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Continuous chlorosulfonation of benzene : I. Phase relations

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CONTINUOUS CHLOROSULFONATION OF BENZENE

I. PHASE RELATIONS

BY

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ABSTRACT

This work presents liquid-liquid equilibria data on a system suitable for continuous chlorosulfonation of benzene. Complete information is presented for the ternary, chlorosulfonic acid - sulfuric acid - carbon tetrachloride. A partial investigation of the ternary systems, chlorosulfonic acid - sulfuric acid - benzenesulfonyl chloride; chlorosulfonic acid - carbon tetrachloride - benzenesulfonyl chloride; and the quaternary system, carbon tetrachloride - benzenesulfonyl chloride - sulfuric acid - chlorosulfonic acid is also presented.

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INTRODUCTION

A. Purpose and Scope

Chlorosulfonation is a common organic reaction. Industrially it finds application in the preparation of dyes and drugs through organic syntheses (e.g. chlorosulfonation of acetanilide for sulfa drugs, o-toluenesulfonyl chloride for saccharin). Commercial processes are batchwise, the economics of which require efficient recovery and utilization of hydrochloric acid from spent, excess chlorosulfonic acid.

This work was initiated to develop a process for continuous chlorosulfonation. It was envisioned that the technique would involve continuous reaction and extraction of the organic product with recycle of the excess chlorosulfonic acid. Such a process may have economic advantages over the batch method.

Benzene to benzenesulfonyl chloride was chosen for study because of the availability of process information and the relative simplicity of the reaction. The problem herein is concerned primarily with the phase relationships between chlorosulfonic acid, benzenesulfonyl chloride, sulfuric acid and carbon tetrachloride at 25°C. It is planned that further work will utilize the information obtained here to develop the process kinetics and reaction scheme.

B. Historical and Theoretical

Chlorosulfonation of benzene (7), (11), (15) toluene (12), naphthalene (10) and related compounds (3), (6), (8), (10), (13), (19), have been reported in the literature. The classical laboratory procedure for the preparation of benzenesulfonyl chloride is described by Gilman and Blatt (7). Industrial methods do not differ much from the laboratory procedure. The German patent (12) describes a process calling for the slow continuous introduction of the hydrocarbons into chlorosulfonic acid at -10°C. The common practice is to carry out the reaction of benzene and toluene at 20-25°C. Use of an inert solvent in chlorosulfonation has also been reported (10), (18). The latter reference is a report of a German technique, discussed below. Data on continuous chlorosulfonation is noticeably lacking. Discussions on continuous sulfonations are available (9), (23) which may serve as a guide to equipment design.

Chlorosulfonation. Chlorosulfonic acid reacts with both aliphatic and aromatic compounds. The reaction may be represented:

$$R{\cdot}H + ClSO_3H \longrightarrow RSO_2OH + HCl \quad (1)$$

$$R{\cdot}SO_2OH + ClSO_3H \rightleftharpoons RSO_2Cl + H_2SO_4 \quad (2)$$

To drive the reaction of the second step as far as possible to the right, an excess (50-150%) of chlorosulfonic acid over the two theoretical moles is always required (10). For chlorosulfonation of benzene, the reaction may be carried out by adding the benzene to the acid, a three to five molar excess of the acid being employed at temperatures of 20-25°C. Hydrochloric acid is liberated throughout the reaction. The addition usually requires two to three hours. At completion, the mixture is quenched on ice and the organic material is extracted from the aqueous acid by carbon tetrachloride or another inert solvent. Recovery of the sulfonyl chloride can be accomplished by distillation. Under 10 mm pressure the sulfonyl chloride boils at 112°C. Properties of this compound are given in Table I. Yields vary from 75-77% based on the benzene charged (7). The excess of chlorosulfonic acid is important, since with small excesses, diphenyl sulfone formation becomes more favorable. The German report (18) shows that increased yields of benzenesulfonyl chloride may be obtained by the addition of sodium chloride to the reaction. The salt removes sulfuric acid as the sodium acid sulfate, driving the reaction to completion. With carbon tetrachloride present, this salt concentration may be reduced. The data are summarized below. (Table II)

TABLE I

Physical Properties of Benzenesulfonyl Chloride

Molecular Weight	176.6
Melting Point	14.5°C.
Boiling Point	251.5°C.
d^{15}_{15}	1.3842

Colorless, oily liquid, with penetrating odor.

Insoluble and stable in cold water.

Soluble in ether and alcohol.

Vapor Pressure Data (14)

t°C.	p (mm Hg)
65.9	1
96.5	5
112.0	10
174.5	100
198.0	200
224.0	400
251.5	760

The rate of hydrolysis has been determined (16) at 25°C. with:

0.053 N H_2SO_4 - 0.014

0.136 N H_2SO_4 - 0.014

0.264 N H_2SO_4 - 0.013

TABLE II

Effect of Additives in Chlorosulfonation of Benzene

Method	Benzene		Chlorosulfonic Acid		NaCl	ϕSO_2Cl	
	Mols	Grams	Mols	Grams	Grams	Grams	%
Gilman and Blatt (7)	2	156	6	700	none	272	76-77
NaCl added	2	156	10.7	1,250	120	318	90
NaCl - CCl_4	2	156	6	700	120	318	90

Solvents. To develop a continuous chlorosulfonation process, it is desirable to perform the reaction in the presence of an inert solvent. The role of the solvent is to extract the product from the reaction medium as it is formed. The solvent should have a high affinity for the organic product and should separate from spent acids without difficulty. Mutual solubilities of acids and solvent must be low. Recovery of the product should be possible by simple means (e.g. solvent evaporation) with recycle of the inert solvent to the reaction. The literature discusses carbon tetrachloride, carbon disulfide and chloroform as solvents for chlorosulfonation (10).

Liquid-liquid equilibria. Some knowledge of the liquid-liquid equilibria in this system is necessary. The kinetics and subsequent process development depend, to a large extent, on the extraction operation. Hence, attention must be given to liquid-liquid relationships. For this work, interest centers on the ternary and quaternary systems. The ternary formed from two pairs of partially miscible liquids is of special concern. Theoretical consideration of both the ternary and quaternary liquid systems are discussed by Treybal (21). Various methods for obtaining and presenting data are also given. Data on four component systems are relatively limited.

A recent review of liquid-liquid extraction (22) cited nine references on four component systems. Brancker, et al. (1), (2) presented data on chloroform-water-acetic acid-acetone at 25°C. A tetrahedral representation was employed to represent the four component equilibrium condition. Chang and Moulton presented data on the system, benzene-ethyl isovalerate-ethyl alcohol-water (4). Other methods of representation have been presented. Cruikshank, et al. (5) described a graphical method using cartesian coordinates where a ternary of three completely miscible liquids is treated with a solvent which is immiscible with one of them. A method that may have application to the four components concerned with herein was published by Prince, et al. (17). The paper is concerned with the correlation of phase compositions in systems where one component is partially miscible with two others and completely miscible with the third. The correlations may have application to the four component system under consideration here namely, carbon tetrachloride, chlorosulfonic acid, sulfuric acid, benzenesulfonyl chloride.

