Thermodynamics

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Euler's theorem

- **A homogeneous function of degree n is one for which $f(\lambda \underline{X}) = \lambda^n f(\underline{X})$**

- **Let $f(x_1,\ldots,x_n)$ is 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,**

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

- **and,**

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

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

Euler's theorem

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

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

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

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

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

Euler's theorem

- **Since $E = E(S, \underline{X})$ is first-order homogeneous, from the postulate**

- **Euler's theorem gives,**

$$E = \left(\partial E / \partial S\right)_{\underline{X}} S + \left(\partial E / \partial \underline{X}\right)_{s} \underline{X}$$
$$= TS + \underline{f} \cdot \underline{X} \quad \text{(the second law)}$$

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

Legendre Transform

- **Assume $f = f(x_1, \ldots, x_n)$ is a natural function of $x_1, \ldots, x_n$.**

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

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

- **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 $u_{r+1}, \ldots, u_n$.**

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 is the chemical potential of species i

Legendre Transform

- **From the first and second law, we have**
$$E = E(S, V, n)$$

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

$$S \times (\text{variable conjugate to } S) = ST.$$

- **Let** $\quad A(T, V, n) = E - TS$ **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,**

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

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

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

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

Maxwell Relations

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

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

Maxwell Relations

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

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

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

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

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

Maxwell Relations

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

- 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** $\dfrac{1}{T} C_p = \dfrac{1}{T} C_v + \left(\dfrac{\partial p}{\partial T} \right)_{V,n} \left(\dfrac{\partial V}{\partial T} \right)_{n,p}$

- **Note that** $\left(\dfrac{\partial x}{\partial y} \right)_z = - \left(\dfrac{\partial x}{\partial z} \right)_y \left(\dfrac{\partial z}{\partial y} \right)_x$

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

- **Therefore**

$$C_p - C_v = -T \left(\partial p / \partial V \right)_{T,n} \left[\left(\partial V / \partial T \right)_{p,n} \right]^2$$

Extensive Function

- **A macroscopic property is extensive if it depends linearly on the size of the system**

- **Consider the internal energy E, which is extensive, how it depends upon S and $\underline{X}$, which are also extensive.**

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

- **Thus, $E(S,\underline{X})$ is a first order homogeneous function of S and $\underline{X}$.**

Extensive Function

- **Euler's theorem gives,**

$$E = \left(\partial E / \partial S \right)_{\underline{\underline{X}}} S + \left(\partial E / \partial \underline{X} \right)_{s} \underline{X}$$
$$= TS + \underline{f} \cdot \underline{\underline{X}}$$

- **And work is**

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

- **This flow naturally to give,**

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

Extensive Function

- **This is, $E = E(S, V, n_1, \ldots, n_r)$, and Euler's theorem yields**

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

- **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**

Mixture/solution

- **Chemical Potential**
- **Partial Molar Property**
- **Partial Pressure**
- **Ideal-Gas Mixtures**
  - **enthalpy of an ideal gas**
  - **entropy of an ideal gas**
- **Gibbs energy of an ideal-gas mixture $G^{ig} = H^{ig} - TS^{ig}$,**

Mixture/solution

- **Because the properties of systems in chemical engineering depend strongly on composition as well as on temperature and pressure,**

- **Need to develop the theoretical foundation for applications of thermodynamics to gas mixtures and liquid solutions**

Mixture/solution

- definition of a fundamental new property called the *chemical potential,* upon which the principles of phase and chemical-reaction equilibrium depend.

