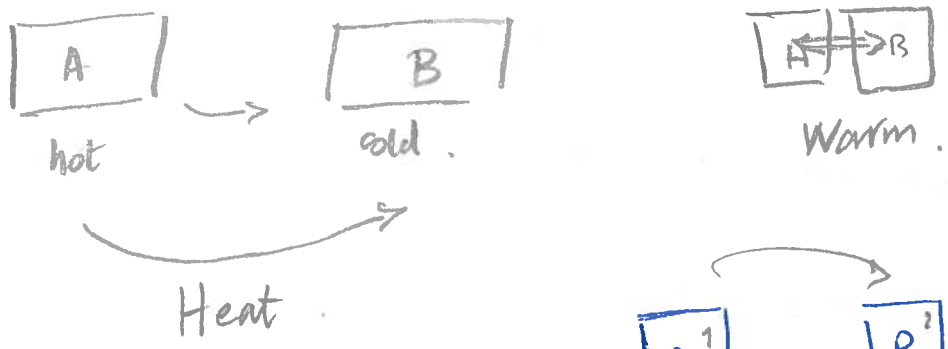
- 3 → n
- H_2 → compo
- g → phase
- $1\,bar$, $100\,^\circ C$ → 2 intensive

I need the path.
- Reversible path. (stay in Equ everywhere in path).
- Irreversible path.

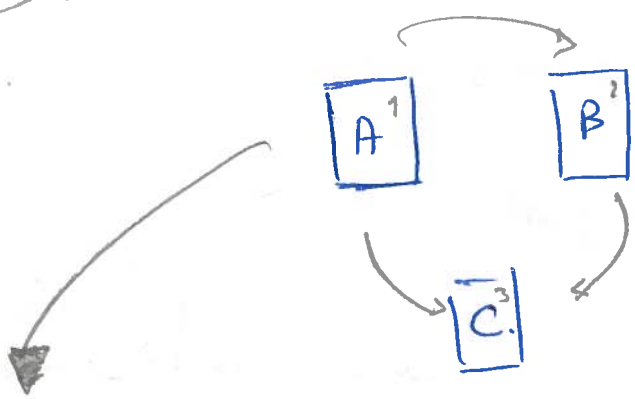


adiabatic: no heat exchange. isothermal: constant T.

isobaric: constant pressure



$T_A > T_B > T_C$



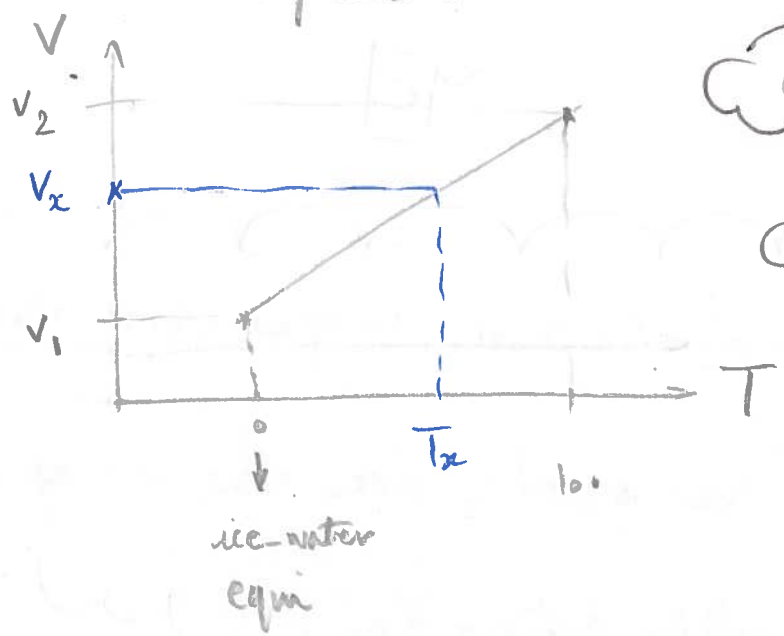
Definition of 0th law: If A & B are in equilibrium and B & C are in equilibrium, then A and C are also in equilibrium and no heat exchange will be between them.

0th law is the point which help us define the temperature and the way we can measure it. B: can be thermometer.

if there is no heat flow between B & C and B & A, thus A & C have the same temperature. How can we check the heat exchange? By volume, colure, conductivity ....

Thermometer $\Rightarrow$ Substance with property.

To make a thermometer, you need two refrence points and a property of a substance and <u>linear</u> relation between those two points.



Centigrade

$\Updownarrow$

volume mercury

Thermodynamics Class * work, heat & First law.

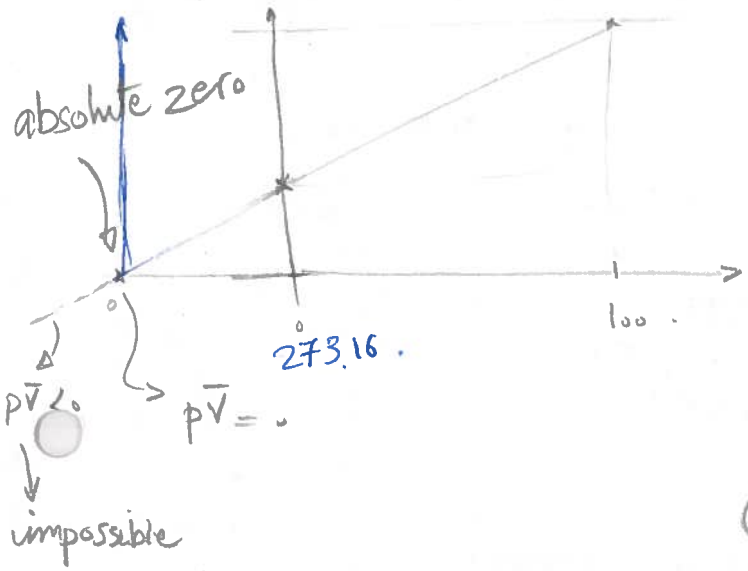
Applied Statistical Mechanics
Abdolhosseini

Ideal gas therm:

Bais therom:

$$\lim_{P \to 0} (P.\bar{V}) = f(t) \Rightarrow \begin{cases} \text{substance : gas} \\ \text{property : } \lim_{P \to 0} (P.\bar{V}) \\ \begin{cases} \text{boiling } (100\,^\circ C) \\ \text{freezing } (\ .\ ) \end{cases} \end{cases}$$

+ linear interpolation.

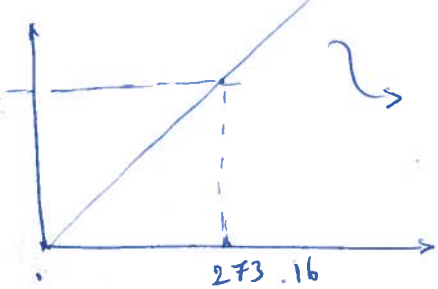


Absolute Zero
$\Rightarrow -273.15\ ^\circ C$

This absolute value is result of linear interpolation and nothing else

$$* \text{ Kelvin Scale: } T(K) = t(^\circ C) + 273.15 \ *$$

Better points: ref $\begin{cases} \text{ok} \rightarrow \text{absolute value.} \\ \text{Triple point of water: } T_{tp} = 273.16\ K \ \&\ P = 6.1 \times 10^{-3} \text{ bar.} \end{cases}$



$$f(t) = \frac{R \cdot f(T_{tp})}{273.16} \cdot T = \lim (P.\bar{V}).$$

$$RT = P\bar{V} \Rightarrow \text{ideal gas.}$$

$V = f(n, p, T) \Longrightarrow V = \frac{nRT}{p}$: for real gas.

$\Downarrow$

equation of state.

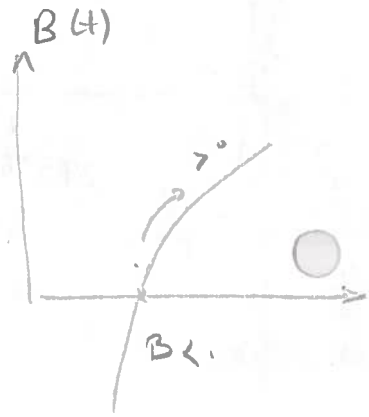
* How to deal with real gases? $\Rightarrow$ modify above ideal gas *

1). $p\bar{V}_{real} = Z\,RT$ & $Z = \frac{\bar{V}_{real}}{\bar{V}_{ideal}}$ $\begin{cases} > 1 : \text{expanding} \\ < 1 : \text{compacting} \end{cases}$

2). virial expansion :

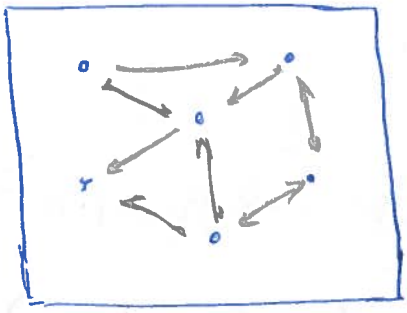
Taylor expansion.

$$\frac{p\bar{V}}{RT} = Z = 1 + \frac{B(T)}{V_{real}} + \frac{C(T)}{V_{real}^2} + \cdots$$



3) Van der Waals equation of state : (1873).

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT \quad : \quad a \,\&\, b = 0 \rightarrow \text{ideal gas}$$



$b \equiv$ volume/mole of hard spheres.

$$p\,(\underbrace{\bar{V} - b}_{\text{actual volume seen}}) = RT.$$

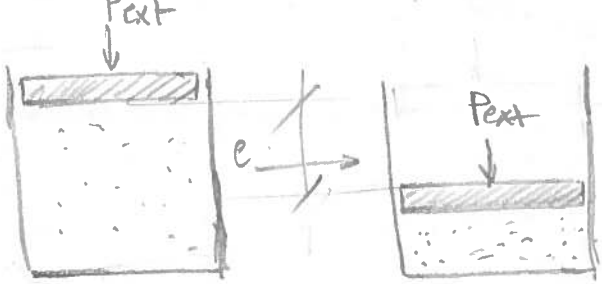
$$\rightarrow \quad P = \left(\frac{RT}{(\bar{V}-b)}\right) - \frac{a}{\bar{V}^2}$$

is less → probability of atoms beeing close to each other.

