# EG3029 Chemical Thermodynamics

## Solution Thermodynamics

# Fundamental Property Relation

- Total Gibbs energy for closed system

$$d(nG) = (nV)dP - (nS)dT$$

- General case of a single-phase, open system

$$d(nG) = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

- Chemical potential of species *i*

$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}$$

# Fundamental Property Relation

- Fundamental property relation for single-phase fluid systems of variable mass and composition:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

- For one mole of solution:

$$V = \left( \frac{\partial G}{\partial P} \right)_{T,x}$$

$$S = -\left( \frac{\partial G}{\partial T} \right)_{P,x}$$

- Enthalpy

$$H = G + TS = G - T\left( \frac{\partial G}{\partial T} \right)_{P,x}$$

# Chemical Potential and Phase Equilibria

- Closed system of two phases ($\alpha$ and $\beta$) in equilibrium:

$$d(nG)^\alpha = (nV)^\alpha dP - (nS)^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$

$$d(nG)^\beta = (nV)^\beta dP - (nS)^\beta dT + \sum_i \mu_i^\beta dn_i^\beta$$

- For system exhibiting $\pi$ phases and $N$ species:

$$\mu_i^\alpha = \mu_i^\beta = \cdots = \mu_i^\pi \qquad i = 1, 2, \cdots, N$$

***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 Properties

- General partial molar property:

$$\overline{M}_i = \left[ \frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j}$$

It is a response function i.e. a measure of the response of the total property *nM* to the addition at constant *T* and *P* of a differential amount of species *i* to a finite amount of solution.

# Partial Properties
## Equations Relating Molar and Partial Molar Properties

- For the total property *M*:

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

$$nM = \sum_i n_i \overline{M}_i$$

- General expression for *dM*:

$$dM = \sum_i x_i d\overline{M}_i + \sum_i \overline{M}_i dx_i$$

- Gibbs/Duhem equation

$$\left( \frac{\partial M}{\partial P} \right)_{T,x} dP + \left( \frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i x_i d\overline{M}_i = 0$$

and at constant *T* and *P*:

$$\sum_i x_i d\overline{M}_i = 0$$

# Partial Properties
## Partial Properties in Binary Solutions

- Partial properties are readily calculated directly from an expression for the solution property as a function of composition at constant *T* and *P*:

$$\overline{M}_1 = M + x_2 \frac{dM}{dx_1}$$

$$\overline{M}_2 = M - x_1 \frac{dM}{dx_1}$$

- In derivative forms:

$$x_1 \frac{d\overline{M}_1}{dx_1} + x_2 \frac{d\overline{M}_2}{dx_1} = 0$$

$$\frac{d\overline{M}_1}{dx_1} = \frac{x_2}{x_1} \frac{d\overline{M}_2}{dx_1}$$

# Ideal-Gas Mixture Model

- ## Useful model because it
  - Has a molecular basis
  - Approximates reality in well-defined limit of zero pressure
  - Is analytically simple

- ## Partial pressure:

$$p_i = \frac{y_i RT}{V^{ig}} = y_i P \qquad (i = 1, 2, \ldots, N)$$

- ## Gibbs's theorem:
  ***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***

# Ideal-Gas Mixture Model

- Properties of ideal-gas mixtures

$$H^{ig} = \sum_i y_i H_i^{ig}$$

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

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

- Ideal gas at constant T:

$$dG_i^{ig} = V_i^{ig} dP = \frac{RT}{P} dP = RT \, d \ln P$$

  and after integration:

$$\mu_i^{ig} = \overline{G}_i^{ig} = \Gamma_i(T) + RT \, d \ln(y_i P)$$

$$G^{ig} = \sum_i y_i \Gamma_i(T) + RT \sum_i y_i \ln(y_i P)$$

# Fugacity and Fugacity Coefficient
# Pure Species

- Chemical potential $\mu$ provides fundamental criterion for phase equilibria (also for reaction equilibria), but the determination of its absolute value is not possible

