free azido-dithiocarbonic acid against standard alkali, with methyl red as indicator; (2) gravimetric determination as silver azido-dithiocarbonate, or as silver chloride; (3) titration with standard silver nitrate solution after the method of either Gay-Lussac or Volhard; (4) titration with standard alcoholic iodine.

Of these, the Volhard method is the one adjudged best for use under ordinary circumstances.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

TERNARY SYSTEMS. III. SILVER PERCHLORATE, TOLUENE AND WATER

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Silver perchlorate, toluene and water give rise to equilibria resembling in many respects those found in the case of the same salt with benzene and water.[2] These resemblances include the formation of a single molecular compound between silver perchlorate and the organic component, $AgClO_4.C_7H_8$; further, systems consisting of three co-existent liquid phases occur, in this instance over a much wider temperature range; and finally, there is a clearly indicated submerged binodal curve for two liquid phases composed of the three components which fails to appear in any of the three 2-component systems.

The Binary System; Silver Perchlorate and Toluene

The ternary system under investigation may be regarded as made up from the three binary systems which can be derived from the three components. Silver perchlorate and water have previously been investigated.[2] Water and toluene proved to be a difficult system to study because of the extremely low mutual solubility of these substances; the only new information as to this pair is the fact that the solubility of water in toluene is too low to be measured by the delicate method described later in this paper and is therefore not more than a few hundredths of a per cent., markedly lower than the value of 0.07% found for water in benzene[3] at 25°. The third pair, however, has been studied over the temperature range —73.5° to +75°.

The silver perchlorate used was prepared from silver nitrate, from which hydrous silver oxide was precipitated by sodium hydroxide and dissolved in 60% perchloric acid.

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[1] The material of this paper was presented by Frederick W. Miller, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1923.

[2] Hill, THIS JOURNAL, **44**, 1163 (1922).

[3] Hill, *ibid.*, **45**, 1143 (1923).

The salt obtained by partial evaporation of the solution above 50° was centrifuged and dried continuously in an oven at 110°; analysis of various samples gave results close to 100%. The toluene was purified by repeated shaking with concd. sulfuric acid, washed with water and dried with calcium chloride. Its boiling point was constant within 0.15°; it was stored over metallic sodium to keep it anhydrous. For the solubility determinations, the salt and toluene in glass-stoppered flasks were tumbled in a thermostat at various temperatures from 0° to 75°; the thermometers used were compared with a standard and corrected. For the lower temperatures, hand stirring in tubes immersed in cooling-baths was used. Samples of saturated solution were removed by a pipet and weighed so that the density could be calculated; they were then diluted with water and titrated with thiocyanate by the Volhard method for the determination of silver. At lower temperatures the solid phase appearing is the compound $AgClO_4.C_7H_8$; this was filtered off on a cooled Büchner funnel and gave upon analysis a silver content in close agreement with the above formula, representing 69.24% of silver perchlorate. Its transition temperature, 22.6°, was established by means of a cooling curve.

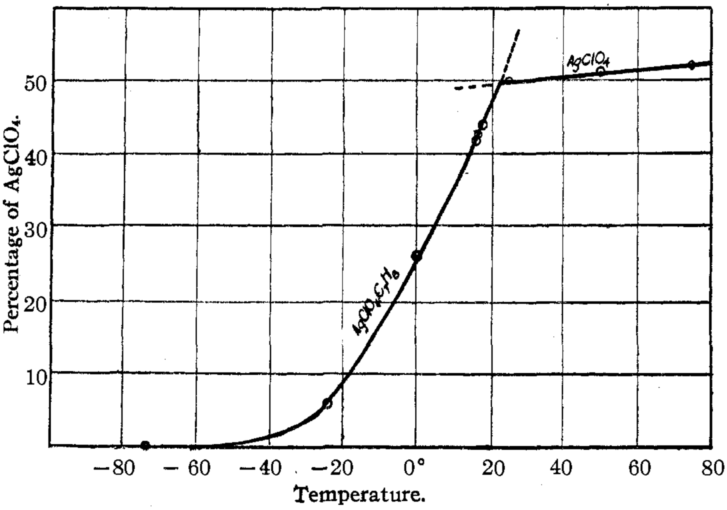

Fig. 1.—Solubility of silver perchlorate in toluene.

The results of the solubility determinations are given in Table I and shown in Fig. 1. Since the solubility of the salt diminishes very rapidly at lower temperatures, being too small for detection at —73.5°, it is probable that the eutectic is only slightly below the freezing point of toluene, given as about —94°.