→ Rearrange $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V}-b) = RT$.

Work ⇒ $W = f \cdot \ell$ → Expansion work:

f → force, ℓ → distance.



$F = P \cdot A$

↓

$W = f \cdot \ell = (P_{ext} A \cdot \ell) = P_{ext} \cdot \Delta V$

P_{ext} → external.

ΔV → Change in volume.

Convention: if you are doing work on the system, then your work should be positive as a convention.

$$W = -P_{ext} \cdot \Delta V \Rightarrow đW = -P_{ext} \cdot dV.$$

very important

$\Delta V < 0 \longrightarrow W > 0$

$\Delta V > 0 \longrightarrow W < 0$

$đW$ → not an exact differential. → You need to know the path.

$$W = +\int_1^2 dW = -\int_1^2 P_{ext}\, dV$$

Example: $Ar(g, P_1, V_1) = Ar(g, P_2, V_2)$ $\begin{cases} V_1 > V_2 \\ P_1 < P_2 \end{cases}$

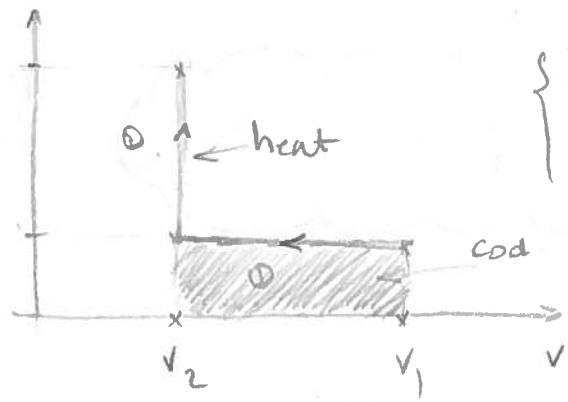
Reversible

Process

$P_{ext} = P_{int}$

very simple consequence.

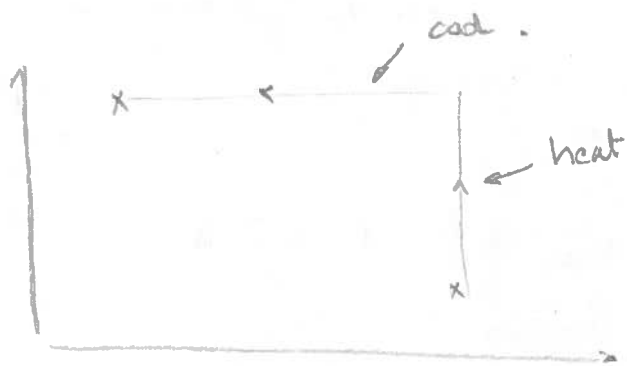
1



$\begin{cases} V_1 \longrightarrow V_2 & : P \text{ const} : \text{isobaric} \\ P_1 \longrightarrow P_2 & : V \text{ constant} \end{cases}$

$PV = nRT$

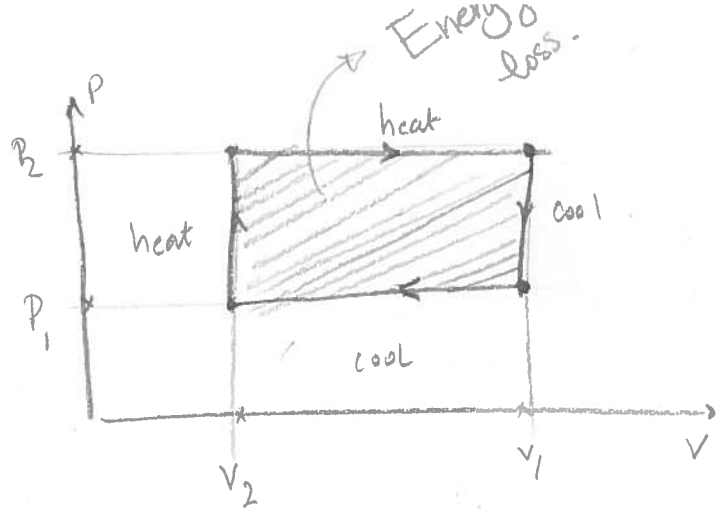
2



$\begin{cases} P_1 \longrightarrow P_2 & : P \text{ constant} \\ V_1 \longrightarrow V_2 & : V \text{ constant} \end{cases}$

$$\begin{cases} W_1 = -\int_{V_1}^{V_2} P_1\, dV = -P_1(V_2 - V_1) = P_1(V_1 - V_2) > 0 \\ W_2 = -\int_{V_1}^{V_2} P_2\, dV = -P_2(V_2 - V_1) = P_2(V_1 - V_2) > 0 \end{cases}$$

$W_1 < W_2 \Longrightarrow$ Work depends on the path you take.



$$W_{total} = W_1 - W_2$$

$$= P_1(V_1 - V_2) - P_2(V_1 - V_2)$$

$$= (P_1 - P_2)(V_1 - V_2) < 0$$

The cycle does work on the surrounding

$$W = \oint dw \neq 0$$ ← path dependent

Def.

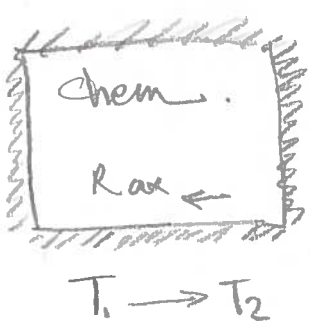
Definition

Heat: is a quantity that flows into a substance and changes it's temperature

heat $\longrightarrow q \Rightarrow$ Convention.

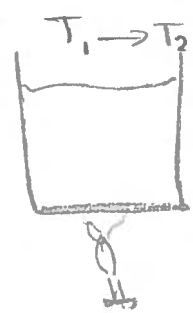
$$T_1 \xrightarrow{q} T_2 : \quad T_2 > T_1 \Rightarrow q > 0$$

①



adiabatic.

no Heat exchange.



So, q depends on the path.

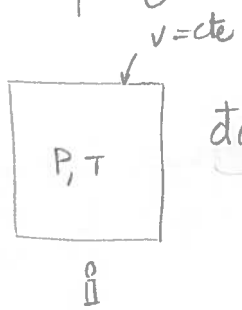
Thermodynamics Class ; Internal energy & expansion work.

Outlines of this session:

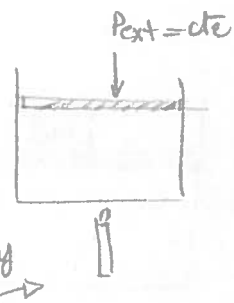
1- heat capacity
2- 1st law
3- $g(P_1, V_1, T) = g(P_2, V_2, T)$
4- $dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{\text{heat cap}} dT + \underbrace{\left(\frac{dU}{\partial V}\right)_T}_{\text{Joule's Free exp.}} dV$. ⇐ $\overbrace{U}^{U(T,V)}$ is internal energy

Heat capacity:

There are 2 ways to increase the temperature.



$đq = C_V \, dT$



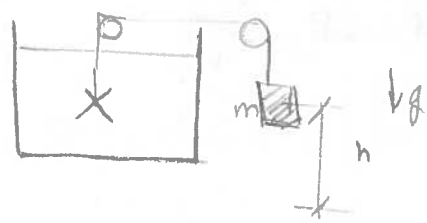
$đq = C_P \, dT$

$$q = \int_{path} C_P \, dT$$

way 1

$$\Delta T = \frac{\Delta q}{C_P}$$

way 2



$w = mgh \Rightarrow \Delta T = w / C_P$

1st law:

1- $\oint (đw + đq) = 0$ → over any closed path.

2- $dU = đq + đw$

path independent

$$\Delta U = \int_1^2 du = U_2 - U_1 = q + w.$$

$\Delta U_{syst} = q + w$

$\Delta U_{sur} = -q - w$

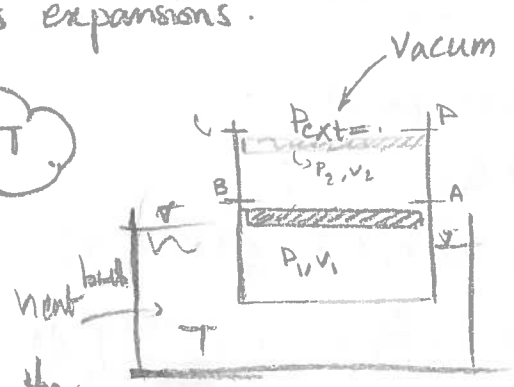
$\Delta U_{universe} = 0$ → Corollary of clausius

Conservation of energy

isothermal gas expansions.

E. Constant T

1. $p_{ext} = 0$



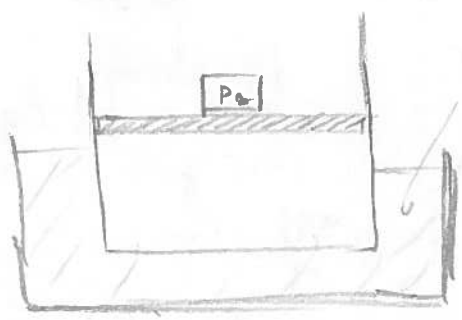
if you remove A-B bolts. then the lid will accelerate to get to CD bolts!