EXPERIMENTAL

A. Apparatus

Extraction and separation of each mixture was carried out in a cylindrical, graduated all-glass separatory funnel. The funnel was graduated to 25 milliliters in half milliliter divisions. Both the top and bottom of the cylinder contained 24/25 tapered joints. The outlet terminated in a fine capillary tip, giving excellent control when separations were made. An air escape line was provided from the top of the funnel (below the point of the stopper) to the tapered joint below the outlet cock. The apparatus was similar to the equipment described in Scientific Glass Company catalogue (item number J 1867).

Additions of the materials to the extractor were made from micropipettes. These were graduated in tenths of a milliliter to a total of 10 milliliters.

Titrations required the use of standard 25 or 50 milliliter burettes.

Chloride titrations were carried out using a Beckman Instruments Inc. automatic titrator (described in Bulletin 239A of the Beckman Instruments Inc.). A titrating accuracy in the range of ±0.5% was obtainable with the instrument.

B. Materials

The materials employed were:

Carbon Tetrachloride Merck	- Merck & Co., Inc., Rahway, N. J. C. P. grade
Sulfuric Acid Merck	- Merck & Co., Inc., Rahway, N. J. Reagent grade 95-98%
Fuming Sulfuric Acid Merck	- Merck & Co., Inc., Rahway, N. J. Free SO_2 - 20.0% - 23.0%
Benzenesulfonyl Chloride	- Matheson Co. Inc., East Rutherford, N. J. B.P. 102-103°/5 mm
Chlorosulfonic Acid	- DuPont and Co. Inc., Wilmington, Del. 98%

100% Sulfuric Acid was prepared from reagent sulfuric acid and fuming sulfuric acid.

C. Procedure*

All materials employed in the experiments were kept in a constant temperature bath at 23-25°C. Prior to mixing, carbon tetrachloride and sulfuric acid were transferred to microburettes and it was assumed that no change in temperature took place. Great care was used to keep the sulfuric acid from contacting the atmosphere. Chlorosulfonic acid and benzenesulfonyl chloride were taken directly from the constant temperature storage by pipettes. The first component added to the extractor in each case was the least dense one. As an example, when working with carbon tetrachloride, chlorosulfonic acid, sulfuric acid, the solvent carbon tetrachloride was added first. The weight of the first component was accurately recorded on an analytical balance. The second component was added in a similar manner and the mixture well shaken. (In the example above, chlorosulfonic acid would have been added next). When proceeding from the one phase system to the two phase system, a technique similar to the cloud point method was used (21). The third, or fourth component was added dropwise with continuous shaking until a

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* The chemicals employed here are very corrosive and the utmost care was required in handling them.

cloudiness appeared. At this cloud point, one or two drops more of the component was added to bring about the phase separation. The point of phase change was selected as the equilibrium condition rather than the cloud point because it was more reproducible. The weight of this component was recorded accurately. At the equilibrium point, the mixture was shaken for five to ten minutes then allowed to come to rest. Equilibrium appeared to be reached within a matter of minutes. When obtaining tie line data, the mixture was allowed to settle for fifteen to thirty minutes. After settling, the bottom layer was drained into a weighed twenty-five milliliter, stoppered flask. The top layer was drained into a similar flask*. The weight of both layers was then accurately determined on the analytical balance. Analysis of either layer could be made.

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* The interface was readily observed because the chlorosulfonic acid imparted a slight straw color to the acid layer.

D. Analytical Methods

Analytical techniques were essentially the same regardless of the system under investigation. To analyze the bottom, or predominately acid layer, a one or two gram aliquot was taken. This aliquot was carefully added dropwise to a known amount of standard 1 normal caustic. Back titration of the excess alkali with standard 1 normal sulfuric acid provided data on total acidity due to both acids. A Volhard analysis using the titrator gave the accurate estimate of chlorosulfonic acid present. With the three component system, chlorosulfonic acid, sulfuric acid and carbon tetrachloride, the weight percentage of each component in the entire bottom layer could be calculated. The upper solvent layer was analyzed in the same manner but the entire layer was used (0.5-15 grams). Carbon tetrachloride was always determined by difference.

The analytical methods for the four component system differed from the above. Here only the top solvent layer was analyzed. The entire layer (0.5-2.0 grams), after weighing, was cooled in an ice bath, then drowned with fifteen to twenty milliliters of deionized water. The total acid content was rapidly determined by titration with standard 1 normal caustic, using a phenolphthalein indicator. Following the titration, fifteen to thirty milliliters of standard 1 normal alkali was added and the mixture heated to reflux for half an hour. This caused the carbon tetrachloride to boil off and the benzenesulfonyl chloride to react with the alkali. Back titration of the excess caustic at room temperature with sulfuric acid provided the data on increased acidity due to the sulfonyl chloride. A Volhard titration with the titrator gave total chloride due to the sulfonyl chloride and to chlorosulfonic acid. Quantities of all materials could then be determined with carbon tetrachloride found by difference. Knowledge of one layer provides the estimate for the other layer.

In the vast majority of runs, material balances were better than 97%. Losses of material occurred when the extractor was not rinsed down after the layers had been cut.

In the titrations as employed above, the acid equivalent of chlorosulfonic was one-third of the molecular weight. The acid equivalent of the sulfonyl chloride was half the molecular weight. The equation involved here may be given as follows:

$$H_2SO_4 + \not{O}SO_2Cl + ClSO_3H \xrightarrow[\text{cold}]{H_2O}$$

$$H_2SO_4 + H_2SO_4 + HCl + \not{O}SO_2Cl \xrightarrow[\text{cold}]{NaOH}$$

$$Na_2SO_4 + Na_2SO_4 + NaCl + \not{O}SO_2Cl \xrightarrow{NaOH}$$

$$Na_2SO_4 + Na_2SO_4 + \not{O}SO_3Na + NaCl + NaOH$$

E. Results

The experimental data are given in the following tables. Information is presented on the ternary systems and the quaternary system. Graphical illustrations are presented in Figures 1 - 4.

TABLE III

Solvent Selection

Vol. % $ClSO_3H$	Solvent Added	Vol. %	Phases	Comments
50.0	Chloroform	50.0	1	
61.5	Chloroform	38.5	1	
28.6	Chloroform	71.4	1	
50.0	Skelly B	50.0	1	Reaction and darkening of mixture
50.0	Tetrachlorethane	50.0	1	Slow reaction
67.0	Ethylene Dichloride	33.0	1	
50.0	Ethylene Dichloride	50.0	1	
30.0	Ethylene Dichloride	70.0	1	
75.0	Ethylene Dichloride	25.0	1	
30.0	Cyclohexane	70.0	2	Slow reaction
30.0	Cyclohexane (pure)	70.0	2	No reaction
10.0	Carbon Tetrachloride	90.0	2	
25.0	Carbon Tetrachloride	75.0	2	

It appears as if carbon tetrachloride is the most suitable solvent.

