Two key problems in thermodynamics:
1. Relate properties to each other, e.g., \( C_p = C_v + R \); how about a general relation \( \Delta p \) between \( C_p = \left( \frac{\partial u}{\partial T} \right)_p \) and \( \Delta p = \left( \frac{\partial u}{\partial T} \right)_T \)?
2. Measure them in the laboratory (independent variables fully characterize a system; e.g., \( P/V \) are not independent).

For one-component systems, need 3 variables:

**Combined First + Second Laws:**
\[
du = Tds - PdV \quad \text{Fundamental Equation}
\]

\( S, V \) always "good" (independent) variables.

Need one more \( \rightarrow N \), number of moles.

Complete expression for \( U(S, V, N) \):
\[
du = \left( \frac{\partial u}{\partial s} \right)_{v,N} ds + \left( \frac{\partial u}{\partial v} \right)_{s,N} dv + \left( \frac{\partial u}{\partial N} \right)_{s,v} dN
\]

where \( \left( \frac{\partial u}{\partial s} \right)_{v,N} = T \left( \frac{\partial u}{\partial s} \right)_{s,N} = -p \)

and \( \left( \frac{\partial u}{\partial N} \right)_{s,v} \quad \text{defines the chemical potential} \)

\[
du = Tds - PdV + \mu dN
\]

most important equation in thermodynamics
What is the chemical potential?
- drives reactions / sensors / taste / smell
- measured by pH meters etc
- increases with concentration, but can be the same for different concentrations (e.g., liq./gas equil.)

Generalization of F.E. for mixtures:
\[ du = r \, ds - P \, dV + \sum_{i=1}^{n} \mu_i \, dN_i \quad n \text{-component mixture} \]

All thermodynamic properties can be obtained from the fundamental equation of a system [see Ex. 5.1]

\[ \boxed{\text{Manipulation of Derivatives } \S 5.2} \]

For well-behaved mathematical functions, can we:

\[ \text{Inversion} \quad \left( \frac{\partial x}{\partial y} \right)_t = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_t} \]

\[ \text{Commutation} \quad \frac{\partial}{\partial x} \left( \frac{\partial x}{\partial y} \right)_t = \frac{\partial}{\partial y} \left( \frac{\partial x}{\partial z} \right)_x = \frac{\partial^2 x}{\partial x \partial z} \]

\[ \text{XYZ-1 "Triple Product"} \quad \left( \frac{\partial x}{\partial y} \right)_t \left( \frac{\partial y}{\partial z} \right)_{x,t} \frac{\partial z}{\partial y} \bigg|_{y,z} = -1 \]

\[ \text{Chain Rule:} \quad \left( \frac{\partial x}{\partial y} \right)_t = \left( \frac{\partial x}{\partial \omega} \right)_t \left( \frac{\partial \omega}{\partial y} \right)_t = \frac{(\partial x/\partial \omega)_t}{(\partial y/\partial \omega)_t} \]

These are functional relationships: \[ x = f(y, z) \]
\[ y = f(x, z) \]
\[ etc \]
Euler's Theorem for Homogeneous Functions

\[ f(\lambda x, \lambda y, z) = \lambda f(x, y, z) \quad \text{homog. of degree 1 with respect to } x, y \text{ only} \]

Then:

\[ f = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} \]

(e.g. \( f = x^2 + y^2 \); \( \frac{\partial f}{\partial x} = 2x \); \( \frac{\partial f}{\partial y} = 2y \)

Proof:

\[ \frac{\partial f(\lambda x, \lambda y, z)}{\partial x} = f = \frac{\partial f(x)}{\partial x} \frac{\partial (\lambda x)}{\partial x} + \frac{\partial f(x)}{\partial y} \frac{\partial (\lambda y)}{\partial x} \]

\[ = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} \quad \text{Q.E.D.} \]

Apply to \( U \), which is homogeneous of degree 1 in all its variables \( U(\lambda s, \lambda v, \lambda n) = \lambda U(s, v, n) \) [extensive]

\[ U = (\frac{\partial U}{\partial s})s + (\frac{\partial U}{\partial v})v + (\frac{\partial U}{\partial n})n \Rightarrow \]

\[ U = TS - PV + MN \quad \text{Euler integrated F.E.} \]

\( U \) is still \( U(s, v, n) \); in this expression,

\[ T = T(s, v, N); P = P(s, v, N); N = N(s, v) \]

Legendre Transformations

\((s, v, N)\) is not usually a convenient set of independent variables.

We often would like to work at \((T, V, N)\)

\((T, P, N)\)

etc.

How do we obtain fundamental equations in other variables?
In principle, from $f(x)$ with $\frac{df}{dx} = w$ we can obtain $g(w)$. But $g(w)$ is not equivalent to $f(x)$!

E.g. $g(x) = x^2 + 2 \Rightarrow w = \frac{df}{dx} = 2x \Rightarrow g(w) = \frac{w^2}{4} + 2$

$\Rightarrow \quad w = \pm 2\sqrt{f-2}$ \quad (1)

From $g(w)$, inversion rule $\frac{df}{dx} = w \Rightarrow \frac{dx}{dg} = \frac{1}{w} \Rightarrow$

$\Rightarrow \quad x = \int \frac{1}{w} \, dg = (1) \int \frac{df}{\pm 2\sqrt{f-2}} = \pm \sqrt{f-2} + c \Rightarrow$

$g = (x-c)^2 + 2 \quad \text{not the same as starting } f(x)$

\underline{Solution}: define new function (transform)

$g(w) = f - xw$

$dg = df - xdw - wdx = -xdw$

new function (first Legendre transform) has the original derivative as variable

The original function $f(x)$ can be obtained unambiguously from $g(w)$ by differentiation:

$dg = -xdw \quad \boxed{g = g + 2w}$