- Fugacity $f$

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

$$f_i^{ig} = P$$

$$G_i - G_i^{ig} = G_i^R = RT \ln \frac{f_i}{P} = RT \ln \phi_i$$

$$\phi_i = \frac{f_i}{P}$$

**Residual Gibbs energy**                **Fugacity coefficient**

# Fugacity and Fugacity Coefficient
# VLE of Pure Species

- Saturated vapour and saturated liquid in equilibrium:

$$G_i^v = \Gamma_i(T) + RT \ln f_i^v$$

$$G_i^l = \Gamma_i(T) + RT \ln f_i^l$$

$$f_i^v = f_i^l = f_i^{sat}$$

***For a pure species coexisting liquid and vapour phases are in equilibrium when they have the same temperature, pressure and fugacity.***

- Fugacity of pure liquid

$$f_i^l(P) = \frac{f_i^v(P_i^{sat})}{P_i^{sat}} \frac{f_i^l(P_i^{sat})}{f_i^v(P_i^{sat})} \frac{f_i^l(P)}{f_i^l(P_i^{sat})} P_i^{sat}$$

$$f_i = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l(P - P_i^{sat})}{RT}$$

**$V_i^l$ is assumed constant**

# Fugacity and Fugacity Coefficient Species in Solution

- For species *i* in a mixture of real gases or in a solution of liquids:

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

- Phases in equilibrium:

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} = \cdots = \hat{f}_i^{\pi} \qquad i = 1, 2, \cdots, N$$

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

- Fugacity coefficient for species in solution: $\hat{\phi}_i = \dfrac{\hat{f}_i}{y_i P}$

# Ideal-Solution Model

- A solution is ideal when:

$$\mu_i^{id} = \overline{G}_i^{id} = G_i(T, P) + RT \ln x_i$$

- Total values of properties:

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

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

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

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

- Lewis/Randall rule

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

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

$$\hat{f}_i^{id} = x_i f_i$$

**Applies to each species in an ideal solution at all conditions of *P, T,* and composition**

# Excess Properties

- If $M$ represents the molar (or unit-mass) value of any extensive thermodynamic property (e.g. V, U, H, S, G, ...), then an excess property $M^E$ is defined:

$$M^E = M - M^{id}$$

**$M$ actual value**
**$M^{id}$ value in ideal solution**

- Fundamental excess property relation

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \frac{\overline{G}_i^E}{RT}dn_i$$

# Excess Properties

| $M$ in Relation to $G$ | $M^R$ in Relation to $G^R$ | $M^E$ in Relation to $G^E$ |
|---|---|---|
| $V = (\partial G/\partial P)_{T,x}$   (11.4) | $V^R = (\partial G^R/\partial P)_{T,x}$ | $V^E = (\partial G^E/\partial P)_{T,x}$ |
| $S = -(\partial G/\partial T)_{P,x}$  (11.5) | $S^R = -(\partial G^R/\partial T)_{P,x}$ | $S^E = -(\partial G^E/\partial T)_{P,x}$ |
| $H = G + TS$ <br> $= G - T(\partial G/\partial T)_{P,x}$ <br> $= -RT^2\left[\dfrac{\partial(G/RT)}{\partial T}\right]_{P,x}$ | $H^R = G^R + TS^R$ <br> $= G^R - T(\partial G^R/\partial T)_{P,x}$ <br> $= -RT^2\left[\dfrac{\partial(G^R/RT)}{\partial T}\right]_{P,x}$ | $H^E = G^E + TS^E$ <br> $= G^E - T(\partial G^E/\partial T)_{P,x}$ <br> $= -RT^2\left[\dfrac{\partial(G^E/RT)}{\partial T}\right]_{P,x}$ |
| $C_P = (\partial H/\partial T)_{P,x}$ <br> $= -T(\partial^2 G/\partial T^2)_{P,x}$ | $C_P^R = (\partial H^R/\partial T)_{P,x}$ <br> $= -T(\partial^2 G^R/\partial T^2)_{P,x}$ | $C_P^E = (\partial H^E/\partial T)_{P,x}$ <br> $= -T(\partial^2 G^E/\partial T^2)_{P,x}$ |

# Excess Properties

- Relations with activity coefficient:

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

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

- Effects of pressure and temperature

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{\overline{V}_i^E}{RT}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,x} = -\frac{\overline{H}_i^E}{RT^2}$$