TABLE IV

Chlorosulfonic Acid - Sulfuric Acid - Carbon Tetrachloride

Run 1

Total Weight	Actual Weight	Weight %	
62.0829 gms	0.7665 gms	10.00	H_2SO_4
61.3164 gms	3.1701 gms	41.25	$ClSO_3H$
58.1463 gms	3.7690 gms	48.80	CCl_4
54.3773 tare	7.7056 total		

Produced a 2 phase system.

Run 2

Total Weight	Actual Weight	Weight %	
65.5406 gms	1.6248 gms	14.50	H_2SO_4
63.9158 gms	7.4677 gms	67.00	$ClSO_3H$
56.9481 gms	2.0630 gms	18.50	CCl_4
54.3851 tare	11.1555 total		

Produced a 2 phase system.

Run 3

Total Weight	Actual Weight	Weight %	
67.2300 gms	0.7933 gms	6.15	H_2SO_4
66.4367 gms	4.4678 gms	34.62	CCl_4
61.9689 gms	7.6366 gms	59.22	$ClSO_3H$
54.3323 tare	12.8977 total		

Produced a 2 phase system.

Run 4

Added more H_2SO_4 to run 3.

Total Weight	Actual Weight	Weight %	
74.7764 gms	8.3397 gms	40.65	H_2SO_4
	4.4678 gms	21.80	CCl_4
	7.6366 gms	37.35	$ClSO_3H$
	20.4441 gms		

Produced a 2 phase system.

Run 5

Total Weight	Actual Weight	Weight %	
66.3903 gms	0.1539 gms	1.30	H_2SO_4
66.2364 gms	4.4084 gms	36.70	CCl_4
61.8280 gms	7.4487 gms	62.00	$ClSO_3H$
54.3793 tare	12.0110 total		

Produced a 2 phase system.

Run 6

Employing an acid mixture of 87.03 weight per cent $ClSO_3H$ and 12.97 weight per cent H_2SO_4.

Total Weight	Actual Weight	Weight %	
104.9056 gms	12.916 gms	78.94	$ClSO_3H$
103.3860 acid mixture	1.925 gms	11.76	H_2SO_4
	1.519 gms	9.29	CCl_4
88.5446 tare	16.360 total		

Produced a 1 phase system.

Run 7

Added more CCl_4 to run 6.

Total Weight	Actual Weight	Weight %	
106.4347 gms	12.916 gms	72.19	$ClSO_3H$
	1.925 gms	10.76	H_2SO_4
	3.048 gms	17.04	CCl_4
	17.889 total		

Produced a 1 phase system.

Run 8

Added more CCl_4 to run 7.

Total Weight	Actual Weight	Weight %	
107.9514 gms	12.916 gms	66.55	$ClSO_3H$
	1.925 gms	9.92	H_2SO_4
	4.565 gms	23.52	CCl_4
	19.406 total		

Produced a 2 phase system. Top layer just visible.

Run 9

Using acid mixture as in run 6.

Total Weight	Actual Weight	Weight %	
110.8396 gms	13.8851 gms	63.34	CCl_4
96.9545 gms	6.9953 gms	31.91	$ClSO_3H$
	1.0425 gms	4.75	H_2SO_4
88.9166 tare	21.9229 total		

Produced a 2 phase system.

Run 9 (continued)

Equilibrium Points

Acid Layer	Actual Weight	Weight %	
	1.7856 gms	19.02	CCl_4
	6.6344 gms	70.66	$ClSO_3H$
	0.9690 gms	10.32	H_2SO_4
	9.3890 total		
Solvent Layer	12.0995 gms	97.31	CCl_4
	0.2609 gms	1.77	$ClSO_3H$
	0.0735 gms	0.82	H_2SO_4
	12.4339 total		

Run 10

Using acid mixture as in run 6.

Total Weight	Actual Weight	Weight %	
106.4346 gms	7.1767 gms	40.95	CCl_4
99.2579 gms	9.0055 gms	51.39	$ClSO_3H$
88.9103 tare	1.3421 gms	7.65	H_2SO_4
	17.5243 total		

Produced a 2 phase system.

Tie Line Data

Acid Layer - 13.3547 gms

Solvent Layer - 3.9470 gms

Assay of Solvent Layer - 2.6 meq total acid
29.68 mg Cl^-

Run 10 (continued)

Equilibrium Points

Solvent Layer	Actual Weight	Weight %	
	0.097 gms	2.46	$ClSO_3H$
	0.042 gms	1.06	H_2SO_4
	3.808 gms	96.48	CCl_4
	3.947 total		
Acid Layer	3.3687 gms	24.72	CCl_4
	8.9580 gms	65.74	$ClSO_3H$
	1.3000 gms	9.50	H_2SO_4
	13.6267 total		

Run 11

Using an acid mixture as in run 6.

Total Weight	Actual Weight	Weight %	
107.1845 gms	4.6828 gms	25.63	CCl_4
102.5017 gms	11.8277 gms	64.73	$ClSO_3H$
88.9113 tare	1.7627 gms	9.64	H_2SO_4
	18.2732 total		

Produced a 2 phase system.

Equilibrium Points

Acid Layer	Actual Weight	Weight %	
	11.7947 gms	68.60	$ClSO_3H$
	1.7027 gms	10.25	H_2SO_4
	3.6361 gms	21.15	CCl_4
	17.1335 total		

Run 12

Using an acid mixture 67.49% $ClSO_3H$ - 32.50% H_2SO_4.

Total Weight	Actual Weight	Weight %	
114.2622 gms	7.5622 gms	28.87	CCl_4
106.7000 gms	12.5758 gms	48.00	$ClSO_3H$
88.0677 tare	6.0562 gms	23.12	H_2SO_4
	26.1945 total		

Produced a 2 phase system.

Equilibrium Points

	Actual Weight	Weight %	
Solvent Layer	6.0537 gms	95.74	CCl_4
	0.2110 gms	3.34	$ClSO_3H$
	0.0583 gms	0.92	H_2SO_4
	6.3230 total		
Acid Layer	1.5085 gms	7.59	CCl_4
	12.3648 gms	62.22	$ClSO_3H$
	5.9979 gms	30.18	H_2SO_4
	19.8712 total		

Run 13

Using acid mixture as in run 12.

Total Weight	Actual Weight	Weight %	
103.6673 gms	8.4559 gms	54.16	$ClSO_3H$
91.1390 gms	4.0722 gms	26.08	H_2SO_4
88.0540 tare	3.0850 gms	19.76	CCl_4
	15.6131 total		

Produced a 2 phase system.

