MME 2010
METALLURGICAL THERMODYNAMICS II

Excess Properties

Activity coefficient is an auxillary function that relates compositions of the components in a real solution to their activities

$$a_i = \gamma_i x_i$$

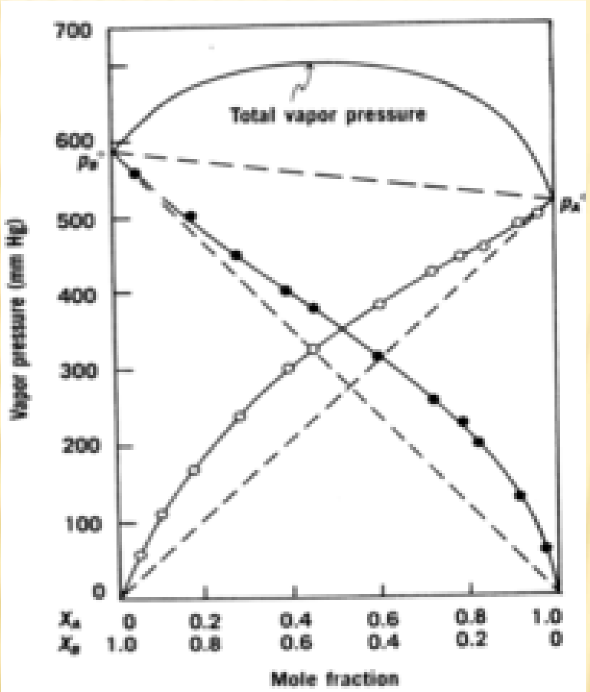
Relationships that are derived for ideal solutions based on the neutrality of the components of the model solution can be adjusted to real solutions by the activity coefficient

Activity coefficient indicates the deviation of components of a real solution from ideal behavior due to the interaction of molecules
A and B molecules attract eachother when their activities are less than their compositions and repel eachother when activities are greater

If $\gamma_A > 1$, solution positively deviates from Raoult's law due to repulsion between two kinds of molecules. Extensive properties of the solution such as volume, enthalpy, Gibbs free energy increase in this case as well as the partial volume, enthalpy and Gibbs free energies of the components

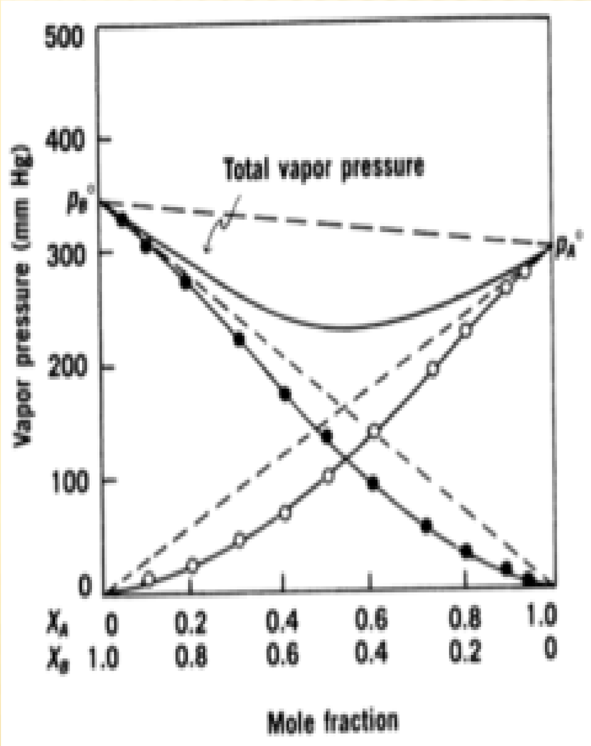
If $\gamma_B < 1$, solution negatively deviates from Raoult's law due to attraction between two kinds of molecules. Extensive properties of both the system and components decrease in this case

Positive deviation from ideality



$\gamma_i > 1$

Negative deviation from ideality



$\gamma_i < 1$

Ideal solution is a model for relating thermodynamic extensive properties to experimental PVT data such as temperature and concentration

$$G^{id} = \sum x_i G_i + RT \sum x_i \ln x_i \qquad \mu_A{}^{id} = G_A + RT \ln x_A$$

$$S^{id} = \sum x_i S_i - R \sum x_i \ln x_i \qquad S_A{}^{id} = S_A - R \ln x_A$$

$$H^{id} = \sum x_i H_i \qquad H_A{}^{id} = H_A$$

Treatment of real liquid solutions in the same way as ideal solutions enables complete determination of their thermodynamic properties and equations of state

For this reason excess properties are derived for measuring the deviations of liquid solutions from ideal solutions:

If M represents the molar value of an extensive thermodynamic property, then an excess property M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution

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

Representation of excess Gibbs free energy which is of most interest is as follows:

$$\boxed{G^E = G - G^{id}}$$

The same form of equation follows for partial properties of a solution

$$\boxed{\overline{G_i}^E = \overline{G_i} - \overline{G_i}^{id}}$$

The difference between the partial molar Gibbs free energy of a component and its free energy at pure state is

$$\overline{G_i} - G_i = RT \ln \frac{a_i}{a_i{}^o} = RT \ln a_i$$

Similarly for ideal solution:

$$\overline{G_i}^{id} - G_i = RT \ln \frac{x_i}{a_i{}^o} = RT \ln x_i$$

Taking the difference between the two equations gives the excess partial molar Gibbs free energy

$$\overline{G_i}^E = \overline{G_i} - \overline{G_i}^{id} = RT \ln \frac{a_i}{x_i}$$

$$\boxed{\frac{a_i}{x_i} = \gamma_i}$$

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

For an ideal solution $\overline{G}_i^{\,E} = 0$, so $\gamma_i = 1$

Since $\overline{G}_i^{\,E}$ is a partial property of the total excess Gibbs free energy of the solution, $\ln \gamma_i$ is also a partial property with respect to G^E/RT

$$\ln \gamma_i = \left[\frac{\partial (nG^E/RT)}{\partial n_i}\right]_{P,T,nj}$$

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

$$\sum x_i \, d \ln \gamma_i = 0$$ at constant T and P

The usefulness of these equations and the excess property concept in general is the ability to calculate the extensive properties V, H, S, G, U of any liquid solution by relating them to ideal solution