- Summability and Gibbs/Duhem equations

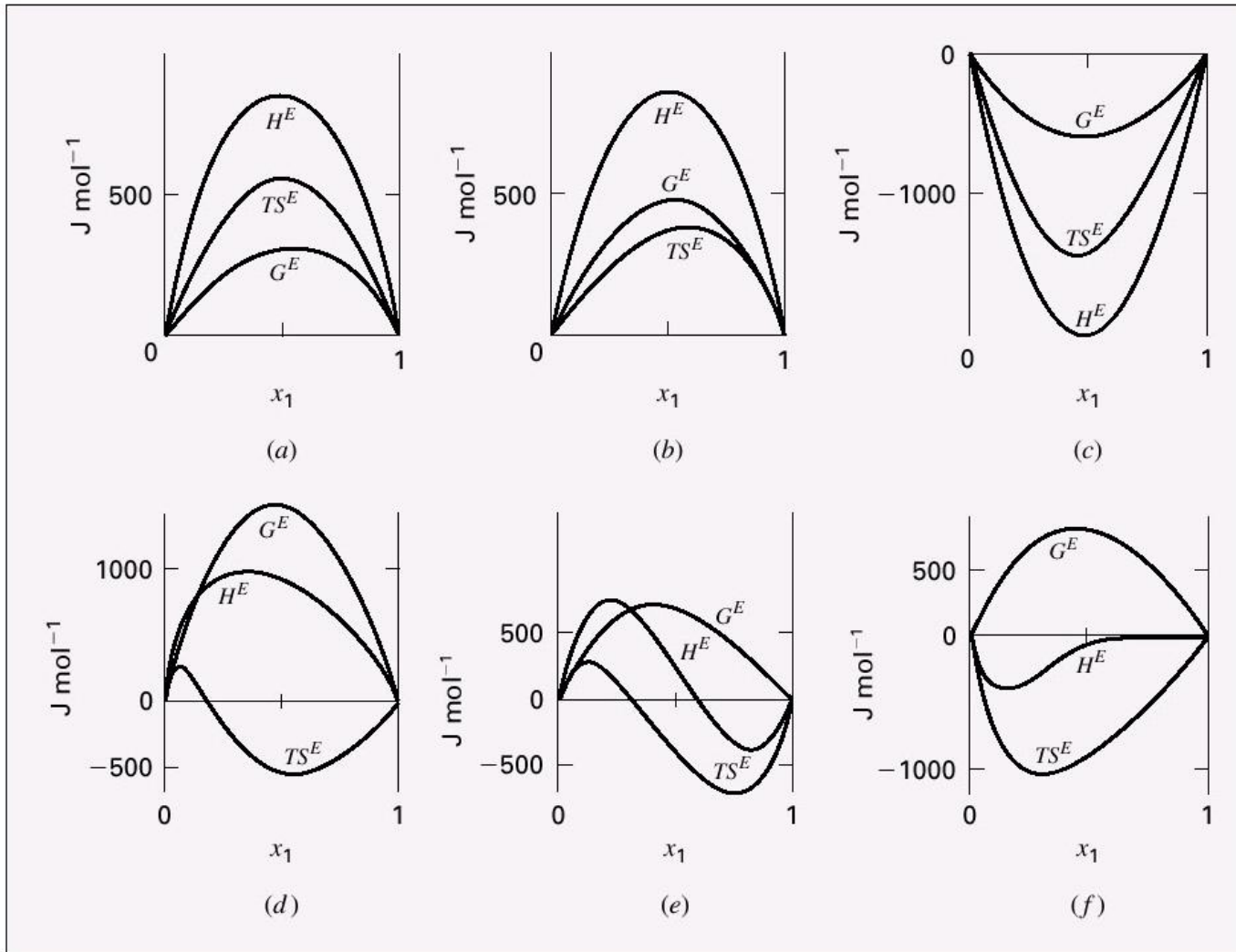$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

$$\sum_i x_i d \ln \gamma_i = 0$$

**const *T, P***

# Excess Properties

- Excess properties can be determined
  - $G^E$ from VLE data
  - $H^E$ from mixing experiments
  - $S^E$ from

