$\Lambda_0 = 39.60$, $K = 0.92 \times 10^{-4}$; for lithium chloride, $\Lambda_0 = 40.00$, $K = 0.0133 \times 10^{-4}$. The general dilution law for sodium iodide in acetophenone then becomes: $c\gamma^2/1-\gamma = 24.82 \times 10^{-4} + 0.140 \times (c\gamma)^{.698}$.

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TERNARY SYSTEMS. II. SILVER PERCHLORATE, ANILINE AND WATER

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The high solubility of silver perchlorate in many organic liquids[2] which are themselves not soluble in water has suggested its use in the study of several ternary systems consisting of the salt, an organic liquid and water; such systems can usually be studied without great difficulty from the low temperature of the ternary eutectic point up to temperatures above the melting point of the organic liquid and water, so that nearly all possible phase complexes involving solid and liquid phases in three-component systems can be assembled without the requirement of a very large temperature range. The system consisting of silver perchlorate, benzene and water has been so studied at an earlier date.[2d] The system containing aniline, here reported on, adds a number of features not found in the system containing benzene, of which the most interesting are the occurrence of a number of additive compounds of silver perchlorate and aniline, the striking insolubility of some of these in water, the existence at various temperatures of four distinct composition areas in which liquid phases appear (although the co-existent liquids are never more than two in number) and the anomalous distribution of silver perchlorate between water and aniline; the salt is found wholly in the aniline phase, thus reversing the distribution relations which it shows between benzene and water,[2c] in which case it is found wholly in the water phase up to considerable concentrations.

The silver perchlorate was made from silver nitrate by precipitation as hydrous silver oxide, solution in perchloric acid and recrystallization. The aniline was prepared from a good grade of commercial material by distillation, the fraction distilling within 0.2° being taken and stored in brown bottles over solid potassium hydroxide. The melting point, as given in Table I, was —6.15°; samples used in other parts of the work were slightly less pure, melting at —6.25° to —6.3°. The analysis of solutions for silver perchlorate content was conducted according to Volhard's method, weighed samples being acidified and titrated with standardized ammonium thiocyanate solution in the

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[1] The material of this paper was contained in the thesis submitted by Rudolph Macy in partial fulfilment of the requirement for the degree of Doctor of Philosophy at New York University.

[2] (a) Gomberg, *Ber.*, **40**, 1867 (1905); (b) *Ann.*, **370**, 160 (1909). Hill, (c) THIS JOURNAL, **43**, 254 (1921); (d) **44**, 1163 (1922); (e) **45**, 1151 (1923).

presence of ferric alum; where the solvent was chiefly aniline, nitric acid was added to complete solution, the sample diluted to about 150 cc. and the titration conducted quickly in order to prevent the interference of a green coloration due to the oxidation of the aniline. In order to determine the composition of a ternary system it is necessary to know the proportion of one other component in addition to the silver perchlorate. This was accomplished for any ternary solution prepared at any temperature by taking a weighed quantity of it, adding known amounts of aniline or silver salt or both, sufficient to bring the composition within the area $C_6\,ts$ of Fig. 3 and allowing the system to come to equilibrium at 25°; a determination of the silver content of this solution gives a fixed point on the curve tS, which previously had been carefully determined, and permits the calculation of the water and aniline in the composition of the original solution. Invariant temperatures were obtained by means of the usual Beckmann freezing-point apparatus, using thermometers calibrated at the boiling point and freezing point of water, at the transition point of sodium sulfate decahydrate and at the temperature of a mixture of ether and solid carbon dioxide, taken as —78°. Solubility equilibria were obtained by stirring ternary mixtures in the same apparatus surrounded by large volumes of water at the desired temperature; where the temperature was considerably removed from that of the laboratory, Dewar flasks were used as the outer containers. For the work at 25° the various complexes were rotated in closed tubes in a carefully controlled thermostat.

The Three Binary Systems

Of the three binary systems on which the ternary system is built up, that consisting of silver perchlorate and water has previously been investigated;[3] it shows a binary eutectic at —58.2°, at which the solid phases are ice and a monohydrate, $AgClO_4.H_2O$, the solution containing 73.9% of the salt; the solubility rises to 86.5% at 42.6°, which is the transition point (redetermined) of the hydrate into anhydrous silver perchlorate. No additional data were sought for this system.

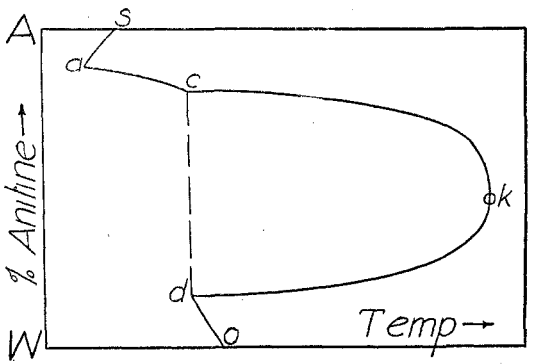

Fig. 1.—Solubility of water and aniline (schematic).

The binary system consisting of aniline and water has been studied by several investigators.[4] More particularly, the compositions of the two conjugate liquids (Curve *ckd*, Fig. 1) have been covered so completely that a repetition seemed superfluous. The mutual solubilities of the liquids at 25°, however, were carefully determined by a new method described under the discussion of the 25° isotherm, with the following results.

[3] Ref. 2 d, p. 1165.

[4] (a) Alexejew, *Wied. Ann.*, **28**, 305 (1886). (b) Rothmund, *Z. physik. Chem.*, **26**, 459 (1898). (c) Kolthoff, *Chem. Weekblad*, **14**, 1081 (1917). (d) Sidgwick, Pickford and Wilsdon, *J. Chem. Soc.*, **99**, 1124 (1911).

	% H_2O by weight	% Aniline by weight
Aqueous phase	96.34	3.66
Aniline phase	5.22	94.78

The figures are quite close to those found by Sidgwick, Pickford and Wilsdon[4d] who find 5.299% of water in the aniline phase and 3.68% of aniline in the aqueous phase. The solubility curves for the solid phases ice and aniline have been carefully repeated and the data are given in Table I and schematically in Fig. 1.