Note that, the work done on the surroundings is zero. ($P_{ext} = 0$).

$$W = -\int_{V_1}^{V_2} p_{ext} \cdot dV = 0$$

$dU = \delta W + \delta Q$

2. $P_{ext} = P_2$

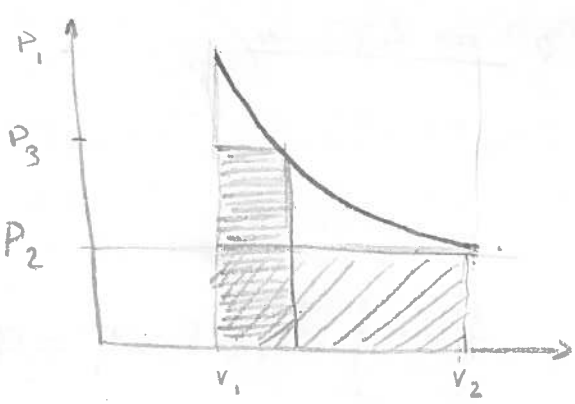


heat bath

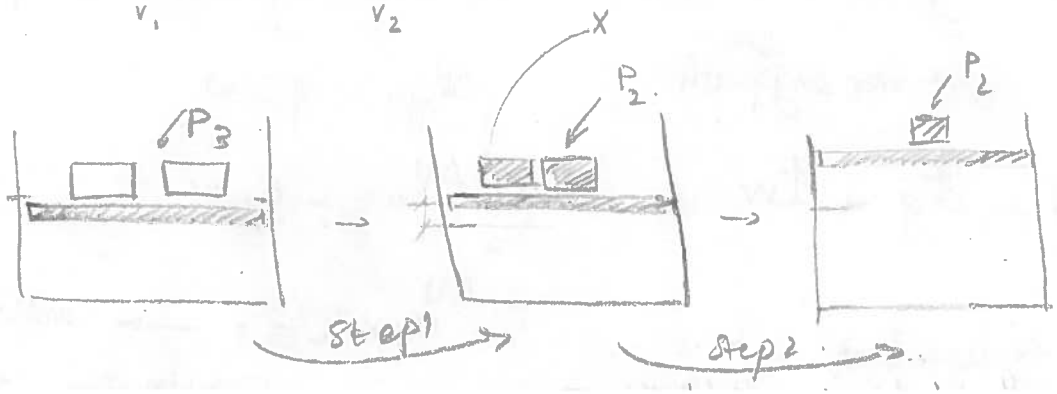
$$W_{(2)} = -\int_{V_1}^{V_2} P_2 \cdot dV = -P_2 (V_2 - V_1) < 0$$

PV ⇒ Energy.

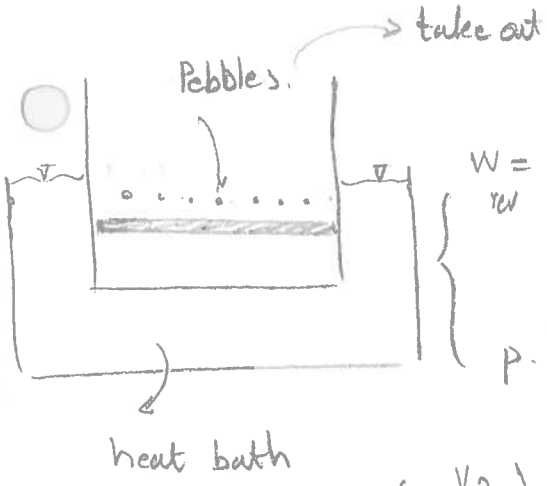
$PV = nRT \rightarrow P = \frac{\bigcirc}{V}$



3.



4. do it reversibly · $p = p_{ext}$ ·

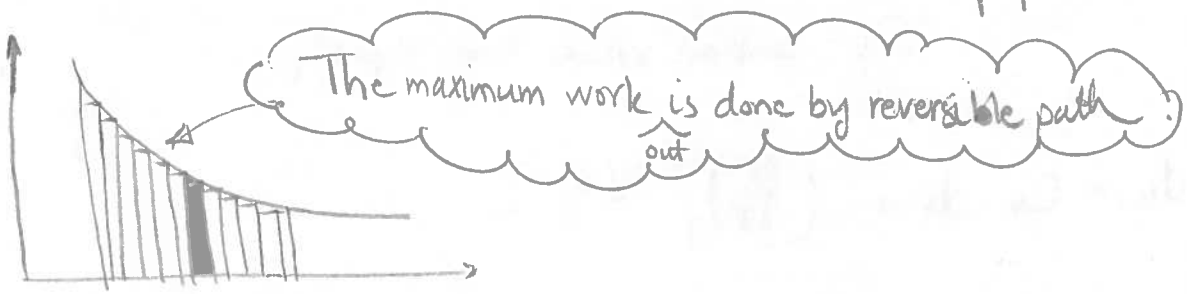


$$\begin{cases} W_{rev} = -\int_{v_1}^{v_2} p \cdot dv = -nRT \int_{v_1}^{v_2} \frac{dv}{v} = -nRT \cdot \ln\left(\frac{V_2}{V_1}\right). \\ p \cdot v = nRT \rightarrow p = \frac{nRT}{v} \end{cases}$$

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{P_1}{P_2}\right)$$

$$W_{rev} = -nRT \cdot \ln\left(\frac{P_1}{P_2}\right) = \boxed{nRT \ln\left(\frac{P_2}{P_1}\right)}$$

The system has done work by bringing up pebbles.



$\Delta U = 0$ (T: cte).

$$\Delta U = q + w$$

The max w out

The max heat in

$$U(T,v) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_v \cdot dT + \left(\frac{\partial U}{\partial v}\right)_T \cdot dv$$

Constraint:

$$\begin{cases} rev: \; dU = đq_{reversible} - p \cdot dv \\ \ldots \end{cases}$$

- adiabatic process: $\because dq = 0 \longrightarrow du = đw_{rev}$.

(close)

$\hookrightarrow$ Be careful about reversibility

- Constant V: $đw = 0 \longrightarrow du = đq_V$.

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

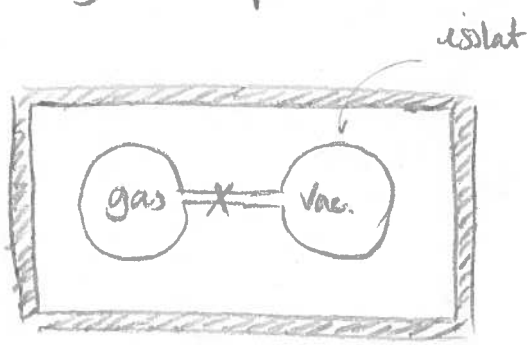
had it before.

$$\hookrightarrow \underbrace{du_V = \left(\frac{\partial U}{\partial T_V}\right)_V dT_V = đq_V}_{C_V}$$

C_V : constant volume heat capacity.

$$du = C_V \cdot dt + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV$$

Joul's free expansion:



isolated

$$\Delta U = \cancel{đq} + \cancel{đw}$$

no volume change.

$$0 = C_V \cdot dT_u + \left(\frac{\partial U}{\partial V}\right)_T dV_u$$

$$\rightarrow \left(\frac{\partial U}{\partial V}\right)_T = -C_V \cdot \frac{dT_U}{dV_u} = -C_V \left(\frac{\partial T}{\partial V}\right)_u$$

$$\begin{cases} \text{ideal gas} \\ \left(\frac{\partial T}{\partial V}\right)_u = 0 \\ \text{real gas} \quad \left(\frac{\partial T}{\partial}\right) = \eta_J \neq 0 \end{cases}$$

$\Delta U = 0 \longrightarrow$ for all isothermal Ideal Gas processes.

$$\Delta U = \int C_v \cdot (T)\, dT$$

$$\Delta U = 0 \longrightarrow -W = +q$$

In simple words, it means that Ideal gas internal energy is a function of Temperature.

Antalpy $\Rightarrow$ $H(T,P) \longrightarrow$ $H = U + PV$ $\Rightarrow$ to study heat transfer constant pressure processes

$$sys(P_1, V_1, T_1) = sys(P_2, V_2, T_2)$$

$$\Delta U = q + w = q_p - P\Delta V \longrightarrow q_p = \Delta U + P\Delta V$$

$$\text{const } P \longrightarrow q_p = \Delta U + \Delta(PV) \longrightarrow q_p = \Delta(\underbrace{U+PV}_{H})$$

This is why we have set $H = U + PV$ to study processes at constant pressure.

$$dH = đq_p$$

You should see this in your dreams!

constant pressure, reversible work

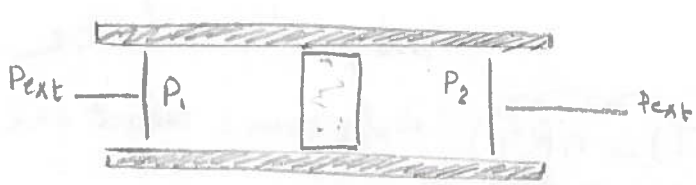
$$dH = \underbrace{\left(\frac{\partial H}{\partial T}\right)_P}_{1^*} dT + \underbrace{\left(\frac{\partial H}{\partial P}\right)_T}_{2^*} dP$$