$$S^E = \frac{H^E - G^E}{T}$$

- All excess properties become zero as either species approaches purity

# Excess Properties



**Figure 11.4:** Excess properties at 50°C for six binary liquid systems: (a) chloroform(1)/n-heptane(2); (b) acetone(1)/methanol(2); (c) acetone(1)/chloroform(2); (d) ethanol(1)/n-heptane(2); (e) ethanol(1)/chloroform(2); (f) ethanol(1)/water(2).
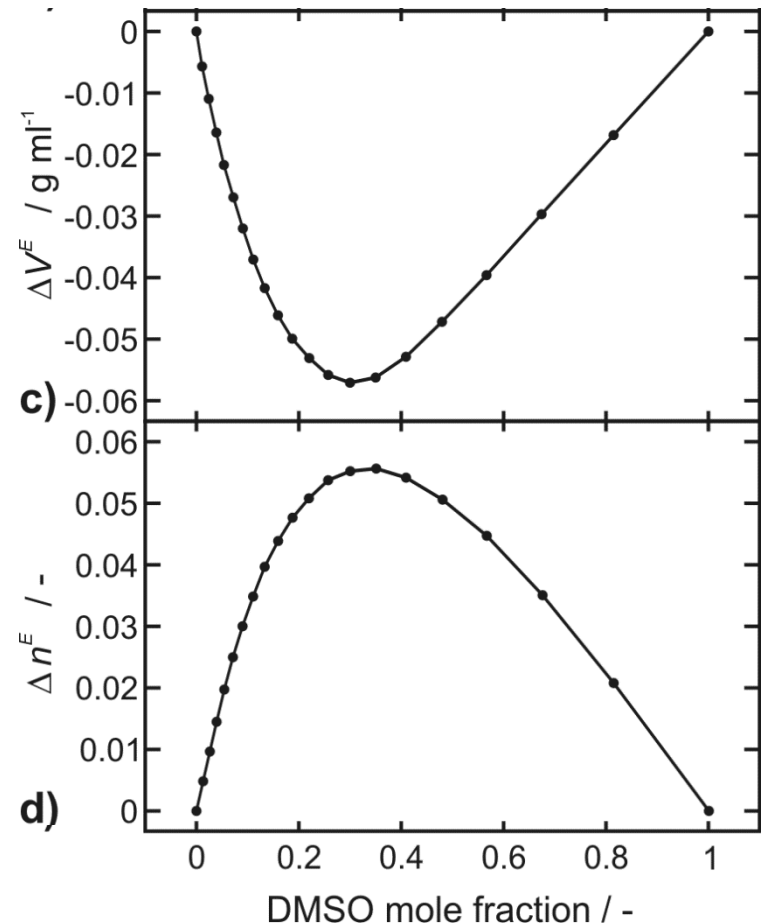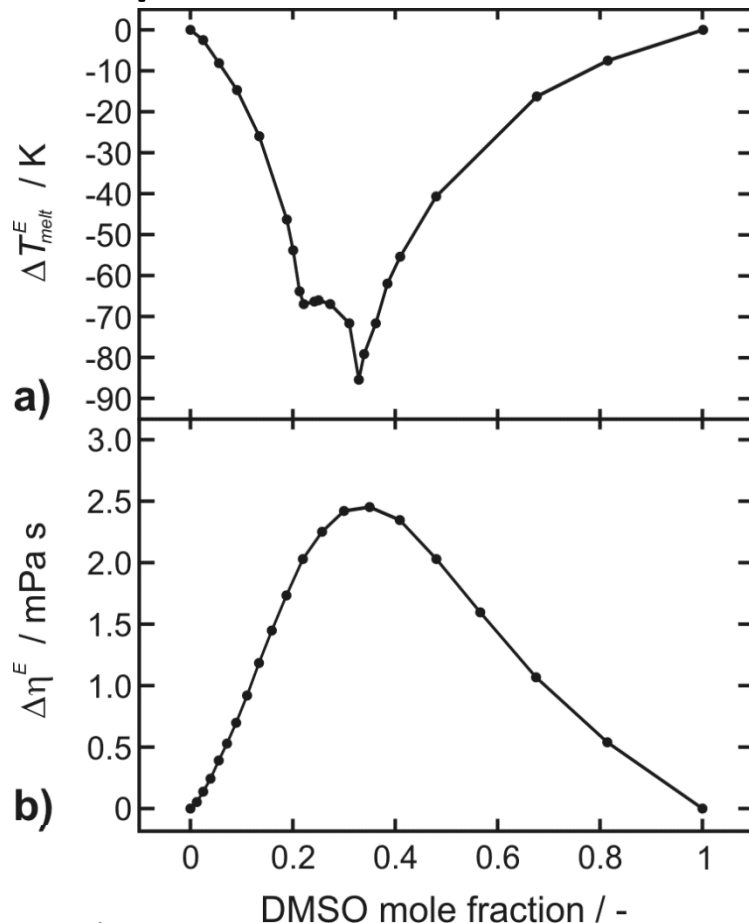
# Current Research: Dimethyl Sulphoxide

