CRITICAL PHENOMENA IN BINARY SYSTEMS.[1]

By Fritz Friedrichs.

In connection with a comprehensive study of various solvates, especially the ammonates, it has seemed desirable to gain preliminary information concerning the behavior of these compounds, and of their solutions, in the neighborhood of the critical temperature of the more volatil component. An additional incentive was found, moreover, in the fact that the critical phenomena in solutions of inorganic salts have received but little attention in comparison with those in organic solutions.

The first investigators to study the critical temperatures of mixtures were Hannay, Cailletet, Villard, and their coworkers.[2] The principal purpose of their researches was to prove the applicability to solutions of Andrews' dictum concerning the continuity of the liquid and gaseous states. In view of the fact that an extended discussion of the older literature is to be found in an article by Centnerszwer, to which reference is made below, it has seemed sufficient for the purposes of the present paper to consider only the more recent literature of the subject. A large mass of facts relative to mixtures of two volatil components has been adduced by Kuenen, who has studied the critical phenomena of gas mixtures from the viewpoint of the work of van der Waals. Among the more recent investigators in the field are Walden, Centnerszwer, Smits, Büchner, Eggink, and Niggli.[3]

Walden and Centnerszwer have investigated the behavior of systems with a very difficultly volatil component, and have shown that, although the solvent power is in most cases retained even after transition into vapor, the ionization approximates zero. A decrease in conductivity had already been noted under somewhat similar conditions by Franklin and Kraus,[4] in the case of solutions of several inorganic salts in ammonia. Walden and Centnerszwer are, moreover, the first, and, singularly

[1] Presented by A. W. Browne at the Rochester meeting of the American Chemical Society, September 12, 1913.

[2] Hannay and Hogarth, *Proc. Roy. Soc.*, **29**, 324 (1879); **30**, 178 (1880); *Chem. News*, **41**, 103 (1880); Hannay, *Proc. Roy. Soc.*, **30**, 484 (1880); Cailletet and Colardeau, *Compt. rend.*, **108**, 1280 (1889); *Ann. chim. phys.*, [6] **18**, 269; Villard, *J. Physique*, [3] October 3 (1884); *Compt. rend.*, **120**, 182 (1895); *Ann. chim. phys.*, [7] **10**, 409 (1897); **11**, 289 (1897); *J. Physique*, [3] **5**, 453 (1897); Pictet, *Compt. rend.*, **120**, 20 (1895).

[3] Walden and Centnerszwer, *Z. physik. Chem.*, **42**, 432–68 (1903); Centnerszwer, *Ibid.*, **46**, 427–501 (1903); Centnerszwer and Pakalneet, *Ibid.*, **55**, 303–314 (1906); Centnerszwer and Zoppi, *Ibid.*, **54**, 689–706 (1906); Smits, *Z. Elektrochem.*, **9**, 663–8 (1903); *Z. physik. Chem.*, **51**, 193–221 (1905); **52**, 587–601 (1905); **54**, 498–509, 513–531 (1906); **67**, 454–63, 464–9 (1909); **76**, 445–9 (1911); Büchner, *Ibid.*, **54**, 665–688 (1906); **56**, 257–318 (1908); Eggink, *Ibid.*, **64**, 449–505 (1908); Niggli, *Z. anorg. Chem.*, **75**, 161–88 (1912); **77**, 321–34 (1912); see also Morey and Niggli, THIS JOURNAL, **35**, 1086–1130 (1913).

[4] *Am. Chem. J.*, **24**, 83–93 (1900), p. 88.

enough, up to the present time the only investigators who have made a complete study of the critical phenomena in a solution of an inorganic salt. As a part of this work, the T,X curve of the system potassium iodide–sulfur dioxide was determined. Centnerszwer showed that the molecular elevation of the critical temperature is independent of the nature of the dissolved substance. The complete diagram of systems with unlimited miscibility of the components in liquid form was studied by Smits for cases in which the solubility curve, throughout its entire course, lies beneath the critical curve, and for cases in which the two curves intersect. Büchner has extended the work to systems showing limited miscibility, and Eggink to systems in which compounds and mixed crystals appear.

Extensive experiments upon the solubility of numerous substances of widely different character in liquid ammonia were carried out by Gore[1] and by Franklin and Kraus,[2] both at —33° and also at temperatures somewhat above room temperature.

Classification.

In the T,X diagrams of binary systems two types of curve are to be distinguished: the solubility curve, which is to be regarded as the boundary line between solid and liquid; and the critical curve, which serves as the boundary between liquid and gas. In systems, the components of which in liquid form show a limited miscibility, a third type of curve appears, namely, the curve of heterogeneous liquids or the miscibility curve. From these facts arises a natural classification of all binary systems into two main groups, according as the components in liquid form are miscible or not.

A. In the case of *unlimited miscibility*, in which only the first two types of curve can appear, two subdivisions are to be recognized, as has already been pointed out by Smits.

(1) The solubility curve, throughout its entire course, lies beneath the critical curve, so that critical phenomena appear only with dilute solutions, and only between liquid and gas. The critical curve may be either a straight line connecting the critical temperatures of the two components; or it may be convex or concave; or it may even show a maximum or minimum, at which the composition of the liquid and gaseous phases are identical. This case is diagrammatically represented in Fig. 1, in which, as in all of the following sketches, no attempt has been made to show any of the numerous complex forms of solubility curve. In each case this curve is shown schematically in its simplest possible form. The fields of the liquid phases are represented by the shaded portions of the diagrams.

(2) The solubility of the system is so slight that the solubility curve

[1] Gore, *Proc. Roy. Soc.*, **20**, 44 (1872).