The high solubility of silver perchlorate (about 50% at room temperature) is without parallel for salts in hydrocarbon solvents and is of the same order of magnitude as that of the alkali metal salts in the alcohols. It stands in a class by itself as an example of high solubility of a highly polar compound in a non-polar solvent, notwithstanding its moderately high melting point,[4] 480°.

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[4] Carnelley, *J. Chem. Soc.*, **45**, 409 (1884).

TABLE I

SOLUBILITY OF SILVER PERCHLORATE IN TOLUENE

Temp., ° C.	Solid phase present	Density of solution	$AgClO_4$, % by wt.
75	$AgClO_4$	1.665	54.60
50	$AgClO_4$	1.576	52.68
25	$AgClO_4$	1.523	50.30
22.6	$AgClO_4 + AgClO_4.C_7H_8$	...	...
18	$AgClO_4.C_7H_8$	1.417	44.11
16.5	$AgClO_4.C_7H_8$	1.388	42.89
16	$AgClO_4.C_7H_8$	1.375	42.00
0	$AgClO_4.C_7H_8$	1.129	26.41
−24.1	$AgClO_4.C_7H_8$	0.920	6.01
−73.5	$AgClO_4.C_7H_8$	.854	0.00

The Ternary System

The data on the ternary system consist of a number of invariant temperatures, determined by the method of cooling curves, and a number of analyses of the liquid ternary solutions, brought to saturation at fixed temperatures in a thermostat or in baths under thermometric control. Saturation was easily attained, since in no case was more than an hour's agitation found to be necessary, and usually 20 minutes of vigorous stirring proved sufficient. For the analysis, the percentage composition with respect to two of the three components is necessary, and only one (silver perchlorate by Volhard's method) could be obtained directly. The percentage of water present was therefore determined by the following indirect procedure. Carefully weighed quantities of toluene and water (the latter in small amounts) were introduced into well-dried, glass-stoppered tubes, treated with an excess of anhydrous silver perchlorate and agitated at 25° to saturation. Pipetted samples were then analyzed for silver perchlorate. Since the solid phase at 25° is the salt uncombined either with toluene, as previously shown, or with water if its total amount is small as is shown later in Fig. 2, it follows that the toluene and water are present in the ternary liquid in the same ratio as originally weighed out. From this experimentation Table II was compiled, which shows that the solubility of the perchlorate rises markedly with the presence of water in the system, although not to so great an extent as when benzene is the organic component.[5] It is possible, therefore, to use the solubility of the per-

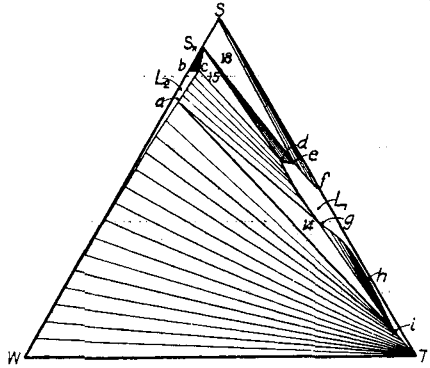

Fig. 2.—Isotherm at 25°.

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[5] Ref. 3, p. 1152.

chlorate in the solution at 25° as a measure of the water content. For the purposes both of accuracy and of ease, the data of Cols. 2 and 4 were plotted and the best straight-line equation was calculated by the method of least squares. The equation is found to be $y = 50.44 + 3.188\,x$, where y is the percentage of silver perchlorate and x the percentage of water. The values thus calculated are given in Col. 5 and are in good agreement with Col. 4.

Table II

Solubility of Silver Perchlorate in Toluene and Water at 25°

Points in Fig. 2	$AgClO_4$, % by wt.	Toluene, % by wt.	Water, % by wt. (found)	Water, % by wt. (calcd.)	Density
e	56.66	41.42	1.92	1.95	1.675
	56.65	41.46	1.89	1.949	1.672
	54.92	43.66	1.42	1.40	1.639
	54.75	43.84	1.41	1.35	1.628
	53.49	45.49	1.02	0.96	1.606
	52.54	46.86	0.60	.66	1.580
f	50.30	49.70	.00	..	1.525

