

Thermodynamics II

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Recap Mixture/solution

- From postulate of internal energy to the definition of heat and the First Law.

$$dE = dQ + dW$$

- From the Newton's Second Law

$$dW = \underline{f} \cdot d\underline{X}$$

- In the reversible case plus

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

Recap Mixture/solution

- From postulate of entropy to the definition of temperature

$$(\partial E / \partial S)_{\underline{X}} \geq 0$$

$$T \equiv (\partial E / \partial S)_{\underline{X}} \geq 0$$

- the Second Law

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

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

$$(\Delta S)_{adiabatic} \geq 0$$

Recap Mixture/solution

- **Combine the First and Second Law,**

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

- **Euler's theorem lead to Gibbs-Duhem Equation**

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

- **From the Legendre transformation lead to Helmholtz free energy**

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

- **And Gibbs free energy**

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

Recap Mixture/solution

- From the definition of chemical potential,

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

- we introduced partial molar property

$$\bar{V}_i = \left[\frac{\partial (nV)}{\partial n_i} \right]_{p, T, n_{i \neq j}}$$

- This allow the calculation of mixture properties at a small deviation

$$dV \Big|_{T, p} = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 + \dots,$$

$$V \Big|_{T, p} = \bar{V}_1 n_1 + \bar{V}_2 n_2 + \dots.$$

Recap Mixture/solution

- 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.
- **This leads to**

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

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 $G^{ig} = H^{ig} - TS^{ig}$,**

Nonideal gas mixtures

Fugacity and Fugacity Coefficient

- For **pure species i** , $dG = -SdT + Vdp$
- At **constant T** , in the **ideal-gas state**,

$$dG_i^{ig} = V_i^{ig} dp = \frac{RT}{p} dp = RT d \ln p$$

- **Integration gives,**

$$G_i^{ig} = \Gamma_i(T) + RT \ln p$$

where $\Gamma_i(T)$ is the integration constant at constant T

- **Ideal gas mixture, recall**

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

Fugacity and Fugacity Coefficient

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i p$$

- For real gas (fluid), **write an analogous**

$$G_i \equiv \Gamma_i(T) + RT \ln f_i$$

- in which pressure p is replaced by a new property f_i , with units of pressure. This equation provides a partial definition of f_i , the **fugacity** of pure species i .

Fugacity and Fugacity Coefficient

- At same T and p

$$G_i - G_i^{ig} = RT \ln \frac{f_i}{p}$$

where $G_i - G_i^{ig}$ is the *residual Gibbs energy*

- The dimensionless ratio f_i / P is another new property, the *fugacity coefficient*, given the symbol ϕ_i .

Fugacity and Fugacity Coefficient

- Therefore,

$$G_i^R = RT \ln \phi_i \quad \text{where} \quad \phi_i \equiv f_i / p$$

- **The definition of fugacity is completed by setting the ideal-gas-state fugacity of pure species i equal to its pressure p .**

Fugacity and Fugacity Coefficient

- The definition of the fugacity of a species in solution is **parallel to** the definition of the pure species fugacity, Recall

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i p$$

- So we have

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i$$

- where \hat{f}_i is the fugacity of species i in solution, **replacing** the partial pressure $y_i p$.

Residual Property

- Define **residual property** as

$$M^R \equiv M - M^{ig}$$

- where M is the molar (or unit-mass) value of a thermodynamic property and M^{ig} is the value that the property would have for an ideal gas of the same composition at the same T and P .

Residual Property

- **Multiply n on both side,**

$$nM^R = nM - nM^{ig}$$

- **Differentiation with respect to n_i at constant $T, P,$ and n_j gives:**

$$\left[\frac{\partial (nM^R)}{\partial n_i} \right]_{p, T, n_j} = \left[\frac{\partial (nM)}{\partial n_i} \right]_{p, T, n_j} - \left[\frac{\partial (nM^{ig})}{\partial n_i} \right]_{p, T, n_j}$$

Residual Property

- each term has the form of a partial molar property, therefore,

$$\bar{M}_i^R = \bar{M}_i - \bar{M}_i^{ig}$$

- Written for the residual Gibbs energy,

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig}$$

- And for same T and P

$$\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{y_i p}$$

Residual Property

- **Using identity** $\mu_i \equiv \left[\frac{\partial (nG)}{\partial n_i} \right]_{p, T, n_{i \neq j}} = \bar{G}_i$
- **then** $\bar{G}_i^R = RT \ln \hat{\phi}_i$
- **Where** $\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i p}$
- **This is the fugacity coefficient of species i in solution**

Residual Property

- For an ideal gas,

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig}$$

is **necessarily zero**;

