Supplemental Notes for Chapter 17
General Treatment of Phase and Chemical Equations

1. Phase rule constrained parameter variability

   - $\mathcal{F} = n + 2 - \pi - r$
   - invariant ($\mathcal{F} = 0$)
   - monovariant ($\mathcal{F} = 1$)
   - divariant ($\mathcal{F} = 2$)
   - other constraints (stoichiometric ratio, “indifferent states”)

2. Matrix/determinant formalism applied to generalized Gibbs-Duhem and reaction equilibrium expressions

   - phase and chemical equilibrium criteria combined
   - Gibbs-Duhem combined with reaction equilibrium criteria to produce a generalized expression for π phases, r reactions and n components

$$\sum_{s=1}^{\pi}\left[-\underline{S}^{(s)}dT + \underline{V}^{(s)}dP - \sum_{i=1}^{n} N_i^{(s)}\, d\mu_i\right] \quad \text{and} \quad \sum_{i=1}^{n}\sum_{k=1}^{r} \nu_i^{(k)} d\mu_i$$

$$-\begin{bmatrix} \underline{S}^{(1)} \\ \\ \underline{S}^{(\pi)} \\ 0^{(1)} \\ \\ 0^{(r)} \end{bmatrix} [dT] + \begin{bmatrix} \underline{V}^{(1)} \\ \vdots \\ \underline{V}^{(\pi)} \\ 0^{(1)} \\ \vdots \\ 0^{(r)} \end{bmatrix} [dP] - \begin{bmatrix} N_1^{(1)} & \cdots & N_j^{(1)} & \cdots & N_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ N_1^{(\pi)} & \cdots & N_j^{(\pi)} & \cdots & N_n^{(\pi)} \\ \nu_1^{(1)} & \cdots & \nu_j^{(1)} & \cdots & \nu_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ \nu_1^{(r)} & \cdots & \nu_j^{(r)} & \cdots & \nu_n^{(r)} \end{bmatrix} \begin{bmatrix} d\mu_1 \\ \vdots \\ d\mu_j \\ \vdots \\ d\mu_n \end{bmatrix} = 0$$

or in shorthand vector notation

$$-\underset{\sim}{S}^{(s)}dT + \underset{\sim}{V}^{(s)}dP - \underset{\approx}{N}_j^{(s)} d\underset{\sim}{\mu}_j = 0$$

3. Invariant systems ($\mathcal{F} = 0$)

- $d\underset{\sim}{\mu}_i = 0$
- mass and mole constraints
- $|\underset{\approx}{N}^{(s)}| \neq 0$ required or the rank of the $N^{(s)}$ matrix must be reduced to avoid an over-constrained system
- indifferent states result if $|\underset{\approx}{N}^{(s)}| = 0$

4. Monovariant systems ($\mathcal{F} = 1$) pressure-temperature variations

- generalized Clapeyron equation
- use Gibbs-Duhem with chemical reactions included
- use a chemical potential or fugacity approach to get

$$\left.\frac{dP}{dT}\right|_{\mathcal{F}=1} = \frac{|\Delta \underset{\approx}{H}|}{T|\Delta \underset{\approx}{V}|} \quad \text{or equivalently} \quad \frac{|\Delta \underset{\approx}{S}|}{|\Delta \underset{\approx}{V}|}$$

$$|\Delta \underset{\approx}{H}| \equiv \begin{vmatrix} H^{(1)} & x_1^{(1)} & x_2^{(1)} & \cdots & x_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ H^{(\pi)} & x_1^{(\pi)} & x_2^{(\pi)} & \cdots & x_n^{(\pi)} \\ 0 & v_1^{(1)} & v_2^{(1)} & \cdots & v_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ 0 & v_1^{(r)} & v_2^{(r)} & \cdots & v_n^{(r)} \end{vmatrix}_{\approx} \qquad |\Delta V| \equiv \begin{vmatrix} V^{(1)} & x_1^{(1)} & x_2^{(1)} & \cdots & x_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ V^{(\pi)} & x_1^{(\pi)} & x_2^{(\pi)} & \cdots & x_n^{(\pi)} \\ 0 & v_1^{(1)} & v_2^{(1)} & \cdots & v_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ 0 & v_1^{(r)} & v_2^{(r)} & \cdots & v_n^{(r)} \end{vmatrix}$$

5. Isobaric monovariant equilibria, temperature-composition variations

-apply $dP = 0$ constraint to the set of generalized Gibbs-Duhem equations and use the Gibbs-Helmholtz relationship to simplify

$$\left[\frac{\partial T}{\partial x_1^{\beta}}\right]_{P,[\alpha,\ldots,\pi]} = \frac{-T|\underset{\approx}{x}_i^{(s)}|\left(\partial\mu_1^{\beta}/\partial x_1^{\beta}\right)_{T,P}}{\left[|\Delta \underset{\approx}{H}| - \overline{H}_1^{\beta}|\underset{\approx}{x}_i^{(s)}|\right]}$$

or with the fugacity introduced

$$\left[\frac{\partial T}{\partial x_1^{\beta}}\right]_{P,[\alpha,\ldots,\pi]} = \frac{-RT^2\left|\underset{\approx}{x}_1^{(s)}\right|\left[\frac{\partial \ln \hat{f}_1^{\beta}}{\partial x_1^{\beta}}\right]_{T,P}}{\left[\left|\Delta \underset{\approx}{H}\right| - \overline{H}_1^{\beta}\left|\underset{\approx}{x}_i^{(s)}\right|\right]}$$

6. Indifferent states and azeotropic behavior ($\mathcal{F} \geq 2$)

$$\left|\underset{\approx}{N}_j^{(s)}\right| \quad \text{or} \quad \left|\underset{\approx}{x}_j^{(s)}\right| = 0$$

- rank of the mole or composition matrix must be reduced which is equivalent to reducing the number of components

- Gibbs-Konovalows' first and second theorems

$$-\underset{\sim}{S}^{(s)}dT + \underset{\sim}{V}^{(s)}dP - \underset{\approx}{N}_j^{(s)}d\mu_j = 0$$

if $\left|\underset{\approx}{N}_j^{(s)}\right| = 0$ and if $dP = 0$ then $dT = 0$ (extremum in T)

or

if $\left|\underset{\approx}{N}_j^{(s)}\right| = 0$ and if $dT = 0$ then $dP = 0$ (extremum in P)

$$\underset{\approx}{N}_j^{(s)} = \begin{bmatrix} N_1^{(1)} & \cdots & N_j^{(1)} & \cdots & N_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ N_1^{(\pi)} & \cdots & N_j^{(\pi)} & \cdots & N_n^{(\pi)} \\ \nu_1^{(1)} & \cdots & \nu_j^{(1)} & \cdots & \nu_n^{(1)} \\ \vdots & & \vdots & & \vdots \\ \nu_1^{(r)} & \cdots & \nu_{\mathrm{j}}^{(\mathrm{r})} & \cdots & \nu_n^{(r)} \end{bmatrix}$$

and

$$\underset{\approx}{x}_j^{(s)} = \begin{bmatrix} x_1^{(1)} \cdots x_j^{(1)} \cdots x_n^{(1)} \\ \vdots \qquad \vdots \qquad \vdots \\ x_1^{(\pi)} \quad x_j^{(\pi)} \cdots x_n^{(\pi)} \\ \nu_1^{(1)} \quad \nu_j^{(1)} \cdots \nu_n^{(1)} \\ \vdots \qquad \vdots \qquad \vdots \\ \nu_1^{(r)} \cdots \nu_j^{(r)} \cdots \nu_n^{(\pi)} \end{bmatrix}$$