In order to analyze any liquid phase formed at any temperature and with any solid phase present, it was necessary only to bring a known weight of the liquid to 25°, add salt, toluene or water in known amount, if necessary, to bring the system within the concentration limits given in Table II, and analyze again for silver perchlorate after the new equilibrium was obtained, calculating the water present from the equation given above and calculating the toluene in the original liquid by subtracting the sum of salt and water from 100%. It was by this method that the practical absence of water from toluene shaken with water was shown, as stated earlier. When the water content was high, a similar method was adopted using the segment *de* of Fig. 2, where the hydrate $AgClO_4.H_2O$ is the solid phase. The ternary system has been studied from temperatures not far above the ternary eutectic up to 99°. The 25° isotherm will first be given in detail, followed by an outline of the various equilibria found to exist from the lowest temperatures to the highest studied.

The 25° isotherm is shown in Fig. 2, which is not drawn exactly to scale because of the low concentration of water and toluene found in the liquid phases. The solubility curve shows three divisions, *ef*, *ed* and *cb*, for the first of which the saturating phase is $AgClO_4$ and for the latter two of which the hydrate $AgClO_4.H_2O$ is the solid phase. The data for the segment *ef* have been given above in Table II. In Table III are given the analyses of the saturated solutions along *ed;* for this curve the equation was found to be $y = 57.877 - 1.2281x + 0.3075x^2$. In the table, S is used for the salt silver perchlorate in solution, T for toluene and W for water.

The point *e* is common to both segments of the solubility curve, representing the composition of the liquid phase in equilibrium with $AgClO_4$ and

TABLE III

SOLUBILITY OF SILVER PERCHLORATE MONOHYDRATE, $AgClO_4.H_2O$, IN TOLUENE AND WATER AT 25°

Points in Fig. 2	S, % by wt.	T, % by wt.	W, % found	W, % calcd.	Density
d	58.34	37.32	4.19	4.34	1.715
	58.11	37.72	4.16	4.17	1.709
	57.96	37.98	4.12	4.06	1.710
	57.56	38.72	3.86	3.72	1.702
	57.44	38.96	3.67	3.60	1.696
	56.95	40.07	2.86	2.98	...
e	56.66	41.51	1.92	1.83	1.675

with $AgClO_4.H_2O$; the experimental data in Tables III and II are in close agreement with the intersection of the two curves as calculated from the equations, which give 56.66% for the concentration of silver perchlorate and 1.95% for the concentration of water. The segment *cb* is very short and the solubility of silver perchlorate at *c* is close to that in pure water, as is shown later in Table VI, Equilibrium 15. The discontinuous solubility curve gives rise to two 4-phase equilibria (isothermally invariant); these are Equilibrium 18, which exists between solid silver perchlorate, solid $AgClO_4.H_2O$, solution and vapor and Equilibrium 15, existing between solid $AgClO_4.H_2O$ vapor and two liquid phases designated by L_2 and L_1. The data for these equilibria are given in Table VI.

In addition to the solubility curve, the 25° isotherm shows two binodal or distribution curves; of these *WcdT* is the curve for the mutual solubility of toluene and water as affected by the presence of silver perchlorate. The data are given in Table IV. The figures in parentheses were obtained by graphic interpolation. The number of interpolated figures is not small, but this method was used here and in Table VI only when the amount of toluene or water was shown to be very small and to vary but little under change of conditions, so that the estimate cannot be in any substantial error.

TABLE IV

BINODAL CURVE *WcdT* AT 25° CONJUGATE SOLUTIONS

		L_1					L_2		
Points in Fig. 2	S. % by wt.	T. % by wt.	W, % by wt.	Density	Points in Fig. 2	S. % by wt.	T. % by wt.	W, % by wt.	Density
T	0.00	100.00	0.00	0.854	*W*	33.34	0.00	66.64	1.344
	.00	100.00	.00	.850		39.37	0.00	60.03	1.436
	.00	100.00	.00	.852		55.21	1.59	43.20	1.730
i	7.37	92.48	.19	.914	*a*	75.57	(2.1)	(22.33)	2.360
g	39.35	56.93	3.70	1.307	*a*	75.57	(2.1)	(22.33)	2.360
	43.44	52.01	4.55	1.372		76.09	(2.2)	(21.71)	2.389
	45.88	49.65	4.77	1.442		76.28	(2.25)	(21.47)	2.421
	49.07	45.98	4.95	1.491		78.00	(2.4)	(20.60)	2.480
	54.08	40.47	5.45	1.574		80.64	(2.45)	(16.91)	...
d	58.34	37.32	4.34	1.715	*c*	84.29	2.52	13.19	2.830

