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THE SYSTEM, SILVER PERCHLORATE-WATER-BENZENE

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Introduction

In a previous communication[1] attention was called to the fact that silver perchlorate has a moderate solubility in benzene, and that the addition of about 1% of water to a complex of salt and saturated solution causes the formation of two liquid phases, each high in benzene but differing in water content and salt content; under certain conditions a third liquid phase is obtained.[2] This ternary system has now been studied from the temperature of the ternary eutectic up to the boiling points of the liquids and in some cases beyond the boiling points. Two compounds have been found, a hydrate of the formula $AgClO_4.H_2O$ and a benzene addition compound of the formula $AgClO_4.C_6H_6$; these two solids, together with the anhydrous salt, benzene, ice, the three liquids and the vapor, give rise to a very considerable number of invariant points and 4-phase equilibria which have been studied. A complete representation of the 3-component system, from its lowest eutectic temperature up to the melting point of the silver perchlorate, is given in the following pages.

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

[2] Professor E. W. Washburn of the University of Illinois made a prior observation of the occurrence of 3 liquid phases in this system, the work being embodied in a Bachelor's thesis presented at that institution by Mr. Russel W. Millar in 1916. Professor Washburn has very courteously left the matter to me for complete investigation.

The Three Binary Systems

Study was made of each of the 3 binary systems from which the ternary system is composed. In the system, silver perchlorate and water, solubility determinations have been made from $100°$ downward to the binary eutectic, the concentration of salt being determined through direct titration by Volhard's method; freezing-point determinations, made by use of the Beckmann apparatus, were carried out to complete the curve from the eutectic to the water axis. The low temperatures required were obtained by use of a cooling bath of solid carbon dioxide and ether.

It was found that the hydrate $AgClO_4 . H_2O$ is stable up to $43°$. The transition point was determined by cooling-point curves, and agrees well with that indicated by the solubility curves given below in Fig. 1. The formation of a hydrate was proved by the observation of a small rise in temperature upon addition of a small amount of water (about 9%) to a quantity of anhydrous salt; the relatively small rise in temperature which was noted indicates qualitatively that the heat of formation is small. The composition of the hydrate was determined by draining crystals at room temperature and drying them over anhydrous silver perchlorate in a very small desiccator; such a system should give a vapor tension in equilibrium with the hydrate.[3] The analysis showed 90.68% and 90.96% of silver perchlorate present, as against 92.00% required by the formula $AgClO_4.H_2O$; the retention of about 1% of water by the crystals is not surprising in view of their very hygroscopic character. The solubility figures are given in Table I.

TABLE I

SILVER PERCHLORATE AND WATER

Solid phase	Temp. °C.	Density	$AgClO_4 \%$ by wt.	$H_2O \%$ by wt.
	480	. . .	100.00	. .
AgClO$_4$...................	99	3.069	88.8	11.2
	75	3.022	88.1	11.9
(AgClO$_4$.H$_2$O(metastable).....	50	2.995	87.2	12.8
AgClO$_4$ + AgClO$_4$.H$_2$O.......	43	. . .	86.5	13.5
AgClO$_4$.H$_2$O...............	25	2.806	84.5	15.5
AgClO$_4$.H$_2$O...............	0	2.667	81.3	18.7
AgClO$_4$.H$_2$O + Ice..........	−58.2	2.315	73.9	26.1
	−40	. . .	70.4	29.6
	−24	. . .	60.3	39.7
Ice......................	−10	. . .	45.2	54.8
	− 3	. . .	26.55	73.45
	− 0.16	. . .	0.96	99.04
	0.0	. . .	0.00	100.0

The eutectic temperature, $−58.2°$, is lower than that of any other true salt in water, and only in the cases of hydrogen chloride in water, po-

[3] Hill, THIS JOURNAL, 44, 546 (1922).

tassium hydroxide in water, and sulfuric acid in water have lower eutectics been found. The solubility of the salt in water is exceedingly high, and the curve, shown in Fig. 1, is made up of two practically straight lines, leading to the melting point of the salt, 480°.[4] The freezing-point determinations at low concentrations of the salt show it to be normally dissociated in water (81.5% at 0.047 N).
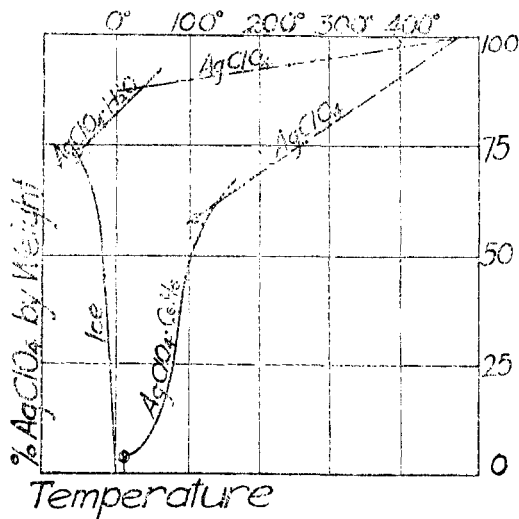

Fig. 1.—Solubility of $AgClO_4$ in H_2O (upper curve);
$AgClO_4$ in C_6H_6 (lower curve).

In determining the solubility curve of the salt in benzene, solutions saturated at temperatures from 25° to 80° were pipetted into flasks and, after weighing, treated with water to extract the silver salt, which was then titrated with standard thiocyanate solution. The determinations at temperatures above 80° were made by sealing weighed amounts of silver perchlorate and benzene in small glass tubes, which were rocked mechanically in a large heating bath of calcium chloride solution in which the temperature was slowly raised; the temperature at which the solid disappeared was taken as corresponding to a saturated solution of the composition taken. The benzene used was purified as noted later, and the cryoscopic determinations made in the usual Beckmann apparatus.

The compound $AgClO_4.C_6H_6$ was found to be the solid phase at all ordinary temperatures. Crystals formed from benzene solution and dried over anhydrous silver perchlorate were found upon analysis to contain 72.14% of $AgClO_4$; calculated from the formula, 72.64%. Attempts to determine the transition temperature of the double compound showed it to be surprisingly high; on being heated in sealed tubes, the compound

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

showed partial liquefaction at 140° to 146°. From the solubility measurements given in Table II it appears that the transition temperature is about 145°, over 60° above the boiling point of benzene.

TABLE II

SILVER PERCHLORATE AND BENZENE

Solid phase	Temp. ° C.	Density	$AgClO_4\%$ by wt.	$H_2O\%$ by wt.
AgClO₄...................	480	...	100.0	..
	(over 160)	...	65.6	34.4
	159	...	64.6	35.4
AgClO₄ + AgClO₄.C₆H₆......	145	...	63.0	37.0
AgClO₄(metastable)........	140	...	62.6	37.4
AgClO₄.C₆H₆...............	138.5	...	60.0	40.0
	115.5	...	50.5	49.5
	92	...	40.1	59.9
	80.3	1.164	32.2	67.8
	50	0.895	10.07	89.93
	25	0.906	5.00	95.00
AgClO₄.C₆H₆ + C₆H₆........	5.12	0.909	3.44	96.56
C₆H₆......................	5.48	...	0.00	100.00

The salt is associated in benzene solution as molecules of double and triple the normal molecular weight, in equilibrium with unassociated molecules; electrolytic dissociation does not occur.[5] This considerable association explains the fact that the eutectic temperature (5.12°) is but slightly lower than the freezing point of pure benzene, 5.48°.[6] The solubility curve rising from the eutectic (Fig. 1), becomes very steep at temperatures above 50°, flattening out again at higher temperatures, and showing a distinct double flexure. The form of the curve is very similar to that observed for salicylic acid and water by Alexejew,[7] in which case the formation of two liquid phases was observed in the metastable region to the left of the solubility curve. In the case of silver perchlorate and benzene, the formation of two liquids was not observed upon undercooling the solutions as much as 30°, but it is evident from the nearly perpendicular character of the curve that changes occur in the solution of the kind which frequently produce 2 liquid phases, which are in the stable region when the solubility curve is perpendicular or inclined toward the vertical axis with increasing concentration, or in the metastable region when the solubility curve does not quite reach the perpendicular. This approach of the curve to a condition demanding 2 liquid phases will be referred to later as explaining in part the occurrence, in the 3-component system including water, of one more liquid phase than would be anticipated from the facts as to the 2-component systems.

[5] Hill, THIS JOURNAL, **43**, 258 (1921).

[6] Richards and Shipley, *ibid.*, **41**, 2002 (1919).

[7] Alexejew, *Wied. Ann.*, **28**, 330 (1886).

For the system, benzene-water, a complete investigation has not yet been made. Herz[8] gives the solubility of water in benzene as 0.21% at 22°, from which value Richards and Shipley[6] dissent on the basis of freezing-point determinations made by them, which give by calculation a solubility of about 0.03% at 5.4° if a normal molecular weight is assigned to water. Three determinations made in the course of my work give 0.077° as the average depression, which is in fair agreement with Richards and Shipley's more carefully determined figure 0.09°. This places the quadruple point at about 5.40°. Clifford[9] has recently obtained, by displacing the water from saturated benzene solutions and weighing the water obtained, figures rising from 0.046% at 21° to 0.113% at 55°, which are a little higher than those of Richards and Shipley; Groschuff has a slightly higher set of figures. By an accurate method described later in this report, a value of 0.06% for the solubility of water in benzene at 25° has been obtained. A careful investigation of this solubility curve is now being conducted in this Laboratory, but it has not appeared necessary to delay this publication until the completion of that work.

For the solubility of benzene in water we have Herz's[8] figure of 0.08% at 22°. Three determinations of the freezing point of water saturated with benzene have given me an average value of 0.037° for the depression, which by calculation gives a benzene concentration of 0.153% at 0°. The upper and lower sections of the solubility curve are, therefore, still open to question; however it appears clear that the mutual solubilities are very low, as indicated in Fig. 2. From the information at hand we should have to deduce that the solubility of water in benzene increases with rising temperature, and that of benzene in water decreases under the same change of conditions.