- therefore

$$\bar{G}_i^R = RT \ln \hat{\phi}_i = 0$$

$$\hat{\phi}_i^{ig} = 1$$

$$\hat{f}_i^{ig} = y_i p$$

The Ideal Solution

The Ideal Solution

- Recall Gibbs energy of an ideal-gas mixture

$$\bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i$$

- We therefore **define** an ideal solution as one for which:

$$\bar{G}_i^{id} = G_i + RT \ln x_i$$

where *id* means ideal solution

The Ideal Solution

- All other thermodynamic properties for an ideal solution **follow from this definition**

$$\bar{S}_i^{id} = - \left(\frac{\partial \bar{G}_i^{id}}{\partial T} \right)_{p, x} = - \left(\frac{\partial G_i}{\partial T} \right)_p - R \ln x_i$$

$$\bar{S}_i^{id} = S_i - R \ln x_i$$

$$\bar{V}_i^{id} = - \left(\frac{\partial \bar{G}_i^{id}}{\partial p} \right)_{T, x} = - \left(\frac{\partial G_i}{\partial p} \right)_T$$

$$\bar{V}_i^{id} = V_i$$

The Ideal Solution

- **Since** $\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id}$

- **Therefore**

$$\bar{H}_i^{id} = G_i + RT \ln x_i + TS_i - RT \ln x_i$$

$$\bar{H}_i^{id} = H_i$$

- **From definition of partial molar property**

$$M^{id} = \sum_i x_i \bar{M}_i^{id}$$

The Ideal Solution

$$G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i$$

$$S^{id} = \sum_i x_i S_i + RT \sum_i x_i \ln x_i$$

$$V^{id} = \sum_i x_i V_i$$

$$H^{id} = \sum_i x_i H_i$$

The Lewis/Randall Rule

- **Recall**

$$G_i \equiv \Gamma_i(T) + RT \ln f_i$$

$$\mu_i \equiv \bar{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

- **SO**

$$\mu_i = G_i + RT \ln(\hat{f}_i / f_i)$$

- **fugacity of a species in an ideal solution**

$$\mu_i^{id} \equiv \bar{G}_i^{id} = G_i + RT \ln(\hat{f}_i^{id} / f_i)$$

$$\hat{f}_i^{id} = x_i f_i \quad \text{or} \quad \hat{\phi}_i^{id} = \phi_i$$

This is the Lewis/Randall Rule

Excess Properties

- If M represents the molar (or unit-mass) value of any extensive thermodynamic property, then **an excess property** M^E is defined as

$$M^E \equiv M - M^{id}$$

- **By definition,**

$$M^E - M^R = -(M^{id} - M^{ig})$$

Excess Properties

- Since an ideal-gas mixture is an ideal *solution* of ideal gases,

$$M^{id} - M^{ig} = \sum_i X_i M_i - \sum_i X_i M_i^{ig} = \sum_i X_i M_i^R$$

- This leads to

$$M^E - M^R = - \sum_i X_i M_i^R$$

- **Note** that excess properties have no meaning for pure species, whereas residual properties exist for pure species as well as for mixtures.
- partial excess property $\bar{M}_i^E = \bar{M}_i - \bar{M}_i^{id}$

The Excess Gibbs Energy and the Activity Coefficient

- **Since**

$$\bar{G}_i \equiv \mu_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

- **And**

$$\bar{G}_i^{id} = \Gamma_i(T) + RT \ln \hat{f}_i^{id}$$

- **Therefore**

$$\bar{G}_i - \bar{G}_i^{id} = RT \ln \frac{\hat{f}_i}{\hat{f}_i^{id}} = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

- Left side is the partial excess Gibbs energy
- Right side is the dimensionless ratio *activity coefficient of species i in solution*, symbol γ_i
- or

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i}$$

$$\bar{G}_i^E = RT \ln \gamma_i$$

Activity and activity coefficient

- Recall the **define** of an ideal solution:

$$\mu_i^{id} \equiv \bar{G}_i^{id} = G_i + RT \ln x_i$$

- We define

$$\mu_i = \mu_i^0 + RT \ln \alpha_i$$

- Where μ_i^0 is the **reference or standard state** chemical potential. The quantity, α_i , is called the "activity" of component i .

