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ten Brinke, G. ; Karasz, F. E.

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Reply to the comments by Morrison^{a)}

G. ten Brinke and F. E. Karasz

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003
(Received 29 November 1982; accepted 23 December 1982)

Our discussion² within the framework of scaling theory showed also clearly that certain qualitative features are essentially a consequence of the stability criterion. In addition to this the symmetry embodied in the scaled equation of state was shown to be essential for the derivation of the explicit Eq. (7). We restricted ourselves to the phase behavior in an isobaric plane, but a similar analysis can be given for an isothermal plane, resulting in a relation between the volume of mixing and the type of phase behavior in this plane, i.e., upper or

lower critical solution pressure. The qualitative results relating the signs of the enthalpy of mixing and the volume of mixing to the type of phase behavior follow, in accordance with Morrison's main conclusion, also from a thermodynamic analysis given by Rowlinson.^{3,4}

The scaling analysis for an isothermal plane results in an expression for the volume of the mixture analogous to Eq. (7) of our previous note.² Combining expressions (3) and (7) of that note with the corresponding ones for an isothermal plane, as indicated in Fig. 1, results in the following equation for the pressure dependence of the critical temperature T_1 :

$$\frac{dT_1}{dP} = \lim_{(T_2, P_2) \rightarrow (T_1, P_1)} T_1 \frac{(\partial V / \partial x_1)_A - (\partial V / \partial x_1)_B}{(\partial H / \partial x_1)_A - (\partial H / \partial x_1)_B},$$

where H , V , and x_1 denote the enthalpy, the volume, and the concentration of component 1. The salient part of this equation can also be written as

$$\lim_{x_{1A} \rightarrow x_{1B}} \left(\frac{\Delta(\partial V / \partial x_1)}{\Delta x_1} \right)_P / \left(\frac{\Delta(\partial H / \partial x_1)}{\Delta x_1} \right)_T,$$

where $\Delta x_1 = x_{1A} - x_{1B}$. Since the numerator and denominator are the operational definitions of the second derivatives of the volume and enthalpy, the given expression for dT_1/dP is equivalent to the one given by Myers *et al.*⁵

FIG. 1. Schematic three-dimensional P, T, x_1 diagram showing a critical line CD . A and B are the points of intersection of the coexistence curve in the isothermic plane through the critical point T_1, P_1 and the coexistence curve in the isobaric plane through the critical point T_2, P_2 . The drawing is for the particular case of UCST behavior with $dUCST/dP > 0$.

^{a)}Reference 1.

¹G. Morrison, *J. Chem. Phys.* 78, 4790 (1983).

²G. ten Brinke and F. E. Karasz, *J. Chem. Phys.* 77, 5249 (1982).

³J. S. Rowlinson, *Liquid and Liquid Mixtures*, 2nd ed. (Plenum, New York, 1969), p. 146.

⁴Y. Suzuki, Y. Miyamoto, H. Miyai, and K. Asai, *J. Polym. Sci. Lett.* 20, 569 (1982).

⁵D. B. Myers, R. A. Smith, J. Katz, and R. L. Scott, *J. Phys. Chem.* 70, 3341 (1966).

Hypervirial calculations of Morse oscillator matrix elements

A. Requena, R. Peña, and J. Zúñiga

Department of Physical Chemistry, University of Murcia, Murcia, Spain
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In a recent paper, Huffaker and Tran¹ propose the use of the standard techniques of the factorization method² to obtain formulas for matrix elements of powers of the quantity

$$y = 1 - \exp(-aq) \quad (1)$$

for bound levels of a Morse oscillator. Expressions for diagonal and off-diagonal matrix elements of y , y^2 , y^3 , and