Fig. 2.—Solubility of water and benzene.

The Ternary System

Methods of Experimentation.—In the analysis of solutions containing the 3 components the silver perchlorate has been determined directly by titration with standard ammonium thiocyanate. No suitable direct method could be found for determining the water or the benzene. The

[8] Herz, *Ber.*, **31**, 2669 (1898).

[9] Clifford, *J. Ind. Eng. Chem.*, **13**, 632 (1921). Groschuff, *Z. Elektrochem.*, **17**, 348 (1911).
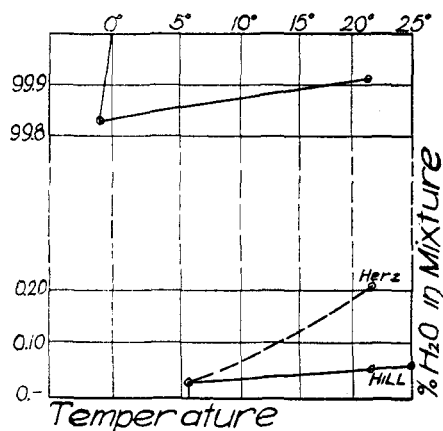
indirect method adopted consists in preparing samples of benzene and water by weighing each of them into a cylinder and using this mixed solvent to determine the solubility of silver perchlorate at 25° in an accurately controlled thermostat; the figures thus obtained, which are given later in Table IV, were plotted so as to give a solubility curve which could be used for reference purposes. The solution obtained in any experiment at any temperature, after determination of its silver perchlorate concentration, was pipetted into a dry cylinder, weighed, treated with excess of anhydrous salt, and agitated at 25° until equilibrium was reached; a sample was titrated for its new content of silver perchlorate, and the point corresponding to this composition on the 25° solubility curve was taken as giving the relative proportions of water and benzene present. This method gives very accurate results in all mixtures except those in which the benzene concentration is below 2%; in these latter cases the solubility curve at 25° is not suited to give accurate readings, since it is almost parallel to the water-benzene axis.

The solid phase present, when its composition was not obvious, was determined by application of phase-rule principles; a complex of salt, water and benzene having given a solution of a certain composition, it follows that a straight line connecting these two points, on the triangular diagram described below, leads to the composition of the solid phase, which, as all the solid phases are either binary compounds or of a single component, is found upon one of the sides of the triangle.

The benzene and silver perchlorate used were carefully purified. The benzene was washed with conc. sulfuric acid and then with water, dried with calcium chloride, then recrystallized, and finally dried and kept over metallic sodium. The principal sample used showed a melting point of 5.432° which is 0.048° lower than Richards' quoted figure of 5.48°. All measurements of temperature involving solid benzene have been corrected by 0.048° to agree with Richards' data. The silver perchlorate used was prepared from silver nitrate by precipitation with sodium hydroxide; the precipitated silver hydroxide after washing was then dissolved in 60% perchloric acid and the solution evaporated on the water-bath to partial crystallization. The mixture was allowed to cool and was filtered at a temperature above 43°, to avoid formation of the hydrate; the crystals were then centrifuged and dried in an electric oven at 105° to 110° for several days before use, on account of their extremely hygroscopic character. Various samples showed upon analysis a purity of 99.6% to 99.8%, determined by titration with standard thiocyanate solution.

Solubility determinations at temperatures other than 25° were made in ordinary Beckmann freezing-point tubes, immersed in a large volume of water at the desired temperature and stirred until equilibrium was reached. The various invariant temperatures were determined in the same apparatus. Thermometers were calibrated at the freezing point and boiling point of pure water and in solid carbon dioxide, which was assumed to be at −78°.

The composition of the various phases has been represented in weight per cent. on the familiar triangular diagram; the vertex representing pure silver perchlorate is indicated by the letter S, that for water by W and

that for benzene by B. The composition of any point within the triangle shows the percentage of salt, water and benzene by its perpendicular distance from the sides opposite to S, W and B respectively. In the diagrams following, the compositions are indicated approximately, and not according to accurate scale, since many points fall so close to the sides of the triangle as to make their correct representation on a small scale confusing to the reader.

The Invariant Equilibria and the Monovariant Equilibria.—Since the gaseous phase is present in all the experiments made, 4 additional phases are necessary to define an invariant equilibrium, or 3 to define a monovariant equilibrium. With 5 solid phases possible and 3 liquids, the number of such equilibria possible is naturally very large. These are of course not all realizable, but the astonishing thing is that so large a number of them are actually met with in this system. For convenience in study, a list of such equilibria realized and studied is given in Table III. The symbol S_H is used for the hydrate $AgClO_4.H_2O$, S_B for the compound $AgClO_4.C_6H_6$, S, W, and B for solid salt, ice and benzene, and L_3, L_2 and L_1 for the 3 liquid phases. The numbers and letters assigned to the various equilibria will be used in the discussion later.

TABLE III
INVARIANT AND MONOVARIANT EQUILIBRIA

Quintuple Point

	°C.	
F	−58.4	$S_H + W + S_B + L_3$
E	−57.8	$W + S_B + B + L_3$
D	− 2.7	$S_B + B + L_3 + L_2$
C	+ 4.98	$S_B + B + L_2 + L_1$
B	+ 5.24	$B + L_3 + L_2 + L_1$
A	+42.1	$S_H + S_B + S + L_3$

Equilibrium		
24		$S_H + W + S_B$
23		$S_H + W + L_3$
22 (3)		$S_H + S_B + L_3$
21 (20)		$W + S_B + L_3$
19		$W + S_B + B$
18		$W + B + L_3$
17 (16)		$S_B + B + L_3$
15 (12)		$S_B + B + L_2$
14		$S_B + L_3 + L_2$
13 (8)		$B + L_3 + L_2$
11		$S_B + B + L_1$
10		$S_B + L_2 + L_1$
9 (7)		$B + L_2 + L_1$
6		$B + L_3 + L_1$
5		$L_2 + L_3 + L_1$
4		$S_H + S_B + S$
2		$S_H + S + L_3$
1		$S_B + S + L_3$

In addition to these 6 invariant and 18 monovariant equilibria, there are 17 divariant equilibria which have been studied (two phases and vapor), and 8 trivariant equilibria (1 phase and vapor); these latter have been realized but not studied. The total number of equilibria existing in this 3-component system is therefore 49.

In order to represent these equilibria a triangular prism can be used. The space figure obtained, however, is too complicated for simple graphic representation. For that reason it seems best to follow the method used by Schreinemakers,[10] in which the various invariant and mono-variant equilibria are shown by their projection upon the base of a tri-angular prism (Fig. 3), and the changes of the system with varying tem-perature are shown by isothermal cross-sections at suitable temperatures (Figs. 4 to 21).

The eutectic for the complete system was found to lie at $-58.4°$, which temperature is represented as Quintuple Point F in Fig. 3. The liquid phase appearing here is low in benzene, and the composition not widely different from that at the eutectic temperature for silver per-chlorate and water alone, $-58.2°$ (Table I). A second quintuple point was found at a temperature only slightly higher than that of Quintuple Point F, namely at $-57.8°$. It was assured by the low temperature and the composition of the liquid phases at the point F that ice and the hydrate $AgClO_4 \cdot H_2O$ were present as solid phases, but the third solid phase could not be directly determined. The point was settled by ap-proaching the quintuple point from mixtures of different total composition. When a phase complex was used which gave the equilibrium $S_H + S_B$ $+L_3$ (Equil. 22) the quintuple point of lower temperature was found. When the equilibrium $W + B + L_3$ (Equil. 18) was used as the path of approach, the higher quintuple point was found. This established that S_B is the third solid phase both at Quintuple Point F, and at E also. At Quintuple Point F $(-58.4°)$ the liquid phase was found by analysis to contain 72.97% of silver perchlorate. The benzene content could not be determined by the method previously outlined, though it was found to be less than 1.6%.

With the composition of the solid and liquid phases determined, it is possible to write the phase reaction which occurs; using the system of notation previously outlined, it becomes,

$$S_H + S_B + W \rightleftarrows L_3 \quad \text{(Quintuple Point F, } -58.4°)$$
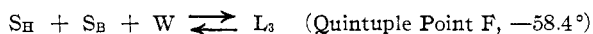
in which the change upon addition of heat is written from left to right. At this temperature there begin 4 monovariant equilibria, of which 1 exists at lower temperatures and 3 exist at higher temperatures. These may be designated as follows.

[10] Schreinemakers, *Z. physik. Chem.*, **25**, 543 (1898).

		Equil.
At lower temperatures.........	S_H + W + S_B	24
At higher temperatures.........	S_H + W + L_3	23
At higher temperatures.........	S_H + S_B + L_3	22
At higher temperatures.........	W + S_B + L_3	21

In Fig. 3, the approximate position of the quintuple point has been represented by F, and the 3 equilibria at higher temperatures by the lines Fh, FA and FE.
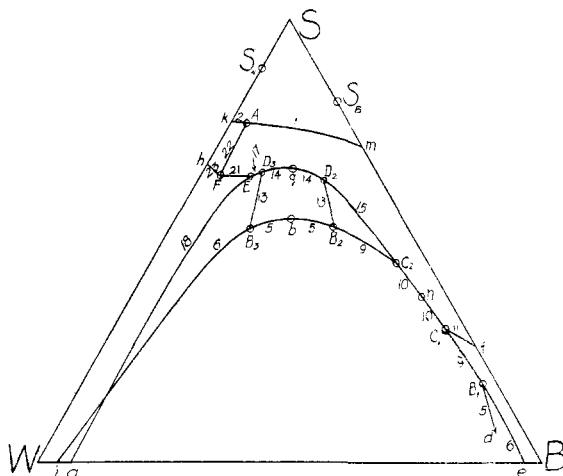

Fig. 3.—Monovariant equilibria (4-phase) in the system, $AgClO_4$-C_6H_6-H_2O.

