Legendre Transformation

$f = f(x, y)$

$df = u \cdot dx + v \cdot dy$ ← the Legendre Transformation : $g(u, y) \equiv f - ux$

$dg = df - u\,dx - x\,du$
$= (u \cdot dx + v \cdot dy) - u\,dx - x\,du$

$= -x\,du + v\,dy$

Example : the internal energy : U

TD 1st Law : $\delta Q + \delta W = dU$

{ reversible : $\delta Q = T\,dS$
hydrodynamic : $\delta W = \delta W_H + \delta W_e + \delta W_D + \delta W_m \cdots$
$= -p\,dV$

$T\,dS - p\,dV = dU$
$dU = T\,dS - p\,dV$ Ans.

U is a function characterized by V, S
↓
U는 Volume 또는 entropy의 변화를 이용해 쉽게 표현이 가능!

Example : the enthalpy : H

(conjugate coordinate)
extensive variable
↓
$dU = T\,dS - p\,dV$

measure & control 하기 쉬운 intensive variable로 바꿔써야?

$df = u\,dx + v\,dy$
$g = f - ux$
$dg = df - u\,dx - x\,du$
$= -x\,du + v\,dy$

$H \equiv U + pV$
$dH = dU + p\,dV + V\,dp$
$= (T\,dS - p\,dV) + p\,dV + V\,dp$

$\therefore dH = V\,dp + T\,dS$ Ans.

H is a function characterized by p, S
↓
H는 P가 일정할 때의 heat quantities로 쉽게 표현.
(또는 control이 가능할 때의)

{ heat capacities
latent heats
heats of reactions

Example: the Helmholtz function, A

extensive variable

$df = u\,dx + v\,dy$
$g = f - ux$
$dg = df - u\,dx - x\,du$
$= -x\,du + v\,dy$

$dU = TdS - pdV$

measure & control 하기 쉬운 variable로 바꾸려고?

$A \equiv dU - TS$
$dA = (TdS - pdV) - TdS - SdT$

$\therefore dA = -SdT - pdV$ Ans.

A is a function characterized by T, V
↳ the partition function in statistical mechanics

Example: the Gibbs function, G

$df = u\,dx + v\,dy$
$g = f - ux$
$dg = df - u\,dx - x\,du$
$= -x\,du + v\,dy$

$dH = TdS + Vdp$
$G \equiv H - TS$
$dG = (TdS + Vdp) - TdS - SdT$

$\therefore dG = -SdT + Vdp$ Ans.

G is a function characterized by T, p
↳ T, p가 independent variables 일때 편함!

e.g. phase transformation, most chemical reactions.

No information is lost in the Legendre Transformation.

The gain is a new function expressed in thermodynamic coordinates amenable to the experimental situation at hand.

J. Willard Gibbs (Mathematical Physics at Yale, 1870s)

Maxwell's Relations

thermodynamic potential functions !

$$dU = -pdV + TdS$$
$$dH = Vdp + TdS$$
$$dA = -pdV - SdT$$
$$dG = Vdp - SdT$$

→

$U = U(V,S)$
$H = H(p,S)$
$A = A(V,T)$
$G = G(p,T)$

Example : $U = U(V,S)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS$$

$$= -pdV + TdS$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_S = -p \ , \ \left(\frac{\partial U}{\partial S}\right)_V = T$$

Ans.

if the internal energy function, U is known, (as a function of V,S) then we can calculate all the other thermodynamic properties (p,T)

Work of simple system	Intensive coordinate (generalized force)	Extensive coordinate (generalized displacement)	Work, J
Hydrostatic system	p	V	$-pdV$
Wire	τ	L	τdL
Surface film	γ	A	γdA
Electrochemical cell	ε	Z	εdZ
Dielectric solid	E	$\mathcal{P}$	$E d\mathcal{P}$
Paramagnetic solid	$\mu_0 \mathcal{H}$	$\mathcal{M}$	$\mu_0 \mathcal{H} d\mathcal{M}$

$$dU = -pdV + TdS$$
$$dH = Vdp + TdS$$
$$dA = -pdV - SdT$$
$$dG = Vdp - SdT$$

→

$$dU = -pdV + \mu_0 \mathcal{H} d\mathcal{M} + TdS$$
$$dH = Vdp - \mathcal{M}\mu_0 d\mathcal{H} + TdS$$
$$dA = -pdV + \mu_0 \mathcal{H} d\mathcal{M} - SdT$$
$$dH = Vdp - \mathcal{M}\mu_0 d\mathcal{H} - SdT$$

a simple system, would not be present.