C_p: Heat Capacity at Constant pressure

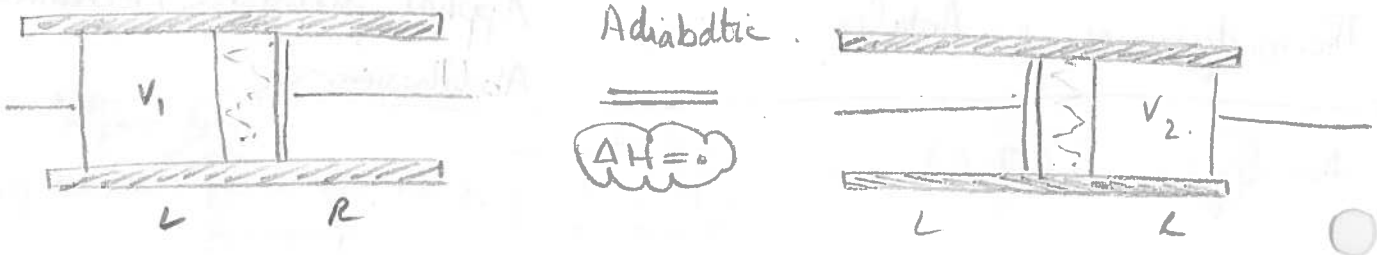
rev

$$1^*) \begin{cases} \left(\frac{\partial H}{\partial T}\right)_P \Rightarrow dH = \underbrace{dq_p}^{2} \;,\; dH = \underbrace{\left(\frac{\partial H}{\partial T}\right)_P dT}^{1} \\ đq_p = C_p\, dT^{3} \xrightarrow{1,2,3} \left(\frac{\partial H}{\partial T}\right)_P = C_p \end{cases}$$

$2^* \longrightarrow$ Jouls - Tompson experiment $\xrightarrow{\text{answers}} \left(\frac{\partial H}{\partial P}\right)_T = ?$



This is irreversible process because $P_1 \neq P_2$



$LH \Rightarrow W = p_1 V_1$

$RH \Rightarrow W = -p_2 V_2$.

$$W_{tot} = W_{LH} + W_{RH} = p_1 V_1 - p_2 V_2 = \boxed{-\Delta(pV) = \Delta U}$$

$$\Delta H = \Delta(U + pV) = \overset{-\Delta(pV)}{\Delta U} + \Delta(pV) = 0 \longrightarrow \boxed{\Delta H = 0}$$

J-T experiment:

$$dH = C_p \cdot dT_H + \left(\frac{\partial H}{\partial p}\right)_T dp_H = 0$$

$$\longrightarrow \left(\frac{\partial H}{\partial p}\right)_T = -C_p \left(\frac{\partial T}{\partial p}\right)_H \longrightarrow \left(\frac{\partial T}{\partial p}\right)_H = \mu_{JT}.$$

{ Constant anthalpy experiments.

$$dH = C_p \cdot dT + \mu_{JT} \cdot dp$$

---

ideal gas: $U(T)$, $pV = nRT$

$$H = U + pV = U(T) + nRT$$

no p dependence.

only cares about the temp.

Thus: $H(T) \rightarrow \left(\frac{\partial H}{\partial p}\right)_T = 0 \Rightarrow \mu_{JT} = 0$

for ideal gas: $dH = C_p \, dT$.

Real gas:

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT. \xrightarrow[\text{at}]{\text{Take}} \left(\frac{\partial H}{\partial p}\right)_T \propto b - \frac{a}{RT}.$$

$$\left(\frac{\partial H}{\partial P}\right)_T \propto -\mu_{JT} \Rightarrow \left(\frac{\partial T}{\partial P}\right)_H \propto \frac{a}{RT} - b$$

$$\rightarrow \frac{a}{RT_{in}} - b = 0 \Rightarrow T_{inv} = \frac{a}{Rb} \longrightarrow \begin{cases} T > T_{inv}: & \frac{a}{RT} - b > 0 \rightarrow \left(\frac{dT}{dp}\right)_H < \\ T < T_{inv}: & -\left(\frac{dT}{dp}\right)_H > 0 \end{cases}$$

$$\begin{cases} \text{most gases}: T_{inv} > 300 \\ T_{inv}(H_2) = 193\,k. \\ T_{in}(He) = 53\,k \end{cases} \longrightarrow \text{Think how you can liquify He?}$$

$$\bar{C}_p = \bar{C}_v + R$$

$$\bar{C}_p = \left(\frac{\partial H}{\partial T}\right)_p, \quad \bar{C}_v = \left(\frac{\partial U}{\partial T}\right)_v.$$

$$\begin{cases} H = U + PV \rightarrow \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial PV}{\partial T}\right)_p \end{cases}$$

C_p

ideal gas: $C_p = \left(\frac{\partial U}{\partial T}\right)_p + \cancel{p}\left(\frac{R}{\cancel{p}}\right) = \left(\frac{\partial U}{\partial T}\right)_p + R$

$$U(T, V(p,T)) \longrightarrow \underbrace{\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V}_{} + \cancel{\left(\frac{\partial U}{\partial V}\right)_T}^{\,0} \cdot \left(\frac{\partial V}{\partial T}\right)_p .$$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + R = C_V + R$$

Thermodynamics Class, Adiabatic Changes

Ideal Gas:

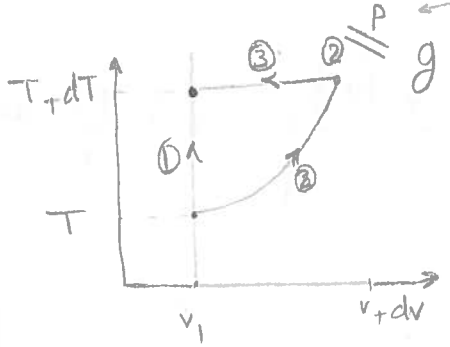
$\bar{C}_p = \bar{C}_v + R \longrightarrow$ let's do it another way!

$pv = RT$

$$g(p, \bar{v}, T) \overset{v \leftarrow c_v}{=} g(p+dp, \bar{v}, T+dT)$$

$$\overset{p \leftarrow c_p}{=} g(p, \bar{v}+d\bar{v}, T+dT)$$

// $T = cte : \Delta u = 0$



$pdv = RdT \Rightarrow dv = \frac{R}{p} dT$

Path (1) const $\underline{v} \longrightarrow d\bar{U} = đq = C_v . dT$

Path(2) const $\underline{p} \longrightarrow d\bar{u} = đq + đw = C_p . dt - p . d\bar{v} = C_p\, dT - R . dT = \underbrace{(C_p - R) dT}_{}$.

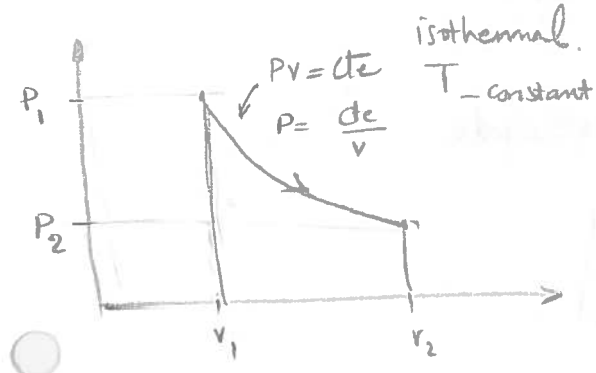
you could say simultaneously $C_v . dT$.

Path(3) Const T $\longrightarrow \cancel{du} = đq + đw$

$$dU_1 = dU_2 + dU_3 \longrightarrow C_v \cancel{dT} = (C_p - R) \cancel{dT} . \Rightarrow \boxed{C_v + R = C_p}$$

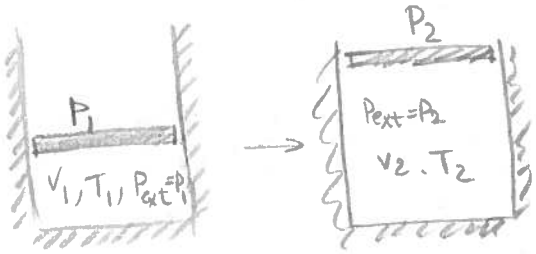
$PV = nRT$

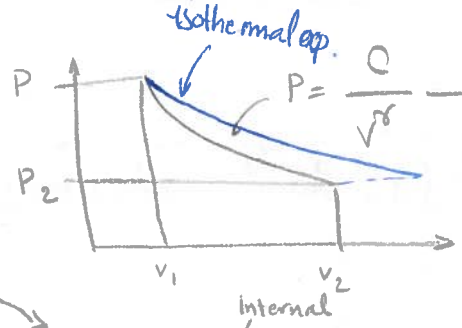
isothermal. T – constant



$$-w_{rev} = \int \frac{nRT}{v} . dv = -nRT . \ln\left(\frac{P_2}{P_1}\right).$$

let's do an adiabatic experiment: (Reversible).





$P = \frac{C}{V^{\gamma}} \longrightarrow$ let's show: $PV^{\gamma} = C$.

adiabatic: $dq = 0$, reversible: $dw = -P_{ext} \cdot dV = -\overset{\text{internal}}{P} \cdot dV$.

Ideal gas = $du = C_v \cdot dt$ I & $PV = RT$

$du = dq + dw = -P \cdot dV$ II

$$\boxed{C_v \cdot dt = -P\, dV}, \quad P = \frac{nRT}{V} \Rightarrow C_v \cdot dt = \frac{RT}{V} \cdot dV$$

$$\boxed{C_v \cdot \frac{dT}{T} = -R \cdot \frac{dV}{V}} \longrightarrow \int_{T_1}^{T_2} C_v \frac{dT}{T} = \int_{V_1}^{V_2} -R \frac{dV}{V} \longrightarrow \cdots$$

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

$$\frac{R}{C_v} = \frac{C_p - C_v}{C_v} = \frac{C_p}{C_v} - 1 = \boxed{\gamma - 1}$$

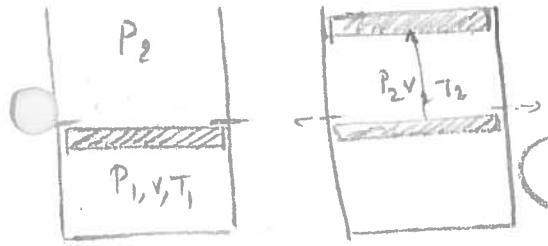
$$T = \frac{PV}{R} \Rightarrow \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{P_2 V_2 / R}{P_1 V_1 / R}\right)$$

$$\longrightarrow P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \longrightarrow PV^{\gamma} = Cte \text{ on the path.}$$

mono-atomic $\begin{cases} C_v = \frac{3}{2} R \\ C_p = \frac{5}{2} R \end{cases} \longrightarrow \boxed{\frac{C_p}{C_v} = \gamma = 5/3}$.

