Auxiliary Functions
Legendre Transforms

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Auxiliary Function

- The term "auxiliary function" usually refers to the functions created during the course of a proof in order to prove the result.
- In thermodynamics, quantities with dimensions of energy were introduced that have useful physical interpretations and simplify calculations in situations where controlled set of variables were used.

Work

- In general, work can be divided into two parts:
  - work of expansion and contraction, and
  - work of the **sum of all other forms**
- Therefore in the reversible case,

$$\underline{f} \cdot d\underline{X} = -pdV + \sum_i \mu_i dn_i$$

where μ_i will be defined as the chemical potential of species i, but not yet at this moment.

Euler’s theorem

- **Euler's homogeneous function theorem**

  States that: Suppose that the function *f* is continuously differentiable, then *f* is positive homogeneous of degree n if and only if

$$f\left(\lambda \underline{x}\right) = \lambda^{n} f\left(\underline{x}\right)$$

- **n= 1, *f* is a first-order homogeneous function**

Euler's theorem

- **Let $f(x_1,\ldots,x_n)$ be a first-order homogeneous function of $x_1,\ldots,x_n$.**
- **Let $u_i = \lambda x_i$**
- **Then $f(u_1,\ldots,u_n) = \lambda f(x_1,\ldots,x_n)$**
- **Differentiate with respect to λ;**

$$\left(\frac{\partial f(u_1,\ldots,u_n)}{\partial \lambda}\right)_{x_i} = f(x_1,\ldots,x_n) \qquad (1)$$

Euler's theorem

- **From calculus,**

$$df\left(u_1,\ldots,u_n\right)=\sum_{i=1}^{n}\left(\partial f/\partial u_i\right)_{u_j} du_i \qquad (2)$$

- **and,**

$$\left(\partial f/\partial \lambda\right)_{x_i}=\sum_{i=1}^{n}\left(\partial f/\partial u_i\right)_{u_j}\left(\partial u_i \partial \lambda\right)_{x_i}$$

$$=\sum_{i=1}^{n}\left(\partial f/\partial u_i\right)_{u_j} x_i \qquad (3)$$

Euler's theorem

- **Substitute back to the first equation,**

$$f(x_1,\ldots,x_n) = \sum_{i=1}^{n} \left(\partial f / \partial u_i\right)_{u_j} x_i \qquad (4)$$

- **Take $\lambda = 1$,**

$$f(x_1,\ldots,x_n) = \sum_{i=1}^{n} \left(\partial f / \partial x_i\right)_{x_j} x_i \qquad (5)$$

- **This is Euler's theorem for first-order homogeneous functions**

Legendre Transform

- **Recall the 2nd law of thermodynamics,**

$$dS = (1/T)dE - (\underline{f}/T)\cdot d\underline{X}$$

$$dE = TdS + \underline{f}\cdot d\underline{X}$$

- **and** $$\underline{f}\cdot d\underline{X} = -pdV + \sum_i \mu_i dn_i$$
- **we arrive at,**

$$dE = TdS - pdV + \sum_i \mu_i dn_i$$

- **Thus,** $E = E(S, V, n_1, n_2, \ldots, n_r)$**, is a natural function of *S*, *V*, and the *n*** **n_i's.**

Legendre Transform

- **However, experimentally, *T* is much more convenient than *S*.**
- **Assume $f = f(x_1,\ldots,x_n)$ is a natural function of $x_1,\ldots,x_n$.**
- **Then,** $f(x_1,\ldots,x_n) = \sum_{i=1}^{n} (\partial f/\partial x_i)_{x_j} x_i$

