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Supplementary References

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Excess Gibbs Energy

For a binary system, Excess Gibbs Energy

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

The values of $\frac{G^E}{RT}$ so calculated are divided by x_1x_2 to provide in addition values

of $\frac{G^E}{x_1x_2RT}$; the two sets of numbers are obtained

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Table 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(P_2^{sat})	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
27,96	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(P_1^{sat})	1,0000	1,000	0,000		0,000	

The four thermodynamic functions for which we have experimental values, $\ln\gamma_1$, $\ln\gamma_2$, $\frac{G^E}{RT}$, and $\frac{G^E}{x_1x_2RT}$, are properties of the liquid phase. Obtained figure shows how each varies with composition for a particular binary system at a specified temperature. This figure is characteristic of systems for which

$$\gamma_i > 1 \text{ and } \ln\gamma_i > 0 \quad (i=1,2)$$

In such a case the liquid phase shows positive deviations from ideal-solution

Property Changes of Mixing

Equations (given before) are expressions for the **properties of ideal solutions**. Each may be combined with the defining equation for an excess property,

$$G^E = G - \sum_i x_i G_i - RT \sum_i x_i \ln x_i$$

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

$$V^E = V - \sum_i x_i V_i$$

$$H^E = H - \sum_i x_i H_i$$

In each of these equations there appears to the right of the equals sign a difference that is expressed in general as $M - \sum_i x_i M_i$. We call this quantity a property change of mixing and give it the symbol ΔM . Thus by definition,

$$\Delta M \equiv M - \sum_i x_i M_i$$

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Where M is molar (or unit-mass) property of a solution and the M_i are molar (or unit-mass) properties of the pure species, all at the same T and P . Equations are now rewritten

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

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

$$V^E = \Delta V$$

$$H^E = \Delta H$$

Where ΔG , ΔS , ΔV and ΔH are the Gibbs energy change of mixing, the entropy change of mixing, the volume change of mixing, and the enthalpy change of mixing. For an ideal solution, each excess property is zero, and for this special case Eqs.

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

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

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

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

Equations (give before) show that **excess properties** and **property changes of mixing** are readily calculated one from the other. Although historically the property changes of mixing were introduced first, because of their direct relation to experiment, it is the excess properties that more readily fit into the theoretical framework of solution thermodynamics. **The property changes of mixing of major interest**, because of their direct measurability, are ΔV and ΔH , and these two properties are identical to the corresponding excess properties.

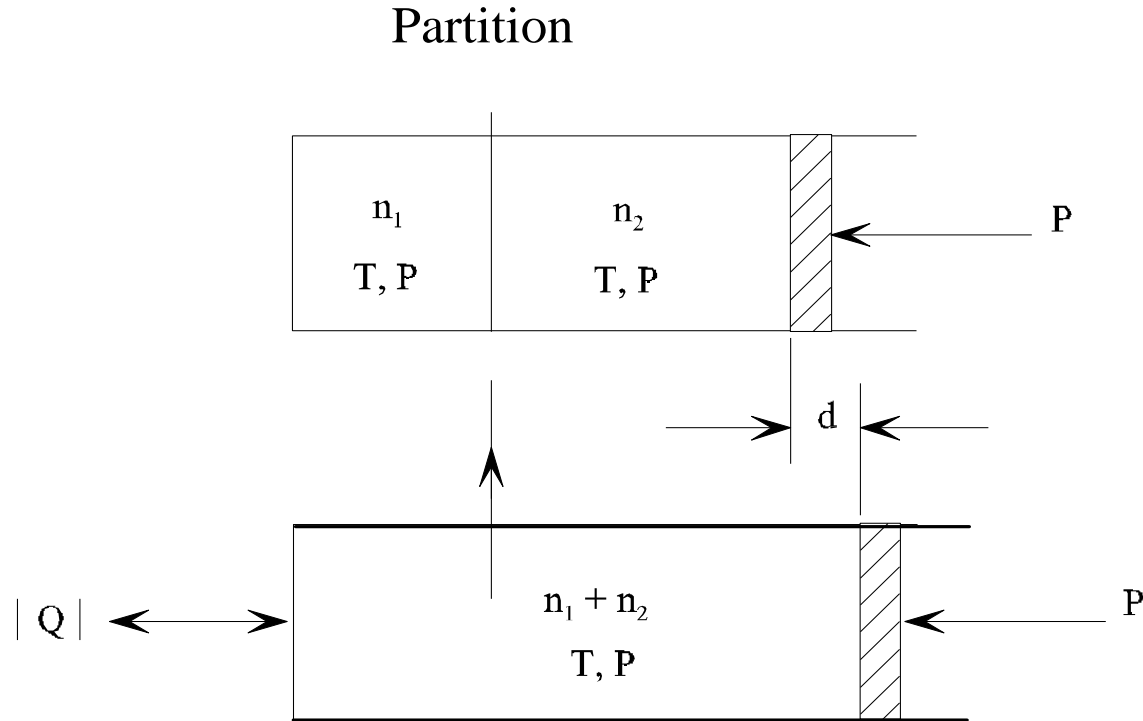


Figure : Schematic diagram of experimental mixing process.

An experimental mixing process for a binary system is represented schematically in Fig. The two pure species, both at T and P, are initially separated by a partition, withdrawal of which allows mixing. As mixing occurs, expansion or contraction of the system is accompanied by movement of the piston so that the pressure is constant. In addition, heat is added or extracted to maintain a constant temperature. When mixing is complete, the total volume change of the system (as measured by piston displacement d) is

$$\Delta V^t = (n_1 + n_2)V - n_1V_1 - n_2V_2$$

Since the process occurs at constant pressure, the total heat transfer Q is equal to the total enthalpy change of the system:

$$Q = \Delta H^t = (n_1 + n_2)H - n_1H_1 - n_2H_2$$

Division of these equations by $n_1 + n_2$ gives

$$\Delta V \equiv V - x_1V_1 - x_2V_2 = \frac{\Delta V^t}{n_1 + n_2}$$

and

$$\Delta H \equiv H - x_1H_1 - x_2H_2 = \frac{Q}{n_1 + n_2}$$

Thus the volume change of mixing ΔV and the enthalpy change of mixing ΔH are found from the measured quantities ΔV^t and Q. Because of its association with Q, ΔH is usually called the heat of mixing.