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \Rightarrow V_2 > V \longrightarrow T_2 < T_1$$ in adiabatic expansion system

Let's do it irreversibly!



adiabatic $dq = 0$

$dw = -p \cdot dv$

$$\left(-w_{irr}\right) < \left(-w_{rev}\right)$$

$$\begin{cases} du = C_v \, dT \\ du = -p_2 \cdot dv \end{cases}$$

$\longrightarrow$ finally: $\underbrace{T_2\left(C_v + R\right) = T_1\left(C_v + \left(\frac{P_2}{P_1}\right)R\right)}$.

$\hookrightarrow < 1$

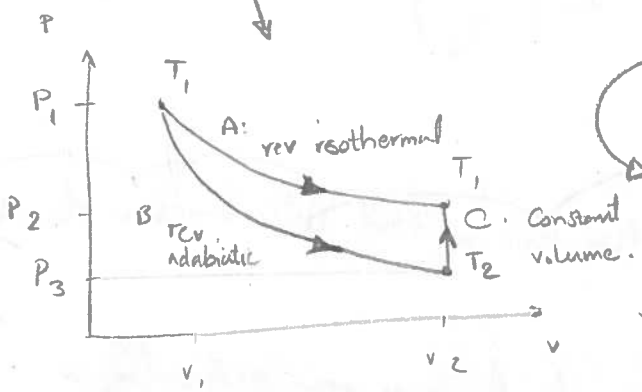
$T_{rev} < T_{irr}$

$T_2 < T_1 \longrightarrow$ qualitatively cooler.

Thermodynamics Class: Thermochemistry.

Thermodynamic Cycles: $\underbrace{\begin{cases}\Delta U \\ \Delta H\end{cases} \quad \boxed{\begin{matrix} q \\ w \end{matrix}}}_{\text{state functions:}}$ → are not state functions. & $dS = \int \frac{dq}{T}$ ⇒ Special function

"ideal gas"



Path A: $\Delta U = 0$, $\Delta H_A = 0$, $dH_A = 0$

$$dw = -p.dv = -RT.\frac{dv}{v}.$$

$$w = -\int_{V_1}^{V_2} \frac{dv}{v} = -RT.\ln\left(\frac{V_2}{V_1}\right).$$

$$q_A = RT.\ln\left(\frac{V_2}{V_1}\right)$$

let's calculate special function for path A:

$$dS = \int \frac{dq_A}{T_1} = R.\ln\left(\frac{V_2}{V_1}\right).$$

Path B: Adiabatic ⇒ $q_B = 0$ Adiabatic.

$$\begin{cases} du = C_v.dT \Rightarrow \Delta U_B = C_v(T_2 - T_1) = w_B \\ dH = C_p.dT \Rightarrow \Delta H_B = C_p(T_2 - T_1). \end{cases}$$

$$ds = \int \frac{dq}{T} = 0$$

Path C : $\Rightarrow w_C = 0$ Constant Volume :

$$\begin{cases} \Delta U = C_v (T_1 - T_2) = q_C \\ \Delta H = C_p (T_1 - T_2) . \end{cases}$$

$$ds = \int \frac{dq_C}{T_1} = \int_{T_2}^{T_1} \frac{du}{T} = \int_{T_2}^{T_1} \frac{C_v dT}{T} = C_v \ln\left(\frac{T_1}{T_2}\right).$$

Comparing Path A and (B+C), we get this notion that state function do not depend on the path, but only on the state which you are actually in.

This is not the case for w & q !

The characteristic of state functions.

Special function :

$$\begin{cases} A : R \ln\left(\frac{V_2}{V_1}\right) & \text{I} \\ B+C : C_v \ln \frac{T_1}{T_1} & \text{II} \end{cases}$$

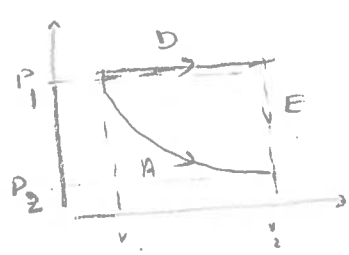
adiabatic reversible path :

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{R/C} \quad \text{III}$$

I, II, III $\rightarrow$ $dS_A = dS_{B+C}$ $\rightarrow$ special function is working like state function

Exercise :

Verify above statements :



Thermochemistry $\Rightarrow$ calculate. ΔH_{rx}.

Constant p + rev $\longrightarrow$ $\Delta H = q_p \Rightarrow \Delta U = q + w \rightarrow$ get w.

$$Fe_2O_3(s, T, p) + 3H_2(g, T, p) = 2Fe(s, T, p) + 3H_2O(l, T, P).$$

$\Delta H_r =$ for isothermal, cons p, reversible work.

$\Delta H_{rx} = H$ (product) $-$ H (reactants).

Refrence Point for H: $\begin{cases} 298.15\,K \text{ 1bar} \\ H = 0 \text{ for every element in the process.} \end{cases}$

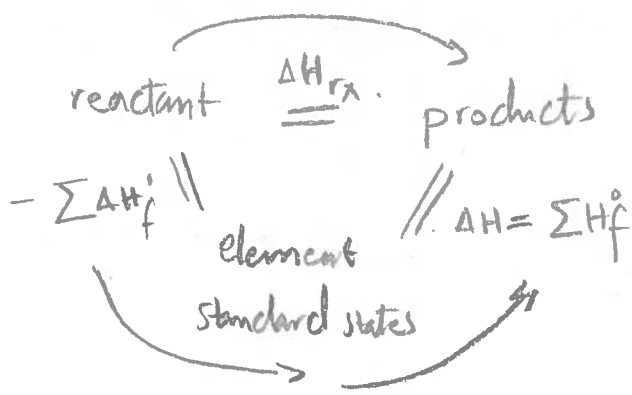
$$\begin{cases} \bar{H}^{\circ}_{H_2(g)}(298.15\,K) = 0 \\ \bar{H}_{E(g)}(298.15\,K) = 0 \end{cases}$$

1bar

ex: HBr ΔH°_f

$\frac{1}{2} H_2(g, T, 1\text{bar}) + \frac{1}{2} Br(l, T, 1\text{bar}) = HBr.$

ΔH_{rx}

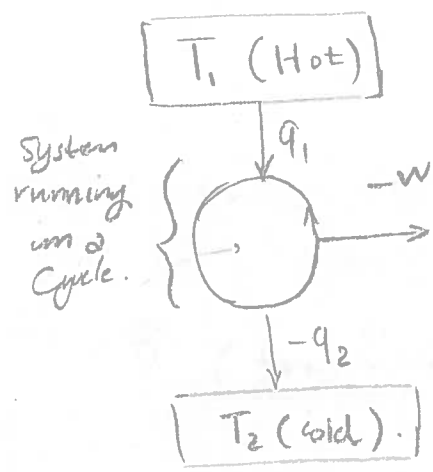


$\Delta H_{rex} = \Delta H_f^{\circ}$ (products) $-$ ΔH_f° (reactants).

Second law: shows the direction of spontaneous change — very important.

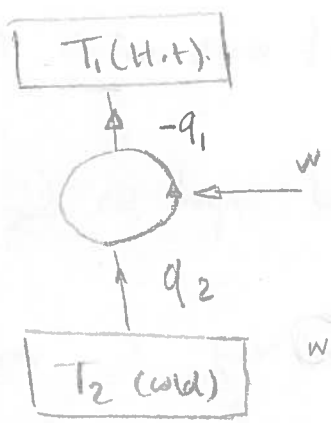
Clausius:
- 1st law: Energy of the universe is constant (1st)
- 2nd law: The Entropy of universe is increasing (2nd.)

Heat Engine:



$q_1 > 0$
$-w > 0$
$-q_2 > 0$
$T_1 > T_2$

Refrigurator



$T_1 > T_2$
$-q_1 > 0$
$q_2 > 0$
$w > 0$

$w = -(q_1 + q_2)$

$-(q_1) > (q_2)$

*

Alternative Statement : All spontaneous processes are irreversible.

Mathematical formula: $\oint \frac{đq_{rev}}{T} = 0$, $\oint \frac{đq_{irrev}}{T} < 0$.

Define: $dS = \frac{đq_{rev}}{T} \Rightarrow \Delta S = \int_1^2 \frac{dq}{T} = S_2 - S_1$

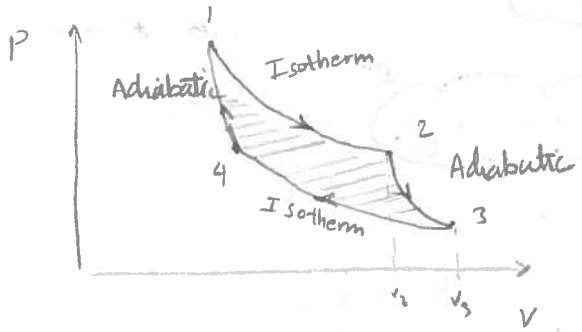
$S \equiv$ Entropy.

Kelvin version of 2nd law:

Kelvin: It's impossible to convert heat to work with a system that opprate in a cycle without wasting amount of it to the reservoir

Thermodynamics / Entropy & Second Thermodynamics law.

