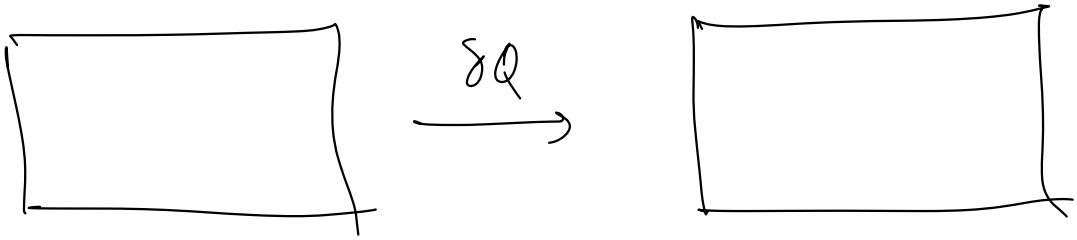
★ for an ideal gas: Which one is larger, C_p or C_V?

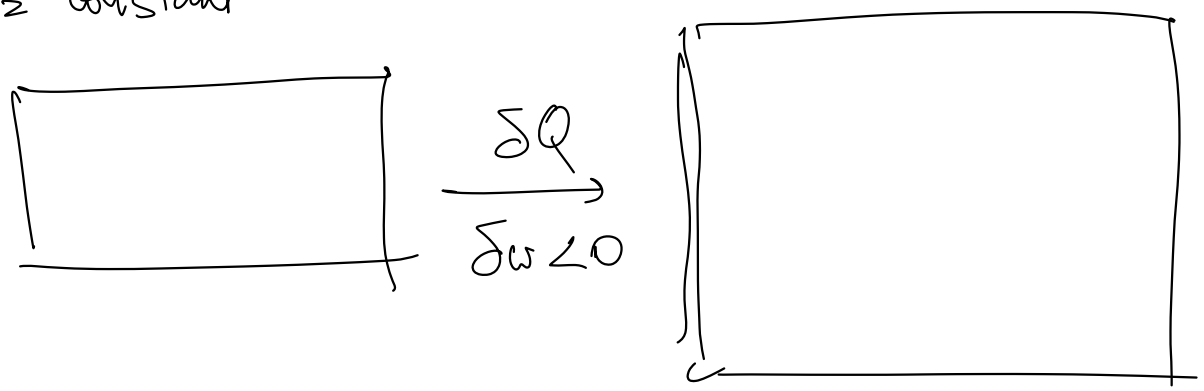
V = constant



$dU = \delta Q$

$\therefore \delta W = 0$

p = constant



$dU < \delta Q$

have to put more heat in to raise the temperature by the same amount

$$C_p > C_V$$

ALWAYS TRUE

What about materials with negative thermal expansion?

$C_p \simeq 6 - 28$ J/mol/K for metals/solides

Dulong & Petit $\longrightarrow C_p \simeq 3R$

$\simeq 25$ J/mol/K

COMING UP NEXT: ① Fundamental relation in thermodynamics
② Mathematical consequences & techniques:

- Euler relation
- Gibbs-Duhem
- Legendre transform
- Maxwell relations
- General math relations between state functions
- Eqm potentials & eqm criteria.

FUNDAMENTAL RELATION IN THERMODYNAMICS:

$$dU = \delta q + (\delta W) \longrightarrow \text{first law}$$

general expression for reversible work: $\delta W = \sum Y_i \, dX_i$

II law: $dS \geq \frac{\delta q}{T}$; $dS = \frac{\delta q_{rev}}{T}$

Since U is a state variable, we can always construct a reversible path between ① & ②

$$\Rightarrow \quad \delta q = T dS$$

$$\boxed{dU = T dS + \sum_i Y_i \, dX_i}$$

Connects all state variables between different equilibrium states.

$S, X_i \longrightarrow$ extensive

$\Rightarrow U(S, X_i) \longrightarrow$ S and X_i are natural variables of the internal energy.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{X_i} dS + \sum_i \left(\frac{\partial U}{\partial X_i}\right)_{S, X_j} dX_i$$

$\left(\frac{\partial U}{\partial S}\right)_{X_i} \longrightarrow T(S, X_i)$

equations of state → EOS

$$\begin{cases} T = \left(\frac{\partial U}{\partial S}\right)_{X_i} \\ Y_i = \left(\frac{\partial U}{\partial X_i}\right)_{S, X_j} \longrightarrow Y_i(S, X_i) \end{cases}$$

All intensive variables are partial derivatives with respect to the extensive variables.

