

$$f(x) : df = w dx \quad g(w) = f - xw$$

$$dg = -x dw$$

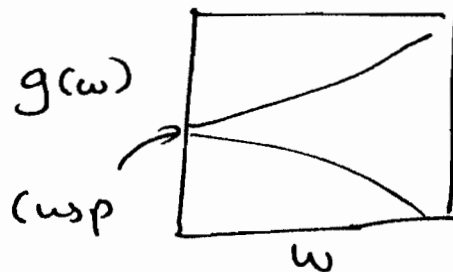
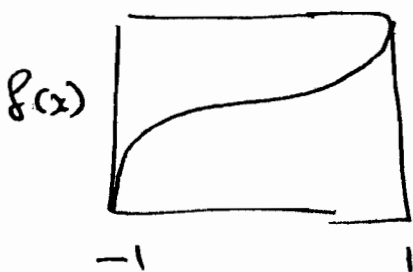
Example 5.4

$$f(x) = x^3 + 1 \quad w = \frac{df}{dx} = 3x^2 \Rightarrow x = \pm \sqrt{\frac{w}{3}}$$

$$g(w) = f - xw = \pm \left(\frac{w}{3}\right)^{3/2} + 1 \mp w \sqrt{\frac{w}{3}} \Rightarrow g(w) = \mp \frac{2w^{3/2}}{3\sqrt{3}} + 1$$

Check  $\frac{dg}{dw} = \mp \frac{w^{1/2}}{\sqrt{3}} = -x \quad \checkmark$

$$g + wx = \mp \frac{2w^{3/2}}{3\sqrt{3}} + 1 \pm w \sqrt{\frac{w}{3}} = \left(\pm \sqrt{\frac{w}{3}}\right)^3 + 1 = x^3 + 1 = f(x) \quad \checkmark$$



multivalued!

Application to thermodynamic functions

$$u(S, V, N) : du = T ds - P dV + \mu dN$$

1<sup>st</sup> transform :  $u - TS \equiv A$  Helmholtz free energy

$$A(T, V, N) \quad dA = -s dT - P dV + \mu dN$$

Reorder,  $u(V, S, N)$ ,  $du = -P dV + T ds + \mu dN$

1<sup>st</sup> transform :  $u + PV \equiv H$  Enthalpy

$$H(P, S, N) \quad dH = v dP + T ds + \mu dN$$

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Legendre Transforms

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$U(S, V, N)$ , 2nd Transform (or 1st Transform of  $A$ )

$$dU = TdS - PdV + \mu dN$$

$$U - TS + PV \equiv G \quad \text{Gibbs free energy}$$

$$G(T, P, N)$$

$$dG = -SdT + v dP + \mu dN$$

$U, A, G, H$  are all equivalent descriptions of the full thermodynamic properties

→ Fundamental Equations in different variables

From Euler Integration,

$$G = U - TS + PV =$$

$$= TS - PV + \mu N - TS + PV = \mu N$$

$$\Rightarrow \boxed{G = \mu}$$

for 1-component systems, chemical potential is the molar Gibbs free energy.

$U(S, V, N) \rightarrow$  after 3 transforms we get 0:

$$U - TS + PV - \mu N = 0 \Rightarrow \boxed{0 = -SdT + v dP - N d\mu}$$

Gibbs-Duhem relationship

Table S.1 summarizes properties for  $U, A, G, H$

Pop Quiz:  $U(N, S, V) \rightarrow$  what is the 1st transform?

Intensive Properties

For 1-component systems simplified relationships for  $\underline{A}$ ,  $\underline{u}$ ,  $\underline{H}$ ,  $\underline{G}$  (intensive forms, e.g.  $\underline{u} = \frac{u}{N}$ ):

$$\begin{aligned} d\underline{u} &= \tau d\underline{s} - P d\underline{v} & d\underline{H} &= \underline{v} dP + \tau d\underline{s} \\ d\underline{A} &= -\underline{s} dT - P d\underline{v} & d\underline{G} &= -\underline{s} dT + \underline{v} dP \end{aligned}$$

first derivatives obtained directly from differential expressions, e.g.  $T = \left. \frac{\partial \underline{u}}{\partial \underline{s}} \right|_{\underline{v}, N} = \left. \frac{\partial \underline{u}}{\partial \underline{s}} \right|_{\underline{v}}$

Instead of  $n+2 = 3$  variables, only 2 intensive variables needed.

