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Binary systems which form crystalline compounds nearly always exhibit negative deviations from the ideal laws for liquid solutions of the type $G = N_1 G_1^0 + N_2 G_2^0$, where N is mole fraction and G may be volume, heat content, vapor pressure or fluidity. The deviations from ideality are often approximately parabolic functions of the molecular composition with the maximum deviation at or near 50 mole percent. In the case of fluidity this type of deviation is observed whatever the composition of the crystalline compound or compounds which occur in the system, leading to the conclusion that there is no correlation between the position of the maximum fluidity deviation and the composition of the crystalline compounds indicated by the freezing point curve. The bearing of this conclusion on the question of compound formation in the liquid is discussed.

BINARY systems which exhibit either maxima or binary reaction points[1] on the freezing point curves are said to form crystalline compounds, and it is usually presumed that the compound (or compounds) is also present to a greater or less extent in the liquid phase. Liquid solutions in such systems nearly always exhibit negative deviations from all the ideal mixture laws:

$$V < V_{ideal} = N_1 V_1^0 + N_2 V_2^0 \quad \text{(contraction)},$$
$$H < H_{ideal} = N_1 H_1^0 + N_2 H_2^0 \quad \text{(evolution of heat)},$$
$$p < p_{ideal} = N_1 p_1^0 + N_2 p_2^0,$$
$$\phi < \phi_{ideal} = N_1 \phi_1^0 + N_2 \phi_2^0,[2]$$

where $V =$ volume, $H =$ heat content, $p =$ vapor pressure, $\phi =$ fluidity (reciprocal of viscosity), $N =$ mole fraction, and the superscript zeros refer to the pure components.

The deviations from these ideal laws are usually approximately parabolic functions of the molecular concentration, and the deviation-composition curves are frequently approximately of the type shown in Fig. 1. Curves of this type for heat of mixing or for volume change on mixing are familiar,[3] and similar curves for vapor pressure deviations can be constructed from vapor pressure data in the literature. Fluidity deviation curves of this type will be given in this paper for the first time, and it will be seen (Figs. 3–14) that these curves are often nearly perfect parabolas, and more frequently so than are curves of heat of mixing and of volume change on mixing.

These deviation-composition curves can often be approximately represented by a function

$$\Delta G = k N_1 N_2,$$

which is the equation of a parabola symmetrical about the line $N_1 = N_2 = \frac{1}{2}$, the constant k being four times the ordinate of the maximum point. Biron[4] first applied this equation to volume changes on mixing, and later it was applied to heats of mixing by Baud.[5] A slightly variant form has recently been given a theoretical deduction for the heat of mixing in regular solutions.[6]

The discussion so far has concerned only negative deviations from the ideal laws. The opposite behavior, i.e., positive deviations from all the ideal laws, is the more common case and

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[1] The term binary reaction point is the more precise term which has been used in the literature recently to designate the melting point of an incongruent melting compound, the older term transition point being reserved for discontinuities in the freezing point curve due to a transition in one of the pure components. Fig. 10 illustrates both these types of discontinuities.

[2] The ideal mixture law for fluidity given above will be demonstrated both theoretically and experimentally in a forthcoming paper. A brief justification follows. It has been shown (Eyring, J. Chem. Phys. **4**, 283 (1936) and Ewell and Eyring, J. Chem. Phys. **5**, 726 (1937)) that flow can be considered as a unimolecular rate process in which the activation energy takes the form of providing a hole for the molecule to flow into. Flow in a binary mixture of liquids can be considered as analogous to two unimolecular chemical reactions which yield the same product proceeding simultaneously in the same vessel. This concept leads directly to the ideal law $\phi = N_1 \phi_1^0 + N_2 \phi_2^0$. As is the case with the other ideal laws, strict adherence is rarely observed.

[3] See Timmermans, *Les Solutions Concentrees* (Masson et Cie., Paris, 1936).

[4] Biron, J. Russ. Phys.-Chem. Soc. **41**, 569 (1909).

[5] Baud, Bull. soc. chim. 4, **17**, 329 (1915).