Run 13 (continued)

Equilibrium Points

Solvent Layer	Actual Weight	Weight %	
	1.6193 gms	97.88	CCl_4
	0.0300 gms	1.81	$ClSO_3H$
	0.0050 gms	0.31	H_2SO_4
	1.6543 total		
Acid Layer	1.4657 gms	10.50	CCl_4
	8.4250 gms	60.36	$ClSO_3H$
	4.0672 gms	29.14	H_2SO_4
	13.9579 total		

Run 14

Total Weight	Actual Weight	Weight %	
111.7956 gms	2.6172 gms	11.03	H_2SO_4
109.1784 gms	16.6384 gms	70.10	$ClSO_3H$
92.5400 gms	4.4800 gms	18.87	CCl_4
88.0600 tare	23.7356 total		

Produced a 2 phase system, just barely separating.

Run 15

Total Weight	Actual Weight	Weight %	
105.4060 gms	0.1912 gms	1.10	H_2SO_4
105.2148 gms	11.1070 gms	64.38	$ClSO_3H$
94.1078 gms	6.0516 gms	34.88	CCl_4
88.0562 tare	17.3498 total		

Equilibrium point - appearance of 2 phases.

Run 16

Total Weight	Actual Weight	Weight %	
116.9440 gms	6.9292 gms	23.97	H_2SO_4
110.0148 gms	18.8318 gms	65.16	$ClSO_3H$
91.1830 gms	3.1407 gms	10.87	CCl_4
88.0423 tare	28.9017 total		

Equilibrium point - appearances of 2 phases.

Run 17

Total Weight	Actual Weight	Weight %	
120.0300 gms	0.5886 gms	1.73	H_2SO_4
119.4414 gms	21.4807 gms	67.22	$ClSO_3H$
97.9607 gms	9.9207 gms	31.05	CCl_4
88.0400 tare	31.9555 total		

Equilibrium point - appearance of 2 phases.

Run 18

Total Weight	Actual Weight	Weight %	
143.1388 gms	37.2000 gms	67.60	H_2SO_4
105.9388 gms	16.3142 gms	29.60	$ClSO_3H$
89.6246 gms	1.5712 gms	2.70	CCl_4
88.0534 tare	55.0854 total		

Produced a 2 phase system.

Run 19

Total Weight	Actual Weight	Weight %	
101.2800 gms	8.6085 gms	65.02	$ClSO_3H$
92.6715 gms	4.6304 gms	34.98	CCl_4
88.0411 tare	13.2389 total		

Borderline on 2 phases.

Run 20

Added to run 19.

Total Weight	Actual Weight	Weight %	
103.9218 gms	0.4535 gms	2.86	H_2SO_4
103.4683 gms	10.7968 gms	67.98	$ClSO_3H$
92.6715 gms	4.6304 gms	29.16	CCl_4
88.0411 tare	15.8807 total		

Equilibrium point - appearance of 2 phases.

Run 21

Total Weight	Actual Weight	Weight %	
100.3228 gms	2.5318 gms	20.63	H_2SO_4
97.7910 gms	8.1510 gms	66.40	$ClSO_3H$
89.6400 gms	1.5926 gms	12.97	CCl_4
88.0474 tare	12.2754 total		

Equilibrium point - appearance of 2 phases.

Run 22

Total Weight	Actual Weight	Weight %	
106.2820 gms	5.4010 gms	29.61	H_2SO_4
100.8810 gms	11.2150 gms	61.48	$ClSO_3H$
89.6660 gms	1.6250 gms	8.91	CCl_4
88.0410 tare	12.8400 total		

Equilibrium point - appearance of 2 phases.

Run 23

Total Weight	Actual Weight	Weight %	
114.2430 gms	8.4146 gms	32.13	H_2SO_4
105.8284 gms	15.6794 gms	59.86	$ClSO_3H$
90.1490 gms	2.0982 gms	8.01	CCl_4
88.0508 tare	26.1922 total		

Equilibrium point - appearance of 2 phases.

Run 24

Total Weight	Actual Weight	Weight %	
103.5822 gms	1.6622 gms	10.70	H_2SO_4
101.9200 gms	11.1570 gms	71.82	$ClSO_3H$
90.7630 gms	2.7146 gms	17.48	CCl_4
88.0484 tare	15.5338 total		

Equilibrium point - appearance of 2 phases.

Run 25*

Total Weight	Actual Weight	Weight %	
94.3320 gms	0.4600 gms	4.12	CCl_4
93.8640 gms	4.5577 gms	40.18	H_2SO_4
89.3063 gms	6.3181 gms	55.70	$ClSO_3H$
82.9882 tare	11.3438 total		

Equilibrium point - appearance of 2 phases.

Run 26

Total Weight	Actual Weight	Weight %	
90.0860 gms	0.5600 gms	7.88	$ClSO_3H$
89.5260 gms	6.5460 gms	92.12	CCl_4
82.9800 tare	7.1060 total		

Produced a 2 phase system.

Run 27

Added $ClSO_3H$ to run 26.

Total Weight	Actual Weight	Weight %	
92.4360 gms	2.9100 gms	30.77	$ClSO_3H$
	6.5460 gms	69.23	CCl_4
	9.4560 total		

Produced a 2 phase system.

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* Runs 25 - 38 employed 99+% H_2SO_4.

Run 28

Total Weight	Actual Weight	Weight %	
90.8245 gms	0.2049 gms	2.61	CCl_4
90.6196 gms	3.3320 gms	42.53	H_2SO_4
87.2876 gms	4.2981 gms	54.86	$ClSO_3H$
82.9895 tare	7.8350 total		

Equilibrium point - appearance of 2 phases.

Run 29

Total Weight	Actual Weight	Weight %	
92.3880 gms	0.7120 gms	7.60	CCl_4
91.6760 gms	5.5274 gms	59.00	$ClSO_3H$
88.5431 gms	3.1329 gms	33.40	H_2SO_4
83.0157 tare	9.3723 total		

Equilibrium point - appearance of 2 phases.

Run 30

Total Weight	Actual Weight	Weight %	
91.2810 gms	0.1860 gms	2.51	$ClSO_3H$
91.0950 gms	7.2263 gms	97.49	CCl_4
83.8687 tare	7.4123 total		

Equilibrium point - appearance of 2 phases.

Run 31

Total Weight	Actual Weight	Weight %	
94.4934 gms	0.1219 gms	1.1	H_2SO_4
94.3715 gms	10.5263 gms	98.9	CCl_4
83.8452 tare	10.6482 total		

Equilibrium point - appearance of 2 phases.

Run 32

Total Weight	Actual Weight	Weight %	
107.4300 gms	3.5150 gms	14.93	$ClSO_3H$
103.9150 gms	13.9130 gms	59.09	H_2SO_4
90.0020 gms	6.1153 gms	25.97	CCl_4
83.8867 tare	23.5433 total		

Produced a 2 phase system.