TABLE I

WATER AND ANILINE

Solid phase	Temperature °C.	Wt. % of $C_6H_5NH_2$	Points (Fig. 1)
Ice	0.00	0.00	*o*
Ice	− .28	1.42	
Ice	− .38	1.87	
Ice	− .51	2.575	
Ice	− .54	2.66	
Ice	− .665	(3.28)	*d* (quadruple point)
Ice	− .665	(95.64)	*c* (quadruple point)
Ice	− .570	96.42	
Ice	− 9.4	96.90	
Ice + $C_6H_5NH_2$	−11.7	97.17	*a* (eutectic point)
$C_6H_5NH_2$	−10.85	97.78	
$C_6H_5NH_2$	−10.02	98.32	
$C_6H_5NH_2$	− 8.87	98.98	
$C_6H_5NH_2$	− 8.41	99.16	
$C_6H_5NH_2$	− 6.15	100.00	*s*

The data for the curve *od* show that aniline has a normal molecular weight in aqueous solution, the average molecular weight being 94.8 when the constant 18.6 is used for water. The curve *as* shows water to be polymerized in aniline solution if its molecular weight is calculated with 58.7 as the freezing-point constant[5] for aniline, and the degree of polymerization increases with increase in concentration. The eutectic point *a* (—11.7°) is slightly higher than that found by Schreinemakers,[6] who gives approximately —12° as the temperature, the compositions not being determined by him. At the quadruple points *d* and *c*, the invariant temperature —0.665 was found, in close agreement with Schreinemakers' value —0.5°; the compositions were obtained by graphic extrapolation of the curves *od* and *ac*.

The binary system consisting of silver perchlorate and aniline has not been investigated before, and is here given completely up to the highest temperatures at which work could be conducted without too rapid oxidation of the aniline by the perchlorate. The results are shown in Fig. 2 and in Table II.

[5] Ampola and Rimatori, *Gazz. chim. ital.*, **27** (I) 35 (1897).

[6] Schreinemakers, *Z. physik. Chem.*, **29**, 581 (1899).

TABLE II

SILVER PERCHLORATE AND ANILINE

Solid phases	Temp. °C.	% $AgClO_4$ by wt.	% $C_6H_5NH_2$ by wt.	Density	Point (Fig. 2)
$C_6H_5NH_2$	−6.15	0.00	100.00	...	*s* melting point
$C_6H_5NH_2 + C_6$	−6.6	0.74	99.26	1.030	*o* eutectic point
C_6	25.0	5.00	95.00	1.063	
C_6	40.0	11.40	88.60	...	
C_6	50.1	17.0	83.0	...	
C_6	60.52	27.06	72.94	...	*c* congruent melting point
C_6	55.0	30.9	69.1	1.281	
$C_6 + C_3$	48.3	33.0	67.0	...	*d* transition point
C_3	56.1	35.0	65.0	1.401	
$C_3 + C_2$	66.6	38.4	61.1	...	*e* transition point
C_2	88	40.0	60.0	...	
$AgClO_4$	480	100.0	0.0	...	*f* melting point

The short curve *so* is the freezing-point curve of aniline, terminating at the eutectic point, *o*. The second solid phase appearing at this point is the double compound, $AgClO_4.6C_6H_5NH_2$, for which the abbreviation C_6 will be used hereafter. Its composition was determined from crystals obtained upon the solubility curve *oc* by filtering them on a Büchner fun-

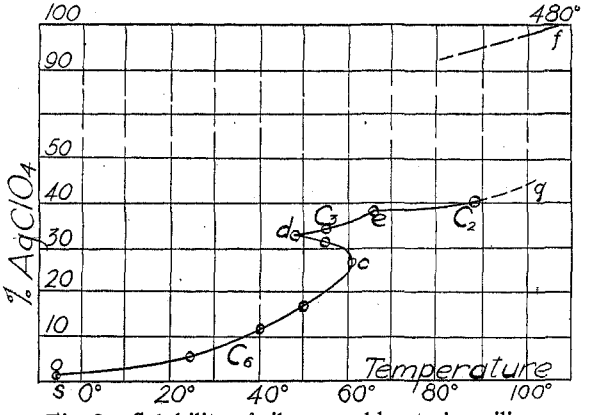

Fig. 2.—Solubility of silver perchlorate in aniline.

nel, freeing from excess of aniline by desiccation over sulfuric acid and analyzing for the silver content by Volhard's method; the silver perchlorate found was 27.03% and 27.08%; that calculated is 27.06%. Crystals which formed from the aniline solution on long standing attained large size and a quite remarkable regularity; a crystal measuring about 2 cm. × 1.5 cm. was the largest obtained. The crystals are not deliquescent in the air (their extremely low solubility in water in contrast with that of the pure perchlorate will be commented on later) and lose their aniline very slowly indeed. The solubility of the compound rises with the temperature as shown on the curve *oc*, until the crystals melt congruently at

60.52°. The two freezing-point curves *oc* and *cd* approach the congruent melting point *c* in such fashion as to make a distinctly sharp bend, which is evidence that the compound C_6 dissociates only slightly into its components upon fusion;[7] expressing the composition in terms of mole-per cent. instead of weight per cent. serves merely to accentuate the sharpness of the bend. The branch *cd*, representing the freezing point of the compound in the presence of an excess of silver perchlorate, is more nearly parallel with the horizontal line expressing the composition of the compound than is the branch *oc*, indicating that the effect of silver perchlorate on the freezing point is more pronounced than that of equivalent amounts of aniline; this result is doubtless connected with the fact that the silver perchlorate unites with aniline in the solution to form a new compound, $AgClO_4.3C_6H_5NH_2$, which appears as a solid phase at the point *d*, increasing the value of the molar fraction $N/N + n$, to which the depression of freezing point is proportional according to Raoult's law, by increasing the number of solute molecules N and at the same time decreasing the number of solvent molecules n according to the reaction, $AgClO_4.6C_6H_5NH_2 + AgClO_4 \longrightarrow 2(AgClO_4.3C_6H_5NH_2)$.

The point *d* in Fig. 2 represents a second eutectic point, at which the two solid phases are the hexa-aniline compound C_6 and the tri-aniline compound, represented by C_3. The composition of this latter compound was determined by analysis of samples obtained from the three-component system discussed later, where it could be obtained at lower temperatures and more easily freed from mother liquor. The solubility curve for C_3 is the line *de*, terminating at 66.6°, which is its transition temperature into the compound $AgClO_4.2C_6H_5NH_2$, called C_2. Solubility determinations of C_2 on the curve *eg* could not be carried much higher, as extensive oxidation of the aniline commences; at 120° the system begins to decompose violently, forming a residue of metallic silver and aniline black. At lower temperatures the odor of nitrobenzene is clearly detectable.

The compounds $AgClO_4.2C_6H_5NH_2$ (C_2) and $AgClO_4.C_6H_5NH_2$ (C_1) were both obtained from the ternary system, and although less stable than the compound C_6 could, nevertheless, be preserved at room temperature for considerable periods and gave analyses in fair agreement with the formulas. The initial change of composition is approximately 1% or 2% during the first few days. There are, therefore, four additive compounds of silver perchlorate with aniline, of which the latter two are too unstable at the temperatures of their equilibria with pure aniline to permit their solubility curves being included in Fig. 2.

The Ternary System

The 25° Isotherm.—The isotherm of the ternary system at 25° was the first part of the work to be completed, and has been used as a reference

[7] For references, see Findlay's "Phase Rule," Longmans, Green and Co., **1923**, p. 118.

isotherm throughout the investigation. In order to present the data of the complete system as briefly as possible, this isotherm will be discussed in some detail and the isotherms at other temperatures much more briefly by means chiefly of diagrams and tables.