[6] Hildebrand and Wood, J. Chem. Phys. **1**, 817 (1933); Vold, J. Am. Chem. Soc. **59**, 1515 (1937).
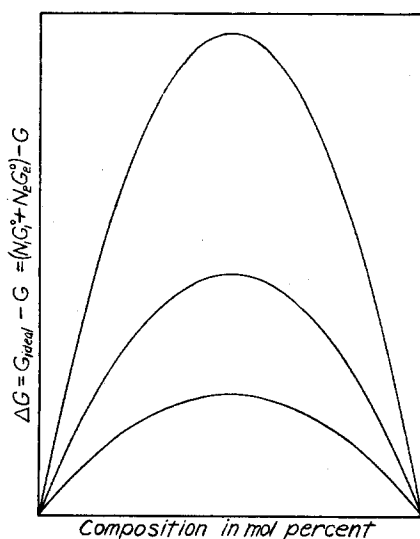
FIG. 1. Type of curves of the negative deviation of a property from its ideal value as a function of composition, where G may be volume, heat content, vapor pressure or fluidity.

FIG. 2. Types of viscosity composition curves given by binary systems which form crystalline compounds, either congruent or incongruent melting.

is exhibited by nonaqueous solutions of non-electrolytes, which have only a eutectic on the freezing point curve, e.g., benzene and carbon disulfide, hexane and ether, carbon tetrachloride and ethyl alcohol, etc. The deviations for these mixtures also have a parabolic form, but in the opposite sense from that shown in Fig. 1 since the observed values of the properties are greater than the ideal values. This type of mixture will be considered in the forthcoming paper mentioned in reference 2, and also aqueous solutions which occupy an entirely separate category.

The viscosity of binary mixtures which form crystalline compounds has been considered at some length by other writers.[7] The leading idea has been to interpret the frequently observed viscosity maxima in terms of compound forma-tion in the liquid. The matter was complicated by the fact that the maximum was practically never at the composition of the compound (or of one of the compounds) indicated by the freezing point curve, and also the position of the maximum usually shifted with temperature. Furthermore,

in other cases where the freezing point curve showed the formation of crystalline compounds there were no maxima at all observed in the viscosity curves, and sometimes the deviation from linear viscosity was actually negative, and sometimes an inflected curve with both positive and negative deviations was observed. Five types of viscosity-composition curves observed are shown in Fig. 2.

According to the view stated earlier, it is the fluidity that is the significant additive property, and if the fluidity is plotted against the molecular concentration, these five types of viscosity curves all give the same type of fluidity curve: uniformly negative deviations from linearity, with or with-out a minimum in the fluidity curve. The presence or absence of a minimum is of no significance since it is the deviation from ideal that is important, and if the fluidity deviations are plotted against the molecular concentration, fairly symmetrical parabolas result in all cases. This is illustrated in Figs. 3–14. The bottom curve in each figure is the freezing point curve, next the viscosity curve, next the fluidity curve,