Run 33

Total Weight	Actual Weight	Weight %	
100.0920 gms	5.0659 gms	31.22	H_2SO_4
95.0261 gms	9.0931 gms	56.04	$ClSO_3H$
85.9330 gms	2.0655 gms	17.73	CCl_4
83.8675 tare	16.2245 total		

Produced a 2 phase system. Total volume 9.6 c.c.

Bottom layer - 9.25 c.c.

Run 34

Added more H_2SO_4 to run 33.

Total Weight	Actual Weight	Weight %	
105.7200 gms	10.6939 gms	49.00	H_2SO_4
	9.0931 gms	41.60	$ClSO_3H$
	2.0655 gms	9.40	CCl_4
	21.8525 total		

Produced a 2 phase system. Total volume 13 c.c.

Bottom layer - 12 c.c.

Run 35

Added more H_2SO_4 to run 34.

Total Weight	Actual Weight	Weight %	
115.9712 gms	20.9451 gms	65.24	H_2SO_4
	9.0931 gms	28.32	$ClSO_3H$
	2.0655 gms	6.43	CCl_4
	32.1037 total		

Produced a 2 phase system. Total volume 18.5 c.c. Bottom 17.5 c.c. Bottom layer appears turbid.

Run 36

Added more H_2SO_4 to run 35.

Total Weight	Actual Weight	Weight %	
125.7152 gms	30.6893 gms	73.34	H_2SO_4
	9.0931 gms	21.73	$ClSO_3H$
	2.0655 gms	4.93	CCl_4
	41.8479 total		

Produced a 2 phase system.

Run 37

Total Weight	Actual Weight	Weight %	
103.2603 gms	0.2213 gms	1.10	CCl_4
103.0390 gms	1.7498 gms	9.15	$ClSO_3H$
101.2892 gms	17.3462 gms	89.75	H_2SO_4
83.9430 tare	19.3173 total		

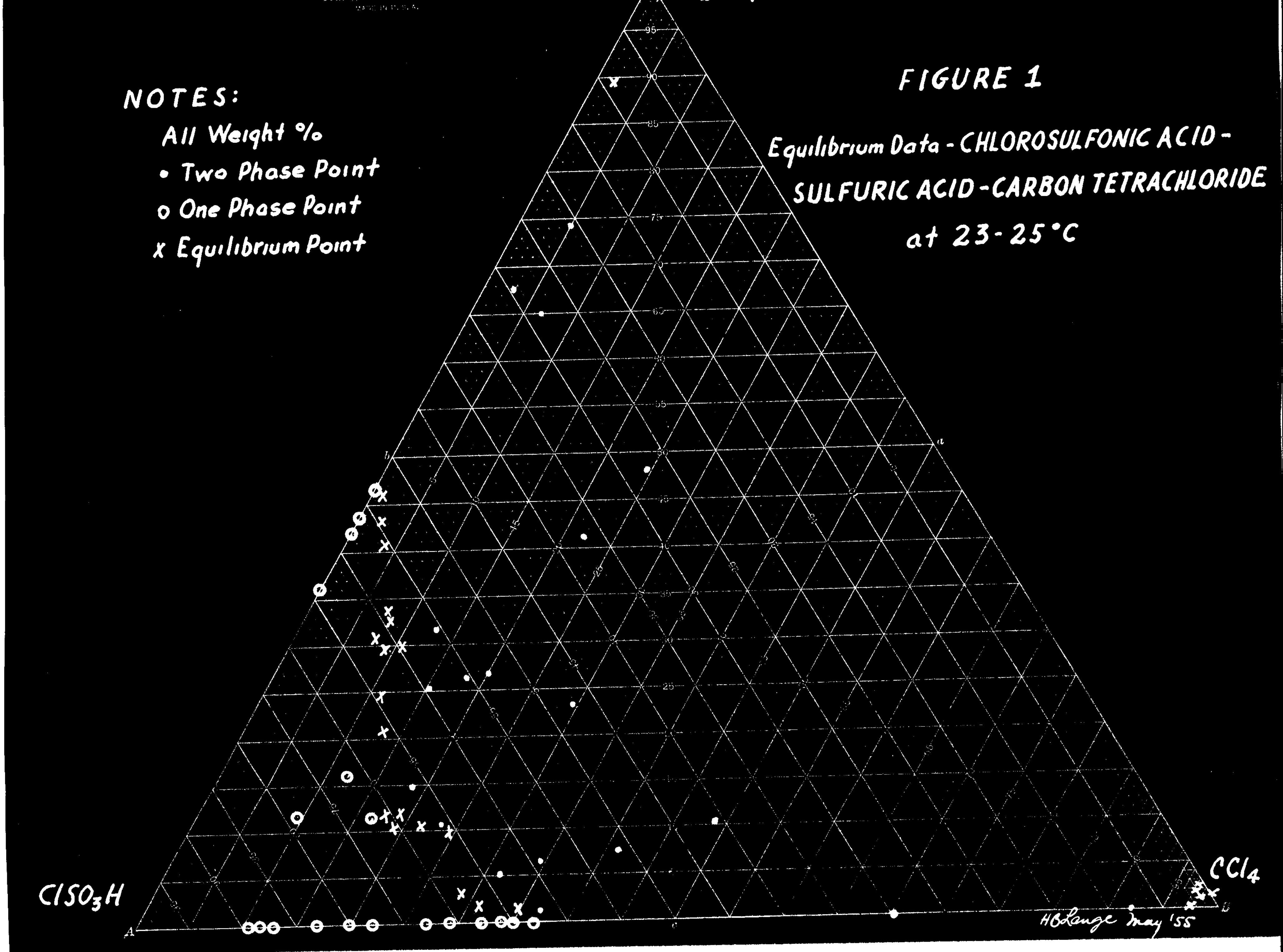
Equilibrium point - appearance of 2 phases.

Run 38

Total Weight	Actual Weight	Weight %	
102.5986 gms	0.3391 gms	1.82	CCl_4
102.2595 gms	18.3152 gms	98.18	H_2SO_4
83.9443 tare	18.6543 total		

Added CCl_4 dropwise.

Equilibrium point - appearance of 2 phases.



