Solution Thermodynamics II

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Postulate U

Joule's paddlewheel experiment

1st law

$$\delta W = \underline{f} \cdot dX$$

$$dU = \delta Q + \delta W$$

$$\delta Q = dE + pdV$$

integrating factor 1/T

$$dS = \frac{1}{T}\delta Q$$

Batch system

$$dH = dU + d(pV)$$

Example 1,2,3,…
Homework 1,2,3,…
Quiz 1,2,3,…

Flow system

Example 1,2,3,…
Homework 1,2,3,…
Quiz 1,2,3,…

Postulate S

$$dS = \left(\frac{\partial S}{\partial E}\right)_{\underline{X}} dE + \left(\frac{\partial S}{\partial E}\right)_{E} d\underline{X}$$

2nd law

Exergy

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

$$\frac{\partial S}{\partial E} \equiv \frac{1}{T}$$

Joule-Thompson expansion

Joule expansion

$$pV = nRT$$

Legendre transform

$$\frac{|Q_2|}{|Q_1|} = \frac{T_2'}{T_1'}$$

$$dH =$$

Thermodynamic temperature scale

$$\left(p + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

$$dA =$$

$$\Delta S = \Sigma \frac{Q_{rev}}{T}$$

$$Z = 1 + B\frac{n}{V} + \cdots$$

$$dG =$$

Thermodynamic Cycles

Equations of state

Continue from I

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

$$dH =$$

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

$$dA =$$

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

$$\overline{\theta}_i \equiv \left[\frac{\partial(n\underline{\theta})}{\partial n_i}\right]_{p,T,n_{i\neq j}}$$

$$-n\left(\frac{\partial\underline{\overline{\theta}}}{\partial T}\right)_{p,n_i} dT - n\left(\frac{\partial\underline{\overline{\theta}}}{\partial p}\right)_{T,n_i} dp + \sum_{i}^{r} n_i d\overline{\theta}_i = 0 \quad \ldots$$

$$\overline{p}_i \equiv \left[\frac{\partial(np)}{\partial n_i}\right]_{p,T,n_j} = \left[p\frac{\partial(n)}{\partial n_i}\right]_{p,T,n_j} = p$$

$$p = \overline{p}_i = \Sigma y_i \overline{p}_i,$$
$$p = \Sigma p_i$$

Solution Thermodynamics

$$\Delta H, \Delta S, \Delta G =$$

Example
1,2,3,…
Homework
1,2,3,…
Quiz
1,2,3,…

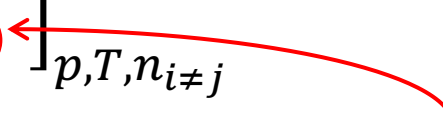Psychrometric appl. ω, φ

$$d\,G_i^{ig}\Big|_T =$$

Term paper

- Title: Thermodynamics knowledge tree
- Name and affiliation
- Abstract
- Introduction: background, what's new, layout
- Theory: work, heat and temperature, 1st and 2nd law, batch and fluid, …
- Diagram: key links
- Summary
- References

Recap Mixture/solution

- **From the definition of chemical potential,**

- **we introduced partial molar property**

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

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

$$\overline{\theta}_i = \left[\frac{\partial(n\underline{\theta})}{\partial n_i}\right]_{p,T,n_{i\neq j}}$$

times dn_i on both sides, therefore, has to be

$$d\theta = nd\,\underline{\theta}\Big|_{p,T} = \overline{\theta}_1 dn_1 + \overline{\theta}_2 dn_2 + \cdots,$$

$$n\,\underline{\theta}\Big|_{p,T} = \overline{\theta}_1 n_1 + \overline{\theta}_2 n_2 + \cdots.$$

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**

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

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 mixtrures

Fugacity and Fugacity Coefficient

- **For for pure species i, at constant T, in the ideal-gas state, the Gibbs' free energy, $dG = -SdT + Vdp$,**

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

- **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**

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

$$\rightarrow \Delta G_i$$

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

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

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

- **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,**

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

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

- **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 $y_i p$.**

- **And for same T and P**

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

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:**

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

Residual Property

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

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

- **Written for the residual Gibbs energy,**

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

- **and**

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

Residual Property

- **Using identity**

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

- **then**

$$\boxed{\overline{G}_i^R = RT \ln \hat{\phi}_i}$$

- **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,**

$$\overline{G}_i^{\,R} \;=\; \overline{G}_i \;-\; \overline{G}_i^{\,ig}$$

  is necessarily zero;

- **therefore**

$$\overline{G}_i^{\,R} \;=\; RT \,\ln \hat{\phi}_i \;=\; 0$$

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

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

The Ideal Solution

The Ideal Solution

- **Recall Gibbs energy of an ideal-gas mixture**

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

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

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

where *id* means ideal solution

The Ideal Solution

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

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

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

$$\overline{S}_i^{\,id} = S_i - R \ln x_i \qquad \boxed{\overline{G}_i^{\,id} = G_i + RT \ln x_i}$$