→ if $U(S, X_i)$ is known ⇒ all thermodynamic EOS can be extracted from U

→ if all sets of EOS are known ⇒ U can be determined through integration.

Rewriting the fundamental equation:

$$dU = TdS + \sum_i Y_i dX_i$$

$$dS = \frac{dU}{T} - \sum_i \frac{Y_i}{T} dX_i$$

⇒ $S(U, X_i)$ → The natural variables of S are U and X_i

* How many equations of state are there?

# of of conjugate pairs + 1 : N work terms + 1

* Ideal Gas: work term → $-pdV$ ⇒ 2 equations of state

$pV = nRT$ → 1 EOS → "Mechanical" EOS

$C_p(T, V)$ → $S(T, V)$ → "Heat" EOS

* How many (independent) variables are there in thermodynamics?

X_i N work terms $\longrightarrow$ $2(N+1)$ variables

Y_i $(N+1)$ equations of state

T
S $\Rightarrow$ $\boxed{(N+1) \text{ degrees of freedom}}$

* Ideal gas: p, V, T, S

2 EOS $\Rightarrow$ 2 independent variables

EULER RELATION

$$\boxed{U = TS + \sum_i Y_i X_i}$$

proof: $U \rightarrow$ homogeneous of 1st order in its extensive variables

Homogeneous functions:

$f \rightarrow$ homogeneous of order r

$$\Rightarrow f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda^r f(x_1, x_2, \dots, x_n)$$

Since U is homogeneous of order 1:

$$U(\lambda S, \lambda X_i) = \lambda U(S, X_i) \longrightarrow \text{restating extensivity}$$

take derivative wrt λ

$$\left(\frac{\partial U}{\partial \lambda S}\right)\left(\frac{\partial \lambda S}{\partial \lambda}\right) + \sum_i \frac{\partial U}{\partial (\lambda X_i)} \frac{\partial (\lambda X_i)}{\partial \lambda} = U(S, X_i)$$

$$\Rightarrow S\frac{\partial u}{\partial(\lambda S)} + \sum_i \frac{\partial u}{\partial(\lambda X_i)} X_i = u(S, X_i)$$

evaluate @ $\lambda = 1$

$$u(S, X_i) = S\frac{\partial u}{\partial S} + \sum_i X_i \frac{\partial u}{\partial X_i} = TS + \sum_i Y_i X_i$$

GIBBS-DUHEM:

Eulers relation $\longrightarrow$ $u = TS + \sum_i Y_i X_i$

$$du = T\,dS + S\,dT + \sum_i (Y_i\,dX_i + X_i\,dY_i)$$

$$du = T\,dS + \sum_i Y_i\,dX_i$$

$$\Rightarrow \boxed{S\,dT + \sum X_i\,dY_i = 0}$$

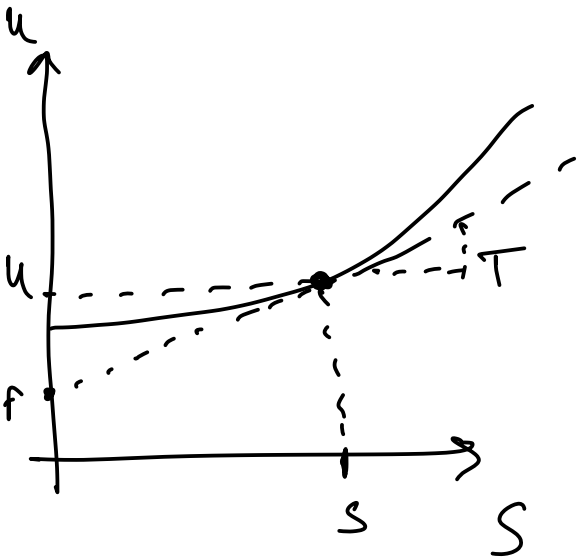
differentials are all intensive

LEGENDRE TRANSFORM: → leads us to characteristic potentials

$U(S, X_i)$ → natural variables are all extensive

extensive variables are usually hard to control.

for instance S → no instrument to directly measure this.



$U(S, X_i)$ at fixed X_i

we would like a function

$\lambda(T, X_i)$ → since this would be practically more useful.