The 25° isotherm is shown schematically in Fig. 3, using tri-linear coordinates. It may be most clearly viewed as consisting of a binodal or distribution curve, *gt–uv*, representing equilibrium between two liquid phases, which curve is cut by a solubility curve, *st–vz–ze–ec–cb–ba*, representing equilibrium between a single liquid phase and a solid phase. These two curves give rise to two separate areas where a single liquid phase exists (the unshaded areas L_1 and L_2 in the diagram) and to a number of triangular areas marked with numbers and representing in each case three phases plus vapor, that is, isothermally invariant equilibria. We will discuss in order the solubility curve, the distribution curve and the various isothermally invariant equilibria.

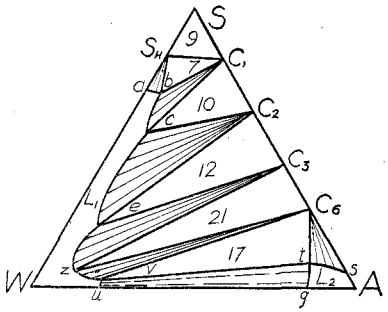

Fig. 3.—Silver perchlorate-aniline-water, 25° isotherm (schematic).

The curve *st* represents the solubility of the compound C_6 in solution consisting of aniline with varying amounts of water, and was carefully determined by weighing selected amounts of the three components into glass-stoppered cylinders, rotating in the thermostat at 25° and analyzing the liquid phase for its content of silver perchlorate. Test runs showed that equilibrium was reached in less than two hours. The total weights of solid phase and liquid phase present were calculated from the equation, $ax + b(w-x) = m$, where w is the total weight of the three components taken, x the unknown weight of the solid phase, a the percentage of silver perchlorate in the compound C_6, b the percentage of silver perchlorate found in the liquid and m the total weight of the silver perchlorate taken. When it is known that all the water taken is in the liquid phase and when the silver perchlorate content of the solution is likewise known by analysis, the aniline content follows. This section of the solubility curve was plotted on cross-section paper and served as a reference curve by which the composition of other ternary solutions could be determined, by adding the component necessary to bring them within the area C_6 *ts* and analyzing the solution for its silver content at 25°.

The data for the complete solubility curve are given in Table III, the four silver perchlorate—aniline compounds which occur as solid phases being represented by C_6,C_3,C_2 and C_1 as before, and the hydrate $AgClO_4 \cdot H_2O$ by the symbol S_H.

TABLE III

SOLUBILITY CURVE *sa* AT 25°

No.	Solid phase	Point (Fig. 3)	$AgClO_4$ Per cent. by wt.	$C_6H_5NH_2$ Per cent. by wt.	H_2O Per cent. by wt.	Density
1	C_6	*s*	5.00	95.00	0.00	1.063
2	C_6		7.18	91.56	1.26	....
3	C_6		8.00	90.00	2.00	...
4	C_6		8.48	88.92	2.60	1.096
5	C_6	*t*	9.42	86.34	4.24	1.106
6	C_6	*v*	trace	4.57	95.43	1.001
7	$C_6 + C_3$	*z*	trace	trace	100	...
8	C_3		1.02	trace	98.98	1.007
9	C_3		2.53	trace	97.47	1.018
10	C_3		5.94	trace	94.06	...
11	C_3		7.03	trace	92.97	1.059
12	$C_3 + C_2$	*e*	8.32	trace	91.68	1.066
13	C_2		10.7	trace	89.3	1.086
14	C_2		21.39	trace	78.61	...
15	C_2		28.55	trace	71.45	1.294
16	C_2		53.71	trace	46.29	...
17	$C_2 + C_1$	*c*	57.13	trace	42.87	...
18	C_1		60.02	trace	39.98	1.859
19	C_1		70.00	trace	30.0	...
20	C_1		81.3	trace	18.7	2.634
21	$C_1 + S_H$	*b*	84.22	trace	15.78	...
22	S_H	*a*	84.5	0.00	15.5	2.806

The solubility of the compound C_6 in the ternary solution is represented not only by the curve *st*, but also by the curve *vz*, which is separated from *st* by the intervening binodal curve. At the point *v*, however, which represents an aqueous solution with a small amount of aniline in it, the solubility of the salt has dropped to an amount too small to be detected even qualitatively; the addition of hydrochloric acid to the filtrate from the solid compound fails to produce a detectable precipitate, so that the surprising conclusion is justified that the double compound $AgClO_4$-$6C_6H_5NH_2$, in the presence of an excess of aniline, is as insoluble as silver chloride. Fig. 3 has accordingly not been drawn to scale, since curves upon the left-hand side of the diagram would be practically coincident with the axes *AW* and *WS*. No measurable quantity of silver perchlorate is found in the solution along the curve *vz*, but at the point *z*, which is an invariant point at which the compound C_3 is also in equilibrium, the amount of silver perchlorate is just sufficient to show a turbidity on treatment with HCl. The continuation of the curve, *ze*, is the segment in which the solid phase is the compound C_3, and represents an excess of silver perchlorate over that required to form the compound C_6; along this curve the solubility is again exceedingly small, so much so that no aniline can be found in the solution by Runge's test. It follows, therefore, that silver

perchlorate can be removed quantitatively from aqueous solution by the addition of aniline sufficient to bring the complex within the areas 17 or C_6 *vz*, while aniline may be removed quantitatively by addition of silver perchlorate sufficient to bring the complex within the areas 21 or C_3 *ze*. The solubility relations thus disclosed are being investigated with a view to their use in the analytical determination of aniline and other aromatic amines by means of silver perchlorate and other silver salts.

The compound C_3, when prepared from solutions along the curve *ze*, forms minute, milk-white needles which decompose in the course of a day into a black crystalline mass under a violet-colored solution which has an odor of nitrobenzene, but if they are filtered quickly from the solution and dried they may be kept for a year without extensive decomposition. Analyses gave the content of silver perchlorate as 45.5%, 41.6% and 43.9%, the formula requiring 42.6%; the variations are doubtless due to incipient decomposition during the brief contact with the solution.

The remaining segments of the solubility curve, *ec*, *cb* and *ba*, represent the compounds C_2, C_1 and S_H, respectively, in equilibrium with liquid phase; in none of these solutions is the aniline detectable by Runge's test. The compounds C_2 and C_1, which were not isolated during the study of the two-component system because the high temperatures promoted decomposition, were readily obtained from the ternary system at 25°, and show moderate stability when dry; for C_2 the analysis showed 53.6% of silver perchlorate as compared with 52.8% required, and for C_1 68.6% as compared with 69.01% required. The hydrate S_H has a short solubility curve, *ba;* it will be noted that uncombined silver perchlorate does not enter into equilibrium with any liquid phase at this temperature.