[2] Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898).

intersects the critical curve. The two points of intersection represent critical end points of the saturated solution. This possibility has been


Fig. 1.   Fig. 2.   Fig. 3.
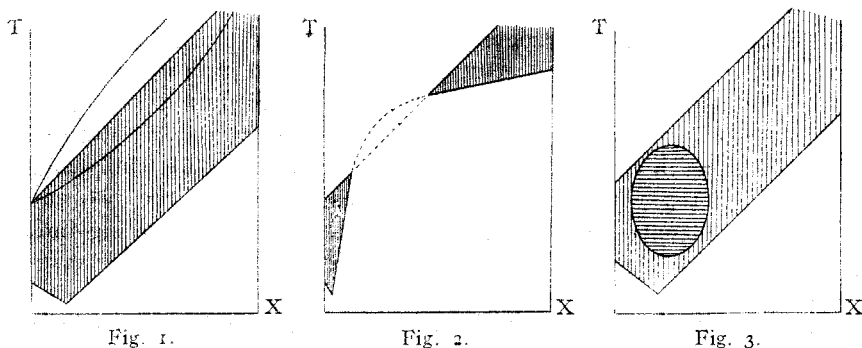
realized in the system anthraquinone–ether, and is schematically illustrated in Fig. 2.

B. In case the *miscibility* of the two components in liquid form is *limited*, so that the system shows all three types of curve, the phenomena become much more complicated. A classification into four subdivisions is possible according to the relative position of the various curves.

(1) The area enclosed by the miscibility curve lies entirely in the field of the dilute solution, and is therefore intersected neither by the solubility curve nor by the critical curve, so that both maximum and minimum (temperatures) of the miscibility curve are stable. This case, which is represented in Fig. 3, is illustrated by the system nicotine–water, which has been investigated by Hudson.[1]

(2) In case the area of limited miscibility is cut by the solubility curve so that the (temperature) maximum remains stable we obtain: (a) when the intersection is symmetrical, the very frequent case of melting under the solution (Fig. 4 or Fig. 5), as example of which may be mentioned the system *p*-toluidine–water; (b) when the intersection is asymmetrical, the

Fig. 4.   Fig. 5.   Fig. 6.
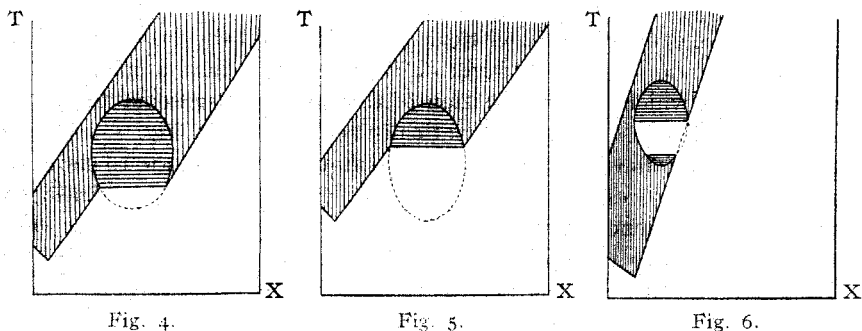
[1] *Z. physik. Chem.*, **47**, 113 (1904).

peculiar condition shown in Fig. 6. As may be seen from the diagram, one of the liquid phases becomes solid at the lower intersection, and then at the upper intersection again becomes liquid. Both maximum and minimum of the miscibility curve are seen to be stable in this case. No actual example of a case of this sort is as yet known.

(3) When the area of limited miscibility is cut only by the critical curve the maximum becomes metastable, while the minimum remains stable (Fig. 7). The number of examples of this type is relatively small,
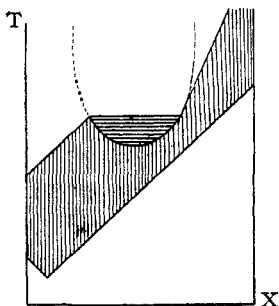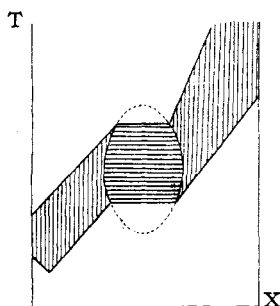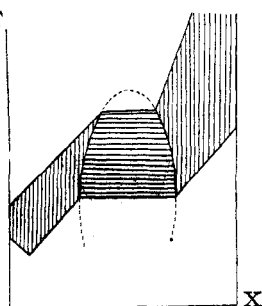

Fig. 7.   Fig. 8.   Fig. 9.

so that it is possible to discuss them briefly. The first case of this sort was discovered by Guthrie[1] for the systems di- and triethylamine–water. Rothmund,[2] in his extensive work upon the T,X diagram of two liquid phases, was able to add only the system β-collidin–water, while Kuenen and Robson[3] met with the same phenomenon in the systems ethyl, propyl, and butyl alcohol–ethane; Aten[4] in the system pyridine–methyl iodide; Büchner[5] in the systems chrysene–ether; thymol, nitrobenzene, and o-nitrophenol (respectively)–carbon dioxide; and Flaschner[6] in the systems methyl and ethyl piperidine–water.

(4) When the area of limited miscibility is cut by both the solubility curve and the critical curve both maximum and minimum become metastable. According to the location of the intersections, with reference to the points at which the coexisting liquid phases show the smallest mutual solubility, or, in other words, the points at which the miscibility curve reaches a (concentration) minimum, and according to the symmetrical or asymmetrical character of the intersections, the systems included in this fourth class may be further grouped into four subdivisions:

(a) The lines of intersection lie on both sides of the temperature of

[1] Phil. Mag., [5] 18, 500 (1884).

[2] Z. physik. Chem., 26, 433 (1898).

[3] Ibid., 28, 342 (1899).

[4] Ibid., 54, 124 (1905).

[5] Ibid., 54, 665 (1906).