Excess properties can be as easily calculated as ideal solution properties provided that activity coefficients are known in addition to concentration

Excess properties are functions of temperature and solution composition

γ_i values are experimentally accessible through vapor/liquid equilibrium data and mixing experiments through which G^E and H^E are obtained respectively

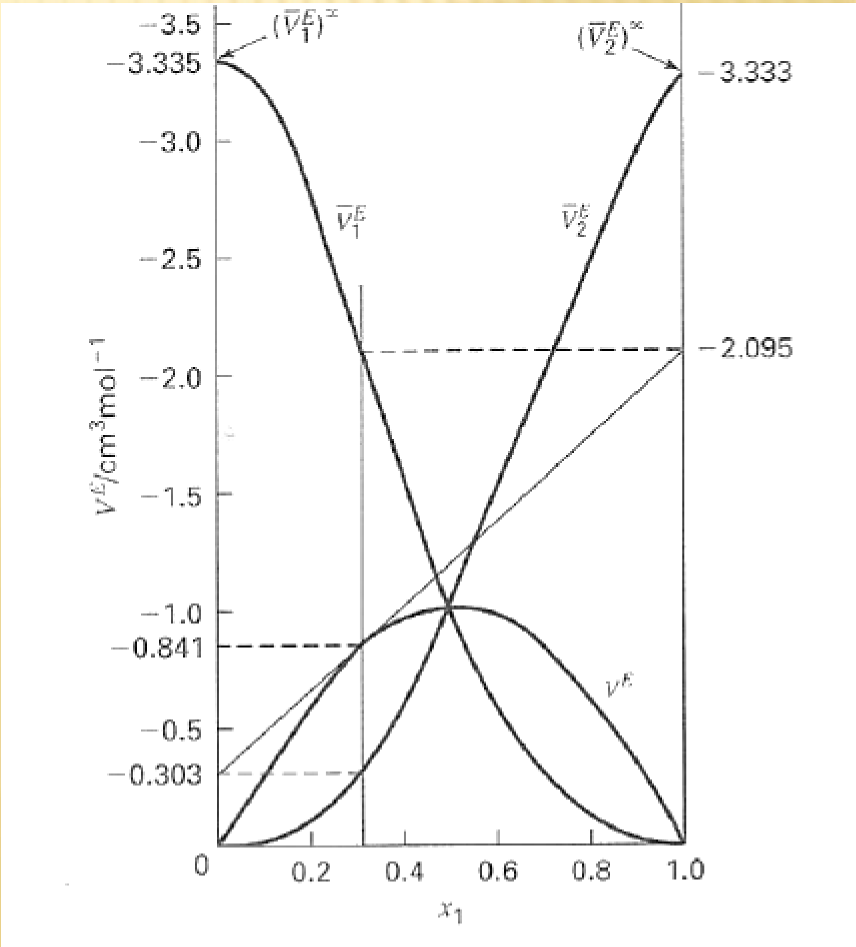
Excess entropy S^E is not measured directly but found from the equation:

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

Example – What is the excess volume of 2000 cm^3 of antifreeze consisting of 30 mol % methanol in water at 25 °C? Molar volumes of pure species and partial molar volumes at 25 °C are given as

V_M= 40.727 cm^3/mol, V_M^P= 38.632 cm^3/mol

V_W= 18.068 cm^3/mol, V_W^P= 17.765 cm^3/mol



Example –Total excess Gibbs free energy in A-B system at 600K has the following values for specific concentrations:

XA	DGe
0	0
0.1	-510
0.2	-1776
0.3	-3405
0.4	-4826
0.5	-5510
0.6	-4826
0.7	-3405
0.8	-1776
0.9	-510
1	0

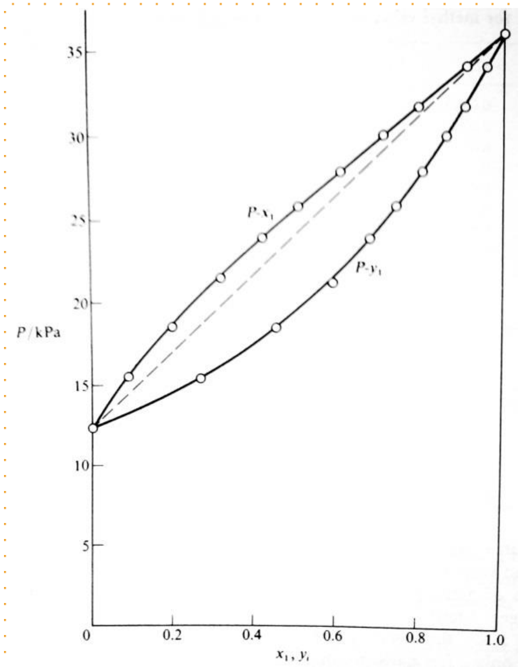
Calculate the partial excess and partial Gibbs free energies of A and B at X_A=0.5.