Maxwell's Relations

exact differential : $Z = Z(x, y)$

$dz = M\,dx + N\,dy$

$\left(\partial M/\partial y\right)_x = \left(\partial N/\partial x\right)_y$

$dU = TdS - pdV$
$dH = TdS + Vdp$
$dA = -SdT - pdV$
$dG = -SdT + Vdp$

→

$\left(\partial T/\partial V\right)_S = -\left(\partial P/\partial S\right)_V$

$\left(\partial T/\partial p\right)_S = \left(\partial V/\partial S\right)_p$

$\left(\partial S/\partial V\right)_T = \left(\partial p/\partial T\right)_V$

$-\left(\partial S/\partial p\right)_T = \left(\partial V/\partial T\right)_p$

↳ Maxwell's Relations

Very useful at any equilibrium state of a hydrodynamic system.

it provides the relationship between measurable quantities and not measurable quantities.
(or difficult to measure)

e.g. $-\left(\partial S/\partial p\right)_T = \left(\partial V/\partial T\right)_p$

we can determine changes of entropy by quantities that can be measured.
(p, V, T)

$\left(\partial S/\partial p\right)_T = -\left(\partial V/\partial T\right)_p = -\beta$ (the volume expansivity)

A positive expansivity ($\beta > 0$)

T 증가 → V 증가 → $\left(\partial S/\partial p\right)_T$ 감소 !!

Ans.

$dU = TdS - pdV$
$dH = TdS + Vdp$
$dA = -SdT - pdV$
$dG = -SdT + Vdp$

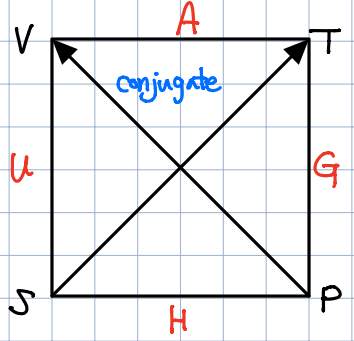
→

$\left(\partial T/\partial V\right)_S = -\left(\partial P/\partial S\right)_V$

$\left(\partial T/\partial p\right)_S = \left(\partial V/\partial S\right)_p$

$\left(\partial S/\partial V\right)_T = \left(\partial p/\partial T\right)_V$

$-\left(\partial S/\partial p\right)_T = \left(\partial V/\partial T\right)_p$



TdS Equation

1st entropy = $S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$TdS = T \cdot \left(\frac{\partial S}{\partial T}\right)_V dT + T \cdot \left(\frac{\partial S}{\partial V}\right)_T dV \quad \leftarrow \because \text{isochoric}$$

reversible, isochoric process: $TdS = \delta Q$

$$\delta Q = T \cdot \left(\frac{\partial S}{\partial T}\right)_V dT \quad \leftarrow \delta Q = C_V dT$$

$$\therefore T \cdot \left(\frac{\partial S}{\partial T}\right)_V = C_V$$

$$TdS = T \cdot \left(\frac{\partial S}{\partial T}\right)_V dT + T \cdot \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\boxed{TdS = C_V dT + T \cdot \left(\frac{\partial P}{\partial T}\right)_V dV}$$

1st TdS equation!

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

2nd: entropy = $S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$TdS = T \cdot \left(\frac{\partial S}{\partial T}\right)_P dT + T \cdot \left(\frac{\partial S}{\partial P}\right)_T dP \quad \leftarrow \because \text{isobaric}$$

reversible, isobaric process: $TdS = \delta Q$

$$\delta Q = T \cdot \left(\frac{\partial S}{\partial T}\right)_P dT \quad \leftarrow \delta Q = C_P dT$$

$$C_P = T \cdot \left(\frac{\partial S}{\partial T}\right)_P$$

$$TdS = T \cdot \left(\frac{\partial S}{\partial T}\right)_P dT + T \cdot \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\boxed{TdS = C_P dT - T \cdot \left(\frac{\partial V}{\partial T}\right)_P dP}$$

2nd TdS equation!