The binodal curve portrayed above shows two peculiarities of considerable theoretical interest: these are, first, the abnormal distribution of silver perchlorate between the toluene phase and the water phase and, second, the interruption by a submerged binodal curve *gi*, giving rise to a 3-liquid system (Equilibrium 14). With respect to the abnormal distribution, it will be seen in Table IV that the salt is found wholly in the aqueous phase (L_2) up to high concentrations; the aqueous solution contains as much as 55% of silver perchlorate when none of the salt can be detected in the toluene phase. A similar one-sided distribution of the strong electrolyte between water and benzene has been discussed in an earlier publication;[6] in the case now reported, however, the anomaly is more striking inasmuch as the solubility of the salt in toluene is so much nearer (50.3%, Table I) to that in water (84.5%)[3] than in the case of benzene, where it is only 5.0%.[3] It is possible to regard the distribution in these cases as evidence for the complete dissociation of an electrolyte at high concentrations, and from that point of view the evidence in this newer case is much more convincing, as was pointed out by Kendall,[7] because of the much smaller solubility ratio. It is evident, however, that these instances require a more detailed explanation than is afforded by the simple hypothesis of complete dissociation, since it has been found that the same salt, when distributed between water and aniline, is found wholly in the organic phase,[8] a fact in complete disagreement with the theory. Compound formation and chemical affinities obviously cannot be disregarded in these cases, and it is probable that they play a large part in all cases of distribution.

The second peculiarity noted is the occurrence of the submerged binodal curve *ghi*, which fails to reach the toluene-salt axis at any temperature. The data at 25° are given in Table V; the figures in parentheses are interpolated.

TABLE V

BINODAL CURVE *ghi* AT 25° CONJUGATE SOLUTIONS

	L_3					L_1			
Points in Fig. 2	S, % by wt.	T, % by wt.	W, % by wt.	Density	Points in Fig. 2	S, % by wt.	T, % by wt.	W, % by wt.	Density
i	7.37	92.48	0.19	0.914	*g*	39.35	56.95	3.70	1.307
	8.97	91.73	.30	.930		36.26	60.69	3.05	1.261
	11.00	88.64	.36	.951		32.18	65.54	2.28	1.210
	16.04	83.17	.79	1.005		26.67	71.73	1.60	...
h	(21)	(77.9)	(1.1)	...	*h*	(21)	(77.9)	(1.1)	...

The curve is found, upon plotting to scale, to have but slight displacement from the tie-line *gi* throughout and to lie very close to the salt-

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[6] Hill, THIS JOURNAL, **43**, 254 (1921).

[7] Kendall, *ibid.*, **44**, 734 (1922).

[8] Hill and Macy, *ibid.*, **46**, 1140 (1924).

toluene axis *ST;* the water content is very small, being less than 0.2% at the point *i*. As shown in a previous paper,[9] it is possible to forecast the occurrence of a submerged binodal curve on addition of a third component when the 2-component system (here silver perchlorate and toluene) shows a steep solubility curve approaching a parallel to the solubility axis, which if actually reached always results in the formation of a second liquid phase in the 2-component system; it is, however, not probable at all that a random choice of the third component will always result in the formation of the closed binodal curve, but we are not yet in position to generalize as to the nature of the third component necessary for such an occurrence.

The binodal curve *ghi* has one of its plait points, *h*, in the stable area; the other would fall in the metastable area within the binodal curve *WcdT*. The crossing of these two binodal curves gives rise to a 3-liquid area, *gai*, within which three liquid phases are co-existent. A similar case was noted for the system: silver perchlorate-benzene-water. These two instances appear to be the only cases known where three co-existent liquids are found in systems containing only two binodal curves. Schreinemakers[10] has predicted the possibility of such systems. As a matter of fact, they will occur in every instance where the merging of two binodal curves, with rise or fall of temperature, occurs at any points upon the curves except at the two plait points; in the latter case only two liquids will result. The occurrence of three co-existing liquids from the merging of three binodal curves[11] has been much more frequently observed.