The mole fractions of a component in a system comprising of a vapor mixture and a liquid solution are given as y_i and x_i

$$\gamma_i = \frac{a_i}{x_i} = \frac{P_i}{x_i {P_i}^{o}} = \frac{y_i P}{x_i {P_i}^{sat}}$$

<u>Modified Raoult's law</u> takes into account the deviations from ideality in the liquid phase and is applicable at low to moderate pressures:

$$\gamma_i x_i {P_i}^{sat} = y_i P$$

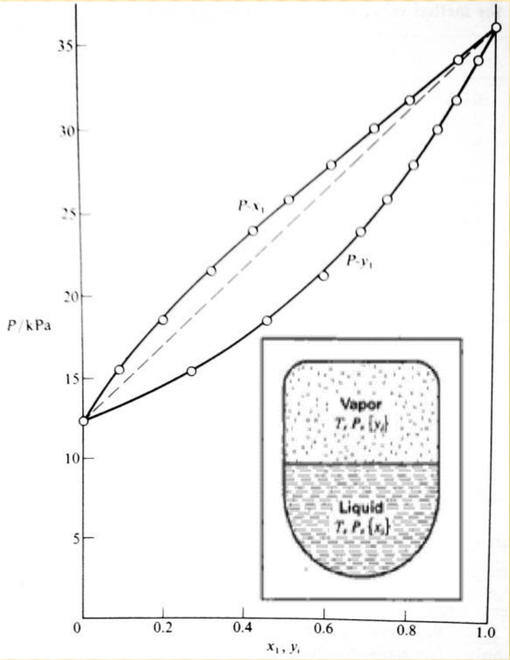


Example – Consider the ethyl ketone – toluene system at 50 C

Table 11.1 VLE Data for methyl ethyl ketone(1)/toluene(2) at 50°C

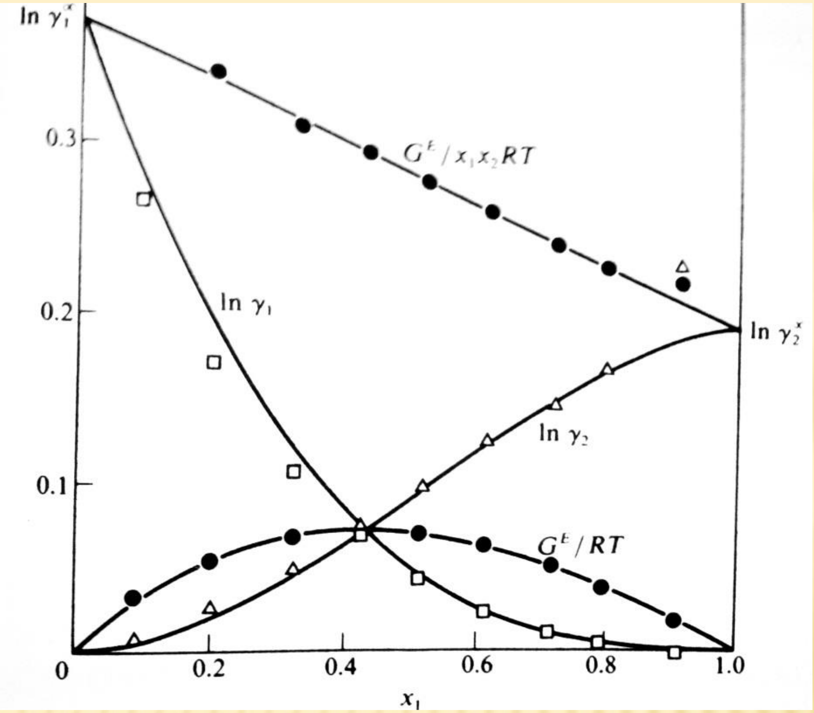
P/kPa	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$	G^E/RT	G^E/x_1x_2RT
12.30†	0.0000	0.0000	......	0.000	0.000	
15.51	0.0895	0.2716	0.266	0.009	0.032	0.389
18.61	0.1981	0.4565	0.172	0.025	0.054	0.342
21.63	0.3193	0.5934	0.108	0.049	0.068	0.312
24.01	0.4232	0.6815	0.069	0.075	0.072	0.297
25.92	0.5119	0.7440	0.043	0.100	0.071	0.283
29.96	0.6096	0.8050	0.023	0.127	0.063	0.267
30.12	0.7135	0.8639	0.010	0.151	0.051	0.248
31.75	0.7934	0.9048	0.003	0.173	0.038	0.234
34.15	0.9102	0.9590	−0.003	0.237	0.019	0.227
36.09‡	1.0000	1.0000	0.000	......	0.000	

† P_2^{sat}
‡ P_1^{sat}



$$\gamma_i x_i P_i^{sat} = y_i P$$

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



The figure is characteristic of systems with positive deviations from Raoult's law,

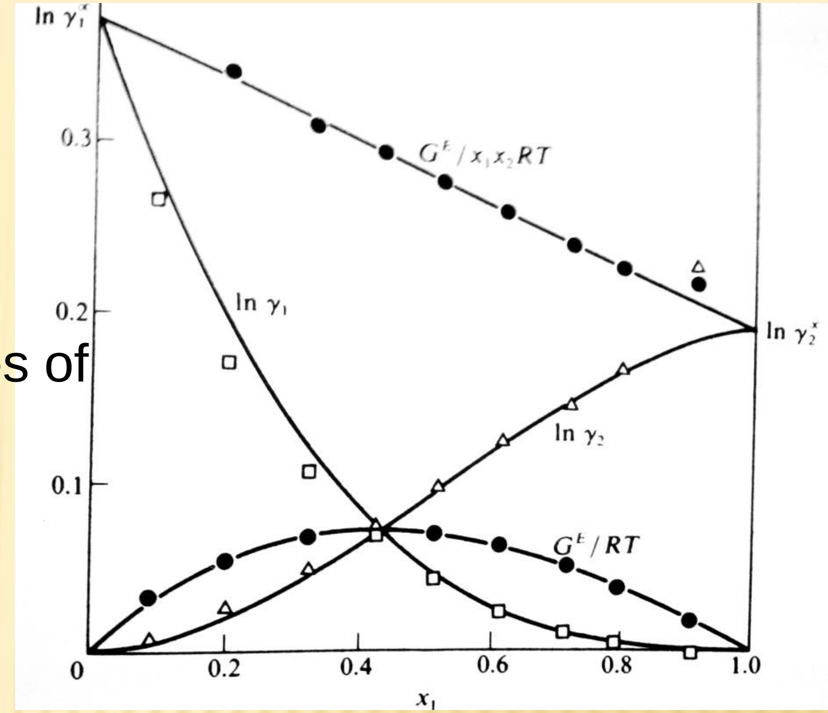
$$\gamma_i \geq 1 \qquad\qquad \ln\gamma_i \geq 0$$

