$\rightarrow$ EOS
$$\begin{cases} T = \frac{\partial U}{\partial S} = T(S, V, N) \\ P = -\frac{\partial U}{\partial V} = P(S, V, N) \\ \mu = \frac{\partial U}{\partial N} = \mu(S, V, N) \end{cases}$$

if these are known. you could recover Fundamental Eq. because of

$$U = TS + \sum_{j=1}^{t} P_j X_j$$

1> The totality of <u>all</u> EOS is equivalent to the Fundamental Eq. & contains all thermo. info.

2> what if one of EOS is unknown? $\rightarrow P_k$

Based on Gibbs – Duhem Relation

$$\sum_{j=0}^{t} X_j \, dP_j = 0 \qquad (X_0 = S, \; P_0 = T)$$

$$\underbrace{\int dP_k}_{P_k} = \int \frac{-\sum_{j \neq k}^{t} X_j \, dP_j}{X_k}$$

$$\Rightarrow P_k = P_k(X_1, \cdots X_t) + \overset{\text{const. (undetermined)}}{P_{k0}}$$

loss of thermo. info.

$$U = \sum_{j \neq k}^{t} X_j P_j + X_k \left(P_k(X_1 \cdots X_t) + \underline{P_{k0}} \right)$$

info. is less than that in Fundamental Eq.

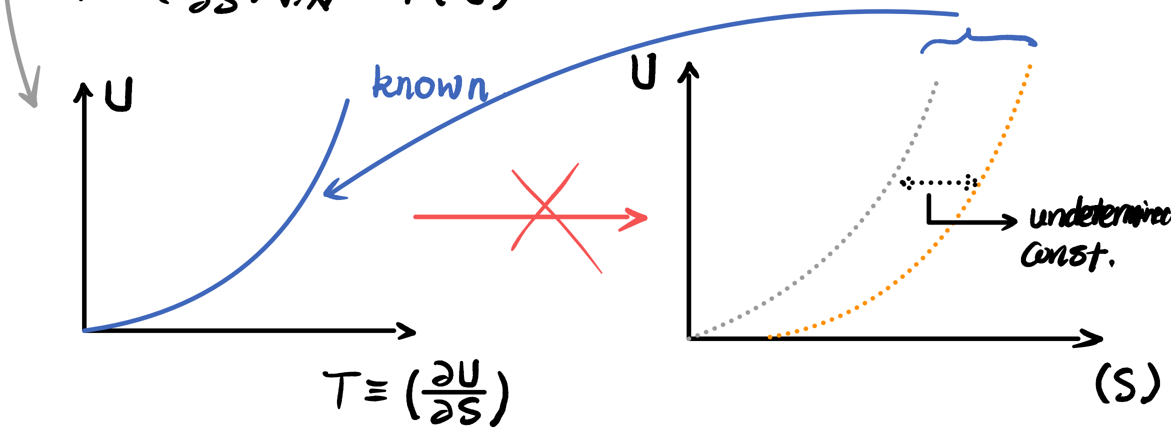
3> what if we know

$U = U(T, V, N)$

$U(S, V, N)$

could we recover $U(S, V, N)$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = T(U)$$



knowledge of $\underline{U(T, V, N)}$ $\not\to$ $U(S, V, N)$

NOT Fundament Eq.

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4. EOS and Fundamental Eq. for common sys.

4-1. Ideal Gas Sys.

- Gas molecules do NOT interact w/ each other.
- can be treated as point mass.
  DO NOT occupy volume.
- collision w/ surface is elastic.

→ $PV = NRT$
  ↳ gas const. : $8.314\ J \cdot K^{-1} \cdot mol^{-1}$

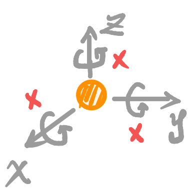
→ $U = cNRT$
  ↳ const. : characterize heat capacity.

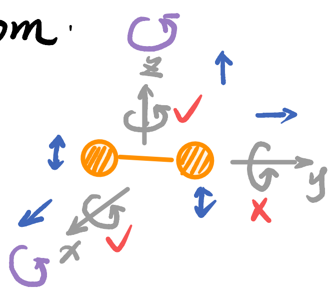
$$c = \lim_{\Delta T \to 0} \frac{Q}{T_f - T_i} = \frac{đQ}{dT}$$

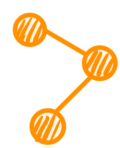
$c = c(T)$

Background — DOF and heat capacity.

Degree of Freedom.







	Monoatomic	Linear	Nonlinear
Translation (x, y, z)	3	3	3
Rotation. (x, y, z)	0	2	3 (x, y, z)
Vibration.	0	$3N-3-2$ (# of atoms)	$3N-3-3 = 3N-6$

Equipartition Theorem.