Euler's theorem for first-order homogeneous functions

$$df = \sum_{i=1}^{n} u_i dx_i \qquad u_i = (\partial f/\partial x_i)_{x_j}$$

- **Let** $g = f - \sum_{i=r+1}^{n} u_i dx_i$

Legendre Transform

- **Then,** $$dg = df - \sum_{i=r+1}^{n} \left(u_i dx_i + x_i du_i \right)$$
$$= \sum_{i=1}^{r} u_i dx_i + \sum_{i=r+1}^{n} \left(-x_i \right) du_i$$
- **Thus, $g = g(x_1,\ldots,x_r,u_{r+1},\ldots,u_n)$ is a natural function of $x_1,\ldots,x_r$ and the conjugate variables to $x_{r+1},\ldots,x_n$, namely $u_{r+1},\ldots,u_n$.**
- **The function *g* is called a Legendre transform of *f*.**

Legendre Transform

- **It transform away the dependence upon $x_{r+1},\ldots,x_n$ to a dependence upon $u_{r+1},\ldots,u_n$.**

- **It is apparent that this type of transformation allows one to introduce a natural function of *T*, *V*, and *n*, since *T* is simply the conjugate variable to *S*; so as to *p* to *V*.**

Legendre Transform

- **From the first and second law, we have**

  $$\boldsymbol{E = E(S, V, n)}$$

- **We construct a natural function of *T*, *V* and *n*, by subtract from the *E*(*S*, *V*, *n*) the quantity**

  ***S* ✕ (variable conjugate to *S*) = *ST*.**

- **Let *A*(*T*, *V*, *n*) = *E* – *TS* called the Helmholtz free energy**
- **Therefore,**

$$dA = -SdT - pdV + \sum_{i=1}^{r} \mu_i dn_i$$

Legendre Transform

- **Let** $G(T, p, n)$ **be the Gibbs free energy**

  $G = E - TS - (-pV)$

- **And** $H(S, p, n)$ **be the Enthalpy**

  $H = E - (-pV) = E + pV$

- **Therefore,**

$$dG = -SdT + Vdp + \sum_{i=1}^{r} \mu_i dn_i$$

$$dH = TdS + Vdp + \sum_{i=1}^{r} \mu_i dn_i$$

Think also about, volume to U pressure to H

Maxwell Relations

- **Armed with the auxiliary, many types of different measurements can be interrelated.**
- **Consider,**

$$\left(\partial S / \partial V\right)_{T,n}$$

- **implies we are viewing *S* as function of the natural function of *T*, *V* and *n*.**

Maxwell Relations

- **If** $df = adx + bdy$**, from calculus,**

$$\left(\partial a / \partial y\right)_x = \left(\partial b / \partial x\right)_y$$

- **Recall** $dA = -SdT - pdV + \mu dn$
- **Then we have**

$$\left(\partial S / \partial V\right)_{T,\, n} = \left(\partial p / \partial T\right)_{V,\, n}$$

- **and**

$$dG = -SdT - Vdp + \mu dn$$

$$\left(\partial S / \partial p\right)_{T,\, n} = -\left(\partial V / \partial T\right)_{p,\, n}$$

Example I

- **Let** $C_v = T\left(\partial S / \partial T\right)_{V,\,n}$
- **then**

$$\left(\frac{\partial C_v}{\partial V}\right)_{T,\,n} = T\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_{V,\,n}\right)_{T,\,n}$$

$$= T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_{T,\,n}\right)_{V,\,n}$$

$$= T\left(\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)_{V,\,n}\right)_{V,\,n}$$

$$= T\left(\frac{\partial^2 p}{\partial T^2}\right)_{V,\,n}$$

Quiz (exercise 1.10)