[6] Ibid., 62, 493 (1908).

minimum miscibility, so that, with rising temperature, the mutual solu-
bility of the liquid phases first decreases and then increases (Fig. 8).
No example of this case is known at the present time.

   (b) The lines of intersection lie above these miscibility minima.   The
solubility, therefore, increases with rising temperature (Fig. 9).   As an
example of this case the system bromoform–carbon dioxide may be men-
tioned.[1]

   (c) The lines of intersection lie beneath the miscibility minima.   The
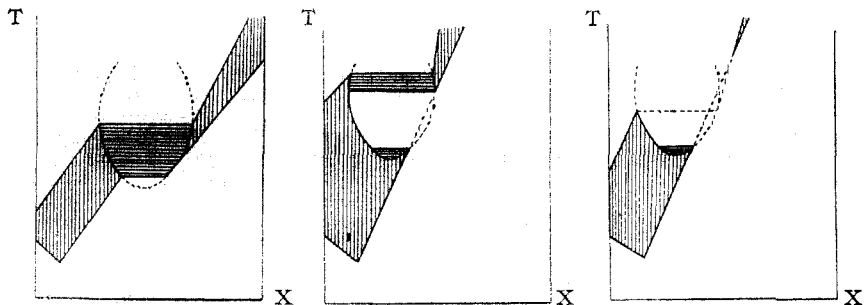solubility, therefore, decreases with rising temperature (Fig. 10).   As an

Fig. 10.   Fig. 11.   Fig. 12.

illustration may be mentioned the systems o-chlornitrophenol, m-chlor-
phenol, and urethane (respectively)–carbon dioxide.[1]

   (d) On the assumption that an asymmetrical intersection may occur,
the temperature minimum of the miscibility curve remains stable, as
shown in Fig. 11.   As in Group B_2b (Fig. 6), one of the liquid phases be-
comes solid at the intersection of the miscibility curve with the solubility
curve, and at the second intersection again becomes liquid.   In case the
solubility curve cuts not only the miscibility curve, but also the critical
curve (Fig. 12), the lower point of intersection is the only quadruple
point, while in place of the upper intersection appears a critical end point
of the saturated solution, entirely analogous to the upper intersection in
Group A_2 (Fig. 2).   As an example of this possibility may be cited the
system potassium iodide–sulfur dioxide, investigated by Walden and
Centnerszwer.[2]

   (5) In case the solubility curve intersects the critical curve, the entire
area of limited miscibility becomes metastable, and the T,X diagrams are
not to be distinguished from those of Group A_2 (Fig. 2).

   In all of the cases discussed above, approximate symmetry of the area
of limited miscibility is assumed, which, however, in many cases seems
not to be in harmony with the facts.   The miscibility (concentration)
minima might easily lie at different temperatures, so that, in the tem-

   [1] Büchner, Loc. cit.
   [2] Loc. cit.

perature interval between them, the two branches of the miscibility curve might be almost parallel. In such a case the thermal coefficient of solubility of each component in the other might be of different signs. It might be further possible that more than one area of limited miscibility, each with its pair of miscible liquid phases, could occur. A simple schematic representation of this case is shown in Fig. 13. From the
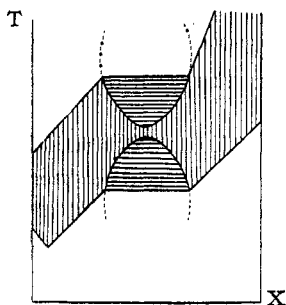

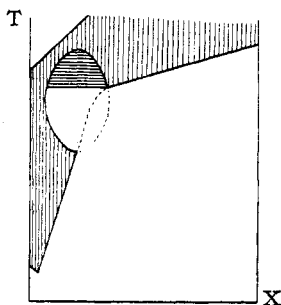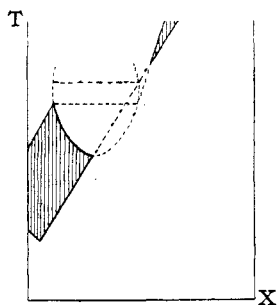Fig. 13.   Fig. 14.   Fig. 15.

great number of possible intersections obtainable in cases of this sort, it may well be possible to explain many of the irregularities observed in the form of actual miscibility curves.

Apparatus and Method.

The apparatus employed in the experiments was in principle the same as that used by Walden and Centnerszwer. A sample of the dried salt was introduced into a tube sealed at one end, and carefully dried ammonia or sulfur dioxide was condensed upon it by means of alcohol and solid carbon dioxide in the manner described by these authors. After the foreign gases had been pumped out, the tube was sealed. The tubes were made of glass obtained from Greiner and Friedrichs, of Stützerbach, Germany, and had an outer diameter of about 7 mm., with walls 1 mm. thick. Tubes of this sort have been found to withstand a pressure of from 120 to 130 atmospheres without danger of explosion. After each tube had been filled it was fastened upon a wheel, which with the aid of an endless cord could be caused to turn slowly at will.

Most of the experiments were carried on with solutions of various concentrations, although no great emphasis was laid upon the exact concentration, since for these experiments the concentration of the liquid phase only is of great importance, and this cannot be calculated with accuracy from the total concentration unless the pressure and the composition of the vapor are known. The experiments may, therefore, be said at the outset to be of a purely qualitative character, and to have been performed for the sole purpose of determining the group to which a given system belongs. The exact diagrams of the systems will be worked

out with the aid of a modified Cailletet apparatus, which is now in process of construction, and will be made the subject of a communication by the author in the near future.

Experimental Results.

Iodine.—Iodine crystals break up, when brought into contact with ammonia at low temperatures, into a reddish brown powder, which on warming dissolves, yielding a faintly yellow solution. From this solution, however, nothing separates again on cooling to —80°. At a temperature slightly above the critical point of ammonia the solution passes unchanged into vapor.