[7] Thorpe and Rodger, J. Chem. Soc. **71**, 360 (1897); Dunstan, ibid. **85**, 817 (1904); **87**, 11 (1905); Thole, Mussel and Dunstan, ibid. **103**, 1108 (1913); Tsakalotos, Bull. soc. chim. [4], **3**, 234 (1908); Bramley, J. Chem. Soc. **109**, 10, 434, 469 (1916); Bingham, *Fluidity and Plasticity* (McGraw-Hill Co., New York, 1922); Kurnakov, Zeits. f. anorg. allgem. Chemie **135**, 81 (1924); Hatschek, *Viscosity of Liquids* (G. Bell and Sons, London, 1928).
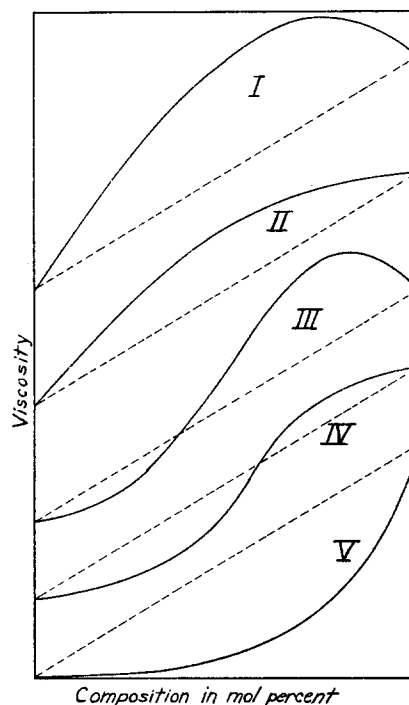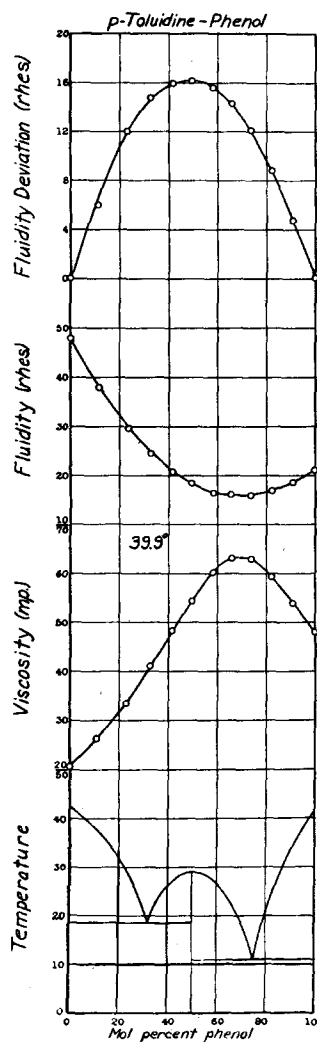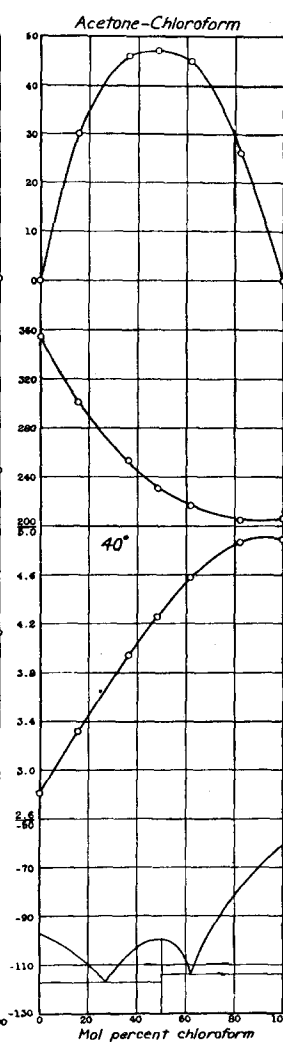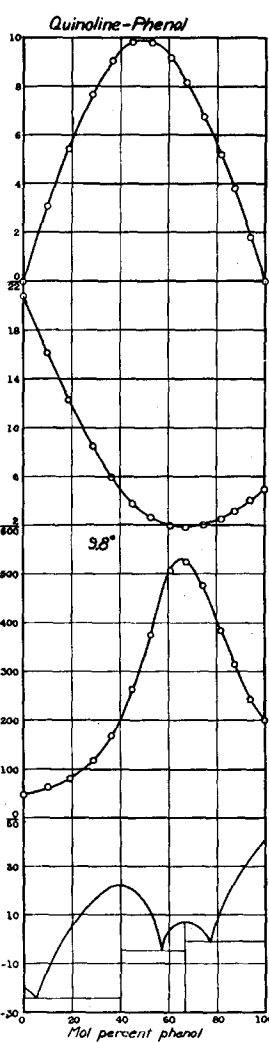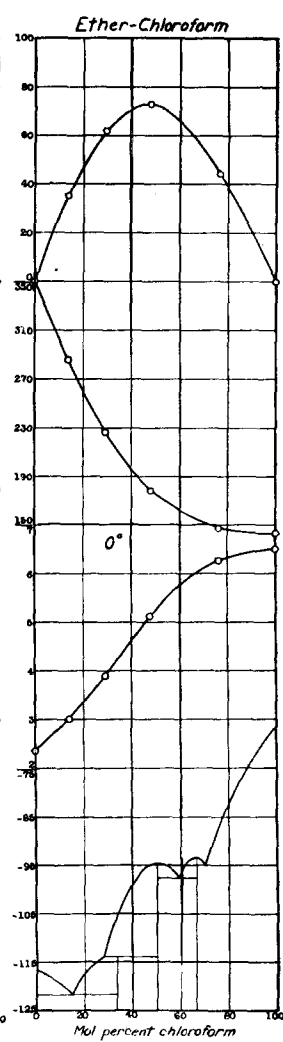
FIG. 3.   FIG. 4.   FIG. 5.   FIG. 6.