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

$$\overline{V}_i^{\,id} = V_i$$

The Ideal Solution

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

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

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

- **From definition of partial molar property**

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

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

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

- **so**
$$\mu_i = G_i + RT \ln(\hat{f}_i / f_i) \qquad \text{(2)} - \text{(1)}$$

- **fugacity of a species in an ideal solution, therefore,**
$$\mu_i^{id} \equiv \overline{G}_i^{id} = G_i + RT \ln\left(\hat{f}_i^{id} / f_i\right)$$

- **Also by definition,**
$$\overline{G}_i^{id} = G_i + RT \ln x_i$$

$$\phi_i \equiv f_i/p$$

$$\hat{\phi}_i \equiv \hat{f}_i/y_i p$$

- **Therefore the Lewis/Randall Rule**
$$\hat{f}_i^{id} = x_i f_i \qquad \text{or} \qquad \hat{\phi}_i^{id} = \phi_i$$

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

Ideal solution is ideal gas mixture which is ideal gas

Ideal solution   ← Ideal gas mixture

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

$$\underline{G}^{ig} = \underline{H}^{ig} - T\underline{S}^{ig},$$

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

$$\underline{S}^{id} = -\sum_i x_i \underline{S}_i - R\sum_i x_i \ln x_i$$

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

$$\underline{S}_i^{ig} - \sum_i y_i \overline{S}_i^{ig} = R\sum_i y_i \ln\frac{1}{y_i}$$

$$H = G + TS$$

$$\underline{H}^{id} = \sum_i x_i \underline{H}_i$$

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

Gibbs free energy connect them all

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**

$$M^{E} \equiv M - M^{id} \longrightarrow \overline{M}_i^{E} = \overline{M}_i - \overline{M}_i^{id}$$

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,**

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

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

The Excess Gibbs Energy and the Activity Coefficient

- **Since**

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

- **And**

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

- **Therefore**

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

- **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**

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

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

Activity and activity coefficient

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

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

- **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.**

Notice, we have activity coefficient then activity

Activity and activity coefficient

- **Thus, for an ideal gas mixture,**

$$\alpha_i^{ig} = \frac{p_i}{p^0} = y_i$$

- **for an nonideal gas mixture,**

$$\alpha_i = \frac{\hat{f}_i}{p^0}$$

- **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

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

$$0 - \left(x_1 \frac{d \ln \gamma_1^*}{dx_1} + x_2 \frac{d \ln \gamma_2^*}{dx_1} \right)$$

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

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

The Gibbs/Duhem equation

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**

Table 13.5: VLE Data for Diethyl Ketone(1)/*n*-Hexane(2) at 65°C

P/kPa	x_1	y_1	$\ln\gamma_1^*$	$\ln\gamma_2^*$	$\left(\dfrac{G^E}{x_1 x_2 RT}\right)^*$
90.15 (P_2^{sat})	0.000	0.000		0.000	
91.78	0.063	0.049	0.901	0.033	1.481
88.01	0.248	0.131	0.472	0.121	1.114
81.67	0.372	0.182	0.321	0.166	0.955
78.89	0.443	0.215	0.278	0.210	0.972
76.82	0.508	0.248	0.257	0.264	1.043
73.39	0.561	0.268	0.190	0.306	0.977
66.45	0.640	0.316	0.123	0.337	0.869
62.95	0.702	0.368	0.129	0.393	0.993
57.70	0.763	0.412	0.072	0.462	0.909
50.16	0.834	0.490	0.016	0.536	0.740
45.70	0.874	0.570	0.027	0.548	0.844
29.00 (P_1^{sat})	1.000	1.000	0.000		
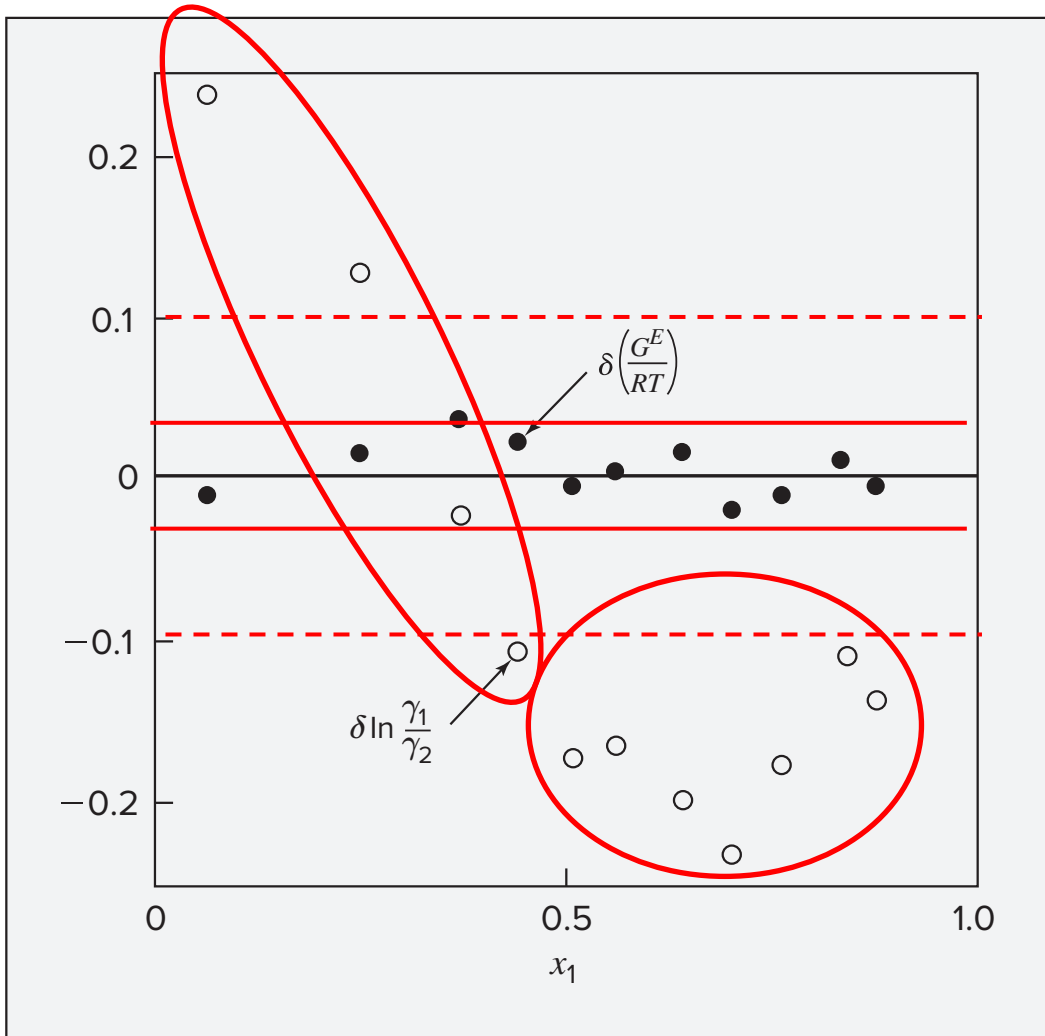
Figure 13.9: Consistency test of data for diethyl ketone(1)/n-hexane(2) at 65°C.