In sulfur dioxide, iodine is slightly soluble in the cold, but very readily soluble at higher temperatures. The solution shows a bright carmine red color, which gradually becomes more bluish with rising temperature, until finally at the critical temperature the violet color characteristic of iodine vapor is obtained. On cooling, abundant crystals, which from their appearance and color seem to be free iodine, separate from the solution. The absorption spectrum of the solution shows a wide band extending from red to violet.

Sulfur.—Rhombic sulfur, obtained by crystallization from carbon bisulfide, shows no solubility or reaction when brought into contact with liquid ammonia at low temperatures. Only when the sealed tube is allowed to warm up does a part of the sulfur dissolve, with formation of a bluish green solution, while the remainder deliquesces. When stirring is avoided, this yields a dark red liquid which readily mixes with the supernatant bluish green liquid, forming a solution of a peculiar dirty red and green color. This solution, which has more the appearance of a colloidal solution than that of a homogeneous phase, was treated with some ammonium chloride, which serves as an electrolyte, and was centrifuged for 15 minutes at a rate of 2400 r. p. m. in the hope of causing separation of the red liquid, but without any result whatever. Investigation with the ultramicroscope, and failure toobta in the Tyndall effect, showed that the solution was optically empty. It was, therefore, to be regarded as a true solution, at least in so far as failure of the Tyndall effect is to be construed as proof of the true character of solutions. Very dilute solutions are of a pure blue color, which changes to green and finally to the dirty red and green color noted above with increasing concentration. The absorption spectra of the very dilute solutions show a narrow absorption band in the yellow, which widens more and more toward the green with increasing concentration. With very high concentration of sulfur, there appears, together with the somewhat brightened wide band, a second sharply defined band in about the same position as that of the first band observed with very dilute solutions. On cooling to —80° neither precipitation nor essential color change could be noted.

When the tubes were heated the bluish green solutions showed no alteration, but retained their color, even after the critical temperature of ammonia was reached. The dirty red and green liquid, on the other hand, slowly assumed a bluish green color with rising temperature, and thereafter behaved like the more dilute solution. Among the other investigators[1] who have studied this system are Gore, Franklin and Kraus, Hugot, and Moissan. All of these investigators noted the red color of a solution of sulfur in ammonia, while Hugot noted also the bluish color mentioned above. Moissan found that a second liquid layer appeared when the solution was heated to higher temperatures, with gradual decoloration of the original solution.

Sulfur is but slightly soluble in liquid sulfur dioxide at room temperature, but is appreciably soluble at higher temperatures. It separates from the solution, on cooling, in the form of long, apparently monoclinic needles. At the critical temperature the solution passes unchanged into vapor.

Phosphorus (yellow).—Yellow phosphorus is only very slightly soluble in ammonia, even at high temperatures. After it has stood for several days, however, the phosphorus is observed to have undergone a change, with formation first of a red and later of a completely opaque reddish brown solution. Concerning the nature of this reaction, or concerning the possible influence of light upon it, nothing definit can as yet be said.

In sulfur dioxide yellow phosphorus is scarcely soluble, although it is somewhat soluble at higher temperatures, as indicated by the appearance of small yellow drops upon the walls of the tube on cooling. In the neighborhood of the critical temperature, the solution becomes somewhat turbid, with separation of a white precipitate. Whether this is to be regarded as an instance of retrograde solubility or as due to a chemical reaction cannot be declared with certainty.

Phosphorus (red).—Red phosphorus is insoluble in ammonia. Even at temperatures above the critical no reaction could be observed. In sulfur dioxide, on the other hand, it appears to be somewhat soluble at high temperatures, since, on cooling, a small amount of red powder (evidently unchanged red phosphorus) was precipitated on the walls of the tube.

Water.—Water[2] is very easily soluble in ammonia. At temperatures as low as —80° no separation of crystals was observed under the conditions of the experiments. The solution, under these conditions, becomes very viscous, and finally solidifies to a gel. On heating, the solu-

[1] Gore, *Proc. Roy. Soc.*, **20**, 44 (1872); Franklin and Kraus, *Am. Chem. J.*, **20**, 820–36 (1898); Hugot, *Ann. chim. phys.*, [7] **21**, 5–87 (1900); Moissan, *Compt. rend.*, **132**, 510–18 (1901).

[2] See Rupert, THIS JOURNAL, **31**, 866 (1909); **32**, 748 (1910); also Smits and Postma, *Chem. Zentr.*, **1910**, I, 1217.

tion passes unchanged into vapor. The miscibility of water with liquid sulfur dioxide is limited, so that at higher concentrations of sulfur dioxide two liquid phases appear, the consolute temperature of which lies at about 40°. On cooling, a solid hydrate, said by Roozeboom[1] to have the composition $SO_2.7H_2O$, separates. This solid melts at about 12°. At the critical temperature the solution passes unchanged into vapor.

Sulfuric Acid.—Approximately 99% pure sulfuric acid shows limited miscibility at room temperature with sulfur dioxide. The consolute temperature of the two liquid phases lies at about 140°. At the critical temperature the solution passes unchanged into vapor.

Ethyl Ether.—Ethyl ether and ammonia show limited miscibility at low temperatures, but the consolute temperature of the two liquid phases lies below room temperature, so that the components at higher temperatures show complete miscibility, which is also the case at the critical temperature.

Sodium Chloride.—Sodium chloride is moderately soluble in ammonia. With rising temperature the salt separates in the form of sharp octahedra, the solubility being therefore retrograde. It is stated by Joannis[2] that at —30° crystals with the composition $NaCl.5NH_3$ separate from a solution of sodium chloride in ammonia. As the result of a hitherto unpublished research conducted by Mr. I. E. Lee in this laboratory, it can be definitly stated that this compound does not exist, but that a compound of the formula $2NaCl.5NH_3$ may be obtained. Sodium chloride is insoluble in sulfur dioxide.