NOTES:
All Weight %
• Two Phase Point
o One Phase Point
x Equilibrium Point
FIGURE 1
Equilibrium Data - CHLOROSULFONIC ACID - SULFURIC ACID - CARBON TETRACHLORIDE at 23-25°C
$ClSO_3H$
CCl_4
H.O. Lange May '55

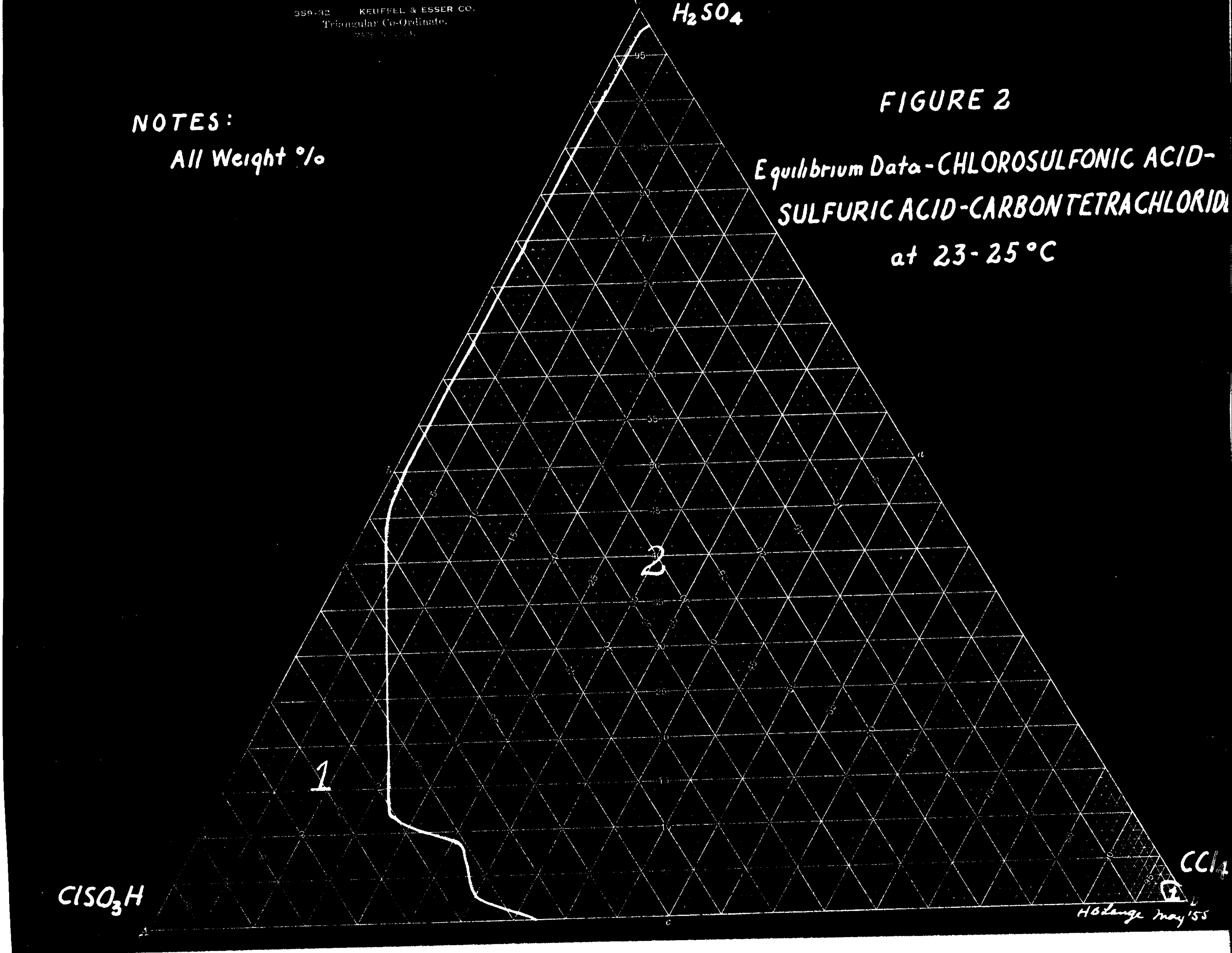

359-32 KEUFFEL & ESSER CO.
Triangular Co-Ordinate.
H_2SO_4
FIGURE 2
NOTES:
All Weight %
Equilibrium Data - CHLOROSULFONIC ACID - SULFURIC ACID - CARBON TETRACHLORIDE at 23-25°C
2
1
$ClSO_3H$
CCl_4
HBLange May '55

TABLE V

Chlorosulfonic Acid - Sulfuric Acid - Benzenesulfonyl Chloride

Run 39

Total Weight	Actual Weight	Weight %	
106.8585 gms	9.1500 gms	48.70	H_2SO_4
97.7085 gms	6.3464 gms	33.72	$ClSO_3H$
94.4000 gms	3.3085 gms	17.58	ϕSO_2Cl
88.0536 tare	18.8049 total		

Produced a 1 phase system.

Run 40

Added more H_2SO_4 to run 39.

Total Weight	Actual Weight	Weight %	
143.9585 gms	46.2500 gms	79.13	H_2SO_4
	6.3464 gms	13.72	$ClSO_3H$
	3.3085 gms	7.15	ϕSO_2Cl
	55.9049 total		

Produced a 1 phase system.

Run 41

Total Weight	Actual Weight	Weight %	
109.4343 gms	9.1513 gms	42.80	H_2SO_4
100.2830 gms	7.8574 gms	36.85	ϕSO_2Cl
95.9140 gms	4.3690 gms	20.35	$ClSO_3H$
88.0566 tare	21.3777 total		

Produced a 1 phase system.

Run 42

Added more H_2SO_4 to run 41.

Total Weight	Actual Weight	Weight %	
127.7343 gms	27.4513 gms	69.18	H_2SO_4
	7.8574 gms	19.80	ϕSO_2Cl
	4.3690 gms	11.01	$ClSO_3H$

Produced a 1 phase system.

Run 43

Total Weight	Actual Weight	Weight %	
97.6358 gms	0.7143 gms	7.45	$ClSO_3H$
96.9215 gms	2.7515 gms	28.72	H_2SO_4
94.1700 gms	6.1153 gms	63.83	ϕSO_2Cl
88.0547 tare	9.5811 total		

ϕSO_2Cl and H_2SO_4 produced a two phase system titrated with $ClSO_3H$ to 1 phase.