The distribution curve, *gt–uv*, representing the mutual solubility of aniline and water, rises from the base line *WA* until intercepted by the solubility curve. The data are given in Table IV.

TABLE IV

THE DISTRIBUTION CURVE (BINODAL CURVE) AT 25°

Aqueous phase (L_1)				Aniline phase (L_2)		
$AgClO_4$ %	$C_6H_5NH_2$ %	H_2O %	Point (Fig. 3)	$AgClO_4$ %	$C_6H_5NH_2$ %	H_2O %
0.00	3.66	96.34	*u* *g*	0.00	94.78	5.22
..	..	...		2.70	92.48	4.82
..	..	...		6.29	89.40	4.31
trace	4.57	95.43	*v* *t*	9.42	86.34	4.24

The points *u* and *g* give the mutual solubilities of aniline and water mentioned earlier. The two liquid layers obtained by agitation at 25° are so nearly of the same density that separation is very slow; they were permitted to stand at 25° for two weeks before analysis. The aniline phase (L_2) was then treated with a known amount of silver perchlorate

sufficient to bring the complex within the area C_6ts (Fig. 3) and analyzed for silver perchlorate, the dependent water content then being read from the curve *st*. The aqueous phase L_1 in turn was treated with sufficient silver perchlorate to bring it within the area C_2ce and analyzed for the content of silver perchlorate; from this the amount of silver perchlorate in the solid phase was calculated, and the amount of aniline present with it as $AgClO_4.2C_6H_5NH_2$ gave the amount of aniline in the original solution *u*. Similar methods were used for the other points on the curves *gt* and *uv*.

The aniline phase L_2 shows no marked peculiarities; with rise of salt content from 0% to 9.42% the solubility of water in the aniline falls only moderately. The aqueous phase L_1, however, is remarkable in that it contains no measurable concentration of salt; that is, the salt distributes itself so as to be found wholly in the aniline phase. Not only is this one-sided distribution found at this temperature, but it is also the case as high as 45°, at which temperature the presence of silver perchlorate becomes just apparent upon the addition of hydrochloric acid. This behavior is in direct contrast with the distribution of the salt between benzene and water,[2c] and also between toluene and water, in both of which cases it is found wholly in the water up to high concentrations. It seems likely that this anomalous behavior is connected in some way with the stability in solution of the three compounds, $AgClO_4.6C_6H_5NH_2$, $AgClO_4.H_2O$ and $AgClO_4.C_6H_5CH_3$;[8] these distribution relations are now being investigated in this Laboratory. A further striking fact for which there is no quantitative explanation is that in the aqueous phase the solubility of the aniline rises markedly from *u* to *v* although the total amounts of silver perchlorate in the phase are always too small to be determined. There must be extensive changes in vapor tension brought about by the presence of minute quantities of silver perchlorate, just as similar extensive changes of vapor tension and solubility of the various solid compounds are indicated along the curves *vz–ze–ec–cb–ba* (Fig. 3) by quantities of aniline all too small to be detected. Such cases emphasize the extensive variation from Raoult's law which are occasionally met.

The Invariant and Monovariant Equilibria, —58.8° to +66°.—The ternary system has been studied as a condensed system from the temperature of the lowest ternary eutectic point, —58.8°, up to +66°, above which decomposition is too rapid to permit accurate measurements. There have been found nine invariant systems (quintuple points) at which there are present in equilibrium a vapor phase and a total of four other phases, solid and liquid. At each of these quintuple points the phase reaction upon addition or subtraction of heat has been determined from the composition of the newly appearing phase; if its composition lies within the

[8] The system consisting of silver perchlorate, toluene and water has been studied and will be reported upon soon.

triangle representing the composition of the three pre-existing phases, the reaction is of the type shown at Quintuple Points A, D, E and G in Table V, while if it falls outside of this triangle reactions of the type of Quintuple Points B, C, F, H and I result; the reaction occurring upon

TABLE V

INVARIANT AND MONOVARIANT EQUILIBRIA IN THE TERNARY SYSTEM

Quintuple point °C.	Phase reaction	Monovariant equilibria		Termination	
A −58.8	$C_1 + S_H + W \rightleftarrows L_1$	d[a] 1	$S_H + C_1 + W$	(exists at lowest temperatures)	
		u 8	$S_H + W + L_1$	$\alpha = -58.2$	binary eutectic, $S_H + W$
		u 6	$C_1 + W + L_1$	$B = -57.8$	quintuple point
		u 7	$C_1 + S_H + L_1$	$H = +42$	quintuple point
B −57.8	$C_1 + W \rightleftarrows L_1 + C_2$	d 5	$C_1 + W + C_2$	(exists at lowest temperatures)	
		d 6	$C_1 + W + L_1$	$A = -58.8$	quintuple point
		u 10	$C_1 + C_2 + L_1$	(not traced above +25°)	
		u 11	$W + C_2 + L_1$	$C = -51.7$	quintuple point
C −51.7	$C_2 + W \rightleftarrows C_3 + L_1$	d 4	$C_2 + W + C_3$	(exists at lowest temperatures)	
		d 11	$C_2 + W + L_1$	$B = -57.8$	quintuple point
		u 12	$C_2 + C_3 + L_1$	$I = +48.7$	quintuple point
		u 13	$W + C_3 + L_1$	$\beta = -0.04$	consolute temperature $L_1 \leftrightarrows L_3$
D −12.0	$C_6 + W + A \rightleftarrows L_2$	d 2	$C_6 + W + A$	(exists at lowest temperatures)	
		u 16	$W + A + L_2$	$\gamma = -11.7$	binary eutectic, $W + A$
		u 15	$C_6 + A + L_2$	$\delta = -6.6$	binary eutectic, $C_6 + A$
		u 14	$C_6 + W + L_2$	$E = -0.67$	quintuple point
E −0.67	$C_6 + W + L_2 \rightleftarrows L_3$	d 14	$C_6 + W + L_2$	$D = -12$	quintuple point
		u 18	$C_6 + W + L_3$	$F = -0.08$	quintuple point
		u 17	$C_6 + L_2 + L_3$	$\phi = 45.8$	consolute temperature $L_2 \leftrightarrows L_4$
		u 19	$W + L_2 + L_3$	$\epsilon = -0.665$	quadruple point $W + A$
F −0.08	$C_6 + W \rightleftarrows C_3 + L_3$	d 3	$C_6 + W + C_3$	(exists at lowest temperatures)	
		d 18	$C_6 + W + L_3$	$E = -0.67$	quintuple point
		u 21	$C_6 + C_3 + L_3$	$G = +35.3$	quintuple point
		u 20	$W + C_3 + L_3$	$\beta = -0.04$	consolute temperature $L_3 \leftrightarrows L_1$
G +35.3	$C_6 + C_3 + L_1 \leftrightarrows L_4$	d 21	$C_6 + C_3 + L_1$	$F = -0.08$	quintuple point
		u 24	$C_6 + C_3 + L_4$	$\pi = 48.3$	transition point $C_6 \leftrightarrows C_3$
		u 22	$C_6 + L_1 + L_4$	$\phi = 45.8$	consolute temperature $L_4 \leftrightarrows L_2$
		u 23	$C_3 + L_1 + L_4$	$I = 48.7$	quintuple point
H +42.0	$C_1 + S_H \leftrightarrows S + L_1$	d 9	$C_6 + S_H + S$	(exists at lowest temperatures)	
		d 7	$C_1 + S_H + L_1$ ($= L_3$)	$A = -58.8$	quintuple point
		u 25	$C_1 + S + L_1$ ($= L_3$)	(not traced above 42°)	
		u 26	$S_H + S + L_1$ ($= L_3$)	$\lambda = 42.6$	transition point $S_H \leftrightarrows S$
I +48.7	$C_3 + L_1 \leftrightarrows C_2 + L_2$	d 12	$C_3 + L_1 (= L_3) + C_2$	$C = -51.7$	quintuple point
		d 23	$C_3 + L_1 + L_2$	$G = +35.3$	quintuple point
		u 28	$C_3 + C_2 + L_2$	$\phi = +66$	transition point $C_3 \rightleftarrows C_2$
		u 27	$L_1 + C_2 + L_2$	(not traced above 48.7°)	