Not consistent with thermos (heavily concentrated on one side)

Models for the Excess Gibbs Energy

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Models for the Excess Gibbs Energy

- **G^E/RT is a function of T, P, and composition,**

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

- **Therefore,**

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

- **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.**

Models for the Excess Gibbs Energy

- **Thus,**

$$\frac{G^E}{RT} = g\left(x_1, x_2, \ldots, x_N\right)$$

- **For binary systems, the function most often represented by a power series in x_1**

$$\frac{G^E}{x_1 x_2 RT} = a + bx_1 + cx_1^2 + \cdots$$

Models for the Excess Gibbs Energy

- **Since $x_2 = 1 - x_1$, therefore,**

$$\frac{G^E}{x_1 x_2 RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots$$

- **This is know as the Redlich/Kister expansion which is the most commonly used polynomial in regular and subregular solution models**

Regular Solution

- **Recall**

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

$$\overline{\Delta G_i^{id}} = RT \ln x_i = \overline{\Delta H_i^{id}} + T\overline{\Delta S_i^{id}}$$

- **Let**

$$\overline{\Delta G_i^{RS}} = \overline{G_i^{RS}} - \overline{G_i^{id}}$$

- **Regular solution is an non ideal solution with small deviation from ideal solution**

- **Regular solution is defined as a solution possesses an enthalpy of mixing but no entropy of mixing.**

Regular Solution

- **That is**

$$\overline{\Delta G^{RS}} = \overline{\Delta H^{RS}} - T\overline{\Delta S^{RS}}$$

$$= \overline{\Delta H^{RS}} - T\overline{\Delta S^{id}}$$

- **Since**

$$\overline{\Delta G_i^{id}} = \overline{\Delta H_i^{id}} - T\overline{\Delta S_i^{id}}$$

- **Therefore,**

$$\overline{G_i^{RS}} - \overline{G_i^{id}} = \overline{H_i^{RS}} - \overline{H_i^{id}} = \overline{\Delta H_i^{RS}}$$

Enthalpy of Regular Solution

- **The word regular implies that the molecules mix in a completely random manner, which means that there is no segregation or preference.**

- **Consider two neighbors in a solution. The probability that one of the neighbors is A or B is simply**

$$P_A = \frac{N_A}{N_A + N_B} = x_A$$

$$P_B = \frac{N_B}{N_A + N_B} = x_B$$

Enthalpy of Regular Solution

- **Therefore the probability that a given ``bond" is A—B type is**

$$P_{(AB)} = P_{AB} + P_{BA} = \frac{2N_A N_B}{\left(N_A + N_B\right)^2} = 2x_A x_B$$

- **If each atom has z nearest neighbors, the number of bonds, total, is**

$$B^{total} = \frac{z}{2}\left(N_A + N_B\right), \quad \underline{B^{total}} = \frac{z}{2}$$