- This leads to the introduction of a new class of thermodynamic properties known as *partial properties.*

Chemical potential

- **Gibbs free energy of a multicomponent mixture is a function of *T*, *P* and each species mole number, therefore, the total differential of the Gibbs free energy,**

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N_i} dT + \left(\frac{\partial G}{\partial P} \right)_{P,N_i} dP + \sum_i^C \left(\frac{\partial G}{\partial N_i} \right)_{P,N_i} dN$$

$$= -SdT + VdP + \sum_i^C \bar{G}_i dN_i \qquad \textbf{(CP1)}$$

Chemical potential

- **Recall**

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

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

- **in extensive function, therefore we have**

$$\mu_i \equiv \left[\frac{\partial (nG)}{\partial n_i} \right]_{p,T,n_{i \neq j}}$$

Chemical Potential and Phase Equilibrium

- **Consider a closed system consisting of two phases in equilibrium.**

- **Within this *closed* system, each individual phase is an *open* system, free to transfer mass to the other, that is**

$$d(nG)^{\alpha} = -(nS)^{\alpha} dT + (nV)^{\alpha} dp + \sum_{i=1} \mu_i^{\alpha} dn_i^{\alpha}$$

$$d(nG)^{\beta} = -(nS)^{\beta} dT + (nV)^{\beta} dp + \sum_{i=1} \mu_i^{\beta} dn_i^{\beta}$$

Chemical Potential and Phase Equilibrium

- **The change in the total Gibbs energy of the two-phase system is the sum of these equations.**

$$d(nG) = -(nS)dT + (nV)dp + \sum_{i=1} \mu_i^{\alpha} dn_i^{\alpha} + \sum_{i=1} \mu_i^{\beta} dn_i^{\beta}$$

$$\sum_{i=1} \mu_i^{\alpha} dn_i^{\alpha} + \sum_{i=1} \mu_i^{\beta} dn_i^{\beta} = 0$$

Chemical Potential and Phase Equilibrium

- **And** $\quad dn_i^\alpha = -dn_i^\beta$
- **Therefore,**

$$\sum_{i=1} \left(\mu_i^\alpha - \mu_i^\beta \right) dn_i^\alpha = 0$$

$$\mu_i^\alpha = \mu_i^\beta \qquad (i = 1, 2, \ldots, N)$$

- **Thus, multiple phases at the same T and P are in equilibrium when the chemical potential of each species is the same in all phases.**

Partial Molar Property

- **Partial Molar Property (θ)**

$$\mu_i / \theta \equiv \left[\frac{\partial (nG / \theta)}{\partial n_i} \right]_{p,T,n_{i \neq j}}$$

- **It is a *response function*, representing the change of total property θ due to addition at constant *T* and *P* of a differential amount of species *i* to a finite amount of mixture/solution.**

Partial Molar Property

- **Let $\underline{\theta}$ be any molar property (molar volume, molar enthalpy, etc.) of a mixture consisting of N_i moles of species i,** $\quad N = \sum_i^C N_i$

- **And partial molar thermodynamic property**

$$\overline{\theta}_i = \overline{\theta}_i\left(T,P,\underline{x}\right) = \frac{\partial\left(N\underline{\theta}\right)}{\partial N_i}\bigg|_{T,P,N_{j\neq i}}$$

- **Therefore,**

$$\underline{\theta} = \sum_{i=1}^{C} x_i \overline{\theta}_i\left(T,P,\underline{x}\right)$$

Partial Molar Property

- **Or**

$$N\underline{\theta} = \sum_{i=1}^{C} N_i \bar{\theta}_i$$

So that, by the product rule of differentiation,

$$d\left(N\underline{\theta}\right) = \sum N_i d\bar{\theta}_i + \sum \bar{\theta} dN_i \qquad \textbf{PM 1}$$

- **substitute G with $N\underline{\theta}$ into Eq. CP 1**

Partial Molar Property

- **substitute G with $N\underline{\theta}$ into Eq. CP 1**

$$dN\underline{\theta} = \left(\frac{\partial N\underline{\theta}}{\partial T}\right)_{P,N_i} dT + \left(\frac{\partial N\underline{\theta}}{\partial P}\right)_{T,N_i} dP + \sum_{i}^{c}\left(\frac{\partial N\underline{\theta}}{\partial N_i}\right)_{P,N_i} dN_i$$

$$= N\left(\frac{\partial \underline{\theta}}{\partial T}\right)_{P,N_i} dT + N\left(\frac{\partial \underline{\theta}}{\partial P}\right)_{T,N_i} dP + \sum_{i}^{c} \overline{\theta}_i dN_i$$