Equilibrium 24 represents the three solid phases S_H, S_B and ice (W) in contact with vapor, of which only the latter is capable of varying in composition. Measurements of vapor tension have not been made in the study of this system. Equilibrium 23, in which S_H, W, and L_3 are present, exists only over a short temperature range, during which the benzene content L_3 drops from an initially small value to zero; that is, the equilibrium ends at the binary eutectic for salt and pure water, at −58.2°. The composition of L_3 at these two points is given below, the benzene content being estimated.

Equilibrium 23.   (S_H + W + L_3)

	Temp. °C.	$AgClO_4$ %	C_6H_6 %	H_2O %	Density
F.............	−58.4	72.97	(0.5)	26.53	. . .
h.............	−58.2	73.98	0.0	26.02	2.345

Equilibrium 22 (hydrate, benzene-compound and solution) exists over a long range of temperature, from −58.4 to +42.1°, at which latter temperature (Quintuple Point A) the hydrate changes to anhydrous salt and solution. During this rise of temperature there is of course a gradual increase in the salt concentration of the solution, but the benzene

concentration is always low, as represented schematically by the line FA. Since this solubility curve presumably parallels very closely the solubility curve of the hydrate in pure water (Table I), it was not thought worth while to make analyses at intermediate temperatures. The composition of L_3 at the extreme temperatures for this equilibrium is as follows.

Equilibrium 22 (3). $(S_H + S_B + L_3)$

	Temp. °C.	AgClO₄ %	C₆H₆ %	H₂O %	Density
F.............	−58.4	72.97	(0.50)	26.53	...
A.............	+42.1	87.12	0.70	12.18	2.956

The remaining monovariant equilibrium beginning at the eutectic is Equilibrium 21 $(W + S_B + L_3)$, which exists over but a short range of temperature, coming to an end with the precipitation of an additional phase, solid benzene, at the invariant temperature −57.8°. The change in composition, with respect to silver perchlorate, is very slight, and the change in benzene concentration is likewise small. It will be remembered that all benzene concentrations found to be less than 1.6% are given only as estimated amounts.

Equilibrium 21 (20). $(W + S_B + L_3)$

	Temp. °C.	AgClO₄ %	C₆H₆ %	H₂O %
F.............	−58.4	72.97	(0.50)	26.53
E.............	−57.8	72.85	(1.00)	26.15

At the new invariant temperature (Quintuple Point E) the composition of the liquid phase is as given immediately above. The appearance of solid benzene from a system consisting of ice, solvate and solution, as represented by the points W, S_B and F in Fig. 3, which do not include the point B in the triangle joining them, can be expressed only by the following phase reaction

$$W + S_B \rightleftarrows B + L_3 \quad \text{(Quintuple Point E } -57.8°\text{)}$$
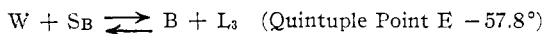
and the monovariant equilibria beginning here are

		Equil.
At lower temperatures..........	$\begin{cases} W + S_B + L_3 \\ W + S_B + B \end{cases}$	20 = 21 19
At higher temperatures.........	$\begin{cases} W + B + L_3 \\ S_B + B + L_3 \end{cases}$	18 17 = 16

The two equilibria existing at lower temperatures require no discussion, as Equilibrium 20 is of course the same as Equilibrium 21, while Equilibrium 19 contains no phase of variable composition except vapor. Equilibrium 18 exists over a long temperature rise, and is represented by the line Ea, which runs close to the SW axis (i. e., there is but little benzene in the solution) and terminates at the eutectic a on the water-benzene axis, which is at 0.037°. Analyses were made at several temperatures.

Equilibrium 18. (W + B + I_3)

	Temp. °C.	AgClO$_4$ %	C$_6$H$_6$ %	H$_2$O %	Density
E	−57.8	72.85	(1.00)	26.15	
	−50	70.31	(0.90)	28.79	
	− 7	33.3	(0.30)	66.4	1.376
a	− 0.037	0.0	0.153	99.84	...

Equilibrium 17, represented by the line ED$_3$, represents the solution in contact with S$_B$ and solid benzene (B), which condition can exist over more than 50° range, ending with the formation of a new liquid phase at −2.7°. This constitutes a new quintuple point having two liquid phases present, represented by D$_3$ and D$_2$. The analyses of L$_3$ are given below.

Equilibrium 17(16). (S$_B$ + B + I_3)

	Temp. °C.	AgClO$_4$ %	C$_6$H$_6$ %	H$_2$O %	Density
E	−57.8	72.85	(1.00)	26.15	...
	−18	72.39	2.20	25.41	2.257
D$_3$	− 2.7	72.18	4.34	23.48	2.243

It will be seen that during rise in temperature there is no substantial change in the salt content of the solution L$_3$ but that the liquid takes up benzene rapidly, so that its composition comes into the region where accurate analyses are possible. The new liquid L$_2$, having its origin at the invariant temperature −2.7°, is represented by the point D$_2$ in Fig. 3, and is widely different in composition from L$_3$. Its composition falls within a triangle drawn connecting the points D$_3$, S$_B$ and B, from which it follows that L$_2$ is produced by reaction of the other three phases.

B + S$_B$ + L$_3$ ⇌ L$_2$ (Quintuple Point D, −2.7°)

	AgClO$_4$ %	C$_6$H$_6$ %	H$_2$O %	Density
Composition L$_3$	72.18	4.34	23.48	2.243
L$_2$	54.36	37.32	8.32	1.644

At Quintuple Point D there originate four monovariant equilibria.

		Equil.
At lower temperatures	S$_B$ + B + I_3	16 = 17
	S$_B$ + B + L$_2$	15
At higher temperatures	S$_B$ + I_3 + L$_2$	14
	B + L$_3$ + L$_2$	13

Of these, Equilibrium 16 is of course the same as 17, which has already been discussed. Equilibrium 14 represents the compound S$_B$ in contact with the two saturated solutions, L$_3$ and L$_2$. As the temperature of this system is raised, L$_3$ is found to decrease in salt concentration and in water concentration, while L$_2$ undergoes exactly the opposite changes. The two liquids are therefore approaching each other in composition, and at some temperature will become consolute. The consolute temperature was

easily determined to be 10.4°; as the 2 liquids are stirred in contact with excess salt and with slowly rising temperature, the emulsion which is seen at lower temperatures passes at 10.4° into the critical opalescence[11] which is characteristic of the coalescence of 2 liquids. The phenomenon is less sharply marked with falling temperatures, since in the latter case the precipitation of excess salt interferes with the observation of the changes in the liquid phases. The changes in composition are indicated in Fig. 3 by the 2 lines D_3g and D_2g and were found by analysis to be as follows.

Equilibrium 14. $(S_B + L_3 + L_2)$

	Temp. °C.		AgClO$_4$ %	C$_6$H$_6$ %	H$_2$O %	Density
D_3	− 2.7	L_3.......72.18		4.34	23.48	2.244
D_2		L_2......54.36		37.32	8.32	1.644
g	+10.4	$L_3=L_2$......64.02		22.72	13.26	1.876

Equilibrium 13 (benzene, L_3 and L_2) also includes 2 liquid phases of variable composition. As the temperature rises, each liquid becomes lower in salt concentration, with small changes in concentration of benzene and water, until at 5.24° a third liquid phase (L_1) appears. This is, however, not the next quintuple point in order, but is one occurring at a higher temperature, and will be discussed as Quintuple Point B a little later. The composition at the beginning and ending of this equilibrium has been determined: in Fig. 3 the two lines D_3B_3 and D_2B_2 represent the same.

Equilibrium 13 (8). $(B + L_3 + L_2)$

	Temp. °C.		AgClO$_4$ %	C$_6$H$_6$ %	H$_2$O %	Density
D_3	−2.7	L_3..........72.18		4.34	23.48	2.244
D_2		L_2..........54.36		37.32	8.32	1.644
B_3	5.24	L_3..........70.30		1.60	28.1	2.141
B_2		L_2..........52.02		35.30	12.68	1.532

Equilibrium 15 represents solution L_2 in contact with the compound S_B and with solid benzene. It may be viewed as the continuation of Equilibria 18, 17 and 14, and will eventually terminate in the binary eutectic for salt and benzene at f; but its progress is again interrupted by the appearance of another liquid phase, which has already been referred to as L_1. This third liquid contains but little salt and its water content is never more than a very few tenths of 1%. The appearance of this phase occasions another quintuple point (C) at a temperature of 4.98°. It is to be noted that although 3 liquid phases are existent at this temperature, they are not coexistent; the 2 coexistent liquids at the quintuple point are L_2 and L_1, both relatively low in water; if the water concentration is increased at this temperature L_1 and the compound

[11] Rothmund, *Z. physik Chem.*, **26,** 446 (1898). Ostwald, "Lehrbuch der allgemein-en Chemie," (2nd Edition), W. Engelmann. Leipsic, **1903,** II, 2, 648.

S_B will eventually disappear and L_3 will appear, giving the monovariant Equilibrium 13. This will be apparent in the isotherm for 4.98°, given later. The data for Equilibrium 15 are as follows, and are represented by the curve D_2C_2 in Fig. 3.

<div align="center">

Equilibrium 15 (12). $(S_B + B + L_2)$

</div>

	Temp. °C.	AgClO₄ %	C₆H₆ %	H₂O %	Density
D₂..........	−2.7	54.36	37.32	8.22	1.644
C₂..........	+4.98	36.86	61.38	1.76	1.276

It is to be noted that with moderate change in water concentration there is relatively large change in salt and benzene concentration, which will be found true of all equilibria represented by points approaching the benzene vertex; both solubility curves and distribution curves in this part of the diagram run nearly parallel to the axis S_B.