and at the top the fluidity deviation curve. It should be noted that the absolute fluidity deviation in rhes (reciprocal poises) is plotted, and not a fractional or percentage deviation.

Figures 3–5 have viscosity curves of type I, Fig. 6 of type II, Figs. 7–8 of type III, Figs. 9–10 of type IV, and Figs. 11–12 of type V. The viscosity curve in Fig. 13 is the trivial case of a straight line. The phase boundaries (not showing solid solutions) have been sketched in under the freezing point curves just to show the compound compositions better. Several types of phase diagrams have been included in the examples: single compound of 1 : 1 composition, single compound of other than 1 : 1 composition,

several compounds in the same system, and both congruent and incongruent melting compounds. The temperature of observation is given in the space between the viscosity and fluidity curves, and it is seen that part of the liquidus is often higher than this temperature, showing super-cooling, especially in mixtures containing phenols. For nearly all these mixtures viscosity data were available at several temperatures, but only one temperature is given in each figure, since the general features of the curves were similar and little was to be gained from the extra drafting involved. The data from which the figures were drawn were taken from various authors (largely those of reference 7) and are all contained in the
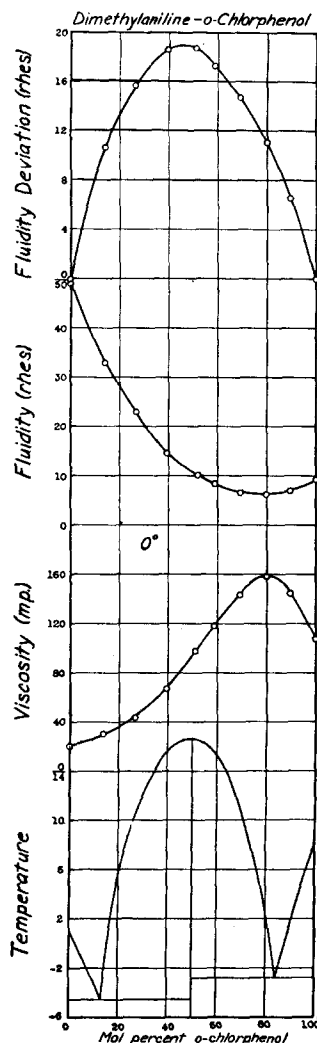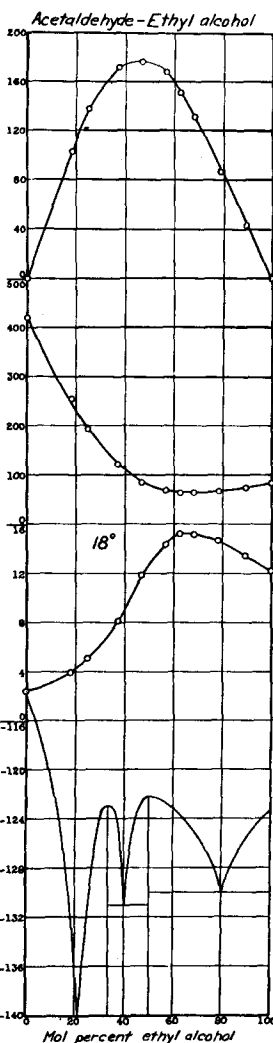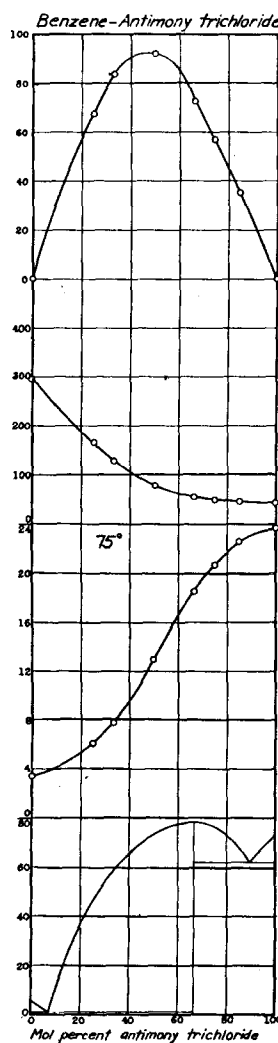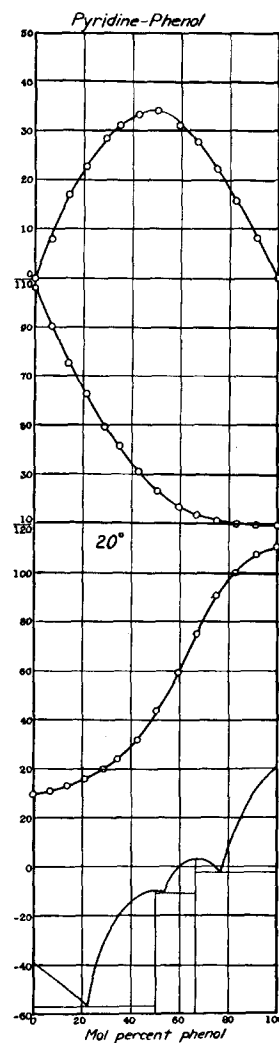
| FIG. 7. | FIG. 8. | FIG. 9. | FIG. 10. |