PM 2

Partial Molar Property

- **Subtracting PM 2 from PM 1,**

$$-N\left(\frac{\partial \underline{\theta}}{\partial T}\right)_{P,N_i} dT - N\left(\frac{\partial \underline{\theta}}{\partial P}\right)_{T,N_i} dP + \sum_i^C N_i d\overline{\theta}_i = 0$$

- **Or,**

$$-\left(\frac{\partial \underline{\theta}}{\partial T}\right)_{P,N_i} dT - \left(\frac{\partial \underline{\theta}}{\partial P}\right)_{T,N_i} dP + \sum_i^C x_i d\overline{\theta}_i = 0$$

This is the generalized Gibbs-Duhem Equation

Partial Molar Property

- **For constant temperature and pressure,**

$$\sum_{i=1}^{c} N_i \, d\overline{\theta_i} \Big|_{T,P} = 0$$

$$\sum_{i=1}^{c} x_i \, d\overline{\theta_i} \Big|_{T,P} = 0$$

- **Substitute θ with G**

$$SdT - VdP + \sum_{i=1}^{c} N_i d\overline{G_i} = 0$$

$$\underline{S}dT - \underline{V}dP + \sum_{i=1}^{c} x_i d\overline{G_i} = 0$$

Partial Molar Property

- **At constant temperature and pressure,**

$$\sum_{i=1}^{C} N_i d\overline{G}_i = 0$$

$$\sum_{i=1}^{C} x_i d\overline{G}_i = 0$$

- **Recall Gibbs-Duhem Equation**

$$-\left(\frac{\partial \underline{\theta}}{\partial T}\right)_{P,N_i} dT - \left(\frac{\partial \underline{\theta}}{\partial P}\right)_{T,N_i} dP + \sum_{i}^{C} x_i d\overline{\theta}_i = 0$$

Partial Molar Property

- **Rearrange,**

$$d\overline{\theta}_i = \left(\frac{\partial \overline{\theta}_i}{\partial T}\right)_{p,\underline{x}} dT + \left(\frac{\partial \overline{\theta}_i}{\partial p}\right)_{T,\underline{x}} dp + \sum_{j=1}^{C-1}\left(\frac{\partial \overline{\theta}_i}{\partial x_j}\right)_{T,p} d\underline{x}_j$$

- **Substitute back to the Gibbs-Duhem Equation**

$$0 = -\left(\frac{\partial \overline{\theta}_i}{\partial T}\right)_{p,N_i} dT - \left(\frac{\partial \overline{\theta}_i}{\partial p}\right)_{T,N_i} dp$$

$$+ \sum_{j=1}^{C} x_i \left[\left(\frac{\partial \overline{\theta}_i}{\partial T}\right)_{p,\underline{x}} dT + \left(\frac{\partial \overline{\theta}_i}{\partial p}\right)_{T,\underline{x}} dp + \sum_{j=1}^{C-1}\left(\frac{\partial \overline{\theta}_i}{\partial x_j}\right)_{T,p} d\underline{x}_j\right]$$

Partial Molar Property

- **Since**

$$\sum_{i=1}^{C} x_i \left(\frac{\partial \bar{\theta}_i}{\partial T} \right)_{p,\underline{x}} dT = \frac{\partial}{\partial T} \bigg|_{p,\underline{x}} \left(\sum_{i=1}^{C} x_i \bar{\theta}_i \right) dT = \left(\frac{\partial \theta}{\partial T} \right)_{p,\underline{x}} dT$$

- **Finally**

$$\sum_{i=1}^{C} x_i \sum_{j=1}^{C-1} \left(\frac{\partial \bar{\theta}_i}{\partial x_j} \right)_{T,P} dx_j = 0$$