Enthalpy of Regular Solution

- **The bond density of A-B type is:**

$$B_{(AB)} = P_{(AB)}B^{total} = zx_Ax_B \qquad \textcolor{red}{\text{AB+BA}}$$

- **If the energy per bond is w$_{(AB)}$ then the enthalpy density (due to the A-B bonds) is:**

$$H^{RS}_{(AB)} = zw_{(AB)}x_Ax_B$$

- **Similarly**

$$H^{RS}_{(AA)} = \tfrac{z}{2}w_{(AA)}x_Ax_A, \qquad P_{(AA)} = x_A^2$$

$$H^{RS}_{(BB)} = \tfrac{z}{2}w_{(BB)}x_Bx_B$$

$$\underline{\Delta H_{mixing}} = \underline{H^{sol}} - \underline{H^{pure}}$$

$$\underline{H_{mix}} = zx_Ax_Bw_{AB} + \left(\frac{z}{2}x_Ax_Aw_{AA} + \frac{z}{2}x_Bx_Bw_{BB}\right)$$

$$\underline{H^{RS}_{(AB)}} = \frac{z}{2}x_Ax_B\left(2w_{AB} + \frac{x_A}{x_Ax_B}x_Aw_{AA} + \frac{x_B}{x_Ax_B}x_Bw_{BB}\right)$$

$$= \frac{z}{2}x_Ax_B\left(2w_{AB} + \frac{1-x_B}{x_Ax_B}x_Aw_{AA} + \frac{1-x_A}{x_Ax_B}x_Bw_{BB}\right)$$

$$\boxed{\underline{H^{id}} = \sum_i x_i\underline{H_i}} \quad = \frac{z}{2}x_Ax_B\left(2w_{AB} + \frac{-x_B}{x_Ax_B}x_Aw_{AA} + \frac{-x_A}{x_Ax_B}x_Bw_{BB} + \frac{x_Aw_{AA} + x_Bw_{BB}}{x_Ax_B}\right)$$

$$\underline{\Delta H^{RS}_{(AB)}} = \frac{z}{2}x_Ax_B(2w_{AB} - w_{AA} - w_{BB})$$

$$= \frac{z}{2}x_Ax_Bw^{RS}$$

Regular Solution

- **According to the definition of Regular solution, entropy of mixing equals to ideal solution**

- **Therefore,**

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

$$\underline{\Delta G_{(AB)}^{RS}} = \underline{\Delta H_{(AB)}^{RS}} - T\underline{\Delta S_{(AB)}^{id}}$$

$$= \frac{z}{2} x_A x_B w^{RS} - T(-R)(x_A \ln x_A + x_B \ln x_B)$$

$$\underline{G}^{E,RS} = \underline{G}^{RS} - \underline{G}^{id} = \Delta\underline{G}^{RS} - \Delta\underline{G}^{id} + \underline{G}^0 - \underline{G}^0$$

$$\underline{G}^{E,RS} = \frac{z}{2} x_A x_B w^{RS} \equiv \omega x_A x_B$$

$$\boxed{\underline{\underline{H^{RS}_{(AB)}}} = x_A \overline{H}^{RS}_A + x_B \overline{H}^{RS}_B} \longrightarrow \boxed{\frac{\partial \underline{\underline{H^{RS}_{(AB)}}}}{\partial x_B} = -\overline{H}^{RS}_A + \overline{H}^{RS}_B}$$

$$x_A \left(\frac{\partial \underline{\underline{H^{RS}_{(AB)}}}}{\partial x_B} \right) = -x_A \overline{H}^{RS}_A + x_A \overline{H}^{RS}_B$$

$$x_A \left(\frac{\partial \underline{\underline{H^{RS}_{(AB)}}}}{\partial x_B} \right) = -x_A \overline{H}^{RS}_A + \left(1 - x_B \right) \overline{H}^{RS}_B = \overline{H}^{RS}_B - \underbrace{x_A \overline{H}^{RS}_A - x_B \overline{H}^{RS}_B}_{\boxed{-\underline{H^{RS}_{(AB)}}}}$$

$$\underline{H^{RS}_{(AB)}} + x_A \left(\frac{\partial \underline{\underline{H^{RS}_{(AB)}}}}{\partial x_B} \right) = \vec{H}^{RS}_B$$

Regular Solution

$$\overline{H}_B^{E,RS} = \underline{H_{(AB)}^{RS}} + x_A \left(\frac{\underline{\partial H_{(AB)}^{RS}}}{\partial x_B} \right)$$

$$= \omega x_A x_B + x_A \left(\frac{\partial(\omega x_A x_B)}{\partial x_B} \right)$$

$$= \omega x_A x_B + x_A \omega (x_A - x_B)$$

$$= \omega x_A^2$$

Regular Solution

- **Since** $\overline{G}_i^{E,RS} = \overline{G}_i^E = RT \ln \gamma_i$

- **Therefore,**

$$\frac{\overline{G}_A^{E,RS}}{RT} = \ln \gamma_A = \frac{\omega}{RT} x_B^2$$

$$\frac{\overline{G}_B^{E,RS}}{RT} = \ln \gamma_B = \frac{\omega}{RT} x_A^2$$

symmetric

Otto Redlich AND A. T. Kister Expansion

- **Recall**

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

- **For binary system,**

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$\frac{d\left(\dfrac{G^E}{RT}\right)}{dx_1} = \ln\left(\frac{\gamma_1}{\gamma_2}\right)$$