[a] The letter "d" indicates equilibria running downward to lower temperatures and "u" those running upward to higher temperatures.

addition of heat is read from left to right. From each of these nine quintuple points there originate four monovariant (four-phase) equilibria; some of these terminate at other quintuple points by the formation of an additional phase, others at fixed points in the three binary systems by

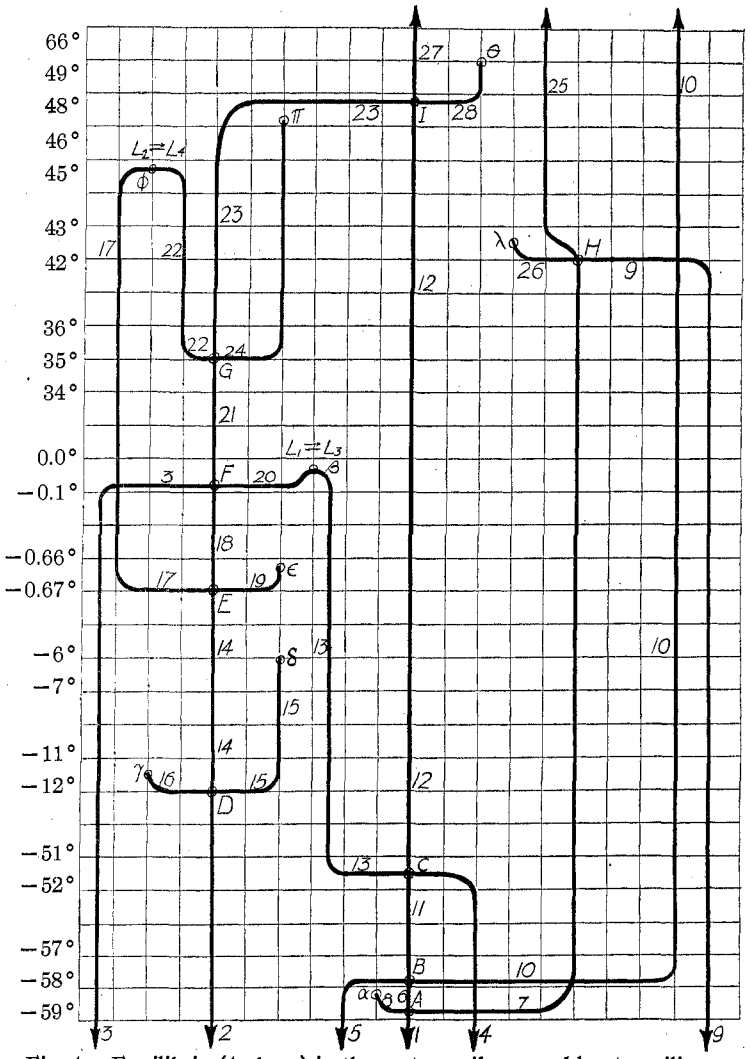

Fig. 4.—Equilibria (4-phase) in the system, silver perchlorate-aniline-water.

diminution of one of the components to zero concentration giving, therefore, a two-component invariant system, while four of them terminate in the ternary area through the coalescence of two liquid phases at consolute temperatures, which are invariant by the added restriction that two liquid

phases shall approach identity at these temperatures. The complete list of nine invariant and 28 monovariant equilibria is given in Table V; the quintuple points are indicated by Roman letters, the monovariant equilibria by Arabic figures, and the fixed points of the binary system and the consolute points by Greek letters. The symbols S_H, C_1, C_2, C_3 and C_6 have already been defined; in addition to these, S is used to indicate solid silver perchlorate, W for ice, and L_1, L_2, L_3 and L_4 for the ternary liquid phases appearing at various positions in the triangular diagrams.

Fig. 4 has been constructed so that the equilibria existing at any temperature may be read directly by noting the perpendiculars crossed by the horizontal corresponding to that temperature; the numbers upon the perpendiculars refer to the monovariant equilibria of Col. 3 of Table V. These equilibria have in most cases been studied at several temperatures between the points of their origin and their termini, and the analytical data of all ternary solutions occurring are given in Table VI which follows, in the order in which they appear in Table V.

TABLE VI

COMPOSITION OF TERNARY SOLUTIONS IN THE INVARIANT AND MONOVARIANT EQUILIBRIA

Point (Table V)	Temp. °C.	$AgClO_4$ %	$C_6H_5NH_2$ %	H_2O %	Density
		EQUIL. 8 ($S_H + W + L_1$)			
A	−58.8	73.88	trace	26.12	...
α	−58.2	73.98	0.00	26.02	2.345
		EQUIL. 6 ($C_1 + W + L_1$)			
A	−58.8	73.88	trace	26.12	...
B	−57.8	73.0	trace	27.0	...
		EQUIL. 7 ($C_1 + S_H + L_1$)			
A	−58.8	73.88	trace	26.12	...
	+25.0	84.22	trace	15.78	...
H	+42.0	86.20	trace	13.80	...
		EQUIL. 10 ($C_1 + C_2 + L_1$)			
B	−57.8	73.0	trace	27.0	...
	+25.0	57.1	trace	42.9	...
		EQUIL. 11 ($W + C_2 + L_1$)			
B	−57.8	73.0	trace	27.0	...
C	−51.7	71.7	trace	28.3	...
		EQUIL. 12 ($C_2 + C_3 + L_1$)			
C	−51.7	71.7	trace	28.3	...
	+25.0	8.32	trace	91.68	...
I	+48.7	L_1 = 1.24	0.10	98.66	...
		L_2 = 40.80	54.88	4.32	...
		EQUIL. 13 ($W + C_3 + L_1$)			
C	−51.7	71.7	trace	28.3	...
β	− 0.04	trace	trace	100.0	...