At the temperature +4.98° the new Quintuple Point C appears. The composition of the liquid phases is as follows.

		AgClO₄ %	C₆H₆ %	H₂O %	Density
C₂..................	L₂	36.86	61.38	1.76	1.276
C₁..................	L₁	5.03	94.71	0.20	0.923

On plotting to scale the positions of the 2 liquid phases and the 2 solid phases S_B and B it appears that L_1 (represented in Fig. 3 by C_1) falls within the triangle made by the other three, whence the phase reaction is the following.

<div align="center">

$S_B + B + L_2 \rightleftarrows L_1$ (Quintuple Point C, + 4.98°)

</div>
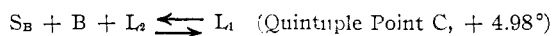
and the 4 monovariant equilibria are

		Equil.
At lower temperatures.............	S + B + L₂	12 = 15
At higher temperatures..........	⎧ S_B + B + L₁	11
	⎨ S_B + L₂ + L₁	10
	⎩ B + L₂ + L₁	9 = 7

Equilibrium 12 is the same as 15, previously discussed. Equilibrium 10 is, like 14, marked by the approach of the two liquid phases toward the same composition as the temperature rises, but it has not been found possible to determine the consolute temperature. It is at least slightly higher than 25°, as will be shown in the discussion of the isotherm at that temperature, but the tendency of the 2 liquids to form very permanent emulsions is displayed for several degrees lower: the opalescence which appears and disappears promptly in the cases of Equilibria 14 and 5 when the consolute temperatures are reached, is found to exist over a wide temperature range in the case of the equilibrium being studied. From the fact that the solubility curve for silver perchlorate rises very sharply on the side of the benzene-salt axis with rise of temperature, it is safe to

estimate that this consolute temperature is not higher than $30°$, which temperature will be adopted provisionally. Analyses of the solutions have been made, which are represented in Fig. 3 by the two lines C_2n and C_1n.

Equilibrium 10. $(S_B + L_2 + L_1)$

	Temp. °C.		AgClO₄ %	C₆H₆ %	H₂O %	Density
C_2........	4.98	L_2	36.86	61.38	1.76	1.276
C_1........		L_1	5.03	94.71	0.20	0.923
	25.00	L_2	31.92	67.03	1.04	1.200
		L_1	10.45	89.34	0.21	0.960
n........	(30.00)	$L_2 = L_1$	(25.00)	(74.0)	(1.00)	...

Equilibrium 11 shows the solution L_1 in contact with solid benzene and the compound S_B. It has but a short temperature range, and ends with the disappearance of water from the liquid phase at the binary eutectic for salt and benzene, the temperature of which is $5.12°$. It is thus to be looked upon as the prolongation of Equilibrium 10, which was the prolongation of Equilibria 15, 14 and 17, which latter had its origin at the ternary eutectic E, $-57.8°$. The curve is shown as C_1 f in Fig. 3, and the analyses are as follows.

Equilibrium 11. $(S_B + B + L_1)$

	Temp. °C.	AgClO₄ %	C₆H₆ %	H₂O %	Density
C_1..............	4.98	5.03	94.77	0.20	0.923
f..............	5.12	3.44	96.56	0.00	0.909

Equilibrium 9 (benzene, L_2 and L_1) continues with rising temperature to the point where, with increase in water and salt content in L_2, the liquid L_3 appears, thus constituting the fifth quintuple point. The changes are represented in Fig. 3 by the two lines C_1B_1 and C_2B_2, and the composition of the 2 liquid phases (L_2 and L_1) is given below, together with that of the third liquid, L_3, at the invariant temperature $5.24°$.

Equilibrium 9 (7). $(B + L_1 + L_2)$

	Temp. °C.		AgClO₄ %	C₆H₆ %	H₂O %	Density
C_1..............	4.98	L_1	5.03	94.77	0.20	0.923
C_2..............		L_2	36.86	61.38	1.76	1.276
B_1..............	5.24	L_1	1.72	98.20	0.077	0.896
B_2..............		L_2	52.02	35.30	12.68	1.532
B_3..............		L_3	70.30	(1.6)	28.1	2.141

At the new quintuple point, $5.24°$, the 4 phases present (with vapor) are solid benzene, L_1, L_2, and L_3. When the composition of these 4 phases as shown above is designated on the triangular diagram, no one of them appears within a triangle constructed upon the other 3; but a line connecting the benzene vertex with L_2, (B_2B) crosses that connecting L_3

and $L_1(B_3B_1)$, from which it follows that the phase reaction is as follows

$$B + L_2 \rightleftarrows L_3 + L_1 \text{ (Quintuple Point } B, 5.24°)$$
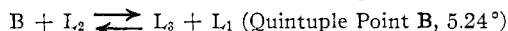
The 4 monovariant equilibria arising at this temperature therefore occur in groups of 2 instead of groups of 1 and 3, and are as follows.

		Equil.
At lower temperatures.............	$\begin{cases} B + L_2 + L_3 \\ B + L_2 + L_1 \end{cases}$	8 = 13 7 = 9
At higher temperatures............	$\begin{cases} B + L_1 + L_3 \\ L_1 + L_2 + L_2 \end{cases}$	6 5

It will be seen that Equilibrium 8 is the same as 13, arising at Quintuple Point D, and 7 is the same as 9, arising at Quintuple Point C, only the 2 equilibria which lead to higher temperatures being new. Equilibrium 6 ($B + L_1 + L_3$) represents the freezing point of benzene in equilibrium with benzene-water solutions containing salt, and obviously must have its terminus at the freezing point of benzene in saturated water-benzene solutions free from salt, namely at 5.40°. The movement of the points representing the liquid phase is given in Fig. 3 by the two lines B_1e and B_3i, in which the point i is only very slightly to the left of a. The value for i is estimated from Fig. 2.

Equilibrium 6. ($B + L_1 + L_3$)

	Temp. °C		AgClO₄ %	C₆H₆ %	H₂O %	Density
B₁.............	5.24	L₃	70.33	(1.6)	28.1	2.141
B₃.............		L₁	1.72	98.20	0.077	0.896
	5.30	L₃	70.24	(1.5)	28.26	2.151
		L₁	1.26	98.67	0.068	0.880
	5.367	L₃	67.7	(1.0)	31.3	...
		L₁	0.56	...	...	...
	5.392	L₃	48.4	(0.5)	51.1	1.643
		L₁	0.0	99.94	0.062	0.875
i.............	5.40	L₃	0.0	(0.12)	99.88	...
e.............		L₁	0.0	99.97	0.03⁶	...

There is here an extremely large variation in the composition of L_3 with a comparatively small change in L_1. This is in accord with the fact that the lines representing the 2 liquids are distribution curves, in which the amount of salt in the one is many thousand times that in the other; this ratio has been shown to be as high as 46000:1 at moderate concentrations.[1] The measurements of this distribution at 25° have been made at various concentrations and appear in Table V.

The equilibrium under discussion involves the melting point of a solid (benzene) in presence of a second liquid phase (water) and in presence of a third component (silver perchlorate) dissolved in the 2 liquids. The conditions governing such a transition point have been studied by Schreinemakers.[12] He arrives at the generalization that the

[12] Schreinemakers, Z. physik. Chem., 25, 305 (1898).

transition point of a solid in the presence of a second (liquid) component is raised by a third component if this latter is more soluble in the dilute than in the concentrated solution. In order to understand this generalization it is necessary to have in mind Schreinemakers' definition that the "dilute" solution is the solution containing the smaller amount of the solid component, and that solubility is the concentration of the third component per unit weight of the third plus the second, or liquid, component. With these definitions in mind, the therorem may be applied to the materials of Equilibrium 6, in which $5.40°$ is obviously the transition point of solid benzene in the presence of a second (liquid) component, water. This transition point should be raised or lowered by the third component, silver perchlorate, according as that substance is more soluble in the dilute (benzene-weak) solution or in the concentrated (benzene-rich) solution. L_3 is obviously the dilute solution. The concentration of silver perchlorate in this phase at $5.24°$, as defined above, is 70.33 divided by 70.33 plus 28.1 (expressed in grams) or 0.71, while in L_1 it amounts to 1.72 divided by 1.72 plus 0.077, or 0.95; that is, it is higher in the concentrated solution L_1, whence it would follow that the transition temperature should be lowered by addition of silver perchlorate. Actually it is lowered from $5.40°$ to $5.24°$, which accords with the requirements of the theorem. In this connection it may be stated that Schreinemakers' exceedingly valuable generalization would be much less liable to misinterpretation if it were phrased so as to consider solubility as the ratio of the third component to the first (or solid) component, in which case a rise in transition point would be required when the salt is more soluble in the concentrated solution.
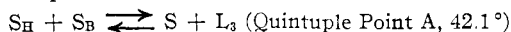
Equilibrium 5, remaining for discussion, is that in which 3 liquid phases coexist. It appears to be a novelty in 3-component systems, in that the other case studied by Schreinemakers,[10] namely, succinic nitrile, ether and water, is one in which all 3 pairs of components are partially miscible. giving at some temperature or temperatures 3 binodal curves, whose intersection gives rise to the isothermal invariant system of 3 liquids. In the case here found, however, water and benzene constitute the only pair of components giving 2 liquid phases and a binodal curve at any temperature known, either above or below the limits within which 3 liquid phases are found. A discussion of this phenomenon will be given later.