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

$$(1-x_1)\frac{d\left(\frac{G^E}{RT}\right)}{dx_1} = (1-x_1)(\ln\gamma_1 - \ln\gamma_2)$$

$$= (1-x_1)\ln\gamma_1 - (1-x_1)\ln\gamma_2$$

$$= \ln\gamma_1 - x_1\ln\gamma_1 - x_2\ln\gamma_2$$

$$= \ln\gamma_1 - \frac{G^E}{RT}$$

$$\frac{G^E}{RT} = x_1\ln\gamma_1 + x_2\ln\gamma_2$$

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

$$(1 - x_2)\frac{d\left(\frac{G^E}{RT}\right)}{dx_1} = (1 - x_2)(\ln \gamma_1 - \ln \gamma_2)$$

$$= x_1 \ln \gamma_1 - (1 - x_2) \ln \gamma_2$$

$$= x_1 \ln \gamma_1 + x_2 \ln \gamma_2 - \ln \gamma_2$$

$$= -\ln \gamma_2 + \frac{G^E}{RT}$$

$$\boxed{\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2}$$

- **Therefore,**

$$\ln \gamma_1 = \left(\frac{G^E}{RT}\right) + \left(1 - x_1\right)\frac{d\left(\dfrac{G^E}{RT}\right)}{dx_1}$$

$$\ln \gamma_2 = \left(\frac{G^E}{RT}\right) - x_1 \frac{d\left(\dfrac{G^E}{RT}\right)}{dx_1}$$

- **Let** $Q = \dfrac{G^E}{RT}$

Otto Redlich AND A. T. Kister Expansion

- **Since $Q = 0$ for $x = 0$ and $x_1 = 1$, each term must contain the factor $x_1(1 - x_1)$.**

- **Introduce the expansion,**

$$\frac{G^E}{RT} = Q = x_1(1 - x_1)\left(B + C(2x_1 - 1) + D(2x_1 - 1)^2 + \cdots\right)$$

- **The coefficients may be determined by**

$$\frac{Q}{x_1(1 - x_1)} = \frac{\ln \gamma_1}{1 - x_1} + \frac{\ln \gamma_2}{x_1}$$

- **This is know as the Redlich/Kister expansion**

Otto Redlich AND A. T. Kister Expansion

- **Or** $\ln\left(\dfrac{\gamma_1}{\gamma_2}\right) = \dfrac{dQ}{dx_1} = B\left(1 - 2x_1\right) + C\left(6x_1\left(1 - x_1\right) - 1\right) + \cdots$

- **Case 1, ideal solution**

$$\ln\left(\frac{\gamma_1}{\gamma_2}\right) = 0$$

- **Case 2, B ≠ 0, C,D,…=0, a form of regular**

- **Case 3, B ≠ 0, C ≠ 0, D,E,…=0, subregular**

- **…**

Excess Gibbs Free Energy and Gibbs-Duhem Equation

If $\underline{G}^{ex}(T,P,\underline{x}) = ax_1x_2$ **then** $\overline{G}_1^{ex} = ax_2^2 = RT \ln \gamma_1$ **,** $\overline{G}_2^{ex} = ax_1^2 = RT \ln \gamma_2$

$$\frac{\partial\left(n\underline{G}^{ex}\right)}{\partial n_1} = \frac{an_1n_2}{n} = \frac{\partial\left(\frac{an_1n_2}{n}\right)}{\partial n_1}$$

$$= a\frac{n}{n^2}\frac{\partial(n_1n_2)}{\partial n_1} - a\frac{1}{n^2}(n_1n_2)$$

$$= \frac{a}{n}n_2\frac{\partial(n_1)}{\partial n_1} + \frac{a}{n}n_1\frac{\partial(n_2)}{\partial n_1} - a\frac{1}{n^2}(n_1n_2)$$

$$= \frac{a}{n}n_2 + \frac{a}{n}n_1\frac{\partial(n-n_1)}{\partial n_1} - a\frac{1}{n^2}(n_1n_2)$$

$$= \frac{a}{n}n_2 - a\frac{1}{n^2}(n_1n_2) = a(x_2 - x_2 + x_2^2) = ax_2^2$$

Excess Gibbs Free Energy and Gibbs-Duhem Equation

$$\underline{G}^{ex}(T,P,\underline{x}) = ax_1x_2 \qquad \overline{G}_1^{ex} = ax_2^2 = RT\ln\gamma_1 \qquad \overline{G}_2^{ex} = ax_1^2 = RT\ln\gamma_2$$

$$\sum_{i=1}^{C} x_i d\overline{G}_i^{ex}\Big|_{T,P} = x_1 d\overline{G}_1^{ex} + x_2 d\overline{G}_2^{ex} = x_1 d\left(ax_2^2\right) + x_2 d\left(ax_1^2\right)$$

$$= 2ax_1x_2\left(dx_2 + dx_1\right) = 2ax_1x_2 d(x_1 + x_2) = 0$$

$$x_1\left(\frac{\partial\ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\ln\gamma_2}{\partial x_1}\right)_{T,P} = x_1\frac{a}{RT}\left[\frac{\partial(1-x_1)^2}{\partial x_1}\right]_{T,P} + x_2\frac{a}{RT}\left[\frac{\partial(1-x_2)^2}{\partial x_1}\right]_{T,P}$$

$$= -\frac{2ax_1}{RT}(1-x_1) + x_2\frac{a}{RT}\left[\frac{\partial x_1^2}{\partial x_1}\right] = -\frac{2ax_1x_2}{RT} + \frac{2ax_1x_2}{RT} = 0$$