Sodium Bromide.—Sodium bromide is but slightly soluble in ammonia at low temperatures, but is very easily soluble at higher temperatures, and passes with the solvent into the vapor phase at the critical temperature.

Sodium Iodide.—Sodium iodide is more soluble in ammonia than the bromide, and, like this salt, passes with the solvent into the vapor phase at the critical temperature. The salt is appreciably soluble in sulfur dioxide. On warming, the solution separates into two liquid phases. At higher temperatures an irreversible reaction takes place.

Sodium Trinitride.—Sodium trinitride is readily soluble in ammonia, and comports itself at the critical temperature similarly to sodium bromide. In sulfur dioxide this salt is insoluble.

Sodium Sulfite.—Sodium sulfite is insoluble in sulfur dioxide.

Potassium Chloride.—At room temperature potassium chloride is distinctly more soluble in ammonia than at lower temperatures. At higher temperatures the solid salt separates out, indicating that the

[1] *Rec. trav. chim.*, **3**, 29 (1884); **4**, 66 (1885); *Z. physik. Chem.*, **2**, 449 (1888); Ostwald, *Lehrbuch*, **2**, II, 894–901.
[2] *Compt. rend.*, **112**, 337–9, 393 (1891).

solubility is retrograde. Potassium chloride is very slightly soluble in sulfur dioxide.

Potassium Bromide.—This salt is more soluble in ammonia than is the chloride. It separates out in the same way at higher temperatures. It is but very slightly soluble in sulfur dioxide.

Potassium Iodide.—In ammonia this salt is very readily soluble, and passes into the vapor phase with the solvent at the critical temperature. The salt is also very soluble in sulfur dioxide, yielding a deep yellow solution. At low temperatures orange-colored crystals separate from the solution. Two compounds with the respective composition $KI.4SO_2$, and $KI.15SO_2$ have been identified by Walden and Centnerszwer.[1] At higher temperatures the solution separates into two liquid phases. The temperature minimum of the miscibility curve was shown to lie at $77.3°$ by the investigators just named. At a temperature somewhat above this point, one of the liquids solidifies to a light yellow crystallin mass, which, on cooling again, liquefies. Concentrated solutions of the salt become turbid after a few days, while more dilute solutions are distinctly more stable.

Potassium Trinitride.—The solubility of potassium trinitride in ammonia, and the behavior of its solutions are very similar to those of potassium bromide. In sulfur dioxide the salt is but very slightly soluble. At $120°$ the salt was found to assume a yellow color, and to explode violently, with evolution of light.

Potassium Cyanide.—Potassium cyanide is slightly soluble in ammonia. On heating to $65°$ a deposition of crystals from the solution takes place. It is insoluble in sulfur dioxide, and on heating becomes coated with a light brown deposit, which does not disappear on cooling.

Potassium Cyanate.—This compound is but slightly soluble in ammonia, and is insoluble in sulfur dioxide.

Potassium Thiocyanate.—In ammonia this salt is very readily soluble, and passes into the vapor phase with the solvent at the critical temperature. It is readily soluble in sulfur dioxide. At $65°$ a second liquid phase appears, in the form of a yellow oil. At $150°$, as the result of some chemical reaction, a slight turbidity of the solution appears, which does not disappear on cooling.

Potassium Ferrocyanide.—This substance, which is insoluble in ammonia, becomes coated in the cold with a reddish brown film, which at higher temperatures turns blue.

Potassium Nitrate.—The salt dissolves with comparative difficulty in ammonia. Precipitation of the solid takes place when the solution is heated.

[1] *Loc. cit.*

Potassium Chlorate.—This salt is slightly soluble in ammonia, and is reprecipitated in the form of crystals at 100°.

Ammonium Chloride.—Ammonium chloride is rather readily soluble in ammonia at ordinary, but only slightly soluble at low temperatures. At about 80° the solution separates into two liquid layers. In sulfur dioxide the salt is insoluble.

Ammonium Bromide.—At ordinary temperatures ammonium bromide is very readily soluble in ammonia. At the critical temperature it passes with the solvent into the vapor phase. It is fairly soluble in sulfur dioxide. At 120° a second liquid layer appears. One of the liquids disappears at 155°, while at 160° the other is changed to a solid.

Ammonium Iodide.—This salt is extremely soluble in ammonia (as would appear from the fact that it deliquesces at atmospheric pressure and room temperature in a current of the gas). The solutions pass unchanged into the vapor state. In sulfur dioxide it is also very soluble, yielding solutions of a faint yellow color. At 40° yellow crystals separate from the solution, although, to judge from the yellow color still shown by the solution, the salt is appreciably soluble even at high temperatures. In the neighborhood of the critical temperature the solution assumes a faint violet color, which still persists after the liquid has been transformed into vapor. On cooling, the violet color disappears completely.

Ammonium Trinitride.—Ammonium trinitride is readily soluble in ammonia. A second liquid phase appears at 110°. With sulfur dioxide this salt forms a yellow oil which shows, with an excess of the solvent, a limited miscibility, thus yielding two liquid layers even at ordinary temperatures. At low temperatures this oil solidifies, forming yellow crystals. It was found impossible to determin the consolute temperature of the two liquids, since at 90° an irreversible reaction takes place, as the result of which the yellow oil is changed into a white, solid mass. On cooling, this does not go back into solution. A further study of this reaction will be undertaken in this laboratory in the near future.

Ammonium Thiocyanate.—This compound is extremely soluble in ammonia, as shown by its deliquescence in a current of the gas at ordinary pressure and temperature.[1] At the critical temperature it passes with the solvent into the vapor phase. In sulfur dioxide the salt is also very soluble. On heating to 100°, a yellow oil separates from the solution, while at 150° a reaction takes place with precipitation of an orange-colored solid mass, which does not go back into solution on cooling.