As the temperature rises, the composition of L_3 and L_2 in equilibrium with L_1, approaches the same value and at $22.4°$ the 2 phases in question coalesce. The temperature is in this case very sharply marked, and the point at which the emulsion gives place to the critical opalescence or the reverse, with rising or falling temperature, can be determined without error of more than $0.1°$. If stirred above the temperature of $22.4°$

the system shows, in addition to the layer of L_1 floating above, a single opalescent layer which retains its opalescent character as long as it contains any admixture of L_1; below the consolute temperature, L_3 and L_2 separate into 2 perfectly clear and transparent phases in the course of a very few minutes. The compositions of the 3 liquids are given below, and the curves representing the direction of the changes are represented in Fig. 3 by the two lines B_3b and B_2b, meeting at the consolute point b, and the third line B_1d, ending at the concentration d at which the system ceases to be monovariant.

Equilibrium 5. $(L_3 + L_2 + L_1)$

	Temp. °C.		AgClO₄ %	C₆H₆ %	H₂O %	Density
B₃..........	5.24	L₃	70.30	(1.6)	28.1	2.141
B₂..........		L₂	52.02	35.30	12.68	1.532
B₁..........		L₁	1.72	98.20	0.077	0.896
b...........	22.4	L₃=L₂ 64.4		18.2	17.4	1.894
d...........		L₁	1.57	98.32	0.09	0.884

The sixth and highest invariant temperature is $42.1°$ (Quintuple Point A). This quintuple point occurs as the result of a change in the monovariant system $S_H + S_B + L_3$ (Equilibrium 22), which has its origin at the eutectic $-58.4°$ and continues over the interval of $100°$ with but slight change in composition of the liquid layers. It will be remembered that the transition point of the hydrate S_H is at $+43.1°$ (Table I) in the presence of water alone, from which it may be deduced that the presence of small amounts of the third component, benzene, will lower the temperature of its change into the anhydrous compound. By the use of cooling curves it was rather sharply determined that this change, in the presence of L_3, is at $42.1°$, only a degree lower than the transition temperature in presence of pure water. The composition of the liquid phase L_3 at this temperature falls outside the triangle joining S, S_B and S_H, from which it follows that the phase reaction is

$$S_H + S_B \rightleftharpoons S + L_3 \text{ (Quintuple Point A, 42.1°)}$$

and the 4 equilibria are

			Equil.
At lower temperatures.............	$\begin{cases} S_H \\ S_H \end{cases}$	$\begin{matrix} + S_B + S \\ + S_B + L_3 \end{matrix}$	$\begin{matrix} 4 \\ 3 = 22 \end{matrix}$
At higher temperatures............	$\begin{cases} S_H \\ S_B \end{cases}$	$\begin{matrix} + S + L_3 \\ + S + L_3 \end{matrix}$	$\begin{matrix} 2 \\ 1 \end{matrix}$

Equilibrium 4 has no liquid phase, and Equilibrium 3 has been discussed. Equilibrium 2 exists over a range of only $1°$, terminating at the transition point of the hydrate in presence of water.

Equilibrium 2. $(S_H + S + L_3)$

	Temp. °C.	AgClO₄ %	C₆H₆ %	H₂O %	Density
A.................	42.1	87.1	0.7	12.2	2.956
k	43.1	86.5	0.0	13.5	...

Equilibrium 1 also terminates at a transition point, that of the compound S_B, but the temperature range is over $100°$, representing the large extent to which the transition point of the compound is lowered by the presence of water.

Equilibrium 1. (S_B + S + L_3)

	Temp., °C.	$AgClO_4$ %	C_6H_6 %	H_2O %
A................	42.1	87.1	0.7	12.2
....	100	84.4	7.3	8.3
m................	145	63.0	37.0	0.0

Of the 24 equilibria originating at the 6 quintuple points, 3 have no phase of variable composition except vapor (24, 19, 4); 12 are denoted twice and represent 6 equilibria existing between quintuple points (22, 21, 17, 15, 13, 9); 3 terminate in the coalescence of 2 liquid phases at a consolute temperature (14, 10, 5); 4 end at the 3 binary eutectics and the quadruple point for benzene and water (23, 18, 11, 6), and the remaining 2 at the transition temperatures of the hydrate and the solid S_B (2, 1). Monovariant equilibria may, therefore, exist over the range of temperature between $-58.4°$ and $145°$.

If the possibilities as to types of invariant and monovariant equilibria are noted, it will be found that the ternary system under discussion affords an instance of each. For invariant equilibria (vapor being assumed present), the three possibilities of type are S S S L, S S L L, and S L L L, where S denotes a solid phase and L a liquid; Quintuple Points F, E and A are of the first type, both C and D are of the second, and B is of the third. For univariant equilibria there are 4 possibilities, namely S S S, S S L, S L L, and L L L, each of which is represented. The system affords at least one example of each general type of invariant or monovariant equilibrium possible for 3 components with 3 liquids.

The Isotherms

A study of the isotherms representing the ternary system shows an interesting gradual growth in complexity, beginning at the eutectic temperature and increasing up to a point between $4.98°$ and $5.12°$, above which temperature conditions become gradually more and more simple until but few phase complexes are possible. These progressive changes will be shown in Figs. 4 to 21.

At temperatures below the eutectic, $-58.4°$, there can exist only solid phases in equilibrium with vapor. When this temperature is reached, however, a liquid phase can exist, the composition of which is represented in Fig. 4 by the point a, quite close to the line SW, since the benzene content is very low. The triangles marked 4 and 19 represent monovariant equilibria involving no liquid, and may exist at temperatures below or above $-58.4°$. The smaller triangles, 21, 22, and 23, repre-

sent equilibria originating at $-58.4°$ and continuing only at higher temperatures; if a phase complex of total composition falling within one of these triangles be prepared, it will fall into solution of the composition a and two solids represented by the other two angles of the triangle.

As the temperature is raised slightly above the quintuple point F, the area representing the solution L_3 becomes larger, spreading out in all directions until at the temperature $-58.2°$ it touches the side SW, thus eliminating the triangle $S_H + W + L_3$ and setting an upper limit to Equilibrium 23. Here the temperature at which the point a has reached the line SW represents of course the binary eutectic for salt and water. At slightly higher temperatures the liquid area takes the general form a b c d as shown in Fig. 5, retaining that shape until the temperature of Quintuple Point E is reached, at $-57.8°$. Here the phase reaction previously discussed is the appearance of solid benzene as a new phase, causing the elimination of Equilibria 19 and 21 and the appearance of the 2 new equilibria, 17 and 18.
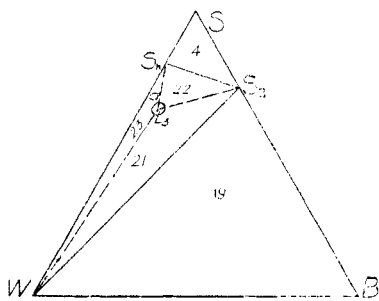

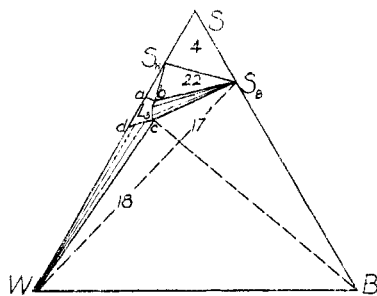Fig. 4.—Isotherm at $-58.4°$ (Quintuple Point F).

Fig. 5.—Isotherm at $-57.8°$ (Quintuple Point E).

As the temperature is further raised, there are but slight changes in this isotherm, which is in form the most persistent of the series; over a rise of about $55°$ the equilibria are those shown in Fig. 5, with the addition only of an area representing solid benzene in contact with L_3, which could be shown by the extension of the point c into a line acting as the base of this triangle. The general form of the area L_3 is, therefore, that shown in Fig. 6: the analyses show that the area is small, and that it does not extend more than 1 or 2% in the direction of the benzene vertex until the next quintuple point is reached, at $-2.7°$. At the point f is shown the approximate location of the newly appearing liquid phase, L_2, the formation of which brings Equilibrium 17 to an end and divides its area into those of the 3 equilibria 13, 14 and 15.

As the temperature is raised above $-2.7°$, the number of fields in the isotherms increases rapidly, and the changes occur with very small increases in temperature. Fig. 7 represents conditions at a temperature

slightly above this quintuple point. The point f of the previous diagram
has widened out into the area f h i of Fig. 7, indicating the range of com-
position which the unsaturated solution L_2 may have. By its extension
into an area it has given rise to several new equilibria; e f g h represents
an area of conjugate solutions, for every point in which there should be
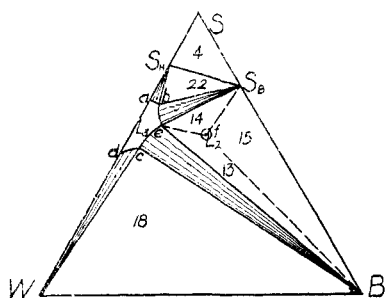drawn a tie-line joining the composition of L_2 with that of its conjugate
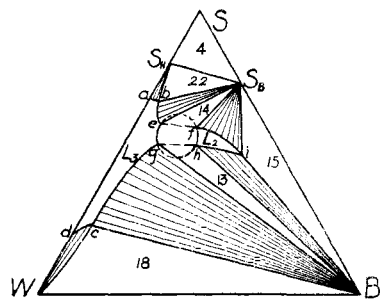

Fig. 6.—Isotherm at −2.7° (Quintuple
Point D).

Fig. 7.—Isotherm above −2.7°.

solution L_3. The isotherm shows 6 isothermal invariant equilibria indi-
cated by the numbered triangles, 6 isothermal monovariant equilibria
consisting of a solid in contact with a liquid and indicated by the shaded
areas, an area of conjugate solutions e f g h, and 2 areas of unsaturated
solutions, L_3 and L_2, a total of 15 fields.