TABLE VI (*Continued*)

Point (Table V)	Temp. °C.		$AgClO_4$ %	$C_6H_5NH_2$ %	H_2O %	Density
		EQUIL. 16 (W + A + L_2)				
D	−12.0		0.88	96.82	2.30	1.042
γ	−11.7		.00	97.17	2.83	...
		EQUIL. 15 (C_6 + A + L_2)				
D	−12.0		0.88	96.82	2.30	1.042
	−10.5		.81	97.88	1.31	1.041
	− 9.6		.80	98.28	0.92	...
δ	− 6.6		.72	99.28	.00	1.030
		EQUIL. 14 (C_6 + W + L_2)				
D	−12.0		0.88	96.82	2.30	1.042
	− 7.8		1.30	96.36	2.34	...
	− 3.6		1.71	95.76	2.53	1.042
	− 1.6		1.95	95.38	2.67	...
E	− 0.67	L_2 =	2.10	95.29	2.61	...
		L_3 =	trace	4.79	95.21	...
		EQUIL. 18 (C_6 + W + L_3)				
E	− 0.67		trace	4.79	95.21	...
F	− .08		trace	trace	100	...
		EQUIL. 17 (C_6 + L_2 + L_3)				
E	− 0.67	L_2	2.10	95.29	2.61	...
		L_3	trace	4.79	95.21	...
	+25.0	L_2	9.42	86.34	4.24	1.106
		L_3	trace	4.57	95.43	1.001
φ	+45.8	L_2	26.4	69.6	4.00	...
		L_3	0.12	0.13	99.75	1.010
		EQUIL. 19 (W + L_2 + L_3)				
E	−0.67	L_2	2.10	95.29	2.61	...
		L_3	trace	4.79	95.21	...
ε		L_2	0.00	95.64	4.36	...
		L_3	.00	3.28	96.72	...
		EQUIL. 21 (C_6 + L_3 + C_3)				
F	− 0.08	L_3	trace	trace	100	...
	+25.00	L_3	trace	trace	100	...
G	35.3	L_3	0.06	0.05	99.89	1.011
		L_4	33.94	62.34	3.72	1.376
		EQUIL. 20 (W + C_3 + L_3)				
F	− 0.08	L_3	trace	trace	100	...
β	− .04	L_3 = L_1	trace	trace	100	...
		EQUIL. 24 (C_6 + C_3 + L_4)				
G	35.3		33.94	62.34	3.72	1.376
	43.0		33.10	65.21	1.69	...
π	48.3		33.0	67.0	0.00	...

TABLE VI (*Concluded*)

Point (Table V)	Temp. °C.		$AgClO_4$ %	$C_6H_5NH_2$ %	H_2O %	Density
		EQUIL. 22 ($C_6 + L_1 + L_4$)				
G	35.3	L_4	33.94	62.34	3.72	1.376
		L_1	0.06	0.05	99.89	1.011
ϕ	45.8	$L_4 = L_2$	26.40	69.6	4.0	...
		L_1	0.12	0.13	99.75	1.010
		EQUIL. 23 ($C_3 + L_1 + L_4$)				
G	35.3	L_1	0.06	0.05	99.89	1.011
		L_4	33.94	62.34	3.72	1.376
I	48.7	L_1	1.24	0.10	98.66	1.012
		L_4	40.80	55.10	4.10	...
		EQUIL. 25 ($C_1 + S + L_1$)				
H	42.0		86.2	trace	13.8	...
λ	42.6		86.5	trace	13.5	...
		EQUIL. 26 ($S_H + S + L_1$)				
H	42.0		86.2	trace	13.8	...
		(not carried further)				
		EQUIL. 28 ($C_3 + C_2 + L_2$)				
I	48.7		40.8	55.1	4.1	...
	66.6		38.4	62.6	0.0	...
		EQUIL. 27 ($L_1 + C_2 + L_2$)				
I	48.7	L_1	1.24	0.10	98.66	...
		L_2	40.80	55.10	4.10	...
		(not carried to higher temperatures)				

The various isotherms for temperatures between —58.8° and +66° are shown schematically in Figs. 5 to 27. From the isotherms and the data of Table VI it is possible to show all the phase reactions occurring

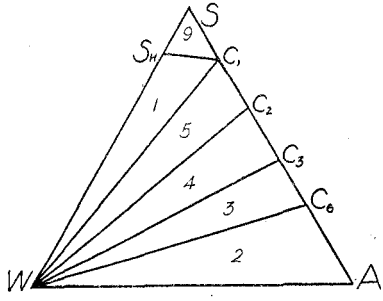

Fig. 5.—Isotherm below —58.8° (schematic).

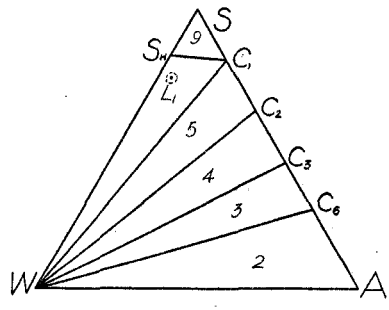

Fig. 6.—Quintuple point A, —58.8° (schematic).

at quintuple points and all the monovariant equilibria coming into existence and terminating within these temperatures, illustrating in a single

ternary system most of the phase relations which are known to exist in three-component systems. Since the relations are fairly obvious in most cases, comment will be limited to a discussion of the appearance and growth of the liquid areas with rising temperature. Liquid first appears at the lowest quintuple point, —58.8° (Fig. 6), its composition being represented by the dot and circle marked L_1; the liquid is high in salt

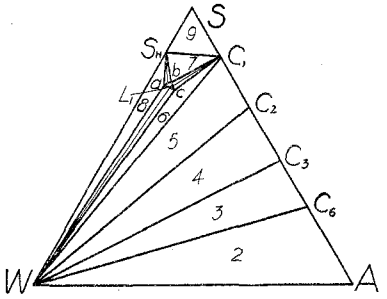

Fig. 7.—Isotherm above quintuple point A (schematic).