The points representing $\ln\gamma_i$ tend toward zero as x_i goes to 1
Thus the activity coefficient of a species in solution becomes unity as the species becomes pure
At the other limit where x_i goes to zero and species i becomes infinitely dilute, $\ln\gamma_i$ is seen to approach some finite limit $\ln\gamma_i{}^\infty$

so at two limiting cases $\lim_{x_1\to 0}\frac{G^E}{RT} = (0)\ln\gamma_i{}^\infty + (1)(0) = 0$

According to the Gibbs-Duhem equation,

$$\sum x_i \, d\ln\gamma_i = 0$$



a direct relation is seen between the slopes of curves drawn through the data points for $\ln\gamma_1$ and $\ln\gamma_2$

$$x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_1} = 0$$

$$\frac{d\ln\gamma_1}{dx_1} = -\frac{x_2}{x_1}\frac{d\ln\gamma_2}{dx_1} = 0$$

The slope of the $\ln\gamma_1$ curve is of opposite sign to the slope of the $\ln\gamma_2$ curve
The slope of the $\ln\gamma_1$ curve is zero when x_1 goes to 1
The slope of the $\ln\gamma_2$ curve is zero when x_2 goes to 1

Excess properties have common features:

- All excess properties become zero as either species approaches purity
- Both H^E and TS^E exhibit different composition dependencies although G^E vs x is nearly parabolic in shape
- The minimum and maximum of the curves often occur near the equimolar concentration

The signs and relative magnitudes of H^E, S^E and G^E are useful for qualitative engineering purposes

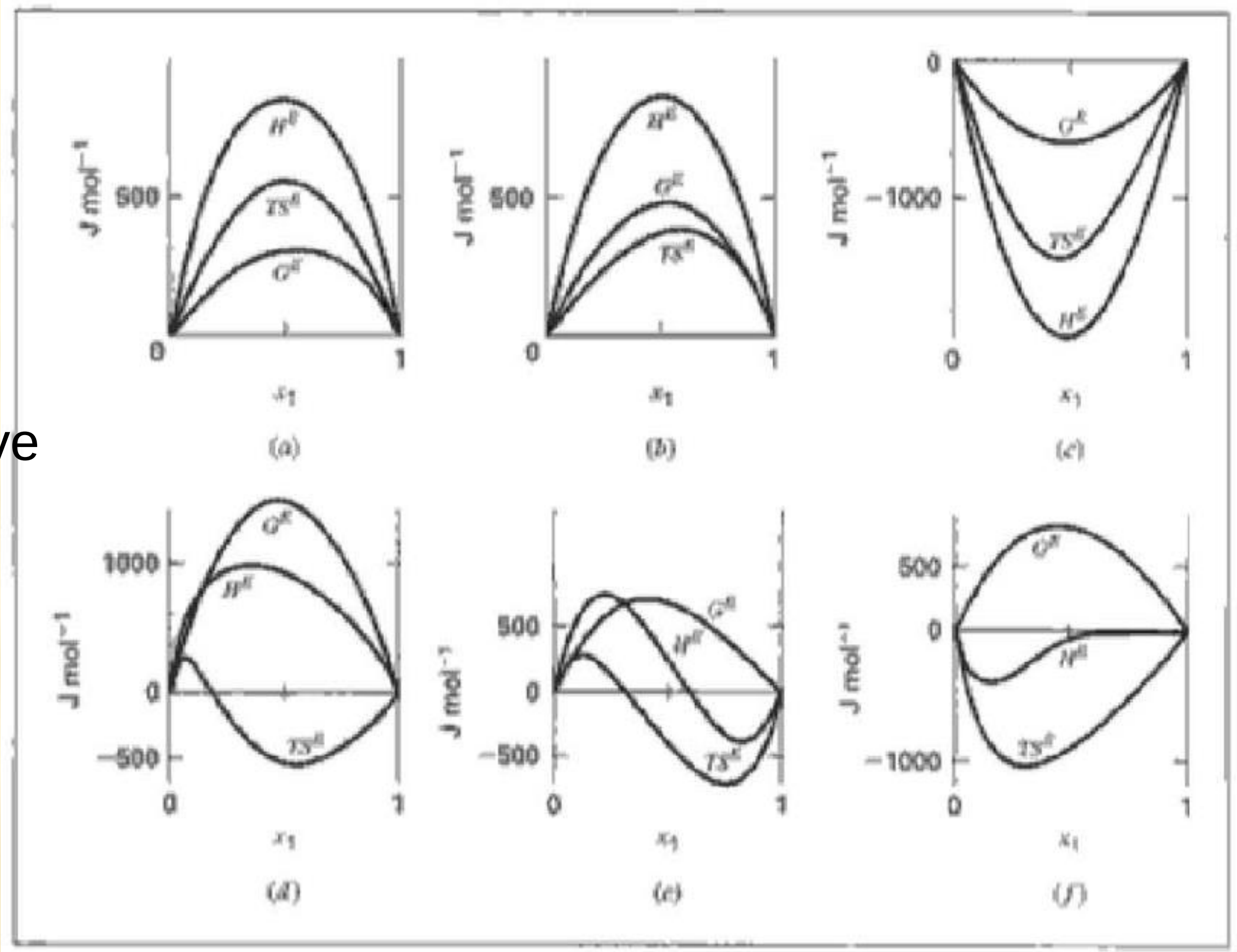


Figure 11.4: Excess properties at 50°C for six binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

Example - Guess the relative spontaneities, activity coefficients and deviations from ideality

a)