↓

How much energy is storaged in each DOF.

- Energy is equally shared among all of its Forms, i.e., Translation, Rotation, Vibration.
- Each energy (at the microscopic level) is given by $\frac{1}{2} k_B T$

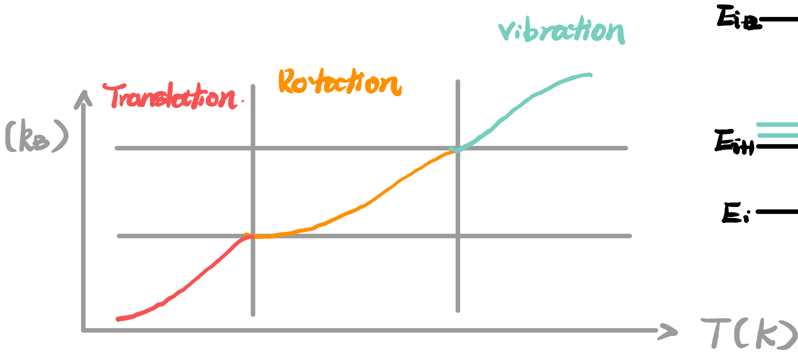
k_B → Boltzman Const.

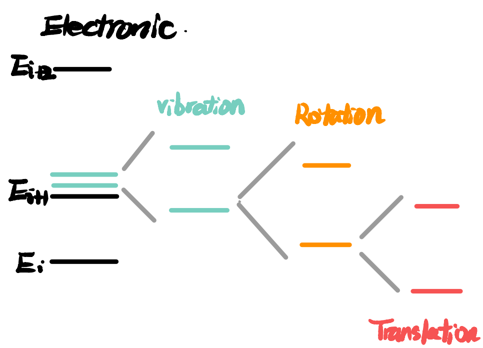
$k_B \cdot N_A$ → (R - gas const.)

→ monoatomic : $\underline{3/2\, k_B T}$ → average heat capacity per molecule

Molecular heat capacity.

$$\frac{3}{2} k_B T \cdot N_A \rightarrow \frac{3}{2} R$$





$$\rightarrow \quad \underbrace{\frac{1}{T}}_{\left(\frac{\partial S}{\partial U}\right)}^{\nearrow F_{j=0}} = \frac{cRN}{U} = \frac{cR}{\underset{\downarrow\ (U/N)}{u}}$$

$$\rightarrow \quad \frac{P}{T} = \frac{RN}{V} = \frac{R}{v}$$

$$F_j = -\frac{P_j}{T} \rightarrow (-P)$$

Based on Gibbs - Duhem Relation.

$$\sum_{j=0}^{t} X_j \, dF_j = 0$$

$$\rightarrow \quad \underset{X_0}{U} \cdot d\Big(\overset{\nearrow F_{j=0}}{\frac{1}{T}}\Big) + \underset{X_1}{V}\, d\Big(\overset{F_{j=1}}{\frac{P}{T}}\Big) - \underset{X_2}{N}\, d\Big(\overset{F_{j=2}}{\frac{\mu}{T}}\Big) = 0$$

$$\rightarrow \quad d\left(\frac{\mu}{T}\right) = \left[U d\left(\frac{1}{T}\right) + V d\left(\frac{P}{T}\right)\right] / N$$

$$= u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right)$$

knowing $\frac{1}{T}$, $\frac{P}{T}$, $\frac{\mu}{T}$

$$\rightarrow \quad S = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \left(\frac{\mu}{T}\right) N$$

Euler Eq.

$$d\left(\frac{\mu}{T}\right) = u \times \left(\frac{-cR}{u^2}\right) du + v \times \left(-\frac{R}{v^2}\right) dv$$

$$= -cR \frac{du}{u} - R \frac{dv}{v}$$

$\rightarrow \frac{u}{T} - \underline{\left(\frac{u_0}{T_0}\right)} = -cR\ln\underline{\frac{u}{u_0}} - R\ln\underline{\frac{v}{v_0}}$

$\rightarrow S = N\underset{\downarrow}{s_0} + NR\ln\left[\left(\frac{U}{U_0}\right)^{c}\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-(c+1)}\right]$

const:

$(c+1)R - \left(\frac{u}{T}\right)_0$

4-2 van der waals sys. (EOS)

Ideal Gas : $PV = NRT$ or $P = \frac{RT}{v}$ ← V/N

→ Point mass : Does NOT occupy volume.

→ Do NOT interact w/ each other.

→ occupy volume.

$\rightarrow P = \frac{RT}{v-b}$ → occupancy of gas molecules.

→ Interactions ("turned on")