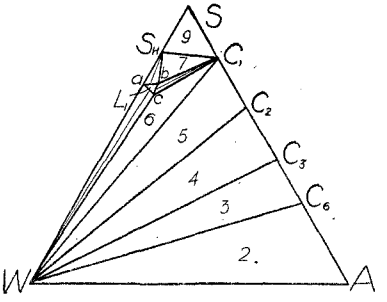

Fig. 8.—Isotherm at binary eutectic α, —58.2° (schematic).

content and extremely low in aniline content. With rise of temperature the liquid area extends downward rapidly (Figs. 7 to 11), always remaining however a narrow strip very close to the *SW* axis. At —12° (Quintuple Point D, Fig. 12) a second liquid area appears (L_2), which is essentially an aniline solution with a few per cent. of salt and mere traces

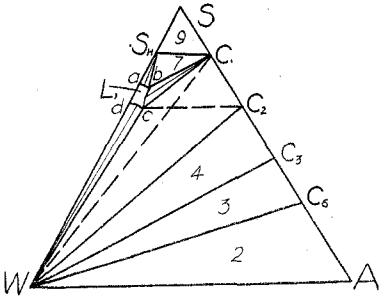

Fig. 9.—Quintuple point B, —57.8° (schematic).

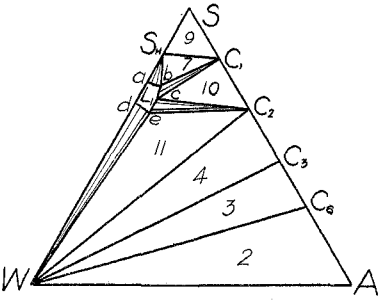

Fig. 10.—Isotherm above quintuple point B (schematic).

of water. This area also increases rapidly, both downward and upward, with rise of temperature. At —0.08° (Quintuple Point F, Fig. 18) a third liquid appears (L_3), essentially an aqueous solution saturated with aniline and containing too little salt to be measured. With rise of temperature the two liquid areas L_1 and L_3 approach each other (Fig. 19), meeting at the consolute temperature —0.04° (Fig. 20). This is a variant

from the method by which two liquids commonly coalesce in ternary systems, since it involves the termination of two monovariant equilibria (13 and 20) whereas commonly there is but a single monovariant equilib-

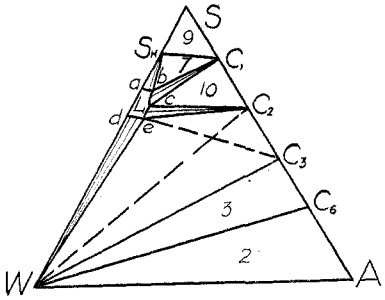

Fig. 11.—Quintuple point C, —51.7° (schematic).

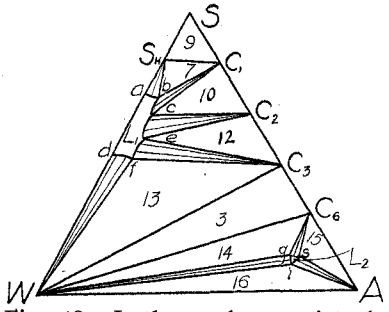

Fig. 12.—Isotherm above quintuple point D, —12° (schematic).

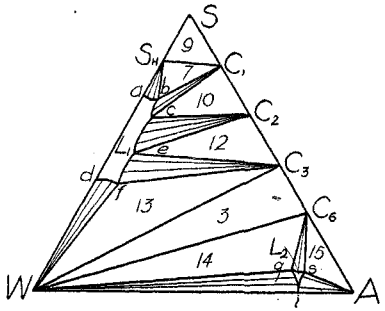

Fig. 13.—Isotherm at binary eutectic γ, —11.7° (schematic).

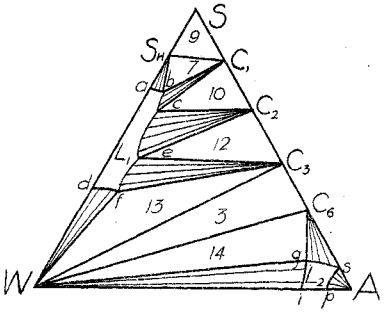

Fig. 14.—Isotherm at binary eutectic δ, —6.6° (schematic).

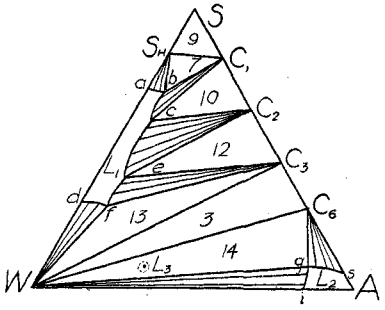

Fig. 15.—Quintuple point E, —0.67° (schematic).

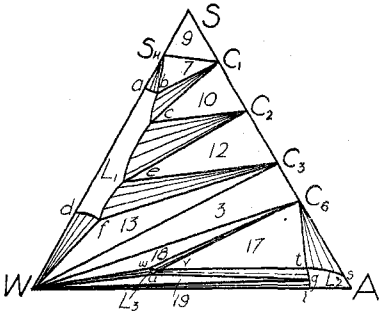

Fig. 16.—Isotherm above quintuple point E (schematic).

rium terminated (two liquids in equilibrium with a solid). Schreinemakers found such an instance at an earlier date[9] in the system consisting

[9] Schreinemakers, *Z. physik. Chem.*, **30**, 479 (1899).

of water, phenol and aniline. The left hand side of the binodal and solubility curve has now been completed (Fig. 20) from the point u representing the solubility of aniline in water up to the point b representing a high

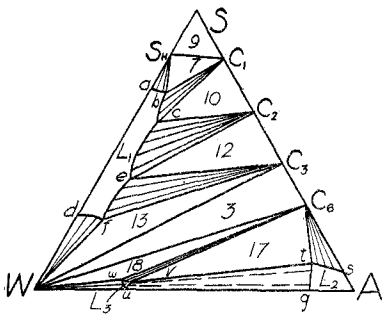

Fig. 17.—Quadruple point ϵ, —0.665° (schematic).

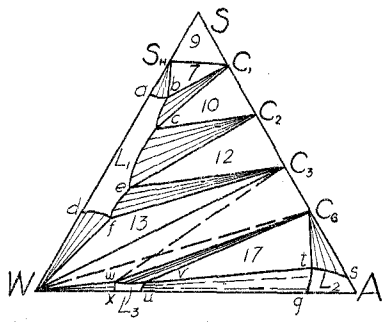

Fig. 18.—Quintuple point F, —0.08° (schematic).

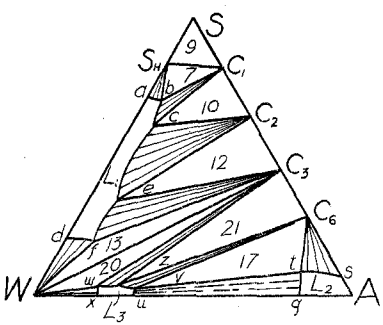

Fig. 19.—Isotherm above quintuple point F (schematic).