Run 44

Total Weight	Actual Weight	Weight %	
97.0528 gms	0.5618 gms	6.50	$ClSO_3H$
96.4910 gms	0.8778 gms	9.80	H_2SO_4
95.6132 gms	7.5286 gms	83.70	ϕSO_2Cl
88.0846 tare	8.9682 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 45

Total Weight	Actual Weight	Weight %	
106.8208 gms	1.1344 gms	6.40	$ClSO_3H$
105.6854 gms	13.2543 gms	70.60	H_2SO_4
92.4311 gms	4.3721 gms	23.00	ϕSO_2Cl
88.0590 tare	18.7608 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 46

Total Weight	Actual Weight	Weight %	
102.7072 gms	0.1410 gms	0.96	$ClSO_3H$
102.5662 gms	12.2876 gms	83.90	H_2SO_4
90.2786 gms	2.1978 gms	15.04	ϕSO_2Cl
88.0808 tare	14.6264 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 47

Total Weight	Actual Weight	Weight %	
99.6200 gms	0.9290 gms	8.05	$ClSO_3H$
98.6910 gms	4.5522 gms	39.42	H_2SO_4
94.1388 gms	6.0611 gms	52.43	ϕSO_2Cl
88.0777 tare	11.5423 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 48

Total Weight	Actual Weight	Weight %	
105.1400 gms	1.5365 gms	8.97	$ClSO_3H$
103.6035 gms	8.7333 gms	51.02	H_2SO_4
94.8702 gms	6.8312 gms	39.91	ϕSO_2Cl
88.0390 tare	17.1010 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 49

Total Weight	Actual Weight	Weight %	
99.7845 gms	0.5392 gms	4.60	$ClSO_3H$
99.2453 gms	0.9032 gms	7.60	H_2SO_4
98.3421 gms	10.2937 gms	87.70	ϕSO_2Cl
88.0484 tare	11.7361 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 50*

Total Weight	Actual Weight	Weight %	
89.0076 gms	0.1006 gms	1.67	$ClSO_3H$
88.9070 gms	0.8805 gms	14.61	H_2SO_4
88.0265 gms	5.0453 gms	83.72	ϕSO_2Cl

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

- -

* Runs 50 - 62 used 99+% H_2SO_4, all others used 98-98.5% H_2SO_4.

Run 51

Total Weight	Actual Weight	Weight %	
89.4109 gms	0.0336 gms	0.52	$ClSO_3H$
89.3773 gms	1.7978 gms	28.10	H_2SO_4
87.5795 gms	4.5665 gms	71.37	ϕSO_2Cl
83.0130 tare	6.3979 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 52

Total Weight	Actual Weight	Weight %	
91.2330 gms	0.0414 gms	0.50	$ClSO_3H$
91.1916 gms	3.1331 gms	38.09	H_2SO_4
88.0585 gms	5.0507 gms	61.41	ϕSO_2Cl
83.1078 tare	8.2252 total		

ϕSO_2Cl and H_2SO_4 produced a 2 phase system titrated with $ClSO_3H$ to 1 phase.

Run 53

Total Weight	Actual Weight	Weight %	
93.7810 gms	6.5330 gms	60.65	H_2SO_4
87.2800 gms	4.2380 gms	39.35	ϕSO_2Cl
83.0100 tare	10.7710 total		

Produced a 1 phase system.

Run 54

Total Weight	Actual Weight	Weight %	
86.3171 gms	0.9560 gms	34.25	H_2SO_4
85.3611 gms	2.0999 gms	65.75	ϕSO_2Cl
83.2612 tare	3.0559 total		

Produced a 2 phase system.

Run 55

Added more H_2SO_4 to run 54.

Total Weight	Actual Weight	Weight %	
87.4861 gms	2.1250 gms	50.35	H_2SO_4
	2.0999 gms	49.65	ϕSO_2Cl
	4.2249 total		

Produced a 2 phase system.

Run 56

Added more H_2SO_4 to run 55.

Total Weight	Actual Weight	Weight %	
90.3297 gms	4.9686 gms	70.40	H_2SO_4
	2.0999 gms	29.60	ϕSO_2Cl
	7.0685 total		

Produced a 1 phase system.

Run 57

Total Weight	Actual Weight	Weight %	
104.8210 gms	20.0878 gms	93.50	H_2SO_4
103.3490 gms	1.4720 gms	6.50	ϕSO_2Cl
83.2612 tare	21.5598 total		

Produced a 1 phase system.

Run 58

Added more ϕSO_2Cl to run 57.

Total Weight	Actual Weight	Weight %	
106.8550 gms	20.0878 gms	85.20	H_2SO_4
	3.5060 gms	14.80	ϕSO_2Cl
	23.5938 total		

Produced a 1 phase system.

Run 59

Total Weight	Actual Weight	Weight %	
94.6140 gms	8.3327 gms	77.47	H_2SO_4
86.2813 gms	2.4238 gms	22.53	$\emptyset SO_2Cl$
83.8575 tare	10.7565 total		

Produced a 1 phase system.

Run 60

Added more $\emptyset SO_2Cl$ to run 59.

Total Weight	Actual Weight	Weight %	
99.4900 gms	7.2998 gms	46.70	$\emptyset SO_2Cl$
	8.3327 gms	53.30	H_2SO_4
	15.6325 total		

Produced a 1 phase system.

Run 61

Total Weight	Actual Weight	Weight %	
105.8775 gms	13.7893 gms	62.33	$\emptyset SO_2Cl$
	8.3327 gms	37.67	H_2SO_4
	22.1220 total		

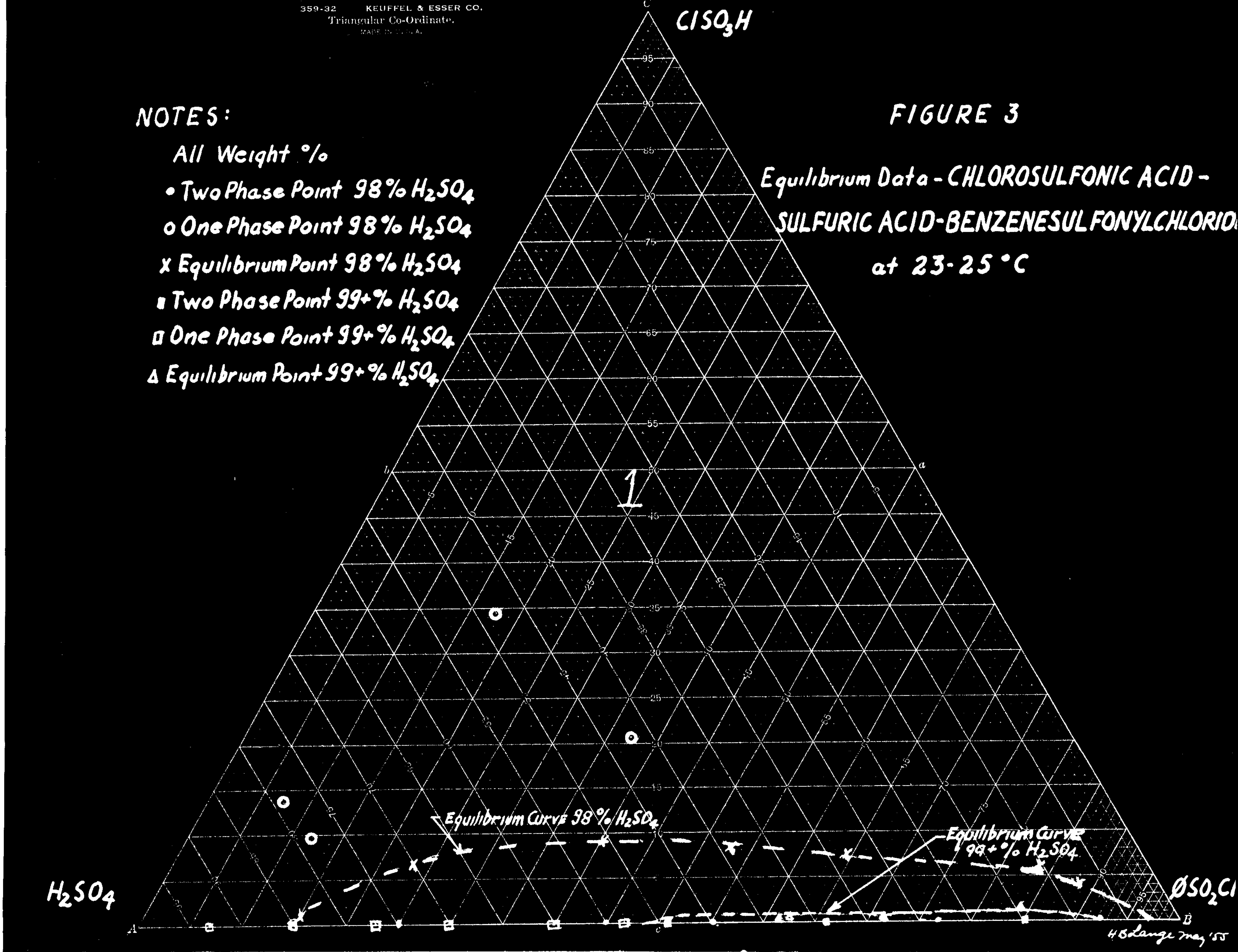
Produced a 2 phase system.