International Critical Tables, except the freezing point data for the systems acetone-carbon tetrachloride, benzene-carbon tetrachloride, and acetone-chloroform.[8]

Numerous examples of each of the five types of viscosity curves could be given, but the figures illustrate all the essential features, and any conclusions based on these examples can be considered as being supported by still others. Type V had been particularly troublesome to explain, but the apparent anomaly is clear when it is seen that *both* viscosity and fluidity curves deviate negatively from linearity. Kurnakov[7]

[8] Wyatt, Trans. Faraday Soc. **24**, 429 (1928); **25**, 43 (1929).

studied two cases of type V, naphthalene with *m*-dinitrobenzene and with *s*-trinitrobenzene, each of which form 1 : 1 compounds, and Hatschek[7] makes particular mention of these apparently anomalous cases. However, the fluidity curves for both these mixtures show negative deviations as would be expected.

The positions of viscosity maxima not only shift with temperature, but the maxima may disappear altogether, and the type of curve change from one temperature to another. For instance, the system pyridine-*p*-cresol gives a viscosity curve of type V at 0, 10, 20, 30°, type IV at 40°, type III at 60, 80, 110°, and dimethyl-aniline-*o*-chlorphenol gives a curve of type III at
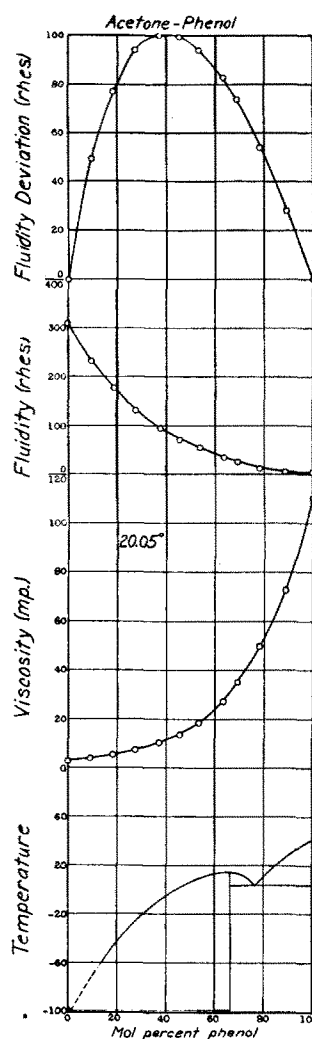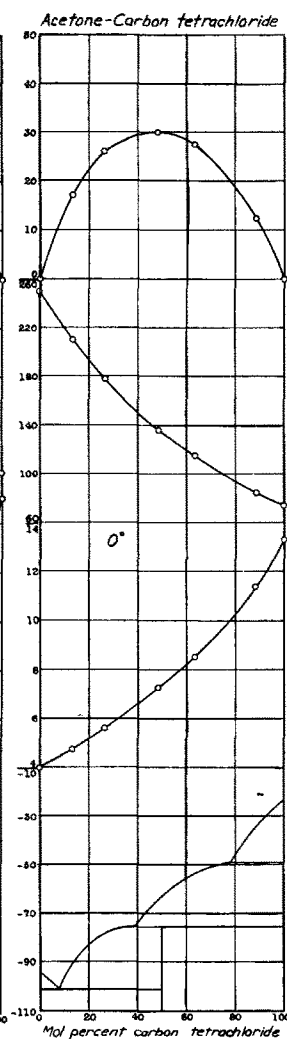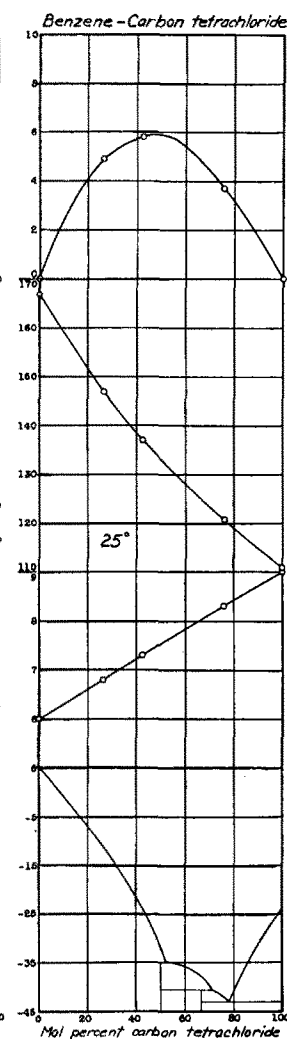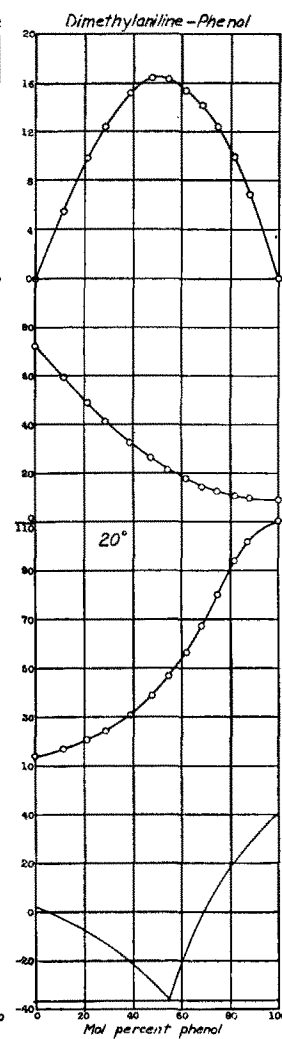
FIG. 11. FIG. 12. FIG. 13. FIG. 14.

0 and 10°, type I at 30, 40, 60, 80°, these irregularities disappear in the fluidity deviation curves. Kurnakov[7] had noticed in some mixtures that the maximum shifted towards the middle of the graph as the temperature was *lowered*, and so he made the generalization that the maximum did not coincide with the composition indicated by the freezing point curve, because the compound was partly dissociated in the liquid and that if the measurements could be made at a low enough temperature the maximum would occur at the expected composition. Bramley[7] made exactly the opposite observation on some other mixtures, namely, that the maximum shifted towards the middle of the graph as the temperature was

raised, and he was led to the opposite generalization. Fig. 15 illustrates Bramley's data for the system pyridine-*o*-cresol. The maxima on the viscosity curves are quite definite when they are plotted on a larger scale and the exact positions of the maxima are indicated by the small arrows. It is seen that the fluidity deviation curves are all of the same form and have their maxima at the same composition, about 46 mole percent *o*-cresol.