Ammonium Nitrate.—The solution of this extremely soluble (deliquescent) salt in ammonia has long been known under the name of Divers

[1] See Bradley and Alexander, THIS JOURNAL, 33, 15–24 (1911).

liquid.   On heating it to the critical temperature the solution passes unchanged into vapor.
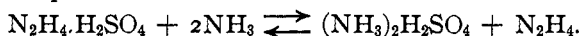
Ammonium Sulfate.—At ordinary temperatures this salt is insoluble in ammonia,[1] although forming with it the compound $(NH_4)_2SO_4.3NH_3$. On heating up to 145° no indication of the decomposition of this compound was observed.   The salt seems to be somewhat soluble at high temperatures.   With sulfur dioxide, under the prevailing conditions, the salt showed neither tendency to dissolve, nor to form a compound.

Ammonium Carbonate.—Ammonium carbonate is practically insoluble in ammonia at low temperatures, as has already been pointed out by Franklin and Kraus.[2]   At higher temperatures, on the other hand, its solubility is quite appreciable.   The solution passes unchanged into the vapor phase.   On cooling, the salt separates from the solution in the form of beautiful crystals.   An excess of the solid salt melts at high temperatures under the solution, forming a second liquid phase.   Since the critical temperature is reached before the two liquids become miscible, the temperature maximum of the miscibility curve is metastable.

Hydroxylamine Hydrochloride.—This compound is readily soluble in ammonia.   The solution separates at 120° into two liquid phases.

Hydrazine Monochloride.—In ammonia this compound is readily soluble, and forms at 105° two liquid phases.

Hydrazine Sulfate.—Hydrazine sulfate reacts with ammonia in accordance with the equation

$$N_2H_4.H_2SO_4 + 2NH_3 \rightleftarrows (NH_3)_2H_2SO_4 + N_2H_4.$$

Since the reaction is reversible,[3] and since hydrazine is very soluble in liquid ammonia, while ammonium sulfate is insoluble at low temperatures, the reaction proceeds quantitatively toward the right in presence of a large excess of ammonia.   For this reason a very high concentration of ammonia was used in the experiment.   It was found that at higher temperatures the voluminous precipitate of ammonium sulfate was partially redissolved, indicating that under these conditions the equilibrium was, to some extent, displaced toward the left.   In sulfur dioxide, neither reaction nor solubility could be observed.

Calcium Chloride.—This salt forms in ammonia its highest ammonate, $CaCl_2.8NH_3$, which was found to be insoluble even at high temperatures. No change in the appearance of this ammonate, that might point toward an inversion into a lower ammonate or into anammonous salt could be observed.

*Barium Nitrate.*—When ammonia is condensed upon barium nitrate

[1] Franklin and Kraus, *Loc. cit.*

[2] *Loc. cit.*

[3] See Browne and Welsh, THIS JOURNAL, **33**, 1728–34 (1911); Browne and Houlehan, *Ibid.*, **33**, 1734–42 (1911); Friedrichs, *Ibid.*, **35**, 244–7 (1913).

a reaction takes place, which is accompanied by a very noticeable swelling of the salt. The composition of this compound, which was found to be readily soluble in ammonia at room temperature, although soluble only with difficulty at low temperatures, cannot be stated at the present writing. On heating the dilute solution to 100°, a second liquid phase appears.

Mercuric Chloride.—Mercuric chloride dissolves with comparative ease in ammonia, but this solution is miscible with ammonia only within narrow limits, so that the use of an excess of ammonia results in the appearance of two liquid phases at room temperature. At low temperatures crystals appear, which according to Franklin[1] are of the formula $HgCl_2.12NH_3$, but which, from results obtained by the author, and soon to be published in detail, are of a composition represented by the formula $HgCl_2.6NH_3$. The composition represented by the formula assigned by Franklin approximates that of the system at the quadruple point, at which the two liquids, solid, and gas coexist. At higher temperatures, or with higher concentration of .ammonia, ammonolysis takes place, as described by Franklin, in accordance with the equation

$$HgCl_2 + 2NH_3 = NH_2HgCl + NH_4Cl.$$
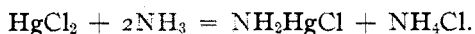
For this reason it was found impossible, without further precautions, to reach the consolute temperature of the two liquid phases. By slightly acidifying the solution with ammonium chloride, however, it was found possible to effect complete mixture of the liquids at 55° without appreciable ammonolysis. On heating to 60°, two new liquid phases appeared. By adding relatively large amounts of ammonium chloride, the consolute temperature of the first pair of liquids was lowered to such an extent that the two components were miscible in all proportions at room temperature.

Mercuric Iodide.[2]—At ordinary temperatures mercuric iodide is very slightly soluble in sulfur dioxide, but it is somewhat more soluble at higher temperatures. At about 130° the red salt undergoes inversion to the yellow modification, a process which is reversed at room temperature only after long standing. As the tube cooled, a small quantity of the solid separated out in the form of needles which were yellow at first, and later red.

Mercuric Cyanide.—In ammonia, mercuric cyanide is very readily soluble (deliquescent). No separation of a second liquid phase was observed to take place when the temperature was raised. In sulfur dioxide the salt is insoluble.

Mercurous Nitrate.—Mercurous nitrate dissolves partially at ordinary

[1] *Am. Chem. J.*, **47**, 361–97 (1912).
[2] See P. Niggli, *Z. anorg. Chem.*, **75**, 161–188; **77**, 321–334 (1912).

temperatures, with formation of a gray precipitate. A second liquid phase appears at 75°.

Cadmium Chloride.—This salt is insoluble both in ammonia and in sulfur dioxide.

Stannous Chloride.—With ammonia this salt forms a yellowish compound of but slight solubility. The solution separates at 120° into two liquid phases. An excess of the solid salt melts at about 100° under the solution.

