

**Textbook:** J. M. Smith, H. C. Van Ness, M.M. Abbott, **Introduction to Chemical Engineering Thermodynamics**, Seventh Edition, McGraw-Hill International Editions, 2005.

### **Supplementary References**

Stanley I. Sandler, **Chemical and Engineering Thermodynamics**, Third edition John Wiley & Sons Inc, 1998.

J. Richard Elliott, Carl T. Lira, **Introductory Chemical Engineering Thermodynamics**, 2nd edition Prentice Hall International Series in the Physical and Chemical Engineering Sciences, 1999.

# **Solution Thermodynamics: Applications**

All the fundamental equations and necessary definitions of solution thermodynamics are given in the preceding chapter. In this chapter we examine what can be learned from experiment.

# Liquid-Phase Properties from VLE Data

## Fugacity

Figure 1 shows a vessel in which a vapour mixture and a liquid solution coexist in vapour/liquid equilibrium. Temperature  $T$  and pressure  $P$  are uniform throughout the vessel, and can be measured with appropriate instruments. Samples of the vapour and liquid phases may be withdrawn for analysis, and this provides experimental values for the mole fractions in the vapour ( $y_i$ ) and mole fractions in the liquid ( $x_i$ ). For species  $i$  in the vapour mixture,  $\hat{f}_i = x_i \hat{\phi}_i P$  is written

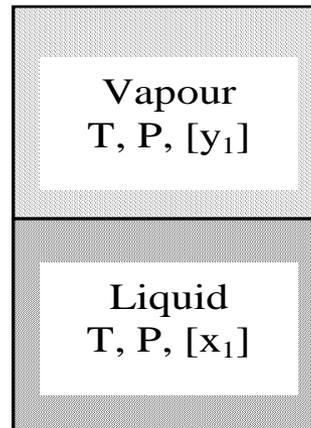


Figure 1 Schematic representation of VLE

$$\hat{f}_i^v = y_i \hat{\phi}_i P$$

For vapour/liquid equilibrium Eq. 10.44 requires that  $\hat{f}_i^v = \hat{f}_i^l$  for each species.

Therefore

$$\hat{f}_i^l = y_i \hat{\phi}_i P$$

We could calculate values of  $\hat{\phi}_i$  by Eq. but for low pressure VLE (up to at least 1 bar) vapour phases usually approximate ideal gases, for which  $\hat{\phi}_i = 1$ . This assumption introduces little error, and reduces the preceding equation to

$$\hat{f}_i^l = y_i P$$

Thus, the fugacity of species  $i$  in the liquid phase is given to a good approximation by the partial pressure of species  $i$  in the vapour phase. In the limit where  $x_i = y_i = 1$ , the total pressure equals the vapour pressure of pure species  $i$ , and  $\hat{f}_i^l = \hat{f}_i^v = P_i^{\text{sat}}$ .

For a binary, system (ketone(1)/toluene (2)), values of the liquid phase fugacities are found from

$$\hat{f}_1 = y_1 P \quad \text{and} \quad \hat{f}_2 = y_2 P$$

where superscript “l” has for simplicity been dropped.

the Lewis/Randall rule, which expresses the composition dependency of the constituent fugacities in an ideal solution:

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

# Activity Coefficient

The activity coefficient is given as following:

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

Thus the activity coefficient of a species in solution is simply the ratio of its actual fugacity to the value given by the Lewis/Randall rule at the same T, P, and composition. For calculational purposes we substitute for both  $\hat{f}_i$  and  $\hat{f}_i^{\text{id}}$  to get

$$\gamma_i = \frac{y_i P}{x_i f_i} = \frac{y_i P}{x_i P_i^{\text{sat}}} \quad (i=1,2,\dots,N)$$

This simple equation is adequate to our present purpose, allowing easy calculation of activity coefficients from experimental low pressure VLE data.

We note in Fig. that the line representing the actual composition dependency of  $\hat{f}_i$  becomes tangent to the Lewis/Randall line at  $x_i = 1$ . This is a consequence of the Lewis/Randall equation, as will be shown presently. We also note that in the other limit  $\hat{f}_i$  becomes zero at  $x_i = 0$ . Thus the ratio  $\hat{f}_i / x_i$  is indeterminate in this limit, and application of l'Hopital's rule yields (*the limit, as  $x$  approaches zero..*)

$$\lim_{x \rightarrow 0} \frac{\hat{f}_i}{x_i} = \left( \frac{d\hat{f}_i}{dx_i} \right)_{x_i=0} \equiv k_i$$