Activity and activity coefficient

- Thus, for an ideal gas mixture,

$$\alpha_i^{ig} = \frac{p_i}{p} = y_i$$

- for an nonideal gas mixture,

$$\alpha_i = \frac{\hat{f}_i}{p}$$

- for an ideal solution mixture,

$$\alpha_i^{id} = x_i$$

Thermodynamic Consistency

- **For Binary experimental data**

$$\left(\frac{G^E}{RT} \right)^* = x_1 \ln \gamma_1^* + x_2 \ln \gamma_2^*$$

$$\frac{d \left(G^E / RT \right)^*}{dx_1} = x_1 \frac{d \ln \gamma_1^*}{dx_1} + \ln \gamma_1^* + x_2 \frac{d \ln \gamma_2^*}{dx_1} - \ln \gamma_2^*$$

- **or**

$$\frac{d \left(G^E / RT \right)^*}{dx_1} = \ln \frac{\gamma_1^*}{\gamma_2^*} + x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1}$$

Thermodynamic Consistency

$$\frac{d(G^E / RT)}{dx_1} - \frac{d(G^E / RT)^*}{dx_1} = \ln \frac{\gamma_1}{\gamma_2} - \ln \frac{\gamma_1^*}{\gamma_2^*} - \left(x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \right)$$
$$\frac{d \delta(G^E / RT)}{dx_1} = \delta \ln \frac{\gamma_1}{\gamma_2} - \left(x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \right)$$

where $N_1 d \ln \gamma_1 + N_2 d \ln \gamma_2 = 0$

Thermodynamic Consistency

- **If a data set is reduced so as to make the residuals in G^E/RT scatter about zero,**

$$\delta \ln \frac{\gamma_1}{\gamma_2} = x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1}$$

- **This is the direct measure of deviations from the Gibbs-Duhem equation. The extent to which a data set departs from consistency is measured by the degree to which these residuals fail to scatter about zero**

Models for the excess Gibbs Energy

- G^E/RT is a function of T , P , and composition, but for liquids at low to moderate pressures it is a very weak function of P . Therefore the pressure dependence of activity coefficients is usually neglected.

Calculated Phase Diagram (CALPHAD)

$$G_m^\Phi = G^0 + G^{id} + G^E$$

$$= \sum x_i G_i^\Phi + RT \sum_i x_i \ln(x_i) + \sum_{i=1}^{c-1} \sum_{j=i+1}^c L_{i,j} x_i x_j$$

$${}^E G_m^\Phi = \sum_{i=1}^{c-1} \sum_{j=i+1}^c L_{ij} x_i x_j$$

$${}^E G_m^\Phi = \sum_{i=1}^{c-1} \sum_{j=i+1}^c {}^0 L_{ij}^\Phi x_i x_j + \sum_{i=1}^{c-1} \sum_{j=i+1}^c {}^0 L_{ijk}^\Phi x_i x_j x_k$$

$${}^0 L_{ij}^\Phi x_i x_j = \left(V_{ij}^{1,\Phi} + V_{ij}^{2,\Phi} T \right) x_i x_j$$

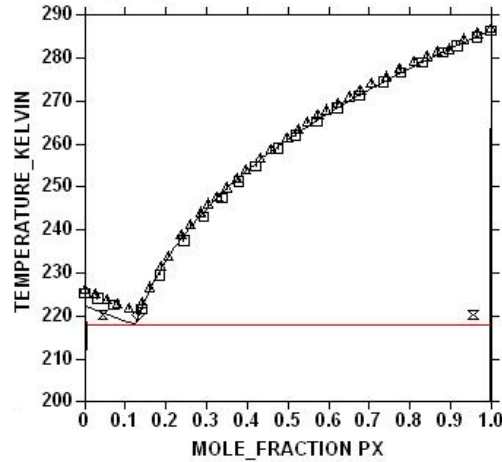
Redlich-Kister formalism

Where $V_{ij}^{1,\Phi}$ and $V_{ij}^{2,\Phi}$ are constants to be identified

Xylene Isomers Solid-Liquid Binary Phase Diagram

THERMO-CALC (2006.08.18:15.43) : EXAMPLE 10.08

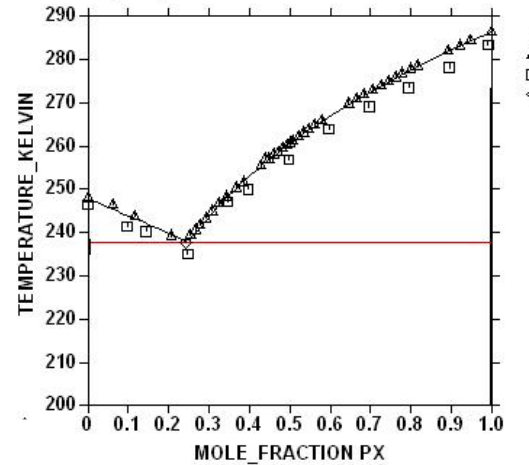
P=100000, N=1;