Carnot Engine / Carnot Cycle: All the pathes are Reversable



$$\begin{cases} 1 \to 2: & \Delta U = q_1 + W_1 \\ 2 \to 3: & \Delta q = 0, \ \Delta U = W_1' \\ 3 \to 4 & \Delta U = q_2 + W_2 \\ 4 \to 1 & \Delta q = 0, \ \Delta U = W_2' \end{cases}$$

Total work out $\Rightarrow W = -(W_1 + W_1' + W_2 + W_2')$

Heat input $\Rightarrow Q = q_1$

Efficiency. $\varepsilon = \dfrac{\text{work out}}{\text{heat in}} = \dfrac{W}{Q} = \dfrac{-(W_1 + W_1' + W_2 + W_2')}{q_1}$ (I)

1st law $\Rightarrow \oint du = 0 \Rightarrow q_2 + q_1 = -(W_1 + W_2 + W_1' + W_2')$ (II)

(I), (II) $\rightarrow \varepsilon = \dfrac{q_1 + q_2}{q_1} = 1 + \dfrac{q_2}{q_1}$ $(q_2 < 0) \longrightarrow \varepsilon < 1$

for an Ideal Gas:

$$\begin{cases} 1 \to 2: \ \Delta U = 0 & q_1 = -W_1 = \int_1^2 P\,dv = \int_1^2 RT_1 \frac{dv}{v} = RT_1 \ln \frac{v_2}{v_1} \\ 2 \to 3: \ \Delta U = C_v(T_2 - T_1) = W_1' & \text{Adiabatic/Rev}: \ \frac{T_2}{T_1} = \left(\frac{v_2}{v_3}\right)^{\gamma - 1} \\ 3 \to 4: \ \Delta U = 0 & q_2 = -W_2 = \int_3^4 p\,dv = RT_2 \ln\left(\frac{v_4}{v_3}\right) \\ 4 \to 1: \ \Delta U = C_v(T_1 - T_2) = W_2' & \text{rev/adiab}: \ \left(\frac{T_1}{\ }\right) = \left(\frac{v_4}{\ }\right)^{\gamma - 1} \end{cases} \Rightarrow \frac{v_4}{v_1} = \frac{v_3}{v_2}$$

$$\begin{cases} \varepsilon = 1 + \dfrac{q_2}{q_1} = 1 + \dfrac{T_2}{T_1} \cdot \dfrac{\ln(V_4/V_3)}{\ln(V_2/V_1)} = \boxed{1 - \dfrac{T_2}{T_1}} < 1 \\ V_4/V_3 = V_1/V_2 \end{cases}$$

$$\frac{q_2}{q_1} = -\frac{T_2}{T_1} \Rightarrow \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \Rightarrow \oint \frac{dq}{T} = 0 \rightarrow \oint dS = 0$$

S is a state function

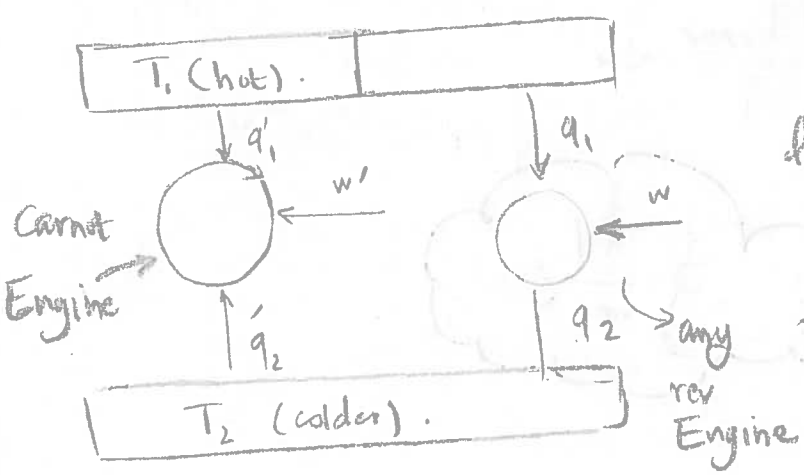
Refrigerator:

Coeff of performance $\eta = \dfrac{q_2}{-w} = \dfrac{q_2}{-(q_2+q_1)} = \dfrac{q_2/q_1}{-(1+q_2/q_1)} = \dfrac{-T_2/T_1}{-(1-T_2/T_1)} =$

$$\rightarrow \eta = \frac{T_2}{T_1 - T_2}$$

Generalized Carnot Results:

$$\varepsilon = -\frac{w}{q_1} \quad \& \quad \varepsilon' = -\frac{w'}{q_1'}$$



let's assume $\varepsilon' > \varepsilon$

Use work of left hand as input work of Right handcycle

Total work out $= 0 \Rightarrow -w' = w > 0$

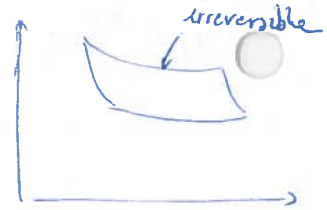
impossible

$$\varepsilon' > \varepsilon \Rightarrow -\frac{w'}{q_1'} > -\frac{w}{q_1} \Rightarrow \frac{w}{q_1'} > \frac{-w}{q_1} \Rightarrow q_1 < q_1' \Rightarrow -(q_1' + q_1) > 0$$

Thus for any Engine / Rev $\Rightarrow \varepsilon = 1 - \frac{T_2}{T_1}$

efficiency is 1 if $T_2 = 0\,K$ which is impossible due to 3rd law.

Irreversible Engine:



$1 \longrightarrow 2$: $(-w_{irrev}) < (-w_{rev}) \Rightarrow w_{irrev} > w_{rev}$.

$$\left.\begin{aligned} \Delta u &= q_{irrev} + w_{irrev} \\ &= q_{rev} + w_{rev} \end{aligned}\right\} \Rightarrow q_{irrev} < q_{rev}.$$

$$\varepsilon_{irrev} = 1 + \frac{q_2}{q_1^{irrev}} < 1 + \frac{q_2^{rev}}{q_1^{rev}} = \varepsilon_{rev}.$$

same rev proc.

It's imp

$\Rightarrow$ $\varepsilon_{irrev} < \varepsilon_{rev}$ Efficiency of a reversible Engine is better. irreversible

$$\frac{dq_{irrev}}{T} < \frac{dq_{rev}}{T} \Rightarrow \oint \frac{dq_{irrev}}{T} < 0$$

$\Rightarrow$ Clausius Inequality $\oint \frac{dq}{T} \leq 0$.

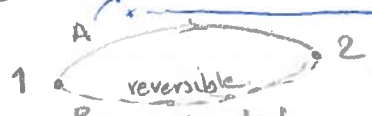
Thermodynamics / Entropy & irreversibility.

$$dS = \frac{dq_{rev}}{T} \rightarrow \oint \frac{dq_{rev}}{T} = 0 = \Delta S_{cycle}$$

$$\oint \frac{dq_{irrev}}{T} < 0$$

Isolated system & irreversible process:

irreversible ⇒ is a spontaneous process.



(not isolated) ⇒ energy or heat or work is inserted to make the system back on not's primary state.

(A) $q_{irrev} = 0$

for the cycle: $\oint \frac{dq}{T} \leq 0$ Because of Being Isolated.

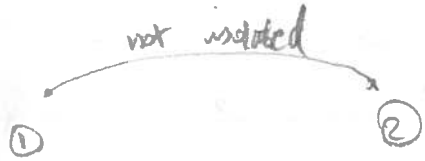
$$\oint \frac{dq}{T_1} = \int_1^2 \frac{dq_{irrev}}{T} + \int_2^1 \frac{dq_{rev}}{T_1} \leq 0 \rightarrow \int_2^1 \frac{dq}{T} = S_1 - S_2 = \Delta S_{backward} = -\Delta S_{forward}$$

$+\Delta S \geq 0$ forward → It means that for this spontaneous change. Entropy is increasing in the system! in the forward process.

Isolated system:
- $\Delta S > 0$ irreversible
- $\Delta S = 0$ reversible.
- $\Delta S < 0$ → never

⇒ which way the system is going if it's isolated in certain situation.

It can depict the direction of time.



$\Delta S^{sys} = S_2^{sys} - S_1^{sys}$: independent of path.

$\Delta S^{surrounding}$.

Irreversible path : consider the whole univ as an isolated system.

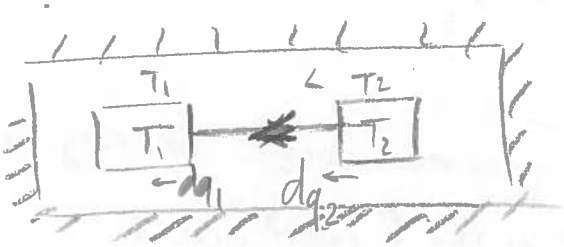
$$\Delta S^{univ} = \Delta S^{sys} + \Delta S^{surr}_{irrev} > 0 \Rightarrow \Delta S^{sur}_{irrev} > -\Delta S^{sys}.$$

Reversible path : $\Delta S^{univ} = \Delta S^{sys} + \Delta S^{surr}_{rev} = 0 \Rightarrow \Delta S^{sur}_{irrev} = -\Delta S^{sys}$.

Entropy of the whole universe never decreases

Calculation of ΔS:

1



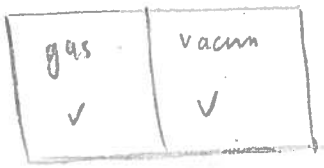
isolated sys: $\Delta u = 0 \Rightarrow dq_1 = -dq_2$

$$dS = dS_1 + dS_2 = \frac{dq_1}{T_1} + \frac{dq_2}{T_2}.$$

$$= dq_1 \left(\frac{T_2 - T_1}{T_1 T_2} \right).$$

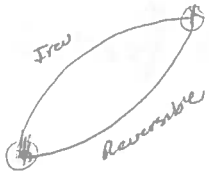
$dS > 0 \longrightarrow$ let's check it ✓

② Joul's expansion: for ideal gas



$1\,mol\,(g, V, T) \overset{ad}{=} 1\,mol\,(g, 2V, T)$.

$w = 0 \quad q = 0 \quad \Delta U = 0$



Reversible press → Compress it back to V isothermally.