Increase in temperature produces no change in form until the tempera-
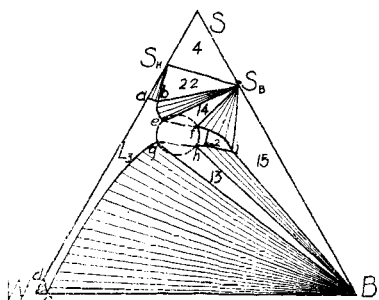ture −0.037° is reached, at which the change is in one particular only.
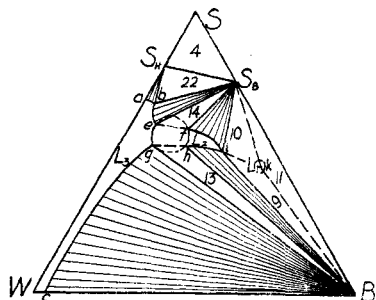

Fig. 8.—Isotherm at −0.037°.

Fig. 9.—Isotherm at +4.98° (Quin-
tuple Point C).

The point c of the previous isotherm has dropped rapidly until as shown
in Fig. 8 it reaches the base line WB, thus terminating Equilibrium 18
(B + W + L_3) which has existed from −57.8° up to this temperature.
The area W d c, representing ice in equilibrium with L_3, is thus reduced
to extremely small dimensions, since the line W c represents only the low
solubility of benzene in water at this temperature, namely 0.153%

(see Fig. 2). The change occurring as the temperature is raised through the small interval to $0°$ is not represented by a drawing; it consists simply in the fall of the point d until it reaches the vertex W. Above this temperature of course the solid phase ice does not appear.

Isotherms will continue to follow the type of Fig. 8, minus the small area W d c, until Quintuple Point C is reached at $+4.98°$. Here the con-
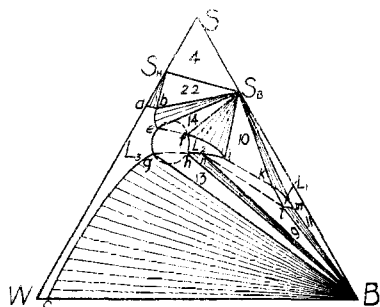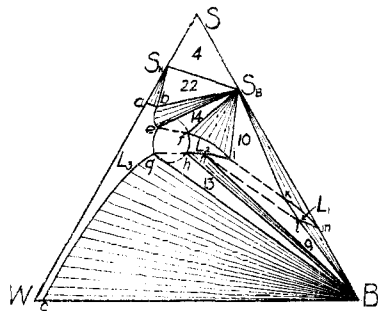

Fig. 10.—Isotherm above 4.98°.   Fig. 11.—Isotherm at 5.12°.

ditions will be as shown in Fig. 9, the change being the appearance of the third liquid phase L_1 at the point k, thus terminating Equilibrium 15 and apportioning its area in the isotherm to the 3 new equilibria, 11, 10 and 9. These represent the new benzene-rich solution in equilibrium with compound and benzene, with compound and L_2, and with L_2 and benzene respectively.

Fig. 10 represents conditions at a slightly higher temperature, at which
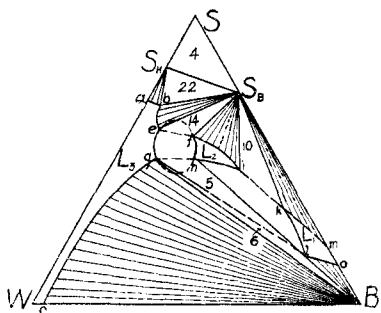
Fig. 12.—Isotherm at 5.24° (Quintuple   Fig. 13.—Isotherm above 5.24°.
Point B).
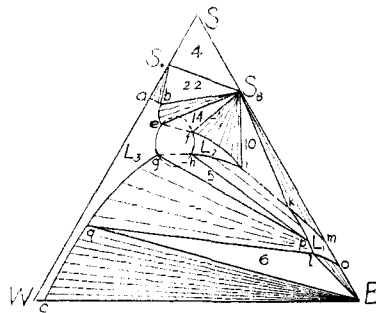
L_1 has increased its dimensions. Here we have again, as in Fig. 7, the addition of new equilibria involving a solid phase and its saturated solution of varying composition (S_B m K and B m l) and also the appearance of L_1 and L_2 as conjugate solutions in the area l n i k. The total of fields occurring at this temperature is 19, which is the largest number met with in the study of this system. It is worth noting that the solid com-

pound S_B can at this temperature be in equilibrium with any one of 8 different phase combinations, and that solid benzene may be in equilibrium with any one of 6, as shown by the number of triangular areas originating at S_B and B respectively. The complexity of the ternary system has thus been increasing from $-58.4°$ up to above $+4.98°$; beginning at the next change, which occurs at $5.12°$, the relationships become more and more simple with rising temperature.

At $5.12°$ the area of unsaturated solutions $L_1(k\ 1\ m)$ has extended until it touches the line of the binary system salt-benzene, eliminating Equilibrium 11; m in Fig. 11 represents the eutectic composition for that pair of components. The changes which now begin may be viewed as resulting from the further extension of $L_1(1\ k\ m)$, which occurs in such fashion as to eliminate several equilibria before it reaches its final characteristic form. The point m moves upward slowly and downward with more rapidity, generating the line m o (Fig. 12). The point 1 moves downward toward the line WB, this movement resulting in a narrowing of the short
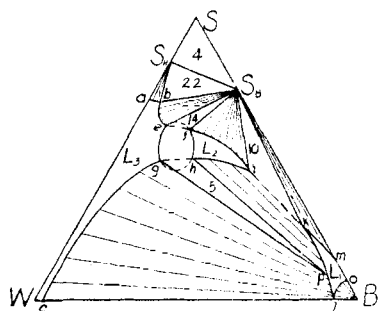

Fig. 14.—Isotherm at 5.40°.   Fig. 15.—Isotherm at 10.4°.
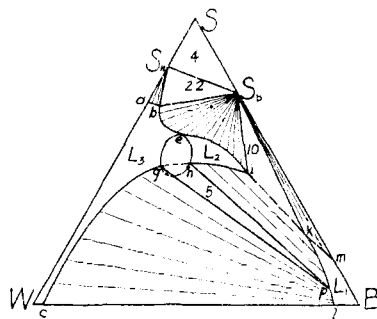
dimension of the triangle l n B(Equilibrium 9) together with a movement of n toward the left, since l and n represent conjugate solutions, in which higher benzene concentration in L_1 is accompanied by lower benzene concentration in L_2. The movement of n, which reduces the triangular area h n B, continues until n coincides with h. At this point the 2 triangles l n B and h n B are reduced to the dimensions of a line, h l, and may be regarded as having disappeared; l, representing a particular composition of L_1, is therefore conjugate with L_2, as represented by the point h, and with L_3 as represented by the point g. At the same time L_3 and L_2 must remain in equilibrium with solid benzene, since nothing has yet occurred to eliminate that equilibrium (13). There are, therefore, 3 liquid phases and 1 solid phase in equilibrium, which with the vapor phase constitute a quintuple point, namely Quintuple Point A (5.24°). Equilibrium 13 of the preceding diagram may now be represented as split up into the 2 equilibria, 5 and 6, originating at this quintuple point, as shown in Fig. 12.

At a temperature above 5.24°, as shown in Fig. 13, the point 1 will have progressed further downward, and the line g 1 of the preceding isotherm will have broadened into g p 1 q, the area of conjugate solutions of L_1 and L_3. The length p 1 is exceedingly short in reality, and g q quite long, since in all of the distribution curves very small changes in L_1 correspond to very large changes in L_3. The system is now slightly less complex than in Fig. 10, the number of fields having been reduced to 18, and the simplicity from now on grows rapidly. Fig. 14 shows conditions at a slightly higher temperature, when the point 1 has completed its migration, meeting the line W B at the binary quadruple point 5.40° (benzene, L_1, L_3, and vapor). Solid benzene can henceforth exist in equilibrium with only one phase, L_1, and the area 1 o B is therefore correspondingly small. Equilibrium 6 has been eliminated by the movement of 1, and the area of conjugate solutions $L_3 - L_1$ (c g p 1) correspondingly enlarged.

Further rise of temperature of 0.08° results in the movement of the point o toward B, which it meets at the melting point of pure benzene,

Fig. 16.—Isotherm at 22.4° and above.   Fig. 17.—Isotherm at 30°.

5.48°, thus removing the area 1 o B, but resulting in no other qualitative change in the isotherm. Above this temperature the chief change is the approach of the points f and e toward each other, representing the gradual approach of L_2 and L_3 toward identical composition. At 10.4°, the consolute temperature, the isotherm has the form of Fig. 15, and Equilibrium 14 ($S_B + L_3 + L_2$) is terminated. L_3 and L_2, therefore, have remained as wholly separated areas of unsaturated solution only from $-2.7°$ to $+10.4°$. As the temperature continues to rise, the points h and g, representing the lower limits of salt concentration in conjugate L_3 and L_2, also approach each other, merging in the point g of Fig. 16 at the sharply defined consolute temperature 22.4°. Equilibrium 5($L_3 + L_2 + L_1$) is thereby ended, and it appears, therefore, that three coexistent liquid phases are found in this system only between the temperatures 5.24° and 22.4°. It is noteworthy that this equilibrium does not show the characteristics of the 3-liquid system studied by Schreinemakers,[10] in

which the areas representing the pairs of conjugate solutions migrate
toward the 2-component axes, and show after reaching their bases the usual
form of 3 binodal curves. In the present system only 1 binodal curve
can be shown to reach its 2-component axis, namely the curve c g i k l
(Fig. 16).