All activity coefficients derived from an excess Gibbs free energy expression that satisfies boundary conditions of being zero at $x_1 = 0$ and 1 will satisfy the Gibbs-Duhem equation.

at $x_1 = 0$ and $x_1 = 1$ $\quad \underline{G}^{ex} = 0 \quad$ then the activity coefficients satisfy $\quad 0 = \sum_{i=1}^{C} x_i d\ln\gamma_i\Big|_{T,P}$

Infinite dilution

- As a solution becomes pure in species *i*, both properties approach pure species property

$$\lim_{x_i \to 1} \theta = \lim_{x_i \to 1} \overline{\theta}_i = \theta_i$$

- In the limit of infinite dilution

$$\lim_{x_i \to 0} \overline{\theta}_i = \overline{\theta}_i^{\infty}$$

- For a binary solution

$$\theta = x_1 \bar{\theta}_1 + x_2 \bar{\theta}_2$$

$$d\theta = x_1 d\bar{\theta}_1 + \bar{\theta}_1 dx_1 + x_2 d\bar{\theta}_2 + \bar{\theta}_2 dx_2$$

- Gibbs-Duhem equation is

$$x_1 d\bar{\theta}_1 + x_2 d\bar{\theta}_2 = 0$$

- Dividing by dx_1, we have the Gibbs-Duhem equation in derivative forms

$$x_1 \frac{d\bar{\theta}_1}{dx_1} + x_2 \frac{d\bar{\theta}_2}{dx_1} = 0$$

- Since $x_1 + x_2 = 1,\quad dx_1 = -dx_2$

- therefore $\dfrac{d\theta}{dx_1} = \overline{\theta}_1 - \overline{\theta}_2$,

$$d\underline{\theta} = \overline{\theta}_1 dx_1 + \overline{\theta}_2 dx_2$$

$$\frac{d\underline{\theta}}{dx_1} = \overline{\theta}_1 + \overline{\theta}_2 \frac{dx_2}{dx_1}$$

$$\underline{\theta} = \overline{\theta}_1 - x_2(\overline{\theta}_1 - \overline{\theta}_2) = \overline{\theta}_1 - x_2 \frac{d\theta}{dx_1}$$

$$\underline{\theta} = \overline{\theta}_2 + x_1(\overline{\theta}_1 - \overline{\theta}_2) = \overline{\theta}_2 + x_1 \frac{d\theta}{dx_1}$$