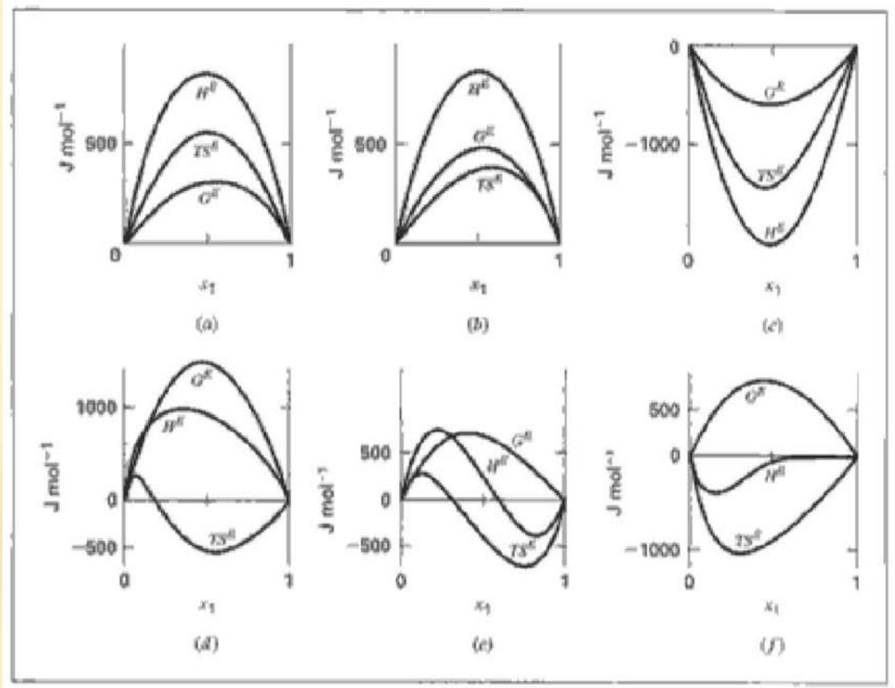
b)

c)

d)

e)

f)



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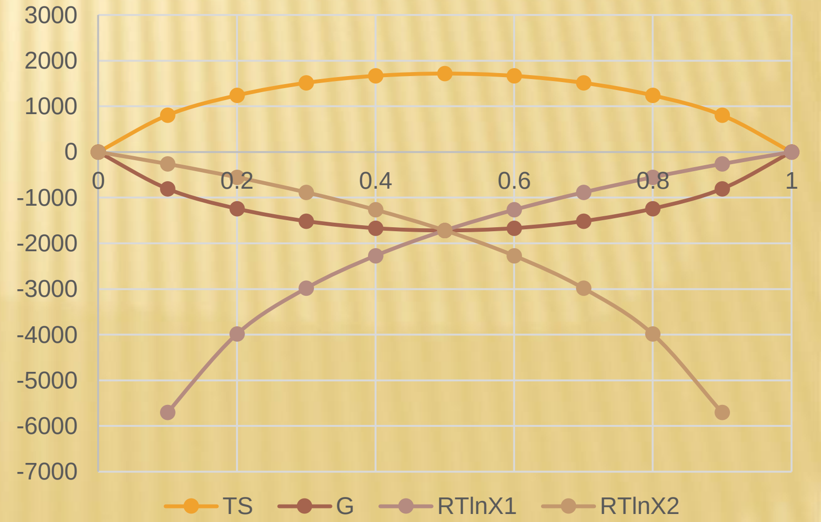
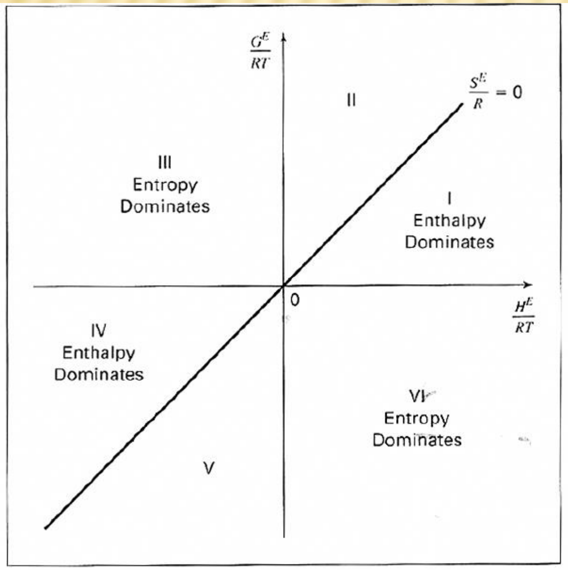


Excess properties of 135 binary liquid mixtures at fixed temperature of 298 K and x_1=x_2=0.5, have been organized by Abbott
Binary organic and aqueous/organic mixtures have been classified based on hydrogen bonding of pure species:

Nonpolar (NP)
Polar but nonassociating (NA)
Polar and association (AS)