If only 1 binodal curve can be completely established, there arises the
interesting question as to why there should be found in this system 3
completely separated areas of solution at temperatures below $10.4°$
(Figures 9 to 15). To account for the separation of the total area of so-
lution into 2 parts (L_1 and L_3) is a simple matter; the binodal curve
c g i k l is intersected at k and i by the solubility curve a b i k m at low
temperatures, and only when the temperature has risen to $30°$ (Fig. 17)
does the solubility curve rise high enough to escape this intersection.
But the further separation of the liquid area into L_3 and L_2 at tempera-
tures below $10.4°$ (Fig. 15) requires a different explanation. The sepa-
ration cannot be due to a second intersection of the 2 curves, although the
almost perpendicular section of the solubility curve below b might at first
suggest such an intersection. If it is assumed that the solubility curve does
have a part descending far enough at any temperature to intersect the
binodal curve, it must be granted that it possesses at the same tempera-
ture also an ascending branch, since the curve must rise to furnish the
upper boundary of the area L_2. If this loop in the solubility curve exists,
its lowermost point must rise with ascending temperature, since the loop
is wholly absent at $25°$ (Fig. 16). In that case, it must on ascending pass
through the binodal curve at the point g (Fig. 16) at a lower temperature
than that at which it reaches the point e (Fig. 15); that is, L_3 and L_2
must become consolute at the concentrations of point g at a lower tempera-
ture than at the point e. But the experimental facts are in direct opposi-
tion to this conclusion; coalescence occurs at e at $10.4°$, and at g at $22.4°$,
the difference of $12°$ being beyond the possibility of experimental error.
It follows then that the hypothesis that the separation of L_3 from L_2
is due to a second intersection of the solubility curve and the binodal
curve is contradicted by the facts.

The rational explanation seems, therefore, to be that, in Fig. 15, there is
a second closed binodal curve e g h, of which the larger portion is in a stable
region and a smaller portion in the metastable region below the binodal
curve g h. At lower temperatures its upper portion is in the metastable
region above the solubility curve a m, as shown by the dotted lines in
Figures 7 to 14. The closed binodal curve may be assumed to have its
beginning at $-2.7°$ (Fig. 6) where its stable part is limited to the 2 points
f and e; with rising temperature it suffers a contraction in the horizontal
dimension and its position in the diagram moves downward, until at $22.4°$
(Fig. 16) it has moved wholly into the metastable area beneath the bi-

nodal curve c k l.   Since its area becomes rapidly less, it may be assumed to shrink to a point at some temperature not far from 30° (Point g, Fig. 17), above which temperature it no longer exists.

This hypothesis of a completely closed binodal curve contradicts no facts observed in this study, and is supported by the analytical determination of some of the points which make up its stable part (Equilibrium 14, Fig. 12; Equilibrium 5, Figs. 9 and 11).   It is further substantiated by the occurrence of a similar area in the system, a silver perchlorate-toluene, and water, which is now being studied in this laboratory.   In this latter case the outlines of the closed curve are very distinctly recognizable.   Schreinemakers[13] has postulated the existence of such completely closed binodal curves as the simplest type of binodal curve but, as far as known to me, curves of this character have not previously been realized.   In the system under discussion, we may regard the curve as experimentally demonstrated, although certain portions of it are in the metastable region and are therefore not realizable.

The occurrence of this second binodal curve is of course something hardly to be anticipated, since it has been shown that only 1 of the 3 pairs of components in the system shows 2 liquid phases.   It is to be recalled however that the curve for the system, silver perchlorate-benzene, (Fig. 1) has very nearly the appearance found where 2 stable liquids occur, and that Alexejew[7] has found the occurrence of 2 liquids in the metastable region for a pair showing a like form of curve.   In the case studied by me the 2 liquids have not been found in the metastable region; but it may be held that the addition of the third component, water, has further accentuated the tendency toward the formation of an additional liquid phase, giving rise to a new and stable liquid phase in the 3-component system.

The form of isotherm shown in Fig. 16 is still existent at 25°, at which temperature a complete series of measurements has been made, covering the solubility curve a m, which is here interrupted over the short distance i k, and the distribution curve c i l.   The measurements for the solubility curve, which are given in Table IV, were used as a basis for calculating solubilities at all other temperatures.

Within certain limits of compositions of solvent, a single metastable solution is obtained—indeed, cannot apparently be avoided.   The experiments numbered 18 to 23 are of this character.   At any such total composition, the liquid should break down into L_1 and L_3 in equilibrium with $AgClO_4.C_6H_6$ (Equilibrium 10), but actually such solutions remained unchanged for indefinitely long periods.   The points 18 to 23 are, however, in no sense indefinite, but fall fairly well upon the smooth curve with no greater error than found in the experiments with the stable solutions.

[13] Schreinemakers, Z. physik Chem., **22**, 93 (1897); **23**, 649 (1897).

TABLE IV

SOLUBILITY CURVE a m AT 25°

No.	Point	AgClO₄ %	C₆H₆ %	H₂O %	Density
		Solid Phase AgClO₄.H₂O			
1	a	84.45	0.0	15.55	2.806
2		84.28	1.19	14.53	2.823
		Solid phase AgClO₄.H₂O + AgClO₄.C₆H₆			
3	b	84.1	1.7	14.2	. . .
		Solid phase AgClO₄.C₆H₆			
4		83.98	1.68	14.34	2.806
5		83.93	1.36	14.71	2.808
6		83.12	1.55	15.32	2.747
7		81.30	1.41	17.29	2.644
8		75.53	7.75	16.62	. . .
9		69.27	15.81	14.91	2.103
10		65.69	22.32	11.98	1.978
11		62.34	27.84	9.81	1.871
12		62.01	28.14	9.85	1.851
13		51.89	43.18	4.94	1.562
14		46.80	50.34	2.86	1.462
15		42.51	55.53	1.96	1.358
16		35.20	63.52	1.28	1.254
17	i	(31.92)	(67.03)	(1.04)	(1.200)
18		31.45	67.54	1.01	1.197
19		25.40	73.90	0.70	1.123
20		15.37	84.29	0.34	1.021
21		14.65	85.01	0.34	1.006
22		13.90	85.82	0.28	1.000
23		10.65	89.13	0.22	. . .
24	k	(10.45)	(89.34)	(0.21)	(0.960)
25		9.55	90.26	0.187	0.949
26		9.38	90.45	0.169	0.9474
27		9.01	90.84	0.15	0.9470
28		8.28	91.60	0.13	0.9367
29		7.31	92.58	0.103	0.9332
30		6.84	93.08	0.074	0.9259
31		6.18	93.77	0.504	0.9221
32		5.96	94.00	0.0361	0.9205
33	m	5.00	95.00	0.000	0.906

The points i and k (Lines 17 and 24), which are the terminations of the areas L_3 and L_1, could not be found by direct methods, because of the formation of these metastable solutions. The points are placed with reasonable accuracy, however, as the points of intersection of the solubility curve with the distribution curve given later in Table V. The best results were obtained by plotting the concentration of silver perchlorate in terms of normality against the water content on a system of rectangular coördinates; a second plot of the water content against the observed densities gave the density at the point of intersection, supplying all data necessary for the

calculation. Experiment 18 falls upon one of these points of intersection within the probable errors of the determinations.

The curve a m as a whole has several points of interest. If the solubility be plotted upon a system of rectangular coördinates, with the concentration of silver perchlorate as ordinate and the percentage composition of the solvent in terms of benzene and water as abscissa, a straight line joining a and m will then show the solubility at any composition calculated as an additive function of its solubility in the pure solvents. The observed solubilities, however, are found to lie far above the straight line throughout its course, indicating that the mixed solvent is more effective than the pure components in any and all ratios.

The solubility curve in Fig. 16 shows two portions which deviate from the simple curve which might be expected to join the points a and m. There is a short section which runs nearly parallel to the W B axis (Experiments 1, 2, 3, Table IV) followed by a nearly perpendicular portion (Experiments 3 to 8). The curve from Experiments 9 to 30 is practically a smooth curve, giving to the L_3 area the general shape of a sickle.

The distribution curve c i k l has also been studied at 25°. The method consisted in weighing the components into a small cylinder, rotating at 25° until equilibrium was established, which usually required less than an hour, and then allowing the vessel to stand until the 2 phases were completely clear, which sometimes required a longer period. Samples of each phase were then titrated for their silver content, and a known weight of L_1 rotated with a weighed quantity of silver perchlorate and analyzed to determine the benzene-water ratio as explained previously. The volumes of both phases in the original experiment were read in the calibrated cylinder, so that the water and benzene content of the phase L_3 was known by subtraction of the composition of L_1 from the known total composition. The method of differences thus used leads of course to noticeable irregularity in those experiments in which the benzene concentration of L_3 is very low. The following table gives the results found. The figures in brackets were found by graphical interpolation.

The points i and k (Line 14) were obtained by interpolation, as explained in Table IV, in which also they occur. Experiment 15 represents again a metastable condition; in this case the solutions were supersaturated with respect to the solid phase $AgClO_4.C_6H_6$, since the points fall above the solubility curve. There are, therefore, two kinds of metastability realizable between the points i and k of Fig. 16, giving, respectively, the metastable liquids described earlier, which should fall at equilibrium into 2 liquid phases each (supersaturation with regard to liquids), and the metastable conjugate solutions of Line 15 (supersaturation with respect to the solid phase). It is interesting to note that the two kinds of metastability have not occurred simultaneously, that is, all points have fallen normally

TABLE V

THE DISTRIBUTION CURVE c 1 AT 25°

Conjugate Solutions

		L_3					L_1		
No.	AgClO₄ %	C₆H₆ %	H₂O %	Density		AgClO₄ %	C₆H₆ %	H₂O %	Density
1 c	0.00	0.08	99.92	. . .	1	0.000	99.95	0.061	. . .
2	50.81	(0.10)	49.09	1.628		0.030	99.91	(0.06)	0.869
3	59.30	(1.00)	39.70	1.821		0.052	99.89	(0.06)	0.870
4	67.73	1.96	30.31	2.050		0.25	99.69	(0.06)	0.873
5	70.52	3.76	25.72	2.127		0.77	99.17	0.06	0.879
6	69.31	11.17	19.51	2.071		1.55	98.37	0.076	0.881
7	60.06	26.15	13.78	1.749		1.59	98.32	0.090	0.881
8	57.88	30.74	11.38	1.653		1.74	. . .	. . .	0.882
9	54.22	36.36	9.42	1.566		1.85	. . .	. . .	0.882
10	46.95	47.57	5.47	1.442		2.90	97.00	0.0969	0.891
11	41.74	55.00	3.26	1.348		4.28	95.61	0.119	0.903
12	38.80	58.62	2.57	1.296		5.80	94.05	0.148	0.916
13	35.28	63.23	1.49	1.218		8.42	91.41	0.168	0.937
14 i	(31.92)	(67.03)	(1.04)	(1.200)	k	(10.45)	(89.34)	(0.21)	(0.960)
15	31.12	68.06	0.82	1.162		13.58	86.13	0.287	0.983

upon the extension of the solubility curve or of the distribution curve, and not within the area between them.