As far as the writer is aware there is not a single example of a system which has a congruent or incongruent melting crystalline compound or compounds which does not give a negative fluidity deviation. There are a very few exceptions to the converse of this generalization
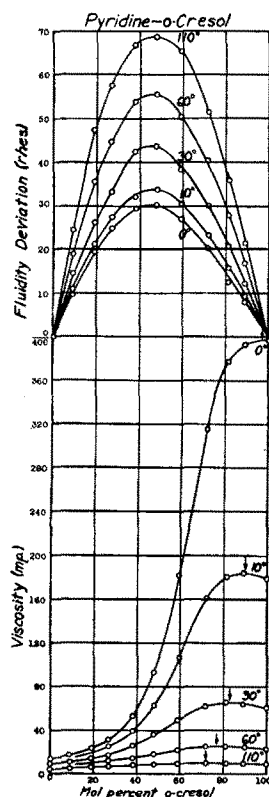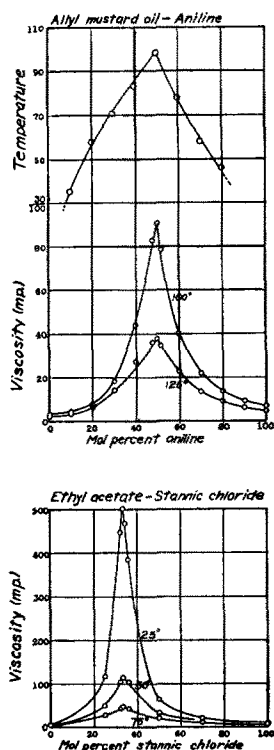
FIG. 15.

FIG. 16.

(omitting aqueous solutions which occupy a separate category), of which Fig. 14 illustrates one. It is very possible that the freezing point curve of this system does not represent true equilibrium, but is a metastable one. There are also a few exceptions to the rule that when the fluidity deviation is negative, the deviations in volume, heat content and vapor pressure are also negative. For example, the system benzene-carbon tetrachloride has a negative fluidity deviation and a small volume contraction, but a small heat absorption and a small positive vapor pressure deviation. However, Vold[6] has recently shown that the heat absorption in this system is much less than would be predicted by the theory assuming only van der Waals forces are active in the mixture.

A different type of viscosity-composition curve is that studied by Kurnakov for the two types of systems: stannic chloride with esters[7] and mustard oils with amines.[9] As shown in Fig. 16 the viscosity curves form sharp cusps at simple

[9] Kurnakov and Zemcuzny, Zeits. f. physik. Chemie **83**, 481 (1913); Kurnakov and Kwjat, ibid. **88**, 401 (1914).

molecular ratios. The freezing point curve for allyl mustard oil and aniline (also shown in Fig. 16) comes to a sharp point at the 1 : 1 composition in contrast to the rounded maxima of the freezing point curves in Figs. 3–12. The freezing point curves of stannic chloride and some esters have been determined by Kurnakov,[7] and it is hard to tell from the data whether they form intersections or sharp maxima at the 1 : 2 composition.

This type of freezing point curve is evidently associated with a more definite type of combination than are the maxima with zero slope at the compound composition. Mustard oils and amines react with great violence and considerable evolution of heat to give substituted thioureas, so that a complete rearrangement and the formation of primary valence bonds has definitely occurred. The reaction between stannic chloride and esters is also quite violent, but nothing is known of the nature of the product. Similar viscosity and freezing point curves would be expected whenever an addition reaction involving the formation of primary valence bonds takes place, e.g., mixtures of ethylene and chlorine. Such systems are characterized by the compound having a much higher melting point and viscosity than either of the end components, and is really two separate systems in one.

DISCUSSION OF THE FLUIDITY DEVIATION CURVES

According to the view stated earlier, any interpretations of the curves of Figs. 3–15 in terms of compound formation in the liquid must come from the fluidity deviation curves. The systems of Figs. 3, 4, 7 and 12 all have 1 : 1 crystalline compounds and the maxima on the fluidity deviation curves also occur at or near the 1 : 1 composition in each case. This would appear to confirm the old assumption that some of the compound exists in the liquid phase and gives rise to the maximum deviation from the ideal at the composition where the concentration of the compound would be greatest according to the principles of homogeneous equilibrium, namely the 1 : 1 composition.