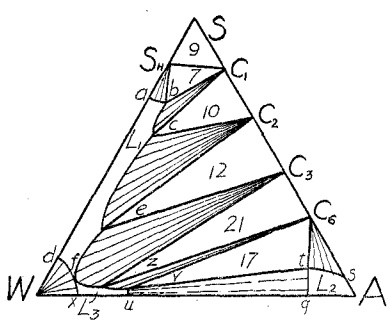

Fig. 20.—Consolute temperature β, —0.04° (schematic).

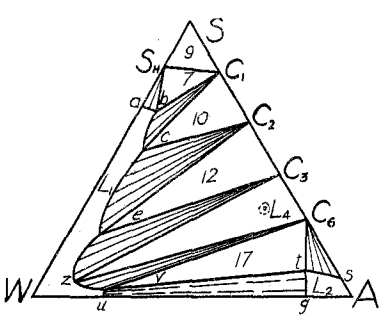

Fig. 21.—Quintuple point G, +35.3° (schematic).

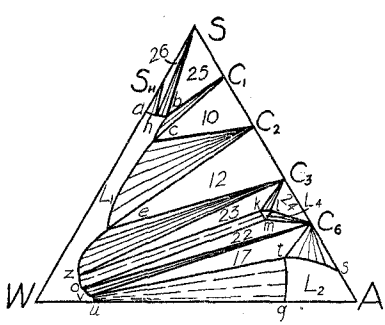

Fig. 22.—Isotherm above quintuple point H, +42° (schematic).

concentration of salt in the aqueous phase. Passing to higher temperatures, at 35.3° (Quintuple Point G, Fig. 21) a fourth liquid area appears (L_4), increasing its extent rapidly with rise of temperature until at 45.8° (Fig

23) it becomes consolute with L_2 by the termination again of two monovariant equilibria (22 and 23) and completes the right-hand side of the

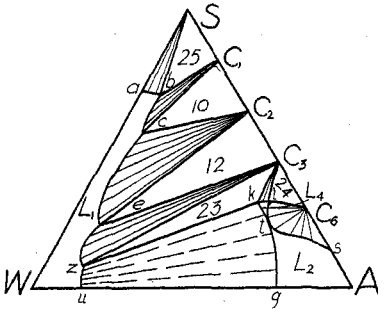

Fig. 23.—Consolute temperature ϕ, +45.8° (schematic).

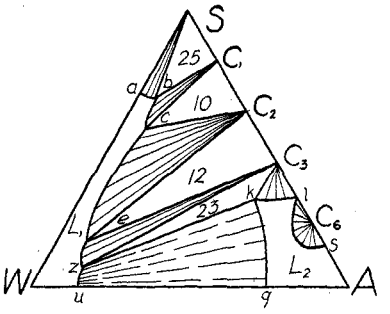

Fig. 24.—Transition temperature π, +48.3° (schematic).

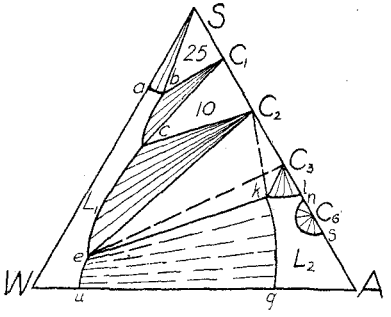

Fig. 25.—Quintuple point I, +48.7° (schematic).

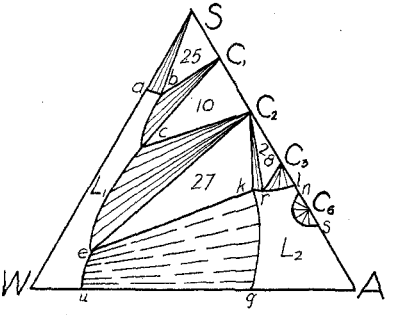

Fig. 26.—Isotherm above quintuple point I (schematic).

binodal curve. It seems probable that if higher temperatures could be attained without decomposition, the rise of the solubility curve (*ab–bc–ce–kl* in Fig. 27) would lead to another consolute point at which the liquids represented by *e* and *k* would coalesce and the binodal curve be complete.

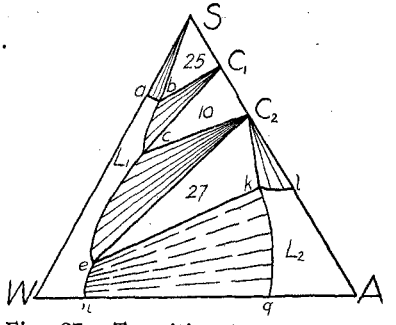

Fig. 27.—Transition temperature θ, +66.6° (schematic).

In the study of this system, a single binodal curve has been observed, and as a result there are never more than two liquid phases co-existent; where benzene was used instead of aniline, a second binodal curve appeared[10] and three co-existing liquids were observed. This behavior of the system containing benzene was attributed to the steep rise of the solubility

[10] Ref. 2 d, p. 1186.

curve of silver perchlorate in benzene, leading to a nearly perpendicular section such as occurs where a binary system forms two liquid phases. In the curve for silver perchlorate and aniline (Fig. 2) no corresponding rise is found, and no corresponding binodal curve appears in the ternary system.

Summary

1. The system consisting of silver perchlorate and aniline has been studied from the eutectic at —6.6° to temperatures slightly higher than 70°, at which extensive decomposition occurs. Four new compounds have been described, namely, $AgClO_4.6C_6H_5NH_2$, $AgClO_4.3C_6H_5NH_2$, $AgClO_4.2C_6H_5NH_2$ and $AgClO_4.C_6H_5NH_2$. Of these only the first is stable in contact with the solution at ordinary temperatures, and has been shown to have a congruent melting-point at 60.52° and a transition point at 48.3°. The other three compounds have been isolated from the ternary system, but not wholly pure. The transition point of $AgClO_4.3C_6H_5NH_2$ is 66.6°; the temperatures for the last two compounds were not obtainable.

2. The system consisting of water and aniline has been studied and the results of previous workers amplified.

3. The ternary system consisting of silver perchlorate, water and aniline has its eutectic at —58.8°, and in a rise of temperature to 66.6° nine invariant equilibria were realized and studied with 28 monovariant equilibria originating from them.

4. Isothermal diagrams have been drawn to represent schematically the equilibria existing in the above-mentioned temperature range.

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ADSORPTION BY ACTIVATED SUGAR CHARCOAL. I. PROOF OF HYDROLYTIC ADSORPTION[1,2]

BY ELROY J. MILLER

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It has been the object of many investigations to determine whether hydrolysis of electrolytes is increased during adsorption from solution by charcoal. It is unnecessary to review in detail the many discrepancies and contradictory results and conclusions existing in the literature on this subject. It is sufficient to state that recent general conclusions arrived at are (1) hydrolysis of electrolytes is not increased during adsorption and (2) when a solution is more acid or more alkaline after ad-

[1] Published by permission of the Director of the Michigan Agricultural College Experiment Station.

[2] Presented at the Milwaukee meeting of the American Chemical Society, September, 1923.