Lead Iodide.—Lead iodide is insoluble in ammonia, and is but slightly soluble in sulfur dioxide, to which it imparts a faint violet tint. No formation of compounds was observed.

Lead Nitrate.—This salt is readily soluble in ammonia. The solution is resolved into two liquid phases at 45°.

Cupric Nitrate.—In place of the anhydrous (and anammonous) salt, the ammonate $Cu(NO_3)_2.4NH_3$ was used. This was prepared by crystallization, first from concentrated aqueous ammonium hydroxide solution, and then from anhydrous liquid ammonia. In order to remove the last traces of water from the blue powder thus obtained, the product was heated to 100° for 4 hours in a current of ammonia, in which it was finally allowed to cool to room temperature. It was found to dissolve readily in ammonia. The deep blue solution separates at 50° into two liquid phases, one of which becomes lighter in color as the temperature rises, while the other becomes darker. At 60° the darker-colored phase solidifies to a deep blue crystallin mass, which is evidently the tetrammonate. In the neighborhood of the critical temperature the upper liquid layer is almost colorless. On cooling, the solid phase again melts at 60° under the solvent, with formation of a second liquid phase. This case is of especial interest because of its adaptability for use as a lecture experiment in connection with the demonstration of critical phenomena of solutions.

Cupric Chloride.—The higher ammonates of this salt are the light blue hexammonate, $CuCl_2.6NH_3$, and the deep indigo-blue tetrammonate, $CuCl_2.4NH_3$. Since an inversion of the former into the latter ammonate beneath the pure solvent—the system is an insoluble one—would become manifest by a deepening of the color of the solid phase, and since, up to a temperature of 145°, no such color change was observed, it would seem reasonable to deny the existence of inversion points upon the dissociation curves in this system, at least below this temperature. Under a solution of ammonium chloride in ammonia the deep blue tetrammonate only is formed, probably because of the lower osmotic ammonia pressure. Even in this case, no inversion into the next lower compound, the green diammonate, could be observed when the temperature was raised.

Cupric Sulfate.—This salt, as is well known, forms with ammonia

compounds containing respectively five, four, two, and one molecules of ammonia. The pentammonate and the tetrammonate possess approximately the same ultramarine blue color, although the former is somewhat darker in color, and, to judge from the increase in volume during absorption of the last molecule of ammonia, somewhat lower in density. On heating, no solubility was noted, nor any tendency whatever toward inversion. In sulfur dioxide the salt is insoluble, and shows no tendency to form a compound. The white salt was observed to undergo no increase in volume, and no change in color.

Cuprous Thiocyanate.—This pure white salt takes on a brown color in ammonia, and forms a hexammonate, which is insoluble. In sulfur dioxide the salt remains white, and is found to be insoluble.

Cobalt Nitrate.—As in the case of cupric nitrate the ammonate was used in place of the anhydrous (and anammonous) salt. This reddish brown compound, which was prepared by the method used for the ammonated cupric nitrate, dissolves in a small amount of liquid ammonia, with formation of a deep red solution. When a large excess of ammonia is used, however, only a small amount of the substance goes into solution. In every case a brown precipitate was observed to form. Inasmuch as complete solution may be effected by acidification with ammonium nitrate, this precipitation is considered to be due to ammonolysis. At higher temperatures the brown precipitate gradually increased in amount, with decoloration of the solution.

Nickel Nitrate.—In this case also, as in that of copper nitrate and that of cobalt nitrate, the ammonated salt, which was prepared in the anhydrous condition by the method outlined above, was used. Contrary to the statement made by Franklin and Kraus,[1] who found the salt to be soluble in liquid ammonia with formation of a purple solution, the ammonated salt, which was obtained in the form of a violet, crystallin powder, was found to be completely insoluble in ammonia. Even at higher temperatures no tendency on the part of the salt to dissolve, or to undergo any change whatever, could be observed.

Silver Chloride.—In the cold, this salt is but slightly soluble in ammonia, although readily soluble at higher temperatures. From dilute solutions a second liquid phase separates at $75°$. An excess of silver chloride, or rather of the triammonate, $AgCl.3NH_3$, melts at $80°$ under the solution, with formation of a second liquid phase.

Silver Bromide.—Silver bromide is more readily soluble in ammonia than is the chloride. The solution separates at $105°$ into two liquid phases.

Silver Iodide.—This compound is the most soluble of the silver halides in liquid ammonia, and is moderately soluble even at low temperatures.

[1] *Loc. cit.*

No formation of a second liquid phase was observed when the solution was heated to 145°. Dilute solutions pass unchanged into the vapor phase at the critical temperature, while more concentrated solutions slowly diminish in volume up to the highest temperatures reached in the experiments.

Silver Trinitride.—So far as its solubility in liquid ammonia is concerned, this salt stands between silver bromide and silver iodide. The dilute solution appears to be rather unstable at high temperatures. Three tubes exploded with great violence at about 100°, but it was found possible to heat the fourth to 110°, at which temperature a second liquid phase was observed to appear. In sulfur dioxide the salt is scarcely soluble. At higher temperatures it becomes dark colored, with evolution of gas, and finally explodes.

Silver Nitrate.—In the cold, silver nitrate is but slightly soluble in ammonia, although more readily soluble at higher temperatures. At 110° the dilute solution separates into two liquid phases.

Discussion of Results.

The foregoing experimental data may be arranged as follows, in accordance with the classification proposed above (pages 1869 *et seq*):

A 1. Unlimited miscibility, with great solubility.—Iodine–, water–, sodium bromide–, sodium trinitride–, potassium iodide–, potassium thiocyanate–, ammonium bromide–, ammonium iodide–, silver cyanide-ammonia. Iodine–, sulfur–sulfur dioxide.

