1st Jan 2024

- No more KTG — starting thermodynamics. from Chem thermodynamics.
- Linking thermodynamics to statistical mechanics.
- Problem in every tutorial - from HW, just one.

Mark distribution to be discussed further later.

- HW planned to be ~~out~~ every week. → to be submitted. (No grading)

○ Ideal Gas:

$$pV = nRT$$

→ Derived empirically from exp (Charles', Boyle's, etc)

→ Experimental / Empirical equation.

○ $U = \frac{3}{2} nRT$

→ KTG

○ $dU = \underbrace{TdS}_{dq} - PdV + \mu dN$ → Not seen (forget about it rn) before

→ Combination of 1st law and 2nd law, in a sense.

Compare

$\Rightarrow U = U(S, V)(N)$

$\Rightarrow dU = \frac{\partial U}{\partial S}\Big|_{V,N} dS + \frac{\partial U}{\partial V}\Big|_{S,N} dV$

Not considering μ

$$\boxed{T \equiv \frac{\partial U}{\partial S}\Big|_{V,N}} \quad \boxed{p = -\frac{\partial U}{\partial V}\Big|_{S,N}}$$

What if we consider μdN?

μdN → Energy taken out or given by taking out or putting in molecules.

$\Rightarrow \mu$ = Chemical potential.

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

Goal: We wish to find $u = u(V, S, N)$ for ideal gas.

Once we know this, we can find T, P, and μ just by taking derivatives

Why these? These are measurable quantities.

We will use the first 2 equations to do this.

$$u = \frac{3}{2} nRT \Rightarrow T = \frac{2u}{3nR}$$

$$\left(\frac{\partial u}{\partial S}\right)_{V,N} = T = \frac{2u}{3nR}$$

$$\Rightarrow \frac{\partial u}{u} = \frac{2}{3} \frac{1}{nR} \cdot dS$$

$$\Rightarrow \ln u = \frac{2}{3} \frac{S}{NR} + f(V,N) \quad \text{(Integrating)} \quad \text{— (I)}$$

$f(V,N)$ → Const of integration.

Now, $pV = nRT$

$$\Rightarrow p = \frac{nRT}{V}$$

$$\left(\frac{\partial u}{\partial V}\right)_{S,N} = -p = -\frac{nRT}{V} = -\frac{2}{3}\frac{u}{V}$$

$$\Rightarrow \frac{\partial}{\partial V}(\ln u)_{S,N} = \frac{1}{u}\left(\frac{\partial u}{\partial V}\right)_{S,N} \quad \text{— (II)}$$

$$\Rightarrow \frac{\partial}{\partial V}(\ln u)_{S,N} = \frac{\partial}{\partial V}\left(\frac{2}{3}\frac{S}{NR} + f(V,N)\right), \text{ from (I)}$$

$$\Rightarrow \frac{\partial}{\partial V}(\ln u)_{S,N} = \left(\frac{\partial f}{\partial V}\right)_{\cancel{S},N}$$

$$\Rightarrow \frac{1}{u}\left(\frac{\partial u}{\partial V}\right)_{S,N} = \left(\frac{\partial f}{\partial V}\right)_{S,N} \quad \text{(from (II))}$$

$$\Rightarrow \left(\frac{\partial u}{\partial V}\right)_{S,N} = u\left(\frac{\partial f}{\partial V}\right)_{S,N}$$

$$\Rightarrow -\frac{2}{3}\frac{u}{V} = u\left(\frac{\partial f}{\partial V}\right)_{S,N}$$

$$\Rightarrow \left(\frac{\partial f}{\partial V}\right)_{N} = -\frac{2}{3}\cdot\frac{1}{V}$$

$\Rightarrow f = -\frac{2}{3}\ln V + g(N)$

$\therefore \ln U = \frac{2}{3}\frac{S}{nR} + \left(-\frac{2}{3}\right)\ln V + g(N)$

We may just write it as $\ln(g(N))$ (Const.)

$$\therefore \boxed{\ln U = \frac{2}{3}\frac{S}{nR} - \frac{2}{3}\ln V + \ln(g(N))}$$

(*) → Using only $pV = nRT$, $U = \frac{3}{2}nRT$

We are going to push dependence of N → There is new stuff there.