- DMSO:
  - Polyfunctional molecule
  - Properties:
    - Melting point: 18 degC
    - Density: 1.1 g/cm$^3$
    - Boiling point: 189 degC
    - Refractive index: 1.479
    - Viscosity: 1.996 cP
  - Applications:
    - Solvent
    - Antifreeze
    - ...
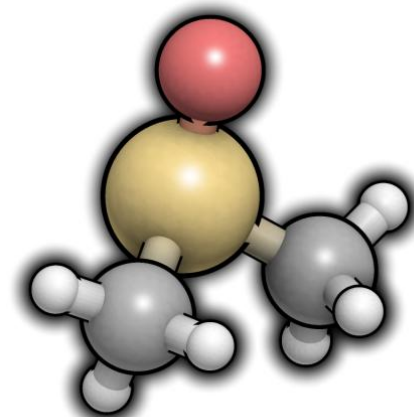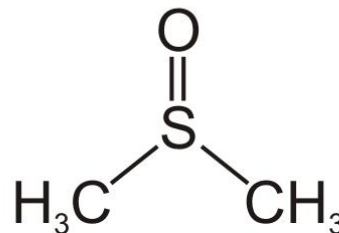


J. Kiefer, K. Noack, B. Kirchner
Hydrogen Bonding in Mixtures of Dimethyl Sulfoxide and Cosolvents
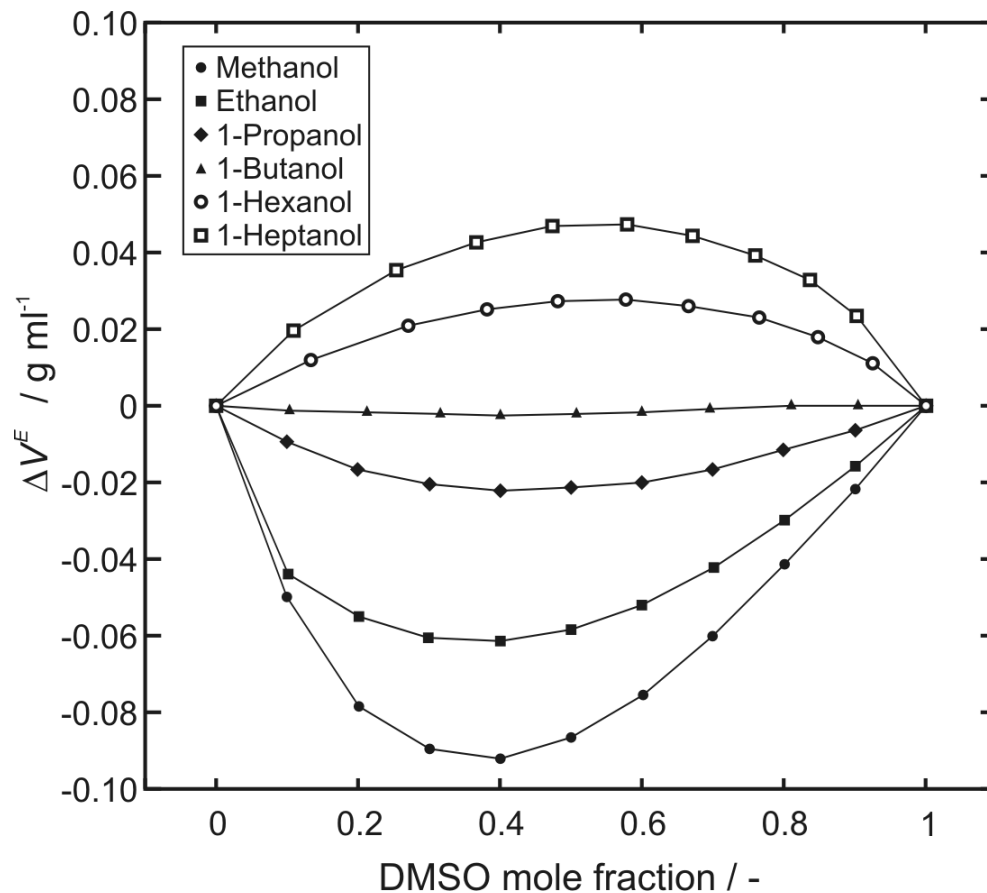*Current Physical Chemistry* **1** (2011) 340-351.