The complete investigation of the ternary system has given seven invariant 5-phase points, designated by the Roman letters A to G, and twenty 4-phase equilibria, designated by numbers. The data are given in compact form below, the letter S standing for solid silver perchlorate, S_c for the solid compound $AgClO_4.C_7H_8$, S_H for the solid hydrate $AgClO_4.H_2O$, T for solid toluene, W for ice, and L_1, L_2 and L_3 for the three liquid phases, L_3 being the phase composed chiefly of toluene, L_2 the phase rich in water, and L_1 the phase intermediate in composition. The lowest quintuple point, A, was not determined by experiment, but is assumed to be practically coincident with the freezing point of toluene, since both salt and water have a negligible solubility in toluene at low temperatures. With the temperature of the quintuple points is given in each instance the phase reaction which occurs (vapor phase being omitted from consideration), written so that the addition of heat is represented by the change from left to right and *vice versa;* the four 4-phase equilibria originating at each quintuple point are given directly following it, the analyses referring to the liquid phase or phases.

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[9] Ref. 2, p. 1187.

[10] Schreinemakers, "Die Heterogenen Gleichgewichte," Roozeboom, Braunschweig, **1911**, vol. 3, pt. 2, p. 34.

[11] Ref. 10, p. 16.

TABLE VI

EQUILIBRIA IN THE TERNARY SYSTEM

Quintuple Point A. Temp. (—94°). $S_o + T + W \rightleftarrows L_3$

Equil. 5. $S_o + T + W$. Exists below —94°. No liquids present. Not studied.
Equil. 2. $W + T + L_3$. Exists from —94° to binary eutectic for W + T. Not studied.
Equil. 3. $S_c + W + L_3$. Exists from —94° to —33.5°. (Quintuple Point C.)

	Temp., ° C.	S, % by wt.	T, % by wt.	W, % by wt.	Density
A	(−94)	(0.00)	100.00	0.00	...
C	−33.5	.73	(99.26)	(.01)	0.894

Equil. 4. $S_c + T + L_3$. Exists from —94° to binary eutectic for S_c + T. Not studied.

Quintuple Point B. Temp., —59.8°. $S_H + S_o + W \rightleftarrows L_2$

Equil. 6. $S_H + S_o + W$. Exists below —59.8°. No liquids present. Not studied.
Equil. 7. $S_o + W + L_2$. Exists from —59.8° to —33.5°. (Quintuple Point C.)

B	−59.8	74.81	(1.00)	(24.19)	2.401
C	−33.5	63.16	(1.75)	(35.09)	...

Equil. 8. $S_H + W + L_2$. Exists from —59.8° to —58.2° (binary eutectic S_H + W)[2].

B	−59.8	74.81	(1.00)	(24.19)	2.401
	58.2	73.98	0.0	26.02	2.345

Equil. 9. $S_H + S_c + L_2$. Exists from —59.8° to +1.25°. (Quintuple Point E.)

B	−59.8	74.81	(1.00)	(24.19)	2.401
	−21.7	79.23	2.11	18.66	2.579
E	+ 1.25	81.30	(2.30)	(16.40)	...

Quintuple Point C. Temp., —33.5°. $S_c + W \rightleftarrows L_3 + L_2$

Equil. 3. $S_o + W + L_3$. Given above.
Equil. 7. $S_o + W + L_2$. Given above.
Equil. 10. $W + L_3 + L_2$. Exists from —33.5° to very slightly below 0° (quadruple point for W + T).

C	−33.5	L_2	63.16	(1.75)	(35.09)	...
		L_3	0.73	(99.26)	(0.01)	.894
	−18.0	L_2	49.44	(1.00)	(59.56)	1.688
		L_3	0.00	100.0	(0.00)	...
	0.0	L_2	.00	0.00	100.00	...
		L_3	.00	100.00	0.00	...

Equil. 11. $S_o + L_3 + L_2$. Exists from —33.5° to —24.1°. (Quintuple Point D.)

C	−33.5	L_2	63.16	(1.75)	(35.09)	...
		L_3	0.73	(99.26)	(0.01)	0.894
D	−24.1	L_2	70.68	(2.00)	(27.32)	2.221
		L_3	6.01	(93.96)	(0.03)	0.920

Quintuple Point D. Temp., —24.1°. $S_c + L_3 + L_2 \rightleftarrows L_1$

Equil. 11. $S_o + L_3 + L_2$. Given above.
Equil. 12. $S_o + L_3 + L_1$. Exists from —24.1° to —15.8° (consolute temp. for $L_3 \rightleftarrows L_1$).

