$\boxed{\text{Thermodynamic Calculus §5.1}}$

Two key problems in thermodynamics:

⇒ relate properties to each other,
e.g. $C_p^{IG} = C_v^{IG} + R$; how about a general relationship between $C_p = (\partial H/\partial T)_P$ and $C_p = \left(\frac{\partial u}{\partial T}\right)_V$

⇒ measure them in the laboratory

From §1.4 : n+2 independent variables fully characterize a system
(e.g. P, V are <u>not</u> independent)
For one-component system, need 3 variables

Combined First + Second Laws:

$$du = TdS - PdV \qquad \text{Fundamental Equation}$$

S, V always "good" (independent) variables
Need one more → 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 $\left(\frac{\partial u}{\partial S}\right)_{V,N} = T \quad \left(\frac{\partial u}{\partial S}\right)_{S,N} = -P$

and $\boxed{\left(\frac{\partial u}{\partial N}\right)_{S,V} \equiv \mu}$ defines the chemical potential

$$\Rightarrow \boxed{\boxed{du = TdS - PdV + \mu dN}}$$

most important equation in thermo
fundamental Equation

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:

$$du = T\,ds - P\,dv + \sum_{i=1}^{n} \mu_i\, dN_i \qquad n\text{-component mixture}$$

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

$\boxed{\text{Manipulation of Derivatives §5.2}}$

For well-behaved mathematical functions, can use:

Inversion $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z}$

Commutation $\frac{\partial}{\partial z}\left(\frac{\partial x}{\partial y}\right)_z = \frac{\partial}{\partial y}\left(\frac{\partial x}{\partial z}\right) = \frac{\partial^2 x}{\partial y\,\partial z}$

XYZ-1 "Triple Product" $\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1$

Chain rule: $\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial w}\right)_z\left(\frac{\partial w}{\partial y}\right)_z = \frac{(\partial x/\partial w)_z}{(\partial y/\partial w)_z}$

These are functional relationships for $\left\{\begin{array}{l} x = f(y,z) \\ y = f(x,z) \\ \text{etc} \end{array}\right.$

Euler's Theorem for Homogeneous functions

$$f(\lambda x, \lambda y, z) = \lambda f(x, y, z)$$ homog. of degree 1 with respect to x, y only

then: $$f = x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y}$$

(e.g. $f = xz^2 + yz$; $\frac{\partial f}{\partial x} = z^2$ $\frac{\partial f}{\partial y} = z$ checks)

Proof: $$\frac{\partial f(\lambda x, \lambda y, z)}{\partial \lambda} = f = \frac{\partial f(\lambda x)}{\partial(\lambda x)}\frac{\partial(\lambda x)}{\partial \lambda} + \frac{\partial f(\lambda y)}{\partial(\lambda y)}\frac{\partial(\lambda y)}{\partial \lambda}$$
$$= x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} \quad \text{Q.E.D.}$$

Apply to u, which is homogeneous of degree 1 in all its variables $u(\lambda S, \lambda V, \lambda N) = \lambda u(S, V, N)$ [u is extensive]

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

$$\Rightarrow \boxed{u = TS - PV + \mu N}$$ Euler-integrated F.E.

u is still $u(S,V,N)$; in this expression,
$T = T(S,V,N)$; $P = P(S,V,N)$; $\mu = \mu(S,V,N)$

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 $f(w)$. But $f(w)$ is not equivalent to $f(x)$!

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

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

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

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

$f = (x-c)^2 + 2$ not the same as starting $f(x)$

Solution: define new function (transform)

$$g(w) = f - xw$$

$$dg = \underbrace{df}_{w\,dx} - x\,dw - w\,dx = -x\,dw$$

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:

$dg = -x\,dw$ $\boxed{f = g + xw}$

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