The distribution curve runs very close to the S W axis up to a concentration of about 65% of silver perchlorate; that is, the amount of benzene in the aqueous layer remains small until the salt concentration becomes very high. It also runs very close to the S B axis up to about 35% of silver perchlorate, showing a correspondingly small amount of water in the benzene layer. The plait point of the curve is in the metastable region between i and k, presumably nearer i than k. As a result of this one-sided location of the plait point, the tie lines for the conjugate solutions are steeply inclined toward the base line W B on the benzene side, which expresses graphically the fact that the distribution of silver perchlorate is largely in favor of the aqueous phase L_3. Investigation of this distribution at moderate concentrations of salt has already been published:[1] at a salt concentration of 2.4 N in L_3, the ratio of salt present in L_3 to that in L_1 is at least 46000 to 1, and at lower total salt concentrations the ratio is higher. The bearing of these facts upon the usual views as to the degree of dissociation of the salt in water has been pointed out. When the salt concentration in L_3 has risen as high as 59% (Line 3), the ratio in the 2 phases is still as high as 1200 to 1.

The measurements given earlier in the study of the various equilibria at different temperatures indicate that the distribution curve has substantially the form appearing in Fig. 16, whether the temperature be high or low; that is, it runs close to the S W and S B axes for considerable distances, and reaches its maximum height at a salt concentration between 60% and 70%.

As the temperature rises above 25° there is no qualitative change in the isotherm until the temperature is reached at which Equilibrium 10 disappears through the approach of the points i and k to identical composition, as shown in Fig. 17. This temperature could not be exactly determined, but is not far from 30°. The point i, which represents the composition of the consolute solutions at that temperature, also represents the plait point of the binodal curve c l. Above this temperature we have a continuous area of unsaturated solution extending from the S W axis to the S B axis, which area grows larger as the temperature rises. At 42.1° the last quintuple point appears, as shown in Fig. 18, resulting in the appearance for the first time of the anhydrous compound $AgClO_4$ as the saturating phase in contact with liquid, thereby terminating Equilibria 22 and 4 and originating the new equilibria 1 and 2. Equilibrium 22 has had an existence over a range of 100°, and Equilibrium 4, containing no liquid phase, over an indefinitely large temperature range. Of the new equilibria, Equilibrium 1 is but short-lived and disappears
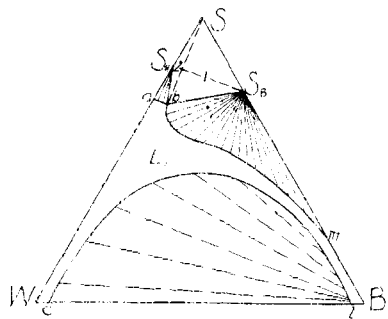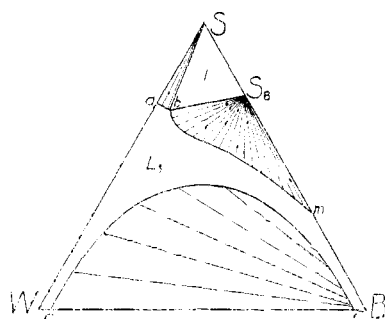

Fig. 18.—Isotherm at 42.1° (Quintuple Point A).

Fig. 19.—Isotherm at 43.1°.

at 43.1° with the final disappearance of the hydrate as a stable phase; Fig. 19 indicates its disappearance at the point a. From this temperature onward the changes consist in a gradual rise of the point a, representing the solubility of anhydrous salt in water, and a much more rapid rise of the point m, showing the rapid rise in solubility of the compound S_B. With these movements there occurs a migration of the point b toward the axis S B, giving rise (as in Fig. 20) to an increasing area S a b in which the anhydrous salt is stable and a diminishing area S_B b m in which the compound S_B can exist. The conditions existing at 100° are shown qualitatively in Fig. 20.

The continued movement of the point b brings it finally to the line S B at 145°, which is the transition point of the compound into the anhydrous salt. The points m and b, therefore, meet at this temperature. The isotherm is shown in Fig. 21, which represents the conditions existing at all higher temperatures. All of the monovariant equilibria have dis-

appeared, and no others can be assumed to appear unless the salt forms either a hydrate or a benzene compound with some fractional portion of a molecule of water or benzene; this is rendered improbable by the results shown in Table I and II. It appears, therefore, that above 145° the system has but 3 fields, that of the saturated solution, S a m, that of the conjugate solutions bounded by the binodal curve c l, and that of unsaturated solution, a m l c. With rise of temperature the solubility curve a m rises toward the apex S, which it should reach at the melting point of the salt, 480°. The binodal curve presumably changes its position but slightly. It is of course highly probable that other less simple changes occur before the temperature of 480° is reached, since the critical temperatures of both water and benzene are lower than that figure.

We are thus able, from these isotherms, to form an accurate picture of the conditions existing in this 3-component system from the eutectic temperature −58.4°, below which no liquids can exist, up to the melting point of the salt, 480°, above which no solid forms can exist.
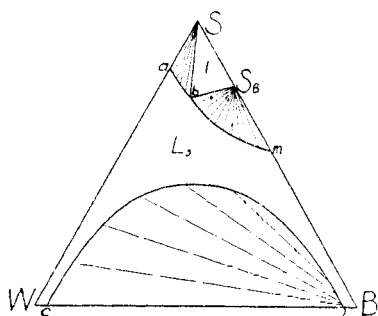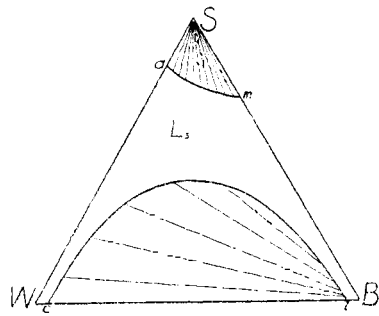
Fig. 20.—Isotherm at 100°.   Fig. 21.—Isotherm at 145° and above.

Summary

1. The system, silver perchlorate-water, has a eutectic point at −58.2°, at which temperature the saturated solution contains 73.9% of the silver salt. This is the lowest known eutectic for a true salt and water. The solubility rises to 88.8% at 99°.

2. The eutectic temperature of the system, silver perchlorate-benzene, is +5.12°, and the solution contains 3.44% of the silver salt. The solubility curve rises steeply with the temperature, almost reaching a perpendicular form between 50° and 145°; at the latter temperature the saturated solution contains 63.0% of silver perchlorate. Attention is called to the likeness between this solubility curve and those which are found where the system gives rise to 2 liquid phases, either in the stable or the metastable region.

3. The hydrate $AgClO_4.H_2O$ has been isolated and its transition

point found to be 43.1°; the compound $AgClO_4.C_6H_6$ has also been iso-
lated and its transition point found to be 145°.

4. The ternary system, silver perchlorate-water-benzene is marked
by the possession of 6 realizable invariant equilibria, and a large number
of monovariant equilibria, affording at least one example of every type
of equilibrium theoretically possible for a ternary system containing vola-
tile components.

5. The ternary eutectic representing 3 solid phases, solution and vapor
is at −58.4°; the eutectic of highest temperature is at 42.1°. The
course of the 24 monovariant equilibria originating at these 2 quintuple
points and the 4 intermediate quintuple points has been studied.

6. Isothermal diagrams have been constructed to show the various
equilibria existing at temperatures between −58.4° and +145°

7. Between 5.24° and 22.4°, 3 coexistent liquid phases can be pre-
pared in stable equilibrium with each other and their vapor. The oc-
currence of two separate fields of unsaturated solution is explained as
due to the intersection of the solubility curve of silver perchlorate with
the binodal curve representing the limited solubility of benzene and water.
The occurrence of a third field is explained as due to the existence, be-
tween −2.7° and +30° (approximately), of an additional closed binodal
curve, which does not extend to any one of the 2-component axes at any
temperature. It appears to be the first demonstrated case of a closed
binodal curve.

New York, N. Y.

A SIMPLE METHOD OF ELECTROMETRIC TITRATION IN ACIDIMETRY AND ALKALIMETRY

By Paul Francis Sharp with F. H. MacDougall

The object of the investigation reported in this paper was to find a
number of constant and reproducible electrodes which would be electro-
motively equivalent to hydrogen electrodes dipping in solutions of various
known concentrations of hydrogen ion. The usefulness of such electrodes
will be at once apparent. If, for example, it becomes necessary to titrate
an unknown acid solution to an end-point which shall be a definite hydro-
gen-ion concentration, the half-cell containing a hydrogen electrode and
the unknown solution is connected with one of our electrodes and alkali
is run into the unknown solution until a galvanometer indicates a zero
e.m.f. The method is applicable especially to all cases in which the ti-
tration is carried to a definite hydrogen-ion concentration, or more gener-
ally to all cases in which the correct potential difference at the electrode
in the solution at the end of the titration is known in advance.