Over the past thirty years an extensive body of data on ternary liquid systems has been published. A survey of these data and, in particular, the considerable experimental work of one of us (AWF) with such systems have revealed certain features of phase diagrams found only in monographs or research papers but which are not general knowledge. The frequency with which some of the features have been observed suggests that there are guiding principles to be followed, and that textbooks are frequently in error in certain matters. In most cases apparent exceptions to these principles have been found to be the result of known or probable impurities. This paper is an attempt to summarize what generalizations have been observed and to draw attention to some examples of novel and fascinating behavior which add interest to a classical subject. It is hoped, at the same time, that it will help to discourage the drawing of unrealistic phase diagrams for instructional purposes. Except where stated, it is understood that ternary systems are being discussed, so that the presence of a fourth substance (especially water), even in small amounts as an impurity, is excluded.

Two Coexisting Phases

The most familiar phase behavior is that in which two of the three liquid components are immiscible or partially miscible, but each is miscible with the third. Addition of a sufficient quantity of the latter increases the mutual solubility of the other two to the point where complete miscibility is attained, as shown in Figure 1 (A) for the system acetic acid-isopropyl ether-water at 23–24°C. The binodal curve or “tie,” XYP, separating the one-phase and two-phase areas, is the locus of the ends of the tie lines. At P, the plait point, the tie lines have shrunk to a point. As applied to isothermal extraction for an unusually favorable situation, B is the original solvent for the solute A, and C is the extracting solvent. The extract lies on YP and the residual solution (raffinate) on XP. For a more common, but less favorable, situation the meanings of B and C are reversed. If the two-phase area is small then it is usually also shallow. Othmer and coworkers (1) observed that the plait point is located at a flatter portion of the binodal curve. While the curve is generally convex, a concavity can occur, as in the system water-sulfuric acid-diethyl ether (2) at 25°C, where chemical interaction between components takes place to some extent. (Such interaction does not destroy the ternary character of the system as long as the composition of all phases at thermodynamic equilibrium can still be expressed in terms of the original three components. In general, a quadrangle is needed to represent the isothermal behavior of truly reciprocal ternary systems, but, with the example mentioned, the composition range studied is confined to a triangle, thus making the latter an adequate means of representation.) It is clear, however, that a concavity cannot occur at the plait point for then the tie lines immediately adjacent to it would have to cross the one-phase area and so result in a contradiction. A symmetrical binodal curve, with a plait point near the apex of the triangle is rare, but observed in the system water-acetone-carbon disulfide at 20–21°C (3) when compositions are plotted in weight per cent. This system also possesses an isopycnic—a phenomenon to be discussed below.

The tie lines, when produced, intersect the side of the triangle on which the binodal curve is based only when that side is also extended, as shown in Figure 1. Alleged examples of tie lines intersecting the unextended side have, in several cases tested, been shown to be the result of impurities (4). Similarly, a tangent to the curve at the plait point does not intersect the unextended side. Alternatively, if straight lines be drawn from the plait point to all three corners of the triangle, only one of these fails to cross the corresponding two-liquid region. Meeting this restriction which, so far as is known, has no thermodynamic proof, requires considerable care in the construction of figures with two or three plait points. Such systems will be discussed below. In these the reverse relation also probably holds, viz., only one plait point can be reached by a straight line from any one corner without crossing its

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**Figure 1.** The system acetic acid(A)-isopropyl ether(B)-water(C) at 23–24°C.
own binodal curve. This correspondence of components (corners) with plait points suggests that more than three plait points are impossible. The slope of the tie lines usually changes steadily with increase in the quantity of distributed component (A). This is to be expected, at least for small additions of A, from the distribution law. In many systems the direction of change of slope reverses as the amount of distributed component increases (6); in a few systems, e.g., water-propionic acid-benzene at 40°C (6) there are at least two reversals. (It is worth observing, however, that changing from weight per cent to mole per cent composition coordinates not only changes the slopes of the tie lines but may even change their sign.)

In many two-phase areas there is, at a given temperature, one tie line connecting phases of equal density (an isopycnic). Total compositions anywhere on such a line have the same overall density as that of the phases. It may be noted that isopycnics are to be avoided in extraction processes, since settling of the layers is prevented. (An interesting lecture demonstration can be arranged by adding traces of colored substances to an isopycnic system in order to make the two phases readily distinguishable (7).) The system water-o-toluidine-propionic acid at 20°C (7) has two isopycnics such that the addition of propionic acid to the immiscible water-o-toluidine system causes the water-rich and o-toluidine-rich layers to change places twice before complete homogenization is attained.

By analogy with isopycnics there are also iso-optics—unique tie lines which join phase compositions that have the same refractive index for a given wave length of light. Such two-phase systems are usually colored. There may be a set of such iso-optics adjacent to each other, all giving differently colored pairs of layers. Figure 2 (8) shows a binodal area in the system benzene-nitromethane-n-heptane at 25°C to be covered with “colored” tie lines. Thus the complete tie line pattern can be observed colorimetrically. The colors are also temperature-sensitive.

