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Comments and Addenda

Multicomponent-Fluid Tricritical Points[*]

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Phenomena in "ordinary" fluid mixtures (such as CH_3OH-H_2O-CO_2) which are analogous to tricritical points in He^3-He^4 mixtures, metamagnets, etc. have been reported for some years in the Soviet physical-chemistry journals. References to these papers are given, together with a brief explanation of why the two types of phase transition are analogous, and reasons why further experiments on the "ordinary" mixtures would be of interest.

Tricritical points in metamagnets, He^3-He^4 mixtures, and NH_4Cl have recently been the subject of several theoretical and experimental investigations.[1] We wish to point out that a very similar type of phase transition has been observed in ordinary liquid mixtures when there are three[2-4] or four[5-8] distinct chemical components present, and the theoretical possibility of such points was discussed as early as 1926[9] (as we learned from Refs. 2 and 3).

Table I lists a number of mixtures in which tricritical points have been observed. Undoubtedly there are still other examples. We have not attempted a systematic search of the literature. Also, since their significance has not been widely appreciated, tricritical points may have been observed in some cases and not reported.

In these mixtures, the tricritical point occurs when *three* coexisting fluid phases *simultaneously* become identical as some appropriate thermodynamic variable is altered. It is thus distinct from ordinary critical points, where two phases become identical, and critical end points, where two phases become identical in the presence of a third phase with dissimilar properties. An appropriate form of the phase rule[9,10] shows that a tricritical point is only to be expected (apart from a special symmetry) in mixtures of three or more components. In a ternary mixture it is an invariant point, with a well-defined temperature, pressure, and composition, while in quaternary mixtures the additional degree of freedom means that a tricritical point will be part of a line of such points (univariant). This means that in a quaternary mixture it is possible to fix the pressure (for example) and observe a tricritical point by varying temperature and composition. Thus in the mixture water-ammonium sulfate-ethanol-benzene a tricritical point can be observed under atmospheric pressure.[5,11]

In metamagnets, etc., the tricritical point also occurs when three "phases" become identical simultaneously, but two of the phases are related by a special symmetry operation (e.g., interchanging the magnetic sublattices of the metamagnet).[12] Hereafter we shall refer to these cases as "symmetrical" tricritical points. Their relationship to the fluid mixtures mentioned in the previous paragraph is conveniently discussed in terms of an approximate phenomenological model (details will be found elsewhere[13]): a Landau[14] expansion of the free energy Ψ in terms of an order parameter ψ,

$$\Psi = a_1\psi + a_2\psi^2 + a_3\psi^3 + a_4\psi^4 + \psi^6 , \tag{1}$$

where the a_j all vanish at the tricritical point. In systems with symmetrical tricritical points, a_1 and a_3 are identically zero by an exact symmetry of the Hamiltonian, though the phase diagram is sometimes drawn (Fig. 2 of Ref. 1, $\zeta = a_1$) with a_1 included as a variable.

In (nonsymmetrical) liquid mixtures, by contrast, a_1 and a_3 may be varied by experiment. (One may think of the a_j as linear combinations

TABLE I. Tricritical points in ternary and quaternary mixtures. Estimates of the tricritical pressure (p_t) and temperature (T_t) are given. The references contain additional information on compositions and molar volumes of mixtures.

Mixture	p_t (atm)	T_t (°C)
Acetic acid, water, butane [a]		191
Methanol, water, carbon dioxide [b]	87	44.6
Ethanol, water, carbon dioxide [c]	91.7	47.4
Methanol, ethane, carbon dioxide [d]	76.5	33.5
Ethane, *n*-hexadecane, *n*-eicosane [e]	55.5	40.7
Water, ammonium sulfate, ethanol, benzene [f]	1	49
Water, phenol, pyridine, *n*-hexane [g]		>162
		>115
Methanol, ethanol, water, carbon dioxide [h]	87.4–91.7	44.6–47.4

[a] Reference 2. No value is given for the tricritical pressure.

[b] References 3(a) and 3(b).

[c] Reference 3(d).

[d] Reference 3(c).

[e] Reference 4. The value of p_t given in Ref. 4(a) seems to be in error.

[f] References 5 and 11.

[g] References 6 and 7. There are apparently two tricritical points, at different compositions. The pressure is presumably vapor pressure. The temperatures given are only lower bounds.

[h] Reference 8. Several points along a line of tricritical points were investigated.

of pressure, temperature, and chemical potentials.) We should emphasize that the identification of Eq. (1) with tricritical points in these mixtures in even a qualitative sense, the sense in which the van der Waals equation correctly describes an ordinary critical point, is tentative, though supported by available data.[13]

An experimental investigation of critical exponents, dynamical properties, etc., near a tricritical point in a mixture would be of interest to see in what way these differ from corresponding properties at an "ordinary" critical point. For example, Riedel and Wegner[15] have suggested that at a tricritical point the exponents will, up to logarithmic corrections, have their "classical" tricritical values, and an experimental test would be most welcome. (At ordinary critical points strong deviations from "classical" values are well known.[16]) Such experiments will not be easy, because of the difficulty of finding the precise location of a tricritical point: two additional thermodynamic degrees of freedom, beyond those encountered at an ordinary critical point, must be controlled.

As for terminology, the name "second-order critical point" used by Kohnstamm[9] has historical precedence, but it seems preferable to use a term suggesting the number, three, of phases which simultaneously become identical. Both "tricritical" (used above) and "third-order critical" point are acceptable possibilities. The situation where four (or more) phases become identical simultaneously has been discussed from the point of view of the phase rule.[10] We know of no experimental examples, and the relationship of such "higher-order critical points" to some others which have been discussed recently[17] is not altogether clear.

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