$$\underline{\theta} = x_1\overline{\theta}_1 + x_2\overline{\theta}_2$$

$$\underline{\theta} = (1 - x_2)\overline{\theta}_1 + x_2\overline{\theta}_2$$

$$\underline{\theta} = x_1\overline{\theta}_1 + (1 - x_1)\overline{\theta}_2$$

- Therefore,

$$\overline{\theta}_1 = \theta + x_2 \frac{d\theta}{dx_1}$$

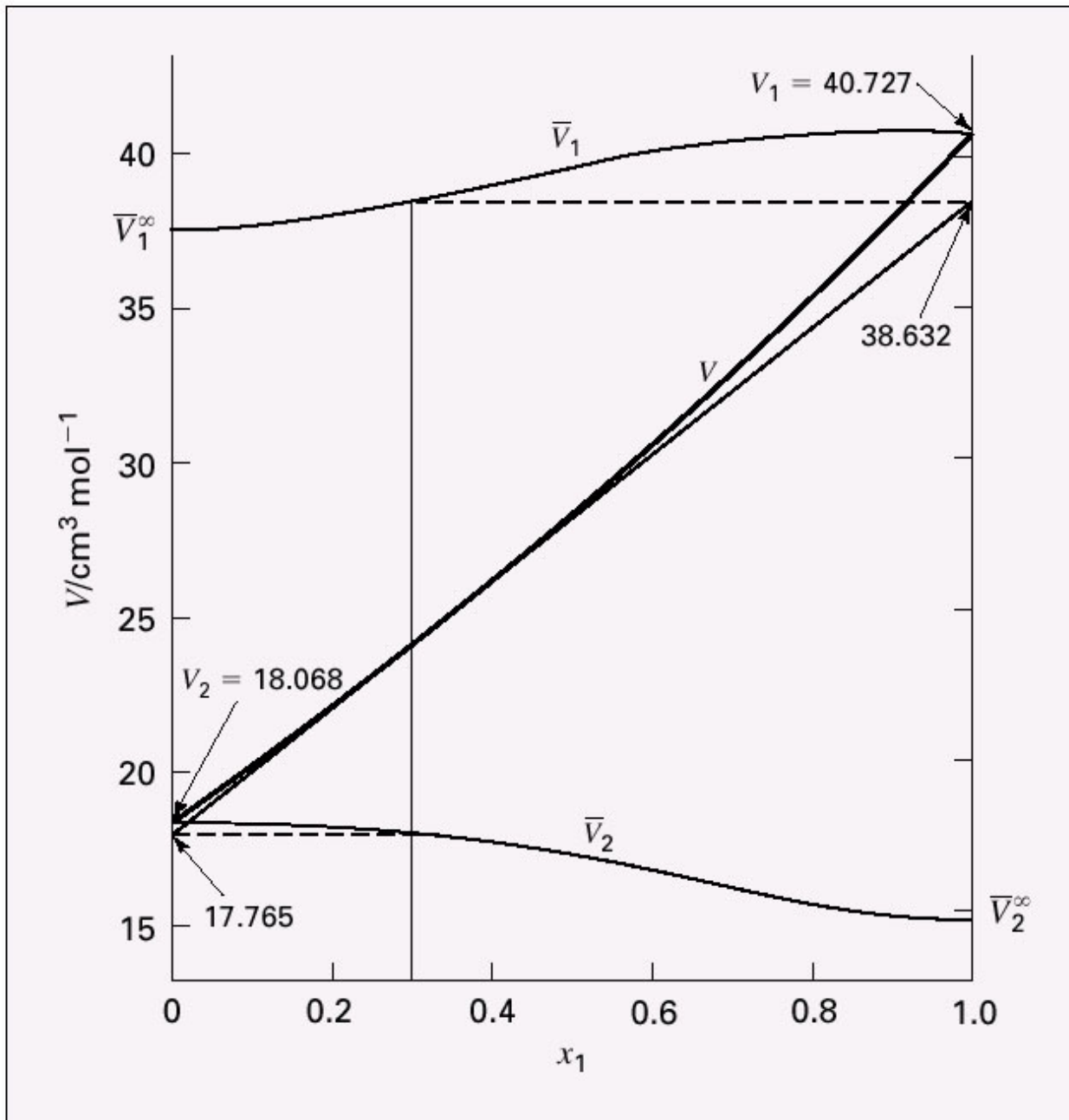$$\overline{\theta}_2 = \theta - x_1 \frac{d\theta}{dx_1}$$

- These equations <mark>can be used</mark> to obtain partial molar properties from experiment solution property.

$$\overline{\theta}_1 = \theta + x_2 \frac{d\theta}{dx_1} \qquad \overline{\theta}_2 = \theta - x_1 \frac{d\theta}{dx_1}$$
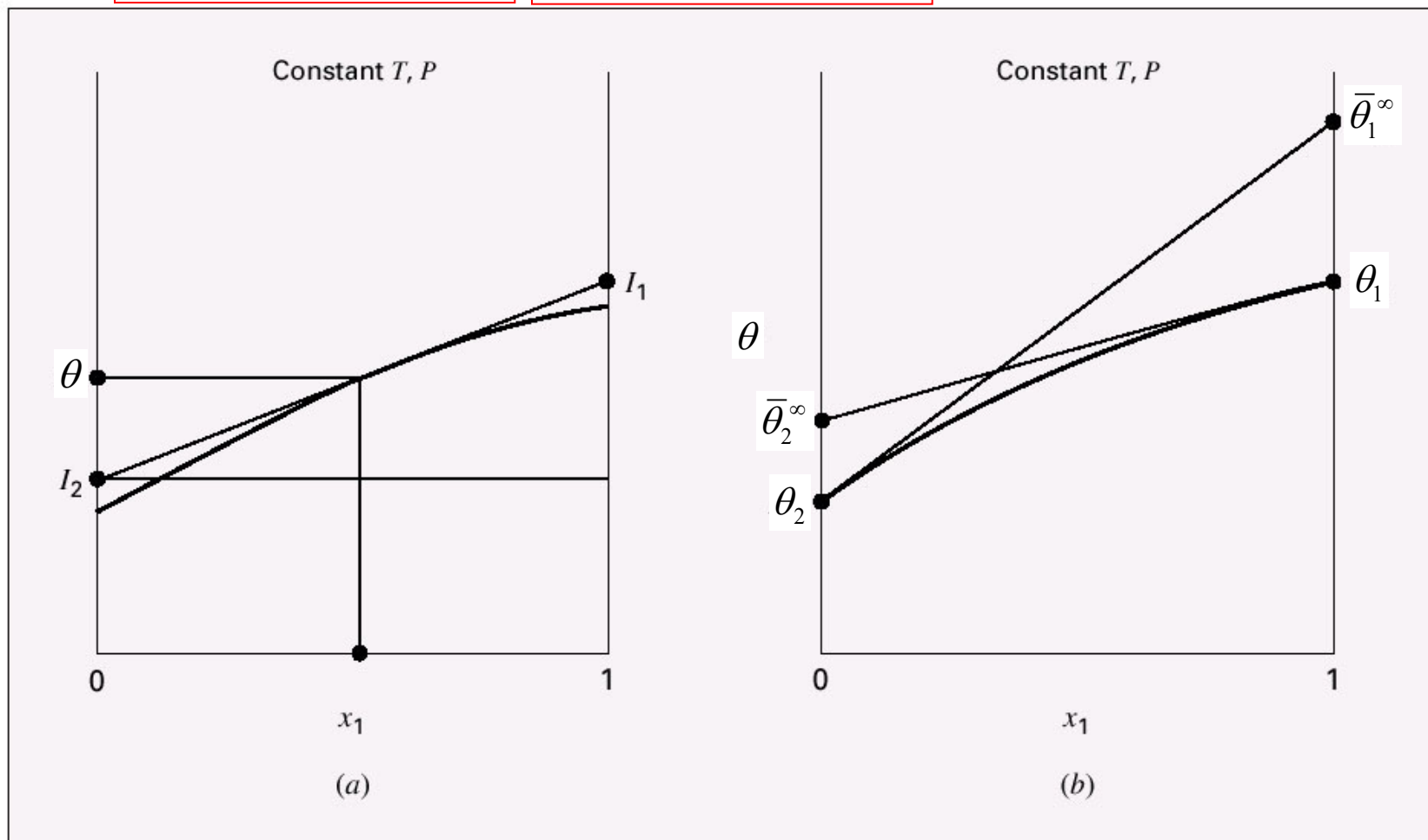
Figure 11.1: (*a*) Graphical construction of Example 11.2. (*b*) Infinite-dilution values of partial properties.