The above description applies, in general, to systems which show two or even three separate binodal areas. In Figure 3 (9) for the system carbon dioxide(l)-methyl phthalate-n-heptane at 21-26°C under pressure, which is typical of many systems, the addition of the third component to the other two exerts an homogenizing effect if not too much is added; continued addition, however, can cause two liquid phases to reappear if the composition of the original mixture lies in a suitable range. Three separate binodal curves are also common if one is not limited to ambient pressures. To show the phenomenon at atmospheric pressure, however, components must be chosen so that the three binary critical solution temperatures are near together—a rare combination. The system ethylene glycol-nitromethane-lauryl alcohol at 29°C (10) is representative (see Fig. 10a, to be discussed later).

When a single two-phase region extends from one binary system to another, either as a result of the merging of two bites or, more commonly, from the enlargement of one bite until it reaches the other side of the triangle, a band results as in Figure 4 for the system furfural-water-ethyl acetate at 25°C (11). This situation is quite common. The short side of the band is often slightly concave. The slope of the tie lines crossing the band, although usually changing steadily as the triangle is crossed, can somewhat rarely reverse the direction of change, as in the system water-hydrogen bromide-n-heptane at 25°C (12).

There are also “island curves,” binodal areas completely surrounded by a one-phase area. These curves are smooth in their entirety, although occasionally drawn erroneously with discontinuities in slope. The three components, taken in pairs, may or may not be

Figure 2. The system benzene-nitromethane-n-heptane at 25°C showing structural colors: a, light blue; b, indigo; c, purple; d, lilac; e, magenta; f, brick red; g, amber; h, amber yellow; i, yellow.

Figure 3. The system carbon dioxide(l)-methyl phthalate-n-heptane at 21-26°C (under pressure).

Figure 4. The system furfural-water-ethyl acetate at 25°C. The dashed line is an isopycnic.
miscible. The island area will have two plait points. The phenomenon is often associated with the reversible formation of a soluble product of chemical reaction between two of the components. In the system water-acetone-phenol between 66° and 92°C (13) there is an island curve, but complete miscibility in all three binaries. The same is true for propionic acid-hydrogen bromide-n-heptane at 0°C (14). Here the island is almost triangular and nearly fills the entire diagram. In the system hydrogen chloride-water-dioxane at 20°C under pressure (14) there is an island near the dioxane corner of the diagram and a small bite on the opposite side near the hydrogen chloride corner as in Figure 5. The tie lines shown in this figure, and those in Figures 8, 9, 10, and 11 are speculative, but have been included for emphasis. It seems improbable that more than one island curve can exist in a genuinely ternary system: although two islands have been reported in the system aniline acetic acid-isooctane at 81°C (15) it would appear that the formation of aniline acetate is not rapid or reversible enough to maintain the true ternary quality of the system.

Three Coexisting Phases

At constant temperature and pressure three coexisting phases (three liquids, two liquids and one solid, one liquid and two solids, etc.) are represented by the corners of a scalene "internal triangle." Only the first two possibilities are pertinent to this discussion.

The coexistence of three liquid phases is illustrated by Figure 6 for the system carbon dioxide-water-phenol at 25°C (under pressure) (9), simplified for the present purpose by omitting the equilibria involving solid phenol. (Inclusion of the latter would have required a region for liquid saturated with solid phenol which would have interrupted, and reduced the size of, the miscibility gap based on the carbon dioxide-phenol side of the triangle.) Similar three-liquid regions are evident in Figures 10b and 11b described below.

The manner in which the borders of two areas, each denoting two-phase equilibria, make contact with a three-phase area is governed by the Schreinemakers rule (16) according to which the tangents of ac and bc at c in Figure 6, for example, must both lie within or both lie without the three-phase regions. The same must be true at the other corners of the internal triangle. This rule is valid regardless of the state of aggregation of the various phases. (Thus it applies to the well known isothermal solubility curves in ternary systems of two salts with a common ion and water at the point representing simultaneous saturation of liquid with two solids.) A proof of the rule is given by Schreinemakers (16) and by Williamson and Morey (17). Figure 7 illustrates an erroneous disposition of the isothermal solubility curves for two salts (B and C) with a common ion and water (A). The reader may wish also to examine Figures 8, 10b, and 11b for conformity with the Schreinemakers rule.

Examples in which the three coexisting phases are
two liquids and one solid are common, and arise, for example, when the components are two miscible or partially miscible liquids, and a solid which is soluble in both of them as in the system aniline-isoctane-naphthalene at 20°C (18). Systems in these categories also arise in connection with the process of salting-out, as with potassium carbonate-water-methanol at 25°C, shown schematically in Figure 8 (19).