# Current Research: Dimethyl Sulphoxide
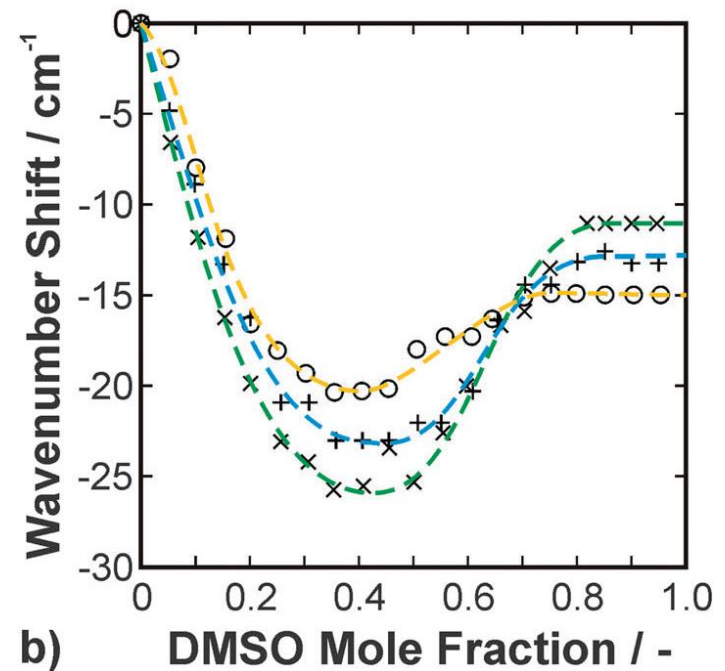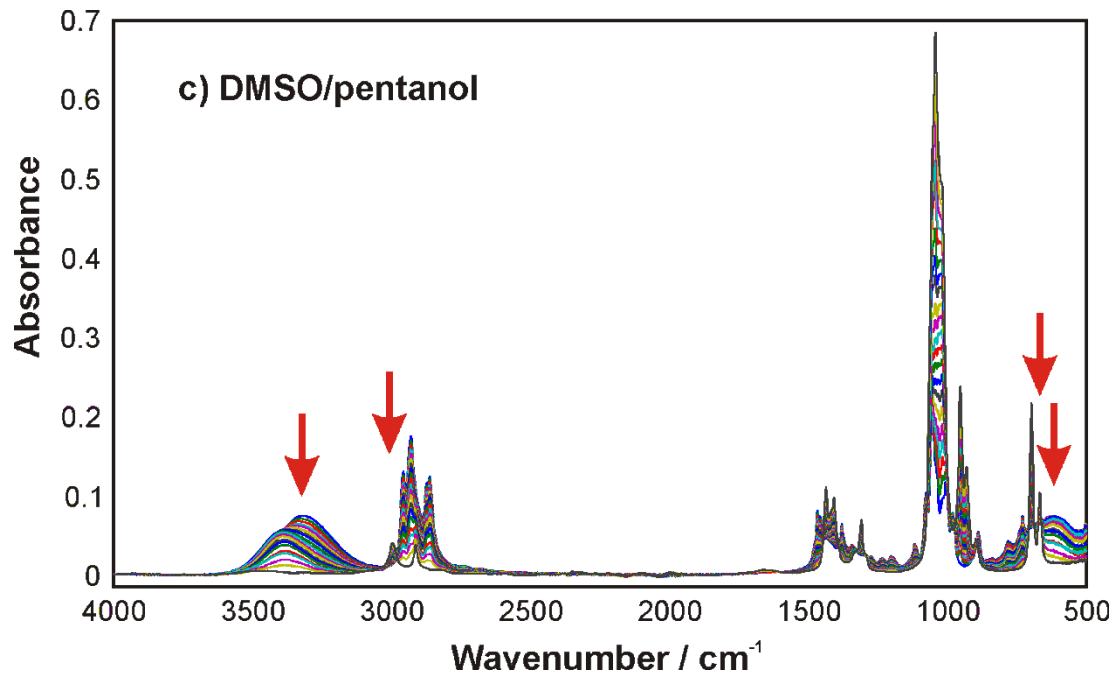
- Aqueous DMSO solutions