B 2. Limited miscibility, with stable temperature maximum on miscibility curve.—Ether–ammonia. Water–, sulfuric acid–sulfur dioxide.

B 3. Limited miscibility, with stable temperature minimum on miscibility curve.—Sulfur–, ammonium chloride–, ammonium trinitride–, hydroxylamine hydrochloride–, hydrazine monochloride–, barium nitrate–, strontium nitrate–, lead nitrate–, stannous chloride–, silver bromide–, silver trinitride–, silver nitrate–ammonia. Ammonium iodide–, ammonium thiocyanate–, potassium iodide–, potassium thiocyanate–sulfur dioxide.

B 4 a,b,c. Limited miscibility, temperature maximum and minimum unstable.—Ammonium carbonate–, silver chloride–ammonia. Ammonium trinitride–sulfur dioxide.

B 4 d. Limited miscibility, asymmetric intersection, stable temperature minimum.—Cupric nitrate–ammonia. Ammonium bromide–, potassium iodide–sulfur dioxide.

In attempting to classify systems that show a retrograde solubility (for example, such systems as sodium chloride–, potassium chloride–, potassium bromide–, potassium trinitride–, potassium cyanide–, potassium nitrate–, potassium chlorate–ammonia), certain difficulties arise. In these systems the salt begins to crystallize from the solution during

warming, even at temperatures considerably below the critical temperature of the solvent. This phenomenon might occur under suitable conditions in three of the groups in the classification given. In Group $A 2$ the separation of the solid salt at temperatures below the critical point of the solvent would be possible, and the solubility curve would in consequence be retrograde, in case the critical curve, which is intersected by the solubility curve, should show a minimum. This would also be possible in Group $B 5$. A third explanation of this phenomenon is based on the assumption that asymmetric intersections may occur. If the lower point of intersection of the solubility curve with the miscibility curve is located very close to the temperature minimum of the latter curve,— or practically coincides with it, so that the lower area of limited miscibility (Fig. 6) becomes infinitly small,— a solid phase will appear in place of one of the liquid phases, and the solubility curve will be partly retrograde. The simplest diagram of this sort is that shown in Fig. 14. The solid phase will, in this case, melt under the solution at the upper point of intersection. Since this melting under the solution has been observed in some of the systems studied, it would seem that the most reasonable explanation might be the mutual intersection of all three of the curves, as is characteristic of Group $B 4 d$, and is illustrated in Fig. 12. On this assumption the system would be best represented by the diagram shown in Fig. 15. This last case shows the transition between Group $B 4 d$, and Group $B 5$.

In most of the systems that show a limited miscibility of the components in liquid form, an approach toward horizontality of the solubility curve could be observed. Attention has already been called to this phenomenon by Büchner[1] and by Eggink.[1] The occurrence of a solubility curve, a part of which is nearly horizontal, may, in fact, be said to point pretty conclusively toward the existence in the system of an area of limited miscibility. On the other hand, the occurrence of such an area in a given system does not, however, necessarily indicate the existence of a partly horizontal solubility curve. In the system ammonium trinitride–ammonia, for example, which shows an area of limited miscibility, the solubility curve is apparently normal.

Summary.

(1) A classification of binary systems which is based upon solubility, miscibility, and critical relations has been proposed.

(2) A number of solutions of inorganic salts in liquid ammonia and in liquid sulfur dioxide have been investigated at temperatures varying between $-80°$ and $+160°$, and have been tentatively arranged in the proposed classification.

(3) The behavior of various ammonates that are insoluble in liquid

[1] *Loc. cit.*

ammonia has been studied at the critical temperature of ammonia, but no indication of decomposition has been obtained.

CORNELL UNIVERSITY,
  ITHACA, N. Y.

THE IONIZATION PRODUCTS FROM THE SALTS OF PHENOL-PHTHALEIN.

BY LUDWIG ROSENSTEIN AND E. Q. ADAMS.

1. Introduction.

Investigations of the properties of dissolved electrolytes, of mixed valence type, are complicated by the probable presence of intermediate ions. Determinations of the concentrations of such ions have been based upon measurements of properties which are modified by all the substances present. Neither measurements of conductivity, of density, of refractive index, of dispersive power, nor of freezing-point lowering and boiling-point raising, uniquely determin the concentration of any one of the substances present; but when one of these substances is colored, its color does uniquely measure its concentration. It, therefore, seems desirable to carry on an investigation of the concentration of intermediate ions by colorimetric measurements.

Most colored substances which might give intermediate ions in solution are unsuited to such measurements in a simple colorimeter, because two or more of the substances present in solution are colored. Cupric chloride, for example, may give three substances—the unionized cupric chloride, cupric ion, and intermediate ion—each of which has a color of its own. It has been found[1] that phenolphthalein is a dibasic acid whose solutions are colored only when the doubly charged ion is formed. As several methods exist for the determination of the concentration of un-ionized substances in the solution, phenolphthalein is entirely suited to an investigation of the concentration of its intermediate ion.

2. Substances Present in Colored Phenolphthalein Solutions.

In phenolphthalein solution, which has been partially converted to the colored form by the addition of alkali, the un-ionized acid and also its mono- and dibasic ions have been assumed to be present. These may each exist in an equilibrium of tautomeric forms, but as a change in hydrogen ion concentration does not affect these equilibria, all tautomeric modifications may be considered together. The un-ionized acid $(H_2C_{20}H_{12}O_4)$ will then be designated by H_2In; the intermediate ion $(HC_{20}H_{12}O_4^-)$ by HIn^-, and the divalent ion $(C_{20}H_{12}O_4^{--})$ by In^{--}. Only

[1] R. Wegscheider, Z. Electrochem., 14, 510 (1908); L. Rosenstein, THIS JOURNAL, 34, 1117 (1912).