But physical input has been exhausted — both equations have been inputted. - - -

Let us increase entropy of system λ times

and the same, $\left.\begin{array}{l} S \to \lambda S \\ V \to \lambda V \\ N \to \lambda N \end{array}\right\}$ $\therefore U \to \lambda U$ (Expected) → Extensivity

$\rightarrow U = g(N)\, V^{-2/3} \exp\left(\frac{2S}{3NR}\right)$ Using these

$U \to g(\lambda N)(\lambda N)^{-2/3} \exp\left(\frac{2\lambda S}{3\lambda NR}\right)$

$\Rightarrow U \to g(\lambda N)(\lambda N)^{-2/3} \exp\left(\frac{2S}{3NR}\right)$

This needs to be λU $\qquad \lambda^{x-\frac{2}{3}} = 1 \Rightarrow x = \frac{5}{3}$

$\rightarrow$ True if $\boxed{g(\lambda N) = \lambda^{5/3} g(N)}$

$\Rightarrow \boxed{g(N) = k \cdot N^{5/3}}$

Fundamental relation of thermodynamics.

$$\Rightarrow \boxed{U = kN\left(\frac{V}{N}\right)^{-2/3} \exp\left(\frac{2}{3}\frac{S}{nR}\right)}$$

Found - goal. (2 empirical eqns, extensitivity)

Find : T, P, μ from this.

Question → Can this be derived from microscopic considerations, without empirical relations?

What if $pV = nRT$ does not ~~hold~~ hold — some other system.

This is the goal of statistical mechanics — to derive this from fundamental physics.

→ This will be derived later in course.

Tutorial Class begins

$F(x, y, z) \rightarrow$ Broadly, a field

In this case, it is a scalar field.

$\vec{E}(\vec{x}, \vec{y}, \vec{z}) \rightarrow$ vector field

(Certain transformation rules).

$$\frac{\partial F}{\partial x} = \lim_{h \to 0} \frac{F(x+h, y, z) - F(x, y, z)}{h}$$

or, notationally as, F_x, $\left(\frac{\partial F}{\partial x}\right)_{y,z}$

all other variables are fixed.

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x} \rightarrow \text{partial derivatives Commute.}$$

Sometimes,

$F(x(t), y(t))$ → Some other variable.

As $t \rightarrow t + \Delta t$, $x \rightarrow x + \Delta x$, $y \rightarrow y + \Delta y$

So, under this change, the new field is,

$$F(x+\Delta x, y+\Delta y) = F(x, y) + \left(\frac{\partial F}{\partial x}\right)_y \Delta x + \left(\frac{\partial F}{\partial y}\right)_x \Delta y$$

$$\Rightarrow \Delta F = \frac{\partial F}{\partial x} \Delta x + \frac{\partial F}{\partial y} \Delta y$$

Or in some other way,

$$\frac{dF}{dt} = \left(\frac{\partial F}{\partial x}\right)_y \frac{dx}{dt} + \left(\frac{\partial F}{\partial y}\right)_x \frac{dy}{dt}$$

If x and y had some other variable dependence, it would be $\frac{\partial F}{\partial t_1}$ and $\frac{\partial F}{\partial t_2}$.

Consider,

All indep of each other.

Constant.

$$F(x_1, \dots, x_n) = C$$

$\Rightarrow$ This cannot be

This is a relation, they can not be independent.

but, $x_1, \dots, x_n$ are functions of independent variables $u_1, \dots, u_n$

In terms of this new variable,

$$F(u_1, \dots, u_n) = C$$

$$dF = \frac{\partial F}{\partial u_1} du_1 + \dots + \frac{\partial F}{\partial u_n} du_n$$

$u_1, \dots, u_n$ are independent variables.

So, $F(u_1 + \Delta u_1, u_2, \dots, u_n) = C$

$$\Rightarrow \frac{\partial F}{\partial u_1} = \lim_{\Delta u_1 \to 0} \frac{F(u_1 + \Delta u_1, \dots, u_n) - F(u_1, \dots, u_n)}{\Delta u_1}$$

$$= 0$$

$$\Rightarrow \frac{\partial F}{\partial u_n} = 0 \quad \Rightarrow \boxed{dF = 0}$$

Essentially saying this in a convoluted way.

$$\Rightarrow \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_n} dx_n = 0$$

Consider,

$$F(x, y, z) = 0$$

$$\Rightarrow dF = \left(\frac{\partial F}{\partial x}\right) dx + \left(\frac{\partial F}{\partial y}\right) dy + \left(\frac{\partial F}{\partial z}\right) dz = 0.$$

take $y = \text{const} \Rightarrow dy = 0$

$$\Rightarrow \boxed{\left(\frac{\partial z}{\partial x}\right)_y = -\frac{(\partial F/\partial x)}{(\partial F/\partial z)}}$$

Similarly,

$$\boxed{\left(\frac{\partial y}{\partial z}\right)_x = -\frac{\frac{\partial F}{\partial z}}{\frac{\partial F}{\partial y}}}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{-\frac{\partial F}{\partial y}}{\frac{\partial F}{\partial x}}}$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

Used later in course.

- [ ] Exact, inexact differentials
- [ ] Lagrange multipliers to optimize functions.