135 binary mixtures were investigated and grouped into 6 binary mixture types



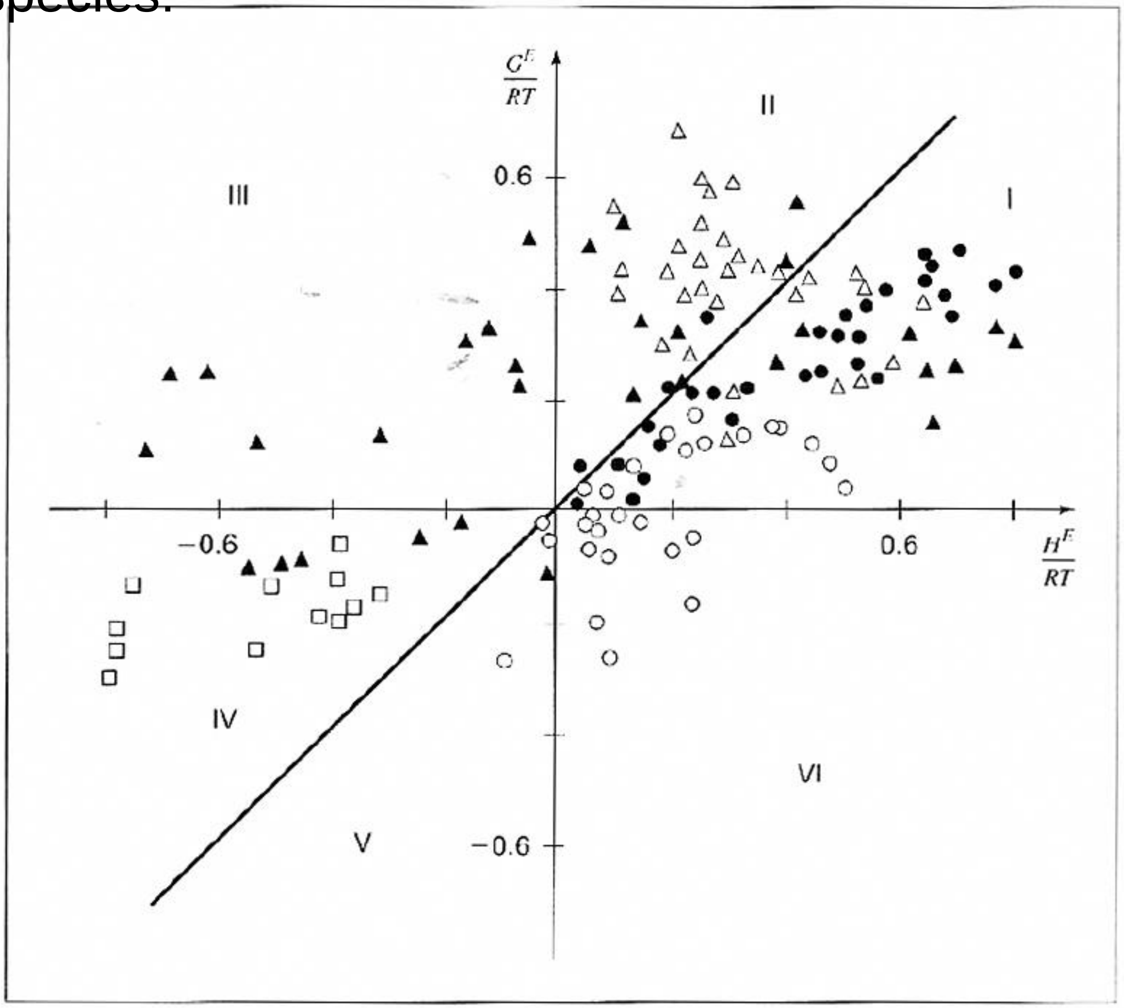


Figure 16.5: Equimolar excess properties for 135 binary mixtures at 298.15 K.
Legend: ○ NP/NP mixtures; ● NA/NP mixtures; △ AS/NP mixtures; ▲ AS/NA and AS/AS mixtures; □ solvating NA/NA mixtures.

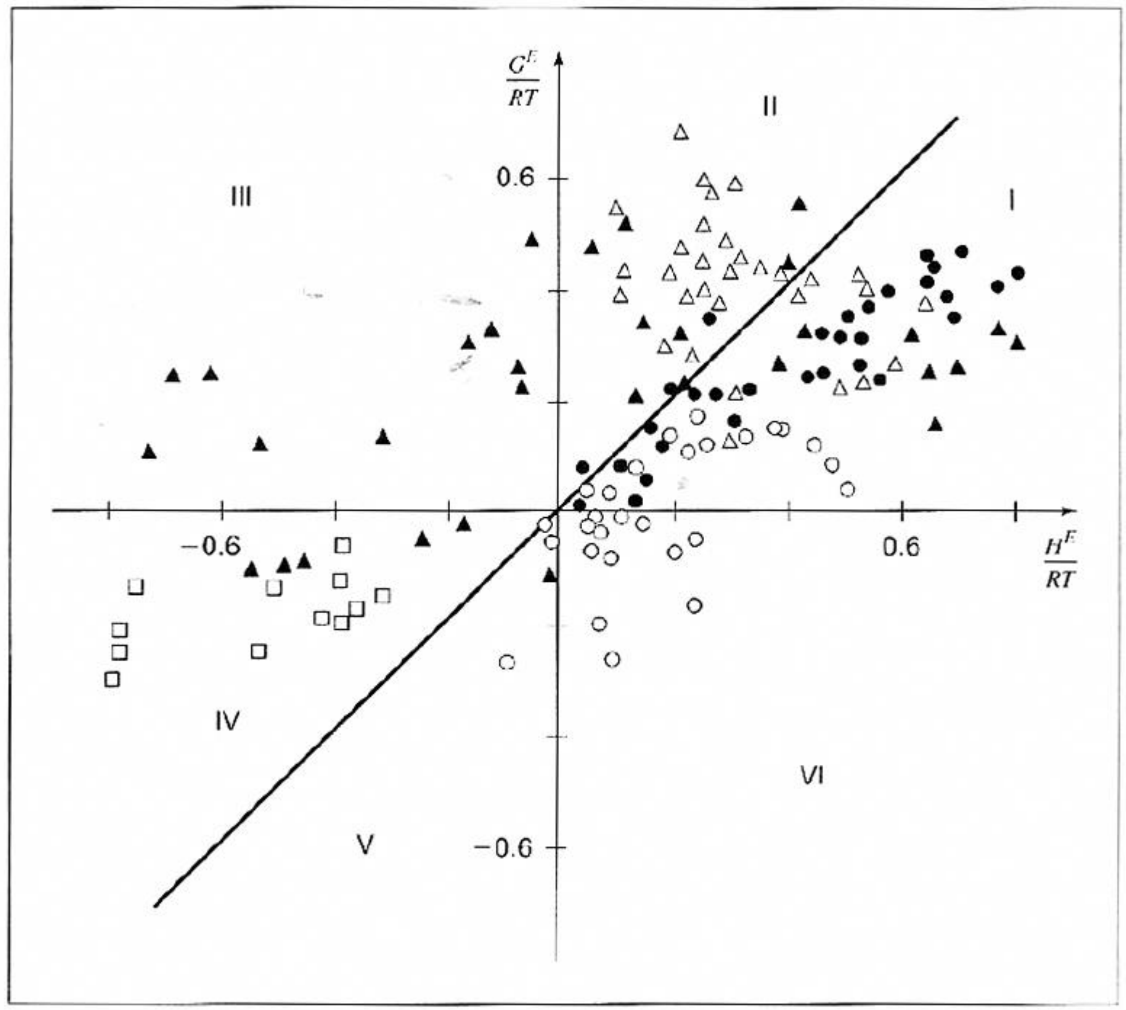
Observed common patterns and norms of excess properties of binary mixtures