# Current Research: Dimethyl Sulphoxide

- Alcoholic DMSO solutions

# Current Research: Dimethyl Sulphoxide

- ## Alcoholic DMSO solutions



c) DMSO/pentanol



b)

# Property Changes of Mixing

- Excess properties approach zero for ideal solutions, but thermodynamic properties might still change upon mixing

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

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

$$\Delta V^{id} = 0$$

$$\Delta H^{id} = 0$$

- Worked example: mixing process for a binary solution

# Activity Models

- Alternative to equations of state
- Typically more accurate when strong intermolecular interactions are present
- Commonly used:
  - Margules equations
  - Van Laar equations
  - Wilson equations
  - Non-Random-Two-Liquids (NRTL)
  - UNIversal QUAsi Chemical (UNIQUAC)

# Activity Models

- ## Basic equations:

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

$$\frac{G^E}{RT} = f(\gamma_i) \quad with \quad \gamma_i = f(x_j)$$

- ## 2 parameter models:

  - Margules equations for binary systems

$$\ln \gamma_1 = x_2^2 \cdot \left[ A_{12} + 2(A_{21} - A_{12})x_1 \right]$$
$$\ln \gamma_2 = x_1^2 \cdot \left[ A_{21} + 2(A_{12} - A_{21})x_2 \right]$$

  - Van Laar equations

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

# Activity Models

- ## 2 parameter models:
  - Wilson equations

$$\frac{G^E}{RT} = -x_1 \ln\left(x_1 + x_2\Lambda_{12}\right) - x_2 \ln\left(x_2 + x_1\Lambda_{21}\right)$$

$$\ln \gamma_1 = -\ln\left(x_1 + x_2\Lambda_{12}\right) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

$$\ln \gamma_2 = -\ln\left(x_2 + x_1\Lambda_{21}\right) + x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

# Activity Models

- ## 3 parameter models:
  - Non-Random-Two-Liquids (NRTL)

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}}$$

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{\left(x_2 + x_1 G_{12}\right)^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[ \tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{\left(x_1 + x_2 G_{21}\right)^2} \right]$$

- UNIversal QUAsi Chemical (UNIQUAC): greater complexity

# Worked example

A liquid binary mixture is in equilibrium with its vapour at 144°C. The liquid mole fraction of component 1 is $x_1$ = 0.6. In addition, the following information is given:

- $\ln \gamma_1 = Ax_2^2$ and $\ln \gamma_2 = Ax_1^2$
- at 144°C, the saturation pressures are $P_1{}^{sat}$ = 75.20 kPa and $P_2{}^{sat}$ = 31.66 kPa
- the system forms an azeotrope at 144°C for which $x_1{}^{az} = y_1{}^{az}$ = 0.294
- the modified Raoult's law is valid

a) Determine the equilibrium pressure of the system.

[9 marks]

b) Determine the composition of the vapour.

[2 marks]

c) Draw a schematic *P-xy* diagram showing the azeotropic behaviour. Indicate how the *P-x* relationship would look like for Raoult's law.

[6 marks]

d) Which is the main problem that is associated with azeotropic mixtures in technical processes? How can it be overcome (give one example)?

[3 marks]