D	−24.1	L_1	34.54	62.60	2.86	1.254
		L_3	6.01	(93.96)	(0.03)	0.920
	−15.8	$L_1 = L_3$	24.60	(75.03)	(0.37)	1.041

TABLE VI (*Continued*)

Equil. 13. $S_c + L_2 + L_1$. Exists from —24.1° to +1.25°. (Quintuple Point E.)

	Temp., ° C.		S. % by wt.	T. % by wt.	W. % by wt.	Density
D	−24.1	L_1	34.54	62.60	2.86	1.254
		L_2	70.68	(2.00)	(27.32)	2.221
	−9.6	L_1	45.86	50.64	3.50	1.458
		L_2	75.80	(2.20)	(22.00)	. . .
	+1.25	L_1	53.08	43.40	3.52	1.597
		L_2	81.80	(2.30)	(16.40)	2.529

Equil. 14. $L_1 + L_2 + L_3$. Exists from —24.1° to above 90°.

	Temp., ° C.		S. % by wt.	T. % by wt.	W. % by wt.	Density
D	−24.1	L_1	34.54	62.60	2.86	1.254
		L_2	70.68	(2.00)	(27.32)	2.221
		L_3	6.01	(93.96)	(0.03)	0.921
	+25	L_1	39.35	56.95	3.70	1.307
		L_2	75.57	(2.1)	(22.33)	2.360
		L_3	7.37	92.48	0.19	0.914
	+90	L_1	53.57	39.33	7.10	1.749
		L_2	77.40	(2.5)	(20.10)	2.401
		L_3	5.14	94.72	0.14	0.861

Quintuple Point E. Temp., +1.25°. $S_o + L_2 \rightleftarrows S_H + L_1$

Equil. 9. $S_H + S_c + L_2$. Given above.

Equil. 13. $S_o + L_1 + L_2$. Given above.

Equil. 15. $S_H + L_1 + L_2$. Exists from 1.25° to 42.2°. (Quintuple Point G.)

	Temp., ° C.		S. % by wt.	T. % by wt.	W. % by wt.	Density
E	1.25	L_1	53.08	43.40	3.52	1.597
		L_2	81.30	(2.30)	(16.40)	2.529
	25.0	L_1	58.34	37.32	4.34	1.715
		L_2	84.29	2.52	13.19	2.830
G	42.2	L_1	64.39	31.16	4.45	1.795
		L_2	86.79	(2.55)	(10.66)	. . .

Equil. 16. $S_H + S_o + L_1$. Exists from 1.25° to 15.2°. (Quintuple Point F.)

	Temp., ° C.	S. % by wt.	T. % by wt.	W. % by wt.	Density
E	1.25	53.08	43.40	3.52	1.597
	10.00	53.43	44.52	2.05	1.596
	15.20	55.04	43.31	1.65	. . .

Quintuple Point F. Temp., 15.2°. $S_H + S_o \rightleftarrows S + L_1$

Equil. 16. $S_H + S_o + L_1$. Given above.

Equil. 1. $S_H + S_o + S$. Exists from 15.2° to lower temps. No liquid phases present. Not studied.

Equil. 17. $S_c + L_1 + S$. Exists from 15.2° to 22.6° (transition point $S_c \rightleftarrows S$).

	Temp., ° C.	S. % by wt.	T. % by wt.	W. % by wt.	Density
F	15.2	55.04	43.31	1.65	. . .
	20.0	54.68	43.88	1.44	1.624
	22.6	. . .	. . .	. . .	. . .

Equil. 18. $S_H + S + L_1$. Exists from 15.2° to 42.2°. (Quintuple Point G.)

	Temp., ° C.	S. % by wt.	T. % by wt.	W. % by wt.	Density
F	15.2	55.04	43.31	1.65	. . .
	25.0	56.66	41.39	1.95	1.674
G	42.2	64.39	31.16	4.45	1.872

TABLE VI (*Concluded*)

Quintuple Point G. Temp., 42.2°. $S_H + L_1 \rightleftarrows S + L_2$

Equil. 15. $S_H + L_1 + L_2$. Given above.
Equil. 18. $S_H + S + L_1$. Given above.
Equil. 19. $S + L_1 + L_2$. Exists from 42.2° to 91.75 (consolute temp. $L_1 = L_2$).

	Temp., ° C.		S, % by wt.	T, % by wt.	W. % by wt.	Density
G	42.2	L_1	64.39	31.16	4.45	1.872
		L_2	86.79	(2.55)	(10.66)	...
	75.0	L_1	70.85	24.14	5.01	2.042
		L_2	87.00	2.71	10.29	2.983
	91.75	$L_1=L_2$	83.00	12.89	5.00	...