About 85% of all mixtures exhibit positive G^E *or* positive H^E(I,II,III, VI); about 70% have positive G^E *and* H^E (I, II)

About 60% of all mixtures fall in I and IV; only 15% in III and VI. Enthalpy is more likely to dominate solution behavior than entropy

NP/NP mixtures concentrate in I and VI, H^E and S^E are normally positive for such mixtures. -0.2< G^E<0.2

NA/NP mixtures usually fall into I, all G^E, H^E and S^E are positive with large values



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Relationship of excess properties with property changes of mixing
Excess properties can be represented in their basic form as

$$G^E = G - \sum x_i G_i^o - RT \sum x_i \ln x_i$$

$$S^E = S - \sum x_i S_i^o + R \sum x_i \ln x_i$$

$$H^E = H - \sum x_i H_i^o$$

$$V^E = V - \sum x_i V_i^o$$

where $M - \sum x_i M_i^o$ is known as property change of mixing ΔM
Excess properties can be rewritten as

$$G^E = \Delta G - RT \sum x_i \ln x_i$$

$$S^E = \Delta S + R \sum x_i \ln x_i$$

$$H^E = \Delta H$$

$$V^E = \Delta V$$

Excess properties and property changes of mixing are readily calculated from eachother

Excess properties are zero for an ideal solution

So total properties of mixing for ideal solutions are derived from excess properties

$$0 = \Delta G^{id} - RT\sum x_i \ln x_i \qquad \Delta G^{id} = RT\sum x_i \ln x_i$$

$$0 = \Delta S^{id} + RT\sum x_i \ln x_i \qquad \Delta S^{id} = -R\sum x_i \ln x_i$$

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

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

Example –Components A-B are mixed to form a solution that deviates positively from an ideal solution and has a standard molar enthalpy of 4000 J/mol. Determine the entropy, enthalpy and Gibbs free energy change of process involving addition of 1 mole of B into 3 moles of A-B solution with X_B= 0.33 initial composition.

Standard enthalpies of formation for A and B are 6000 J/mol and 12000 J/mol

Standard entropies of A and B are 10 J/mol K and 20J/mol K respectively

Property changes of mixing have common features:

- Each ΔM is zero for a pure species
- The Gibbs energy change of mixing ΔG is always negative
- The entropy change of mixing is always poisitive

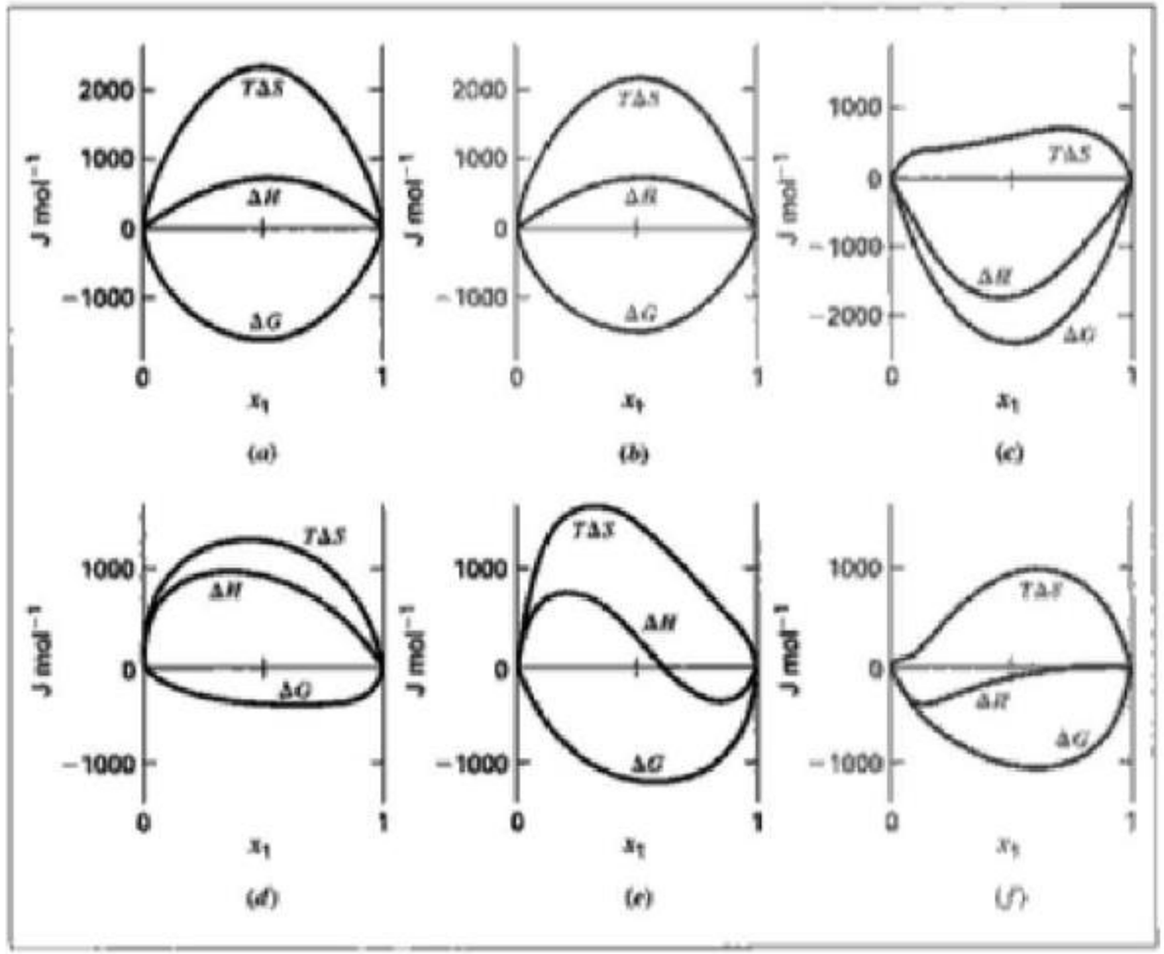


Figure 12.13: Property changes of mixing at 50°C for six binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

