Extended Phase Rule for Non-reactive, Multiphase, Multicomponent Chemical Systems

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A comprehensive phase rule[1] has been developed for non-reacting, multicomponent, multiphase systems, which considers, in addition to phase-intensive variables such as temperature (T), pressure (P) and phase compositions (x), system-intensive variables such as overall or total density ρ^T, overall composition (X), and phase volume fractions such as the liquid volume fraction (LVF). This extended phase rule, incorporating as it does overall density and composition, is of use to engineers who design chemical processing equipment and to theoreticians and experimenters concerned with the nature and study of thermodynamic equilibrium. It uniquely describes, for example, multi-phase thermodynamic paths followed by experimentalists studying systems of three or more components. For the phase rule: the number of degrees of freedom is given as ${}^of = C + 1$, where C is the number of components. This phase rule is for a relative thermodynamic system; that is, one in which relative phase sizes are relevant. It is in contrast to Gibb's phase rule and Duhem's theorem for open and closed systems respectively. The Gibbs phase rule is incorporated into the present formulation. Application examples are:

1) description of two-phase experimental paths for a ternary system (${}^of = 3+1 = 4$. Variables are X_1, X_2, P, and T)[2],
2) theoretical and experimental papers for obtaining binary mixture critical densities (${}^of = 2+1 = 3$. Variables are X_1, ρ^T, and T)[3,4],
3) isoplethic path method to obtain critical lines of binary azeotropic mixtures, (${}^of = 2+1 = 3$. Variables are X_1, LVF (= ½), and P)[5],
4) isoplethic paths utilized to correlate two-phase binary-mixture surface tension data, (${}^of = 2+1 = 3$. Variables are X_1, LVF (= ½), and T)[6].

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[4] L.J. Van Poolen, V.G. Niesen, *Fluid Phase Equilibria*, **66** 161 (1991).
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[6] L.J. Van Poolen and C.D. Holcomb, "Liquid Volume Fraction Model for Vapor-Liquid Surface Tension Data for the Binary Mixtures {Ar + Kr} and {CH_4 + Kr)", (to be published).