Derivatives (in terms of measurements)

Some 1st derivatives of f.e.s are not measurable:

$$\text{e.g. } \underline{s} = - \left. \frac{\partial \underline{A}}{\partial T} \right|_{\underline{v}} = - \left. \frac{\partial \underline{G}}{\partial T} \right|_{P}$$

Many second derivatives are directly measurable:

$$\begin{aligned} \left. \frac{\partial^2 \underline{A}}{\partial T^2} \right|_{\underline{v}} &= - \left. \frac{\partial \underline{s}}{\partial T} \right|_{\underline{v}} = - \frac{1}{T} \left. \frac{\partial \underline{u}}{\partial T} \right|_{\underline{v}} = - \frac{C_v}{T} \\ \left. \frac{\partial^2 \underline{G}}{\partial T^2} \right|_{P} &= - \left. \frac{\partial \underline{s}}{\partial T} \right|_{P} = - \frac{1}{T} \left. \frac{\partial \underline{H}}{\partial T} \right|_{P} = - \frac{C_p}{T} \end{aligned} \left. \vphantom{\begin{aligned} \left. \frac{\partial^2 \underline{A}}{\partial T^2} \right|_{\underline{v}} \\ \left. \frac{\partial^2 \underline{G}}{\partial T^2} \right|_{P} \end{aligned}} \right\} \text{heat capacities}$$

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(4)

$$\frac{\partial^2 G}{\partial P^2} = \left. \frac{\partial \underline{V}}{\partial P} \right|_T = -\kappa_T \underline{V}$$

where  $\kappa_T \equiv -(\partial \underline{V} / \partial P)_T / \underline{V}$  isothermal compressibility

Cross Second Derivatives (remember Maxwell):

$$\frac{\partial^2 G}{\partial T \partial P} = - \left. \frac{\partial \underline{S}}{\partial P} \right|_T = \left. \frac{\partial \underline{V}}{\partial T} \right|_P = \alpha_P \underline{V}$$

where  $\alpha_P \equiv (\partial \underline{V} / \partial T)_P / \underline{V}$  coefficient of thermal expansion

$$\frac{\partial^2 A}{\partial T \partial \underline{V}} = - \left. \frac{\partial P}{\partial T} \right|_{\underline{V}} = - \left. \frac{\partial \underline{S}}{\partial \underline{V}} \right|_T \quad (\text{measurable})$$

$$\frac{\partial^2 U}{\partial \underline{S} \partial \underline{V}} = - \left. \frac{\partial P}{\partial \underline{S}} \right|_{\underline{V}} = \left. \frac{\partial T}{\partial \underline{V}} \right|_{\underline{S}} \quad (\text{also measurable})$$

pop quit: suggest exp. to measure this

etc

Derivatives with respect to "unnatural" variables can be obtained from the differential expressions

-e.g.  $\left. \frac{\partial \underline{U}}{\partial \underline{V}} \right|_T = ?$   $\underline{V}, T$  not natural for  $\underline{U}$

$$d\underline{U} = T d\underline{S} - P d\underline{V} \Rightarrow \left. \frac{\partial \underline{U}}{\partial \underline{V}} \right|_T = T \left. \frac{\partial \underline{S}}{\partial \underline{V}} \right|_T - P$$

$$= T \left. \frac{\partial P}{\partial T} \right|_{\underline{V}} - P \quad (\text{measurable } \checkmark)$$

see

$(\partial^2 A / \partial T \partial \underline{V})$  above