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

slope of a line: $T = \frac{y_2 - y_1}{x_2 - x_1} = \frac{U - f}{S}$ → intercept of the line @ $S=0$

$$\Rightarrow \boxed{f = U - TS}$$

differential of f:

$$df = dU - TdS - SdT$$

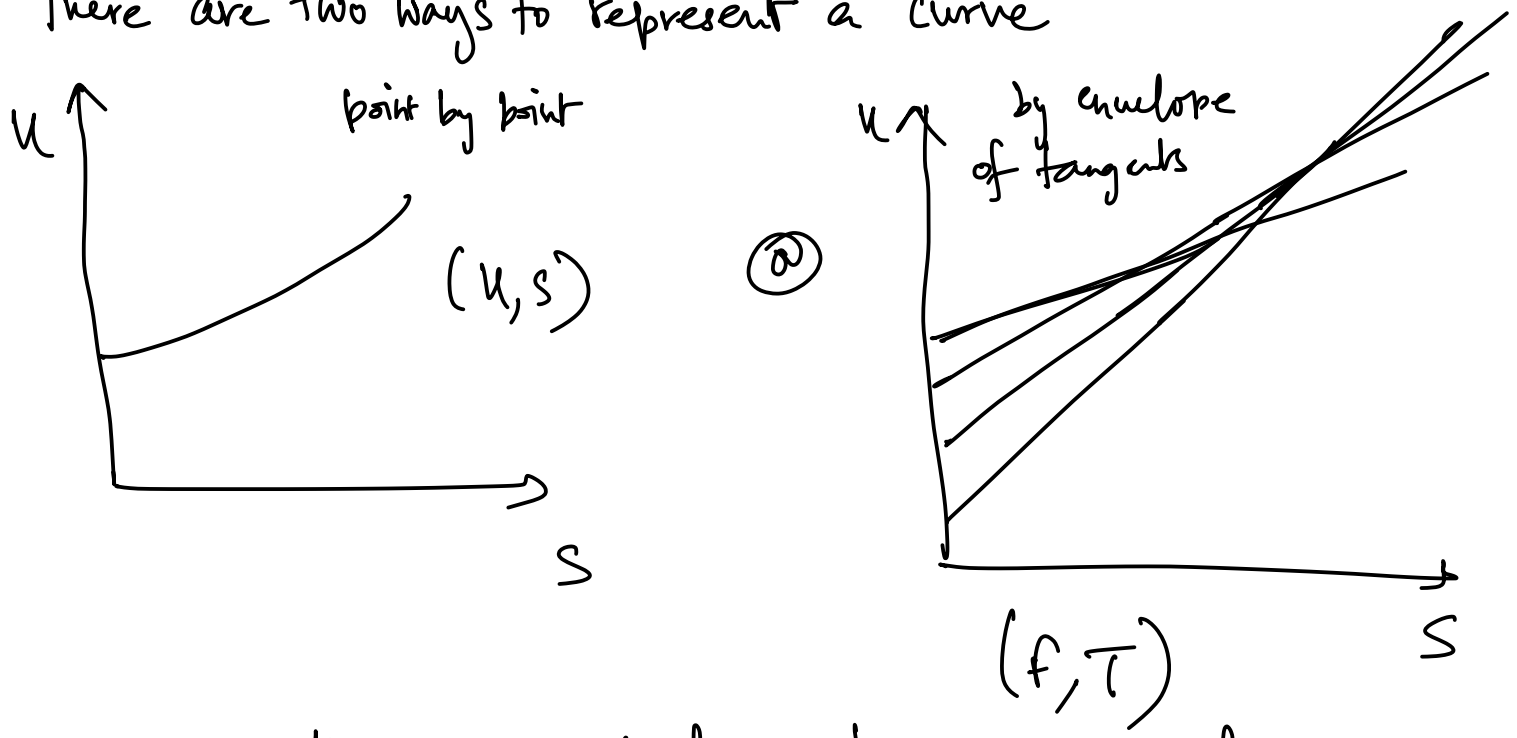
$$= TdS + \sum_i Y_i dX_i - TdS - SdT$$

$$\boxed{df = -SdT + \sum_i Y_i dX_i}$$

natural variables of f: $(T, X_i) \Rightarrow f(T, X_i)$

Does f contain the same information as U?

There are two ways to represent a curve



* when controlling T instead of S it is more practical to specify (f, T) instead of (U, S)

| need to specify the slope T and intercept f

$\Rightarrow$ Performing a Legendre transform is equivalent to switching from a point-by-point description to an envelope of tangents.

ANY TIME WE CONTROL AN INTENSIVE VARIABLE

$\Rightarrow$ subtract off a conjugate pair from U to get a new characteristic potential

$$f = U - TS$$

TS → conjugate pair