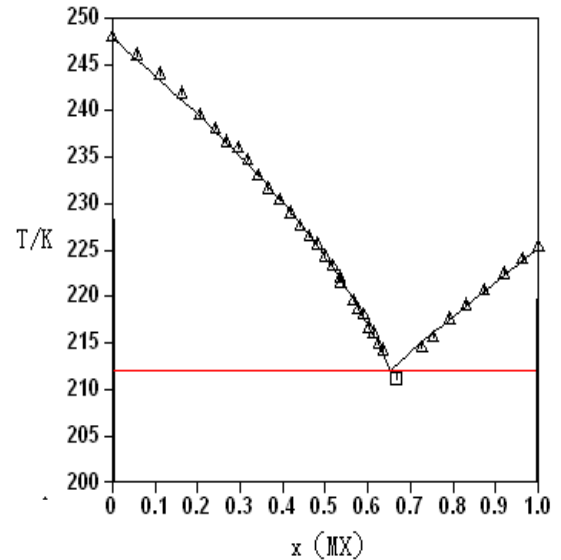
mX-pX

THERMO-CALC (2006.08.21:13.24) : EXAMPLE 10.10

P=100000, N=1;



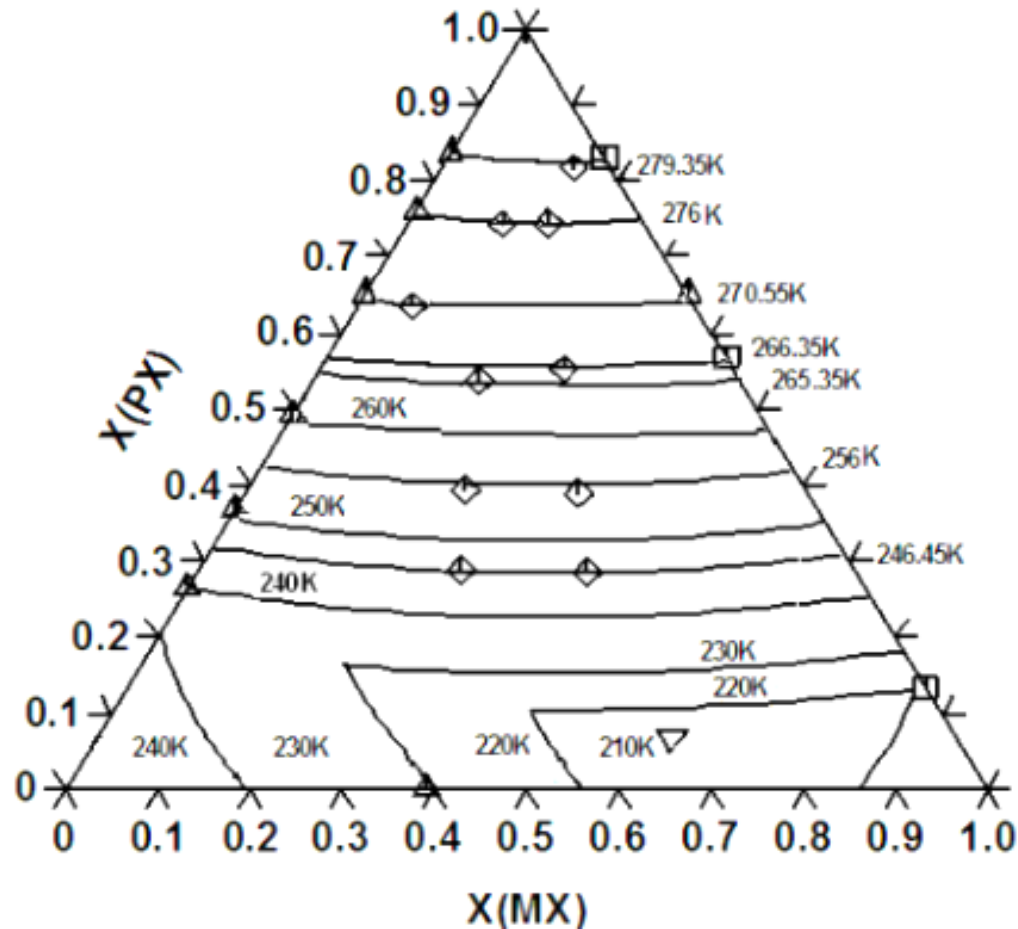
oX-pX



oX-mX

o,p,m 邻对间

Xylene Isomers Solid-Liquid Ternary Phase Diagram



Calculated Phase Diagram (CALPHAD)

Liquid	Solid
${}^0L_{OX,MX}^{Liq} = 6594.84 - 26.5515T$	${}^0L_{OX,MX}^S = 0.595190 + 101.609T$
${}^0L_{MX,PX}^{Liq} = 5219.46 - 16.8047T$	${}^0L_{MX,PX}^S = 0.418037 + 76.1079T$
${}^0L_{OX,PX}^{Liq} = 3760.90 - 11.2476T$	${}^0L_{OX,PX}^S = 0.430147 + 79.0478T$
${}^0L_{OX,MX,PX}^{Liq} = 31018.52 - 110.822T$	${}^0L_{OX,MX,PX}^S = 0.00859893 + 0.00385954T$