$$\overline{V}_1 = V + x_2 \frac{dV}{dx_1}$$

$$\overline{V}_2 = V - x_1 \frac{dV}{dx_1}$$

Figure 11.2: Molar volumes for methanol(1)/water(2) at 25°C and 1(atm). Numerical values relate to Ex. 11.3.

$$\lim_{x_i \to 1} V = \lim_{x_i \to 1} \overline{V}_i = V_i$$

$$\lim_{x_i \to 0} \overline{V}_i = \overline{V}_i^{\infty}$$

Example

$$H = 400x_1 + 600x_2 + x_1x_2\left(40x_1 + 20x_2\right)$$

$$x_2 = 1 - x_1$$

$$H = 600 - 180x_1 - 20x_1^3$$

$$\frac{dH}{dx_1} = -180 - 60x_1^2$$

$$\overline{H}_1 = H + x_2\frac{dH}{dx_1} \qquad \overline{H}_2 = H - x_1\frac{dH}{dx_1}$$

$$\overline{H}_1 = 420 - 60\,x_1^2 + 40\,x_1^3 \qquad \overline{H}_2 = 600 + 40\,x_1^3$$

$$\overline{H}_1^{\infty} = 420 \qquad \overline{H}_2^{\infty} = 640$$

Activity Coefficient Model

$$ln\,\gamma_i = \overline{G_i^{ex}} \,/\, RT \qquad \underline{G}^{ex} \,/\, RT = \sum_i x_i\,ln\,\gamma_i$$

- **Random mixing assumption (Wohl's expansion):**

$$\frac{\underline{G}^{ex}}{RT\sum_i q_i x_i} = \sum_i \sum_j a_{ij} z_i z_j + \sum_i \sum_j \sum_k a_{ijk} z_i z_j z_k + \dots..$$

  - **Redlich-Kister model**
  - **Margules model**
  - **van Laar model**

Margules' Equations

•**While the simplest Redlich/Kister-type correlation is the Symmetric Equation, but a <mark>more accurate</mark> equation is the Margules correlation:**

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2$$

•**let,**

$$\ln \gamma_1^\infty = \lim_{x_1 \to 0} \frac{G^E}{RTx_1x_2} \qquad \left.\frac{G^E}{RTx_1x_2}\right|_{x_1 \to 0} = A_{12} \qquad x_1 \to 0, x_2 \to 1$$

•**so that**

$$A_{12} = \ln \gamma_1^\infty$$
$$A_{21} = \ln \gamma_2^\infty$$

Margules' Equations

•If you have Margules parameters, the activity coefficients can be derived from the excess Gibbs energy expression:

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2$$

•to yield:

$$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$$

$$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$$

•These <mark>empirical equations</mark> are widely used to describe binary solutions. A knowledge of A_{12} and A_{21} at the given T is all we require to calculate activity coefficients for a given solution composition.

Van Laar Correlation

- **Another two-parameter excess Gibbs energy model was developed from an expansion of (RTx$_1$x$_2$)/G^E instead of G^E/RTx$_1$x$_2$. The end results are:**

$$\frac{G^E}{RTx_1x_2} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2}$$

- **for the excess Gibbs energy and:**

$$\ln\gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2} \qquad \ln\gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}$$

- **for the activity coefficients.**

- **as** $x_1 \rightarrow 0$, $\ln\gamma_1^\infty = A'_{12}$ **as** $x_2 \rightarrow 0$, $\ln\gamma_2^\infty = A'_{21}$