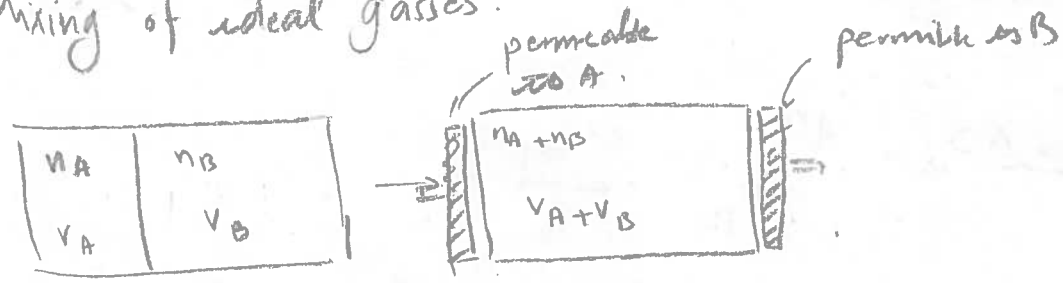
$$\Delta U = 0 \to \Delta S_{backward} = \int \frac{dq}{T} = \int \frac{-dw}{T} = \int_{2V}^{V} \frac{P\,dV}{T} = \int \frac{R\,dV}{V} = R \ln(1/2).$$

$$\Delta S_{forward} = R \ln 2 > 0 \Rightarrow \text{Spontaneous}$$

In microscopic terms: $S = R/N_A \cdot \ln \Omega$ → # distinct microscopic states.

$$\Delta S = \frac{R}{N_A} \cdot \ln 2^{N_A} = R \cdot \ln 2 \text{ as had it before.}$$

Mixing of ideal gasses:



$$n_A A(g, V_A, T) + n_B B(g, V_B, T) = (n_A A + n_B B)(g, V, B)$$

Reversible compression demixing:

$$\Delta S_{demixing} = -\Delta S_{mix} \quad : \quad \Delta U_{demix} = 0 = q_{rev} + w_{rev}.$$

$$dw_{rev} = -P_A\,dV_A - P_B\,dV_B \quad . \quad \Delta S_{1} = \int \frac{dq_{rev}}{} = \int^{V_A} \frac{P_A\,dV_A}{} + \int^{V_B} \frac{P_B\,dV_B}{}$$

$= n_A \ln(V/V_A) + n_B \ln(V/V_B)$.

Mole fractions: $X_A = \frac{n_A}{n}$, $X_B = \frac{n_B}{n}$.

$= \frac{V_A}{V}$, $V = \frac{V_B}{V}$.

Thus

$$\Delta S_{demix} = nR\left(X_A \ln X_A + X_B \ln X_B\right) \Big/ \Delta S_{mix} = -nR\left(X_A \cdot \ln X_A + X_B \ln X_B\right) > 0$$

Heat or Cool at Const. V: $A(T,V) = A(T_2,V)$. for any system.

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_v \cdot dT}{T} = C_v \ln\left(\frac{T_2}{T_1}\right) \begin{cases} \Delta S > 0 & T_2 > T_1 \\ \Delta S < 0 & T_2 < T_1 \end{cases}$$

Reversible phase change: $H_2O(l, 100, bar) = H_2O(g, 100, bar)$.

$$q_p = \Delta H_{vap} \longrightarrow \Delta S_{rev} = q^{vp}/T_p = \frac{\Delta H_{vap}}{T_p}.$$

$H_2O(l, -10\,^\circ C, 1\,bar) = H_2O(S, -10, 1\,bar)$. spontaneous irreversible.

heating Π^{rev} $\quad$ rev $\|$ Cooling. $C_p(s)\,dT$.

$$H_2O(l, 0, bar) \overset{rev}{=} H_2O(s, 0, 1\,bar)$$

$q^{rev} = \Delta H_{fus}$.

$dq_{rev} = C_p(l)\,dT$

$$\Delta S = \Delta S_{heat} - \Delta S_{fus} + \Delta S_{cool} = \int_{T_1}^{T_{fus}} \frac{C_p\, dT}{T} - \frac{\Delta H_{fu}}{T_{fu}} + \int_{T_{fus}}^{T_1} \frac{C_p(s)\, dT}{T}$$

$$dS = -\frac{\Delta H_{fus}}{T_{fus}} + \int_{T_1}^{T_{fus}} \left[C_p(l) - C_p(s)\right] \frac{dT}{T} \approx -\frac{\Delta H_{fus}}{T_{fus}} + \left[C_p(l) - C_p(s)\right] \ln($$

Thermodynamics / Fundamental equation, absolute S and Third law.

* ~~Applied Statistical Mechanics, Abdolhosein~~ *

$du = đq + đw \longrightarrow$ This is a path dependent term! $\therefore$ [example: $du = C_v dT - C_v \eta_v dV$]

$du = [\ \ldots\ldots\ldots\ ]$ $\quad dT, dP, dS, dH.$

$\rightarrow T, P, S, H.$

Consider reversible process at constant pressure.

$$\left.\begin{aligned} du &= đq^{rev} - p\,dv \\ \text{2nd law: } đq &= T.ds \end{aligned}\right\} \Rightarrow du = T.ds - p\,dv$$

$\downarrow$

Awsom! ☺

$\Rightarrow$ So: $U = U_{(S,V)}$. $\quad \left(\frac{du}{ds}\right)_V = T, \quad \left(\frac{du}{dv}\right)_S = -P$

$$\begin{cases} H = U + pV \longrightarrow dH = dU + d(pV) = T\,ds - V\,dP \\ H = H(S,P). \end{cases}$$

$\left(\frac{dH}{ds}\right)_P = T, \quad \left(\frac{dH}{dP}\right)_S = V.$

$$\begin{cases} dU = T\,dS - p\,dv \longrightarrow dS = \frac{1}{T}dU + \frac{P}{T}.dv. \\ du = C_v.dT + \left(\frac{dU}{dv}\right)_T dv \longrightarrow dS = \frac{1}{T}C_v\,dT + \left[\frac{P}{T} + \left(\frac{dU}{dv}\right)_T\right]dv \end{cases}$$

$\left(\frac{dS}{dT}\right)_V = \frac{C_v}{T}$; Also $\left(\frac{dS}{dT}\right)_P = \frac{C_P}{dT}$.

Consider $S(T,p)$:

$$dU = TdS - pdV \Rightarrow dS = \frac{dU + pdV}{T}$$

constant T & ideal gas $\Rightarrow dU = 0 \longrightarrow dS = \frac{p\,dV}{T} = \frac{nR}{V} \cdot dV$

$\hookrightarrow d(nRT) = d(pV) = 0 \longrightarrow pdV + V.dp = 0 \longrightarrow dS = -nR\frac{dp}{p}$

$\longrightarrow$ if we know: $S(p^\circ, T)$ then S in arbitrary pressure

$$S(p,T) = S(p^\circ;T) - \int_{p^\circ}^{p} \frac{nR\,dp}{p} = S(p^\circ, T) - nR\ln(p/p^\circ)$$

1mol & $p = 1$bar

* ——————————— *

Starting at 0 kelvin:

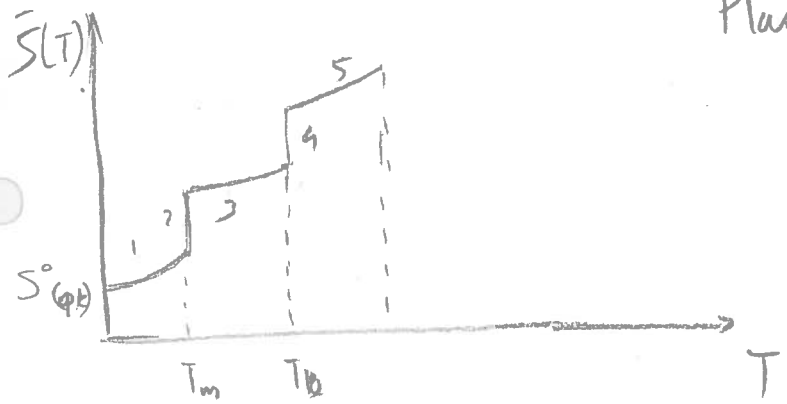
$$A(\text{solid } 0K, 1\text{bar}) \overset{1}{=} (\text{solid}, T_m, 1\text{bar}) \overset{2}{=} (l, T_m, 1\text{bar}).$$

$$\overset{3}{=} (l, T_b, 1\text{bar}) \overset{4}{=} (g, T_b, 1\text{bar}) \overset{5}{=} (g, T, 1\text{bar}) \overset{6}{=} (g, T, p).$$

$$\bar{S}(T,p) = \bar{S}(0K) + \Delta S^1 + \Delta S^2 + \Delta S^3 + \dots + \Delta S^6.$$

$$= \bar{S}^\circ(0K) + \int_0^{T_m} \frac{\bar{C}_p(s)}{T} dT + \frac{\Delta H_{fus}}{T_m} + \int_{T_m}^{T_b} \frac{C_p(l)}{T} \cdot dT$$

$$+ \frac{\Delta H_v}{T} + \int_{T_b}^{T} \frac{C_p(g)}{T} dT - R \cdot \ln(p/1)$$



Plank (1911) $T \to 0K \Rightarrow S \to 0K$.
perfect.

for every pure substance in it crystalline state.

$$S = R/N_A \cdot \ln \Omega$$ ← macroscopic state #

Corollary of Cannot reach absolute 0K°

(g, 1m, ideal) $= p = \frac{RT}{V}$ ⟶ Start (T_1, V_1).

cool irreversibly, adiabatic expansion:

$$dU = TdS - pdV, \quad dS = \frac{dU}{T} + \frac{R}{V} \cdot dV$$

$$dS = \frac{C_v}{T} dT + R \cdot \frac{dV}{V} = C_v\, d(\ln T) + R\, d(\ln V).$$

$$\to \Delta S = C_v (\ln T_2 - \ln T_1) - R(\ln V_2 - \ln V_1).$$

$$\Delta S = C_v \cdot \ln \frac{T_2}{T_1} - R \ln(V_2/V_1).$$

$$S = \int_0^{T_m} \frac{C_p(s)}{T} dT.$$

→ ∞ : $T \to 0K$?

