

## AZEOTROPIC DATA FOR BINARY MIXTURES

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Binary homogeneous (single-phase) liquid mixtures having an extremum (maximum or minimum) vapor pressure  $P$  at constant temperature  $T$ , as a function of composition, are called azeotropic mixtures, or simply azeotropes. The composition is usually expressed as mole fractions, where  $x_i$  for component  $i$  in the liquid phase and  $y_i$  for component  $i$  in the vapor phase are identical. Mixtures that do not show a maximum or minimum are called zeotropic. A maximum (minimum) of the  $P(x_i)$  or  $P(y_i)$  curves corresponds to a minimum (maximum) of the boiling temperature  $T$  at constant  $P$  plotted as a function of  $x_i$  or  $y_i$ , [see  $T(x_i)$  and  $T(y_i)$  curves, Types I and II, in Fig. 1]. Azeotropes in which the pressure is a maximum (temperature is a minimum) are often called positive azeotropes, while pressure-minimum (temperature-maximum) azeotropes are called negative azeotropes. The coordinates of an azeotropic point are the azeotropic temperature  $T_{az}$ , pressure  $P_{az}$ , and the vapor-phase composition  $y_{1,az}$ , which is the same as the liquid-phase composition  $x_{1,az}$ .

In the two-phase liquid-liquid region of partially miscible (heterogeneous) mixtures, the vapor pressure at constant  $T$  (or the boiling temperature at constant  $P$ ) is independent of the global composition  $x$ , of the two coexisting liquid phases between the equilibrium compositions  $x'$  and  $x''$  ( $x' < x < x''$ )

and is impossible by ordinary distillation, even with an infinitely large number of stages.

Following eq. (1) azeotropic behavior will always occur in homogeneous binary systems when the vapor pressure ratio  $P_1^s/P_2^s$  is equal to the ratio of the activity coefficients  $\gamma_1/\gamma_2$ .

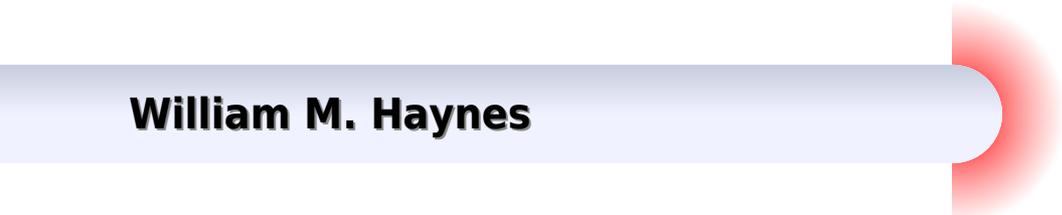
Various thermodynamic methods based on  $g^E$ -models (Wilson, NRTL, UNIQUAC) or group contribution methods (UNIFAC, modified UNIFAC, ASOG, PSRK) can be used for either calculating or predicting the required activity coefficients for the components under given conditions of temperature and composition (Reference 2).

Because of the importance of azeotropic data for the design of distillation processes, compilations have been available in book form for quite some time (References 3-7). The most recent printed data collection was published in 1994 (Reference 8). A revised and extended version appeared in 2004 (Reference 9).

A collection of approximately 47,400 zeotropic and azeotropic data sets, compiled from 6600 references, are stored in a comprehensive computerized data bank (Reference 10). The references from the above-mentioned compilations and from the vapor-liquid equilibrium part of the Dortmund Data Bank (Reference 11) were supplemented by references found from CAS online

# Azeotropic Data For Binary Mixtures

**William M. Haynes**



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