- **For Binary**

$$\sum_{i=1}^{2} x_i \sum_{j=1}^{C-1} \left(\frac{\partial \bar{\theta}_i}{\partial x_1} \right)_{T,p} dx_1 = 0 \qquad x_1 \left(\frac{\partial \bar{\theta}_1}{\partial x_1} \right)_{T,p} + x_2 \left(\frac{\partial \bar{\theta}_2}{\partial x_1} \right)_{T,p} = 0$$

Ideal-Gas Mixtures

- **Ideal gas** $\quad p = \dfrac{nRT}{V^t} \quad p_i = \dfrac{n_i RT}{V^t}$

$$\frac{p_i}{p} = \frac{n_i}{n} = y_i \quad or \quad p_i = y_i p \quad (i = 1,2,\ldots,N)$$

- p_i is known as the *partial pressure* of species i

$$\overline{V}_i^{\,ig} = \left[\frac{\partial\left(nV^{ig}\right)}{\partial n_i}\right]_{T,p,n_i} = \left[\frac{\partial\left(nRT \,/\, p\right)}{\partial n_i}\right]_{T,p,n_i}$$

$$\frac{RT}{P}\left(\frac{\partial n}{\partial n_i}\right)_{n_j} = \frac{RT}{P}$$

Ideal-Gas Mixtures

- **A partial molar property (other than volume) of a constituent species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.**

$$\overline{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i) \ \ when \ M_i^{ig} \neq V_i^{ig}$$

Ideal-Gas Mixtures

- **Since the enthalpy of an ideal gas is independent of pressure,**

$$H_i^{ig}(T, p_i) = H_i^{ig}(T, p)$$
$$\overline{H}_i^{ig}(T, p) = H_i^{ig}(T, p)$$
$$\overline{H}_i^{ig} = H_i^{ig}\ (pure\ value\ at\ mixture\ T, p)$$
$$H^{ig} = \sum_i y_i H_i^{ig}$$

- **For ideal gases, this *enthalpy change* of *mixing* is zero.**

Ideal-Gas Mixtures

- **The entropy of an ideal gas does depend on pressure, is given as**

$$dS_i^{ig} = Rd \ln p \qquad at\ const\ T$$

- **Therefore, integration from p_i to p**

$$S_i^{ig}(T, p) - S_i^{ig}(T, p_i) = -R \ln \frac{p}{p_i} = R \ln y_i$$

Ideal-Gas Mixtures

- **Recall** $\overline{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i)$ *when* $M_i^{ig} \neq V_i^{ig}$

- **Therefore,**

$$\overline{S}_i^{ig}(T,p) = S_i^{ig}(T,p) - R \ln y_i$$

$$\overline{S}_i^{ig} = S_i^{ig} - R \ln y_i$$

- **Where** S_i^{ig} **is** the pure-species value at the mixture T and P.

Ideal-Gas Mixtures

- **By the summability relation**

$$S_i^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

$$S_i^{ig} - \sum_i y_i S_i^{ig} = R \sum_i y_i \ln \frac{1}{y_i}$$

- **the left side of the second equation is the *entropy change* of *mixing* for ideal gases. Since *l/y$_i$* > 1, this quantity is always positive, in agreement with the second law.**

Ideal-Gas Mixtures

- **For the Gibbs energy of an ideal-gas mixture $G^{ig} = H^{ig} - TS^{ig}$,**

- **for partial properties is**

$$\overline{G}_i^{ig} = \overline{H}_i^{ig} - \overline{T}S_i^{ig}$$

$$\overline{G}_i^{ig} = H_i^{ig} - TS_i^{ig} + RT \ln y_i$$

$$\mu_i^{ig} \equiv \overline{G}_i^{ig} = G_i^{ig} + RT \ln y_i$$

Recap Mixture/solution

- **Gibbs free energy of a multicomponent mixture**
- **Chemical Potential**
- **Partial Molar Property**
- **Partial Pressure of Ideal-Gas**
- **Ideal-Gas Mixtures**
  - **enthalpy of an ideal gas**
  - **entropy of an ideal gas**
- **Gibbs energy of an ideal-gas mixture $G^{ig} = H^{ig} - TS^{ig}$,**