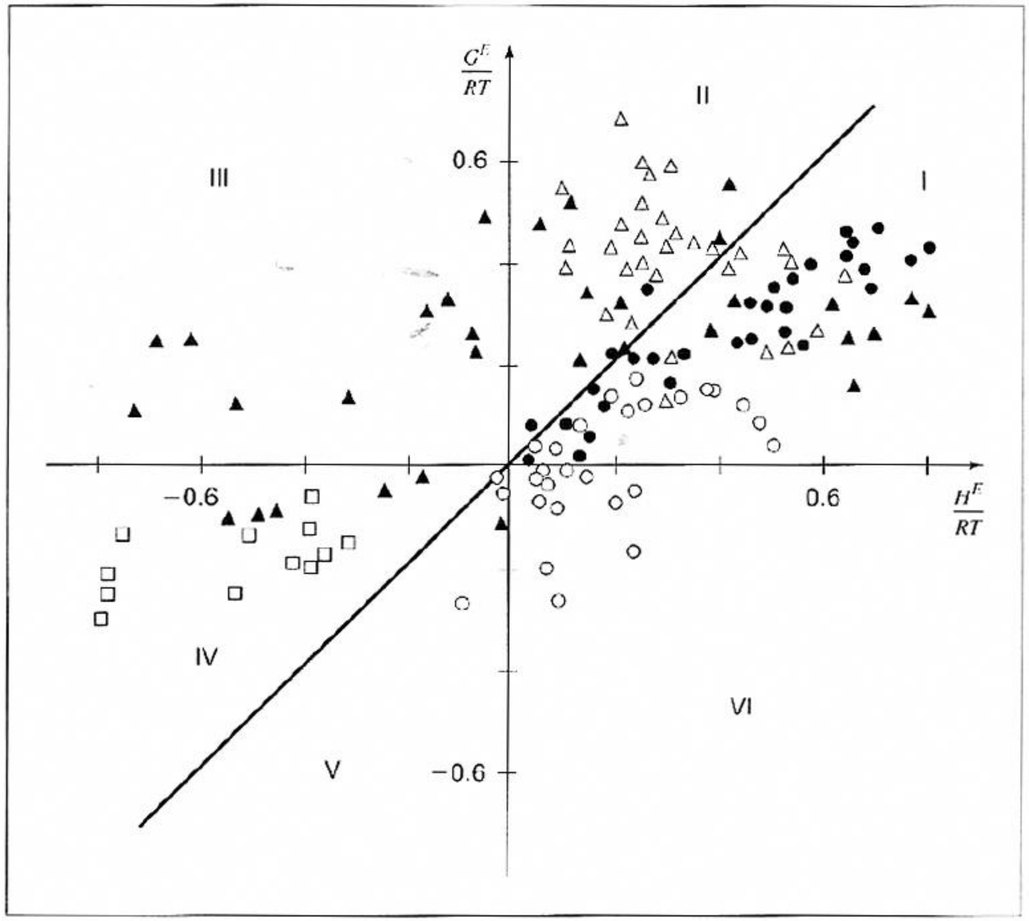
Molecular basis for mixture behavior
The relations between excess properties and property changes of mixing enables discussion of the molecular phenomena which give rise to observed excess property behavior

Excess enthalpy which equals enthalpy of mixing reflect differences in the strengths of intermolecular attraction between pairs of unlike species and pairs of like species.

Interactions between like species are disrupted in a standard mixing process and interactions between unlike species are promoted

More energy (ΔH) is required in the mixing process to break like attractions if the unlike attractions are weaker than the average of those between like species
In this case mixing is endothermic, $\Delta H = H^E > 0$
$\Delta H = H^E < 0$ if the unlike attractions are stronger and mixing process is exothermic

Observations made from Abbott's analysis of NP/NP binary mixtures is that dispersion forces are the only significant attractive intermolecular forces for NP/NP mixtures. Dispersion forces between unlike species are weaker than the average of dispersion forces between like species. Hence a positive excess enthalpy is usually observed for NP/NP mixtures



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Example – The excess enthalpy or heat of mixing for a liquid mixture of species 1 and 2 at fixed T and P is represented as

$$H^E = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) \text{ J/mole}$$

Determine expressions for $\overline{H^E}_1$, $\overline{H}_1$ and $\overline{H^E}_2$, $\overline{H}_2$ as functions of x_1

$$\overline{H}_1^{\,E} = H^E + x_2 \frac{dH^E}{dx_1}$$

$$\overline{H}_2 - H_2{}^o = \int_{(\overline{H}_1)_{X2=1}}^{(\overline{H}_1)_{X2=a}} \left(\frac{1 - x_2}{x_2}\right) d\overline{H}_1$$

The fundamental excess property relation and its derivations

Gibbs free energy is a generating property for all other related properties

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

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

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT} d(nG) - \frac{(nG)}{RT^2} dT$$

Since $G = H - TS$,

$$d\left(\frac{nG}{RT}\right) = \frac{(nV)dP + (nS)dT + \sum_i \mu_i dn_i}{RT} - \frac{nH - TnS}{RT^2} dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT} dP - \frac{nH}{RT^2} dT + \sum \frac{\overline{G_i}}{RT} dn_i$$

$$\boxed{d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum \ln \gamma_i \, dn_i}$$

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

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum \ln\gamma_i \, dn_i$$

$$\ln\gamma_i = \left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{P,T,nj}$$

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

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