Equil. 20. $S_H + S + L_2$. Exists from 42.2° to 43.1° (transition temp. $S_H \rightleftarrows S$).

G	42.2	86.79	2.55	10.66	...
	43.1	86.5	0.00	13.5	...

From the data given above it is easily possible to construct a complete series of diagrams showing all of the phase complexes capable of stable existence between about —94° and +91.75°. The multiplicity of equilibria results from the evolution of the solubility curves for the three solids, S_c, S_H and S and the two binodal curves, these being the characteristic parts of the system. Liquid areas appear consecutively at three widely different temperatures and of widely different compositions; L_3, being substantially liquid toluene, appears at the ternary eutectic, Quintuple Point A (about —94°); L_2, which is substantially an aqueous solution of silver perchlorate, appears at Quintuple Point B (—59.8°); L_1, which is of intermediate composition, appears at Quintuple Point D (—24.1°). The areas for these liquid phases increase with rise of temperature, L_3 and L_1 becoming consolute at —15.8° (Equil. 12) and completing the submerged binodal curve *ghi*, while L_2 and L_1 do not become consolute until the temperature +91.75° is reached (Equil. 19), at which temperature the larger binodal curve *WcdT* is completed. The 3-liquid system (Equil. 14) comes into existence at —24.1° (Quintuple Point D) and remains stable up to 90°, which is approximately the boiling point of the system under atmospheric pressure; the fact that the three liquids have up to that temperature shown no marked tendency to reach the same composition makes it probable that they can co-exist up to much higher temperatures. 3-Liquid systems arising from the merging of two binodal curves have, therefore, now been realized in two instances; in the first (silver perchlorate-benzene-water)[2] the temperature range is 17°, while in the case reported here the range is something greater than 110°.

Summary

1. The solubility of silver perchlorate in toluene has been determined from —73.5° to +75°. At room temperature (25°) the solubility is 50.3%. Below 22.6° the solid phase is the compound $AgClO_4.C_7H_8$.

2. The ternary system, silver perchlorate-toluene-water has been studied from the ternary eutectic at —94° up to +91.75°. There exist seven quintuple points, each of which was determined, and twenty 4-phase equilibria.

3. The system shows, in addition to the solubility curves for the three solid phases (silver perchlorate, its hydrate and its compound with toluene), two binodal curves, one of which is submerged and does not reach any of the two-component axes at any temperature.

4. The intersection of the two binodal curves, at certain points which are not their plait points, gives rise to a 3-liquid system which is stable from —24.1° to above +90°.

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[Contribution from the Departments of Pharmacology and Tropical Medicine, Harvard Medical School]

THE SULFUR CONTENT OF ARSPHENAMINE AND ITS RELATION TO THE MODE OF SYNTHESIS AND THE TOXICITY. V.[1]

By W. G. Christiansen, A. J. Norton and J. B. Shohan

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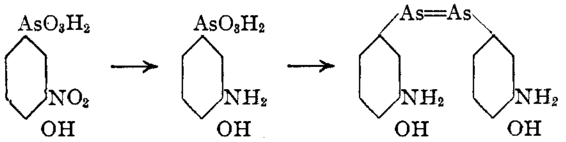
Previous studies[2] in this Laboratory have shown that when 3-nitro-4-hydroxyphenylarsonic acid is reduced to arsphenamine base by means of sodium hydrosulfite as indicated in Reaction 1, the experimental conditions under which the nitro acid is reduced to the amino acid are of great importance in determining the toxicity and sulfur content of the reaction product.



(1)

Evidence has also been reported[3] of the formation of a very soluble by-product during the reduction of the nitro group; it was hypothetically suggested[4] that sulfamic acids are formed and that the latter give rise to the sulfo-arseno compounds which are present as impurities in the arsphenamine obtained when the nitro group is reduced under the least favorable

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[1] This is a continuation of an investigation which was commenced under a grant from the United States Interdepartmental Social Hygiene Board; the work has been under the general direction of Dr. Reid Hunt.

[2] Christiansen, This Journal, (a) **43**, 2202 (1921); (b) **44**, 847 (c) 854 (d) 2334 (1922); (e) **45**, 1316 (f) 1807 (1923).

[3] Ref. 2 a, p. 2206.

[4] Ref. 2 d, p. 2338.