The manner in which a change in temperature can cause two-phase regions to interact with each other has been a matter of speculation for some time. It is only recently that sufficient experimental data have been available to provide examples in support of the speculation. Three such types of interaction may now be distinguished: (1) external contact of two binodal curves at a "col," (2) external contact of two binodal curves at a "subcol," and (3) eruption of one two-phase area from within another.

The first of these modes arises when the two binodal areas first make contact at their plait points. This is illustrated in Figure 9a,b,c representing schematically the relations of the system nitrobenzene-methanol-isoctane at 15.0, 14.1 and 14.0°C (20). Points P₁ and P₂ are the plait points. The name col or saddle point, found at 14.1°C, derives from the appearance of the solid model obtained when a temperature axis is erected on the composition triangle. Careful experimental study has shown that at the col temperature the two curves which have just made contact, Figure 9b, do not have a common tangent as sometimes postulated, but appear as two nearly straight lines intersecting at a finite angle. Thereafter, the borders of the resulting band are highly concave but have no cusps, Figure 9c.

The second mode of contact arises when two binodal areas make contact involving only one of the two plait points. Figures 10a and 10b show schematically the sequence of events in the system nitromethane-ethylene glycol-lauryl alcohol at temperatures just above and just below the subcol temperature, 28.5°C, respectively (10). The subcol tie line ab, Figure 10a, splits to form the internal triangle a'ab' of Figure 10b. It is to be noted that one of the contacting curves—the one the plait point of which is not involved in the contact—

![Figure 9](image1.png)

![Figure 10](image2.png)
must be concave at the point where the merger occurs, in order not to contravene the Schreinemakers rule given above.

The third kind of behavior is shown in Figures 11a and 11b, which illustrate schematically the system nitroethane-ethylene glycol-lauryl alcohol (10) at temperatures just above and just below the temperature at which the new binodal area erupts from within the old, also a subcool temperature, 16.5°C. (The phase relationships are actually slightly more complex than shown, because of the presence of solid lauryl alcohol, m.p. 22.7°C. The equilibria involving this solid have been omitted from the diagram for simplicity, but the omission does not affect the liquid-liquid equilibria features under consideration.)

**Presence of a Fourth Substance**

The presence of small amounts of a fourth substance can exert a profound influence on the phase behavior of the other three. The location of plait points, for example, is very sensitive to impurities. The fourth substance is sometimes deliberately introduced in appreciable quantities by, for example, replacing one of the components of a ternary system by a solution of the fourth substance in that component. The system is now quaternary (21), but certain features of ternary systems may be retained under these circumstances.

Consider, for example, the use of an aqueous salt solution in place of pure water in the ternary system water-alcohol-acid. Let us suppose that the alcohol and water are partially miscible and that the addition of sufficient acid produces homogeneity, just as the addition of A in Figure 1 makes the partially miscible system B-C homogeneous. When the water is replaced by salt solution the triangular diagram is still adequate for expressing all compositions if the salt solution, alcohol, and acid are mixed in proportions such as to give a single liquid phase. When, however, the proportions are such as to give more than one phase (the only situation of interest in heterogeneous equilibrium) it is not, in general, possible to describe all the phase compositions in terms only of the three variables salt solution, alcohol, and acid, and therefore not possible to represent them by a point within the triangle—unless the salt/water ratio is the same in every phase as it is in the original solution represented by the corner of the triangle. The latter event is unlikely since the salt would tend to enter the water-rich layer to a greater extent than the alcohol-rich layer.

In spite of the inability to represent even two-phase equilibria, one can still plot "phase boundary curves" on triangular diagrams in such cases. These are curves resembling XYP of Figure 1. Total compositions lying outside of the "bite" area give a single phase of the same composition; total compositions lying within the area give more than one phase, but the compositions of these phases cannot be accurately represented since such phases are not ternary. As they cannot be plotted they do not necessarily lie on the phase boundary curve and, strictly, tie lines cannot be drawn across the area. The curve is not, therefore, a binodal curve, and the comments made earlier concerning the shape of binodal curves are not applicable to it. Nevertheless, it is possible to plot a plait point under these circumstances, since it, too, lies on the edge of an area of homogeneity.

Phase boundary curves frequently consist of reverse curves with concavities, as shown by Figure 12 for the system toluene-aqueous acetic acid- n-heptane at 25°C (21). When anhydrous acetic acid is used, the three components, acetic acid, toluene, and n-heptane, are miscible in all proportions, so the phase diagrams consist of an empty triangle. When 98% acetic acid (in water) is used, however, partial miscibility develops between the aqueous acid and the heptane. When 97% acetic acid is used partial miscibility also develops.
between the aqueous acid and the toluene, as seen in Figure 12. By regarding water as an impurity in this system one can readily appreciate the drastic influence on liquid-liquid equilibria of the presence of soluble impurities.

**Literature Cited**