- **Derive an analogous form for (15 Mins)**

$$\left(\frac{\partial C_p}{\partial V} \right)_{T,n}$$

solution

$$\left(\frac{\partial C_p}{\partial p}\right)_{T,n} = T\left(\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_{p,n}\right)_{T,n}$$

$$= T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_{T,n}\right)_{p,n}$$

$$= T\left(\frac{\partial}{\partial T}\left(-\frac{\partial V}{\partial T}\right)_{p,n}\right)_{p,n}$$

$$= -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{p,n}$$

Example II

- **Let** $$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,\,n}$$
- **Viewing *S* as a function of *T*, *V* and *n***
- **We have**

$$(dS)_n = \left(\frac{\partial S}{\partial T}\right)_{V,\,n}(dT)_n + \left(\frac{\partial S}{\partial V}\right)_{T,\,n}(dV)_n$$

$$\left(\frac{\partial S}{\partial T}\right)_{p,\,n} = \left(\frac{\partial S}{\partial T}\right)_{V,\,n} + \left(\frac{\partial S}{\partial V}\right)_{T,\,n}\left(\frac{dV}{\partial T}\right)_{n,\,p}$$

Maxwell Relations

- **Hence** $$\frac{1}{T}C_p = \frac{1}{T}C_v + \left(\frac{\partial p}{\partial T}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{n,p}$$
- **Note that** $$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x$$ Euler's chain rule
- **So** $$(\partial p/\partial T)_{V,n} = -(\partial p/\partial V)_{T,n}(\partial V/\partial T)_{p,n}$$
- **Therefore** $$C_p - C_v = -T(\partial p/\partial V)_{T,n}\left[(\partial V/\partial T)_{p,n}\right]^2$$

Euler's theorem

- **From the 2nd law of thermodynamics,**

$$E = E\left(S, \underline{X}\right)$$

- **the internal energy *E* is extensive, it depends upon *S* and *X̲*, which are also extensive.**

$$E\left(\lambda \underline{X}\right) = \lambda E\left(S, \underline{X}\right)$$

- **Thus, *E*(*S*,*X̲*) is a first order homogeneous function of *S* and *X̲*.**

Euler's theorem

- **Therefore, from Euler's theorem, Eq.5,**

$$E = \left(\partial E / \partial S\right)_{\underline{X}} S + \left(\partial E / \partial \underline{X}\right)_s \underline{X}$$

$$= TS + \underline{f} \cdot \underline{X}$$

where $\underline{X}$ is a vector means system volume

- **And work is,**

$$\underline{f} \cdot d\underline{X} = -pdV + \sum_i \mu_i dn_i$$

Extensive Function

- **This flow naturally as we gave earlier,**

$$dE = TdS - pdV + \sum_{i=1}^{r} \mu_i dn_i$$

- **That is, $E = E(S, V, n_1, \ldots, n_r)$**

- **and Euler's theorem yields,**

$$E = TS - pV + \sum_{i=1}^{r} \mu_i n_i$$

Extensive Function

- **Its total differential is**

$$dE = TdS + SdT - pdV - Vdp + \sum_{i=1}^{r} \left(\mu_i dn_i + n_i d\mu_i \right)$$

- **Therefore,**

$$0 = SdT - Vdp + \sum_{i=1}^{r} \left(n_i d\mu_i \right)$$

This is the Gibbs-Duhem Equation

Extensive Function

- **Recall the definition of Gibbs free energy**

  ***G* = *E* – *TS* – (–*pV*)**

- **Apply Euler's theorem gives,**

$$dG = \left(TS - pV + \sum_{i=1}^{r} \mu_i dn_i \right) - TS - pV$$

$$= \sum_{i=1}^{r} \mu_i dn_i$$

- **For one component system $\mu = G/n$, Gibbs free energy per mole**

Quiz (exercise 1.14)

- Show that for a one component p-V-n system

$$\left(\frac{\partial \mu}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T$$

- where *v* is the volume per mole. [Hint: show that $d\mu = -sdT + vdp$, where *s* is the entropy per mole.

solution

- The Gibbs-Duhem Equation,

$$0 = SdT - Vdp + \sum_{i=1}^{r} (n_i d\mu_i)$$

- Implies, for one component,

$$d\mu = sdT - vdp$$

- Hence,

$$\left(\frac{\partial \mu}{\partial v}\right)_T = -s\left(\frac{\partial T}{\partial v}\right)_T + v\left(\frac{\partial p}{\partial v}\right)_T$$