

STATISTICAL MOLECULAR THERMODYNAMICS

Christopher J. Cramer

Video 10.8

Regular Solutions

PARTIAL PRESSURE IN NON-IDEAL SOLN'S

Recall that for an ideal solution:

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j$$

which we derived from Raoult's law applied to the more general:

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln \frac{P_j}{P_j^*}$$

which holds equally for a nonideal solution, except: $P_j \neq x_j P_j^*$

For nonideal solutions, partial pressure data are often fit by a more complex expression, namely:

$$P_1 = x_1 P_1^* \exp(\alpha x_2^2 + \beta x_2^3 + \dots)$$

ACTIVITY AND ACTIVITY COEFFICIENT

Ideal solution: $\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j$

Non-ideal solution: $\mu_j^{sol} = \mu_j^*(l) + RT \ln a_j$

$$a_1 \rightarrow 1 \text{ as } x_1 \rightarrow 1 \text{ (} x_2 \rightarrow 0 \text{)}$$

$$a_1 = x_1 e^{\alpha x_2^2 + \beta x_2^3 + \dots}$$

activity

$$a_j = \frac{P_j}{P_j^*}$$

$$a_j \neq x_j$$

(if non-ideal)

The *activity coefficient* is defined as (a measure of the deviation from ideality):

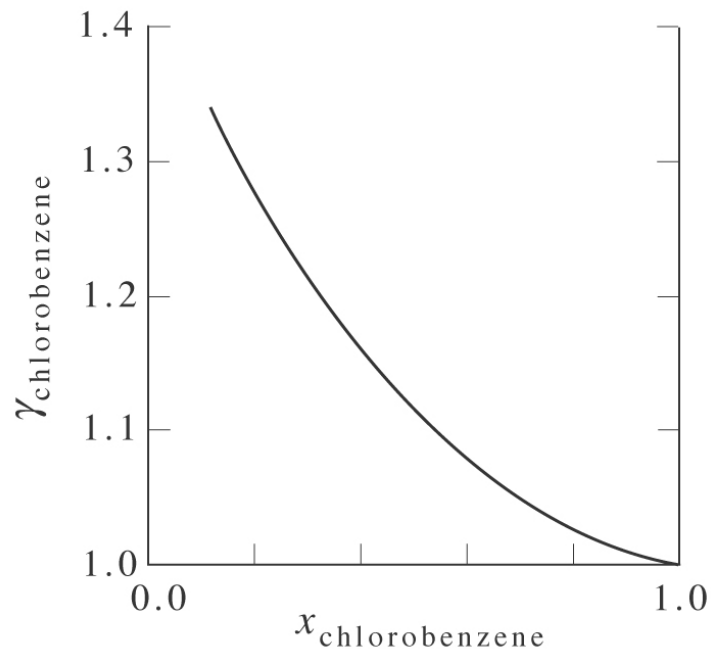
$$\gamma_j = \frac{a_j}{x_j}$$

The activity coefficient is unity at all concentrations for an ideal solution

NON-IDEAL SOLUTION EXAMPLE

Chlorobenzene + 1-nitropropane at 75 °C

$x_1 \longrightarrow$	0.119	0.289	0.460	0.691	1.00	$\nearrow P_j^* = 119 \text{ torr}$
P_1/torr	19.0	41.9	62.4	86.4	119	
a_1	0.160	0.352	0.524	0.726	1.00	$\longrightarrow a_j = \frac{P_j}{P_j^*}$
γ_1	1.34	1.22	1.14	1.05	1.00	$\searrow \gamma_j = \frac{a_j}{x_j}$



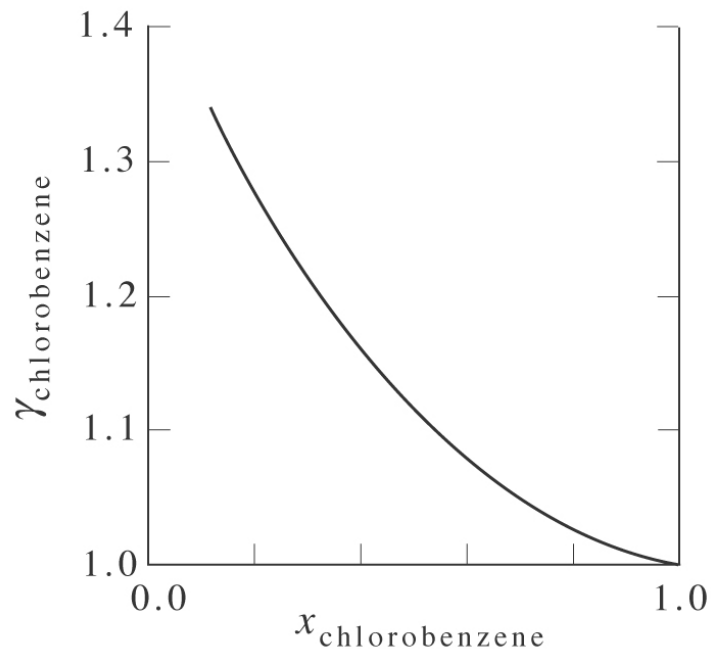
Self-assessment

Is this a positive or negative deviation from Raoult's Law (i.e., ideal behavior)?

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Self-assessment Explained

Since $a_1 > x_1$, then $a_1 P_1^* > x_1 P_1^*$, which is positive deviation from Raoult's Law behavior at non-unit activity

EXCESS FREE ENERGY OF MIXING

Recall that the Gibbs free energy of mixing of a 2-component solution is given by:

$$\Delta_{mix} G = n_1 \mu_1^{sol} + n_2 \mu_2^{sol} - n_1 \mu_1^* - n_2 \mu_2^*$$

For a non-ideal solution, we use activity instead of mole fraction, thus:

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln a_j$$

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j + RT \ln \gamma_j$$

$$\gamma_j = \frac{a_j}{x_j}$$

Inserting into equation above:

$$\frac{\Delta_{mix} G}{RT} = \underbrace{n_1 \ln x_1 + n_2 \ln x_2}_{\text{ideal}} + \underbrace{n_1 \ln \gamma_1 + n_2 \ln \gamma_2}_{\text{excess}}$$

REGULAR SOLUTION

$$G^E = \Delta_{\text{mix}} G - \Delta_{\text{mix}} G^{\text{id}}$$

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

molar value

Excess Gibbs free energy of mixing

A *regular solution* is one where the excess *entropy* of mixing is zero, but the excess *enthalpy* of mixing is *non-zero*. This implies an excess Gibbs free energy of mixing, which can be either negative or positive. Expressed more intuitively, the two molecules mix fully randomly, but their energies of interaction with one another are different.

$$\bar{S}^E = 0 \quad \bar{H}^E \neq 0 \quad \bar{G}^E \neq 0$$

$$dU = \delta q + \delta w$$



Next: Regular Solution Theory