However, Figs. 7 and 11 illustrate systems where the single crystalline compound is not an equimolecular one, and Figs. 5, 6, 8, 10 and 13

where there are several crystalline compounds, and in all these the maximum in the fluidity deviation curve occurs at or near the 1 : 1 composition. The system acetone-phenol shows the greatest variation from the 1 : 1 composition with the maximum at about 40 mole percent phenol. Numerous other examples of these types could be cited confirming this observation.

These observations lead to the conclusion that there is no correlation between the position of the maximum fluidity deviation and the composition of the crystalline compounds indicated by the freezing point curve. The negative fluidity deviation, usually accompanied by volume contraction, evolution of heat and a negative vapor pressure deviation shows that the net attractive forces are greater in the mixture than in the pure components, and the symmetrical character of the fluidity deviation curves for all these different systems is significant. It indicates that *if* a compound is present in the liquid it is the equimolecular one regardless of what the crystalline compounds in the system may be.

This brings up a long moot question: Is there compound formation or not in the liquid? For example, is an equimolar mixture of acetone and chloroform at $-90°$ composed of acetone molecules plus chloroform molecules plus a certain amount of acetone·chloroform molecules, or only molecules of the two end components? The former view has usually been tacitly assumed. In systems of the type shown in Fig. 16, compound formation involving primary valence bonds is quite definite, and the contrast between this behavior and that of the systems in Figs. 3–14 indicates that there is a difference of kind as well as of magnitude between the two types of systems.

If primary valence bonds are excluded, there remain hydrogen bonds, and dipole and van der Waals forces with which to explain the observed attractions. The negative deviations in the systems of Figs. 3, 5, 7, 8, 10, 11 and 14 can be explained by the formation of hydrogen bonds, oxygen or nitrogen donating electrons to hydroxyl or amino hydrogen. Glasstone[10] has discussed compound formation between tri- and tetra-halogenomethanes, and ethers and ketones. He concluded that there was a donation of electrons by ketone or ether oxygen to the hydrogen of

chloroform or bromoform (which seems improbable, but possible), and to a chlorine of carbon tetrachloride (which seems still more improbable). However, there still remain the mixtures of benzene with carbon tetrachloride and with antimony trichloride, and a more reasonable view of all these mixtures where hydrogen bond formation is not a factor is a geometrical one according to which the molecules in the mixture are able to pack more closely giving a reduction in volume and an enhancement of the van der Waals attraction.

Irrespective of possible explanations, the lower fluidity definitely indicates a more orderly structure in the mixture than would be present in a completely random mixture of the pure components, and an arbitrary definition of compound formation in the liquid could be given in terms of the magnitude of the free energy difference between the partially ordered state and the completely random state as compared to kT.

The enhanced attractive forces which give rise to negative deviations from the ideal laws are apparently also responsible for the formation of crystalline compounds, but the composition of the compound (or compounds) in the crystal appears to be dictated chiefly by steric considerations. Pairs of substances with identical functional groups often form different compound, for instance, acetone forms 1 : 1 compounds with catechol and hydroquinol, but a 2 : 1 compound with resorcinol; and methyl oxalate forms a 1 : 4 compound with phenol, a 4 : 1 compound with hydroquinol, and no compounds at all with catechol, resorcinol or pyrogallol. When several compounds are formed in a system, e.g., ether-chloroform, the same attractive forces are probably responsible for all the compounds being formed, but several molecular ratios are evidently geometrically convenient in the crystal. The same question arises here as in the liquid: Is the crystal a molecular lattice of acetone·chloroform molecules, or a molecular lattice of acetone molecules and chloroform molecules in equimolecular proportions? Obviously, a knowledge of the crystal structure of some of these addition compounds would throw some light on the nature of the liquid.

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[10] Trans. Faraday Soc. **32**, 200 (1936).