$T \Rightarrow 0K \Rightarrow C_p(s) \Rightarrow 0 \longrightarrow dT = \frac{dq_p}{C_p \to 0}$

→ any contact $(dq_p) >$ ↓ system's temp increases.

$$dw_{IRev} > dw_{Rev}$$

$$(*) \quad đq_{IRV} < đq_{RV} \rightarrow \int_1^2 \frac{đq_{IRV}}{T} < \int_1^2 \frac{đq_{RV}}{T} = S(2) - S(1)$$

$$= \Delta S = dS$$

$$\boxed{dS > \frac{đq_{IRV}}{T}}$$

Criterion for Spontaneous Change

Thermodynamics – Criteria for spontaneous change.

How do we know if a change will happen spontaneously?

$\text{State}_{(T,P)}^{A} = \text{State}_{(T,P)}^{B}$ $\quad \Delta S = ? \quad \Delta U = ? \quad \Delta H = ?$

Clausius inequality: $dS > \dfrac{đq}{T_{surr}}$. for irreversible spontaneous process.

Spontaneous chemical changes:

① $2H_2O_2 \rightarrow 2H_2O + O_2$. $\begin{cases} \Delta H = -209\,kJ. \\ \Delta S = +132\ J/K \end{cases}$

② $3H_2 + N_2 \rightarrow 2NH_3$ $\begin{cases} \Delta H = -92\,kJ \\ \Delta S = -198\ J/K \end{cases}$

③ $NaCl(s) + 4.00\,H_2O(l) \rightarrow Sol(NaCl.H_2O)$ $\begin{cases} \Delta H > 0 \\ \Delta S > 0 \end{cases}$ انرژی‌های سیستم کمتر از انرژی‌های آن‌ها است. ای‌ام که PdV و TdS است.

{ Let's revise our view toward an spontaneous change.

Definition of Equilibrium state

no spontaneous changes can occur to to any other state.

1st law $du = đq + đw$

2nd law $\Rightarrow ds > đq/T_{surr}$ for spontaneous

$\Rightarrow du < T_{surr}.ds - p_{surr}.dv$

Condition for spontaneous change.

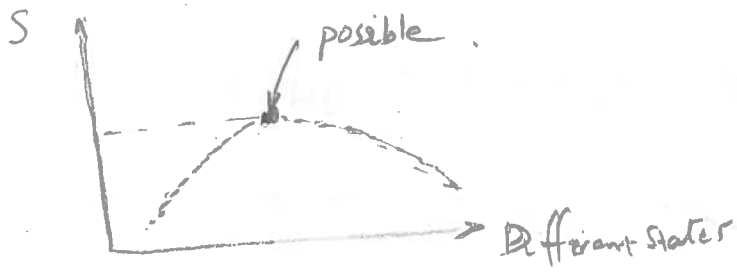
$$\boxed{du + p_{surr}\,dv - T_{surr}.ds < 0}$$

in terms of controlable and state func!

Applied Statistical Mechanics. A.L.Ahmadian

Equilibrium under different conditions

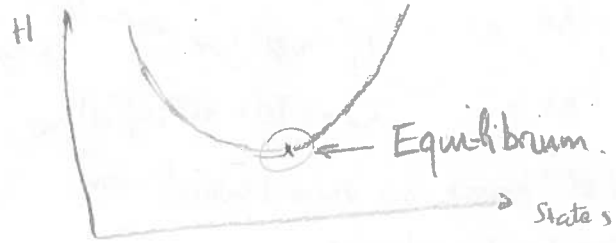
① isolated system $\Rightarrow T_{sur} \cdot dS > 0$ — $\boxed{(dS)_{U,V} > 0}$



$\mathcal{S} > 0$

② Constant $(S, V) \rightarrow (dU)_{S,V} < 0$: condition for spontaneous change.

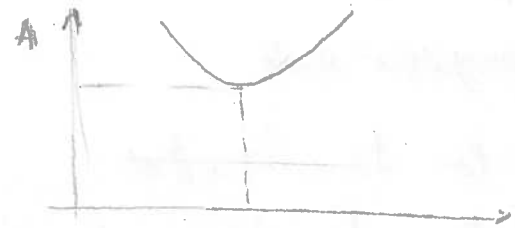
③ constant $(S, P) \longrightarrow dU + p\,dV < 0 \Rightarrow d(U + pV) = dH < 0$ | criterion for spontaneous change.



④ Constant $(T, V) \Rightarrow dU - TdS < 0 \longrightarrow d(U - TS) < 0$

$A = U - TS \longrightarrow dA < 0$

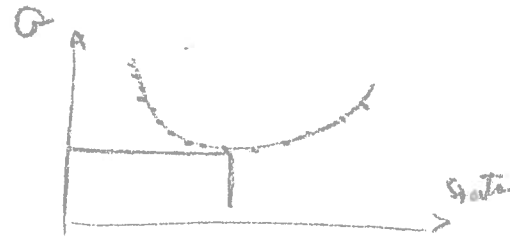
↳ Helmholtz free energy



⑤ constant (Temp & Pres).

$$dU + p\,dv - T\,ds < 0 \longrightarrow d(U + pV - TS) = 0$$

$G = U + pV - TS$: Gibbs Free Energy.



$$G = H - TS = A + PV \longrightarrow \underline{(dG)_{p,T} < 0}$$

↓

our equilibrium criterion for spontaneous change.

Thermodynamics / Gibbs Free Energy.

$G = U + PV - TS = H - TS = A + PV$. Gibbs free energy.

Relate thermodynamics quantities to equ. state (p, v, T) sets.

$$\left\{\begin{array}{ll} dU = T.dS - p.dv & ; U(S,v) \\ dH = TdS + v.dp & , H(S,P) \\ dA = -S.dT - p.dv & , A(T,v) \\ dG = -S.dT + v.dp & G(T,P) \end{array}\right\} \Rightarrow$$

Fundamental Equ of Thermodynamics.

State function

State variables.

Example.
$$\left\{\begin{array}{ll} \left(\frac{dA}{dT}\right)_v = -S & ; \quad \left(\frac{dA}{dv}\right)_T = -P \\ \left(\frac{dG}{dT}\right)_P = -S & ; \quad \left(\frac{dG}{dP}\right)_T = v \end{array}\right.$$

S depence on v + P:

$$\boxed{dS = \frac{dq^{rev}}{T} = \frac{C_v\, dT}{T} \quad \text{const } v} \qquad \left(\frac{dS}{dT}\right)_v = \frac{C_v}{T}$$

$$= \frac{C_p\, dT}{T} \quad \text{const } P \qquad \left(\frac{dS}{dT}\right) = \frac{C_p}{T} \rightarrow \Delta S = \int^{T_2} \frac{C_p}{T} dT = C_p \ln\left(T_2/T_1\right)$$

Abolhosseini, Applied Statistical Mechanics.

$$\frac{d^2A}{dV\,dT} = \frac{d^2A}{dT\,dA} \Rightarrow \text{order doesn't matter}$$

$$\left[\frac{d}{dV}\left(\frac{dA}{dT}\right)_V\right]_T = -\left(\frac{dS}{dV}\right)_T$$

$$=$$

$$\left[\frac{d}{dT}\left(\frac{dA}{dV}\right)_T\right]_V = -\left(\frac{dP}{dT}\right)_V$$

Equation of state.

Take: $pV = nRT \rightarrow \left(\frac{dP}{dT}\right)_V = \frac{nR}{V} = \left(\frac{dS}{dV}\right)_T$

case: constant T

① → ②

$V_1 \rightarrow V_2$

$$\Delta S = S(T, V_2) - S(T, V_1)$$

$$= \int_{V_1}^{V_2} \left(\frac{dS}{dV}\right)_T dV = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1}$$

$$\frac{d^2G}{dP\,dT} = \frac{d^2G}{dT\,dP} \overset{\text{like}}{\Rightarrow} \left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P$$

equation of state.

case const P

① → ②:

$$\Delta S = \int_{P_1}^{P_2} \frac{nR}{P}\, dP = nR \ln(P_2/P_1)$$

$$\left(\frac{dU}{dV}\right)_T = ? \qquad dU = TdS - p.dV$$

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{dS}{dV}\right)_T - P = T\underbrace{\left(\frac{dP}{dT}\right)_V - P}_{\text{from equation of state}}$$

ideal gas $\longrightarrow \left(\frac{dP}{dT}\right)_V = \frac{nR}{V} = \frac{P}{T} \longrightarrow \left(\frac{dU}{dV}\right)_T = \cancel{T}\cdot\frac{P}{\cancel{T}} - P = 0$

So, for ideal gas U is not function V at constant T

This is the thing that Joul showed it before -

For H : $dH = TdS + V.dp$

Joul's Tompson Exp.

$$\left(\frac{dH}{dP}\right)_T = T\left(\frac{dS}{dP}\right)_T + V = -T\left(\frac{dV}{dT}\right)_P + V$$

the case of an ideal gas: $\left(\frac{dV}{dT}\right)_P = \frac{V}{T} \rightarrow \left(\frac{dH}{dP}\right)_T = -T\left(\frac{V}{T}\right) + V = 0$

V-W Gas Case:

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \longrightarrow P = \frac{RT}{V-b} - \frac{a}{V^2} \longrightarrow \left(\frac{dP}{dT}\right)_V = \frac{R}{V-b}.$$

$$\left(\frac{dU}{dV}\right)_T = \frac{RT}{V-b} - P = \frac{a}{V^2} > 0 \Rightarrow U(T\&V) \leftarrow \text{This a result}$$