Run 62

Added $ClSO_3H$ to run 61.

Total Weight	Actual Weight	Weight %	
105.9205 gms	0.0430 gms	0.19	$ClSO_3H$
	13.7895 gms	62.21	$\emptyset SO_2Cl$
	8.3327 gms	37.60	H_2SO_4
	22.1652 total		

Produced a 1 phase system.



359-32 KEUFFEL & ESSER CO.
Triangular Co-Ordinate.
FIGURE 3
Equilibrium Data - CHLOROSULFONIC ACID - SULFURIC ACID - BENZENESULFONYLCHLORIDE at 23-25 °C
NOTES:
All Weight %
• Two Phase Point 98% H2SO4
o One Phase Point 98% H2SO4
x Equilibrium Point 98% H2SO4
▪ Two Phase Point 99+% H2SO4
□ One Phase Point 99+% H2SO4
Δ Equilibrium Point 99+% H2SO4
ClSO3H
H2SO4
ØSO2Cl
Equilibrium Curve 98% H2SO4
Equilibrium Curve 99+% H2SO4
1
H B Lange May '55

TABLE VI

Chlorosulfonic Acid - Carbon Tetrachloride - Benzenesulfonyl Chloride

Run 63

Total Weight	Actual Weight	Weight %	
92.9590 gms	2.5990 gms	28.60	$ClSO_3H$
90.3600 gms	2.4527 gms	27.00	ϕSO_2Cl
87.9073 gms	4.0313 gms	44.40	CCl_4
83.8760 tare	9.0830 total		

Produced a 1 phase system.

Run 64

Added more CCl_4 to run 63.

Total Weight	Actual Weight	Weight %	
97.7391 gms	2.5990 gms	18.78	$ClSO_3H$
	2.4527 gms	17.71	ϕSO_2Cl
	8.8115 gms	63.51	CCl_4
	13.8632 total		

Produced a 1 phase system.

Run 65

Added more CCl_4 to run 64.

Total Weight	Actual Weight	Weight %	
100.1202 gms	2.5990 gms	16.01	$ClSO_3H$
	2.4527 gms	15.04	ϕSO_2Cl
	11.1926 gms	68.85	CCl_4
	16.2443 total		

Produced a 1 phase system.

Run 66

Added more $ClSO_3H$ to run 65.

Total Weight	Actual Weight	Weight %	
110.6624 gms	13.1412 gms	49.15	$ClSO_3H$
	2.4527 gms	9.15	ϕSO_2Cl
	11.1926 gms	41.70	CCl_4
	26.7865 total		

Produced a 1 phase system.

Run 67

Total Weight	Actual Weight	Weight %	
103.5012 gms	6.5399 gms	13.80	$ClSO_3H$
96.9613 gms	9.0039 gms	19.00	ϕSO_2Cl
87.9574 gms	31.8614 gms	67.20	CCl_4
56.0960 tare	47.4052 total		

Produced a 1 phase system.

Run 68

Total Weight	Actual Weight	Weight %	
110.2308 gms	6.9786 gms	12.27	ϕSO_2Cl
103.2522 gms	13.0277 gms	22.89	$ClSO_3H$
90.2245 gms	36.8784 gms	64.83	CCl_4
53.3461 tare	56.8847 total		

Produced a 1 phase system.

Run 69

Added more $ClSO_3H$ to run 68.

Total Weight	Actual Weight	Weight %	
122.4862 gms	6.9786 gms	10.10	ϕSO_2Cl
	25.2831 gms	36.60	$ClSO_3H$
	36.8784 gms	53.30	CCl_4
	69.1401 total		

Produced a 1 phase system.

Run 70

Total Weight	Actual Weight	Weight %	
96.0167 gms	0.4758 gms	1.27	ϕSO_2Cl
95.5409 gms	7.6282 gms	20.35	$ClSO_3H$
87.9127 gms	29.3875 gms	78.47	CCl_4
58.5252 tare	37.4915 total		

Produced a 2 phase system.

Run 71

Added ϕSO_2Cl to run 70.

Total Weight	Actual Weight	Weight %	
96.6667 gms	1.1258 gms	2.95	ϕSO_2Cl
	7.6282 gms	20.00	$ClSO_3H$
	29.3875 gms	77.05	CCl_4
	38.1415 total		

Produced a 2 phase system.

Run 72

From 4 component data - run 82.

Actual Weight	Weight %	
1.9253 gms	29.38	$ClSO_3H$
2.3150 gms	35.22	CCl_4
2.3130 gms	35.20	ϕSO_2Cl

6.5533 total

Produced a 1 phase system.

Run 73

From 4 component data - run 83.

Actual Weight	Weight %	
1.4082 gms	20.70	$ClSO_3H$
3.7028 gms	54.40	CCl_4
1.6804 gms	24.70	ϕSO_2Cl

6.7914 total

Produced a 1 phase system.

Run 74

From 4 component data - run 84.

Actual Weight	Weight %	
1.0035 gms	14.40	$ClSO_3H$
5.1245 gms	73.50	CCl_4
0.8454 gms	12.10	ϕSO_2Cl

6.9734 total

Produced a 1 phase system.

Run 75

From 4 component data - run 85.

Actual Weight	Weight %	
2.5175 gms	30.00	$ClSO_3H$
2.6262 gms	31.35	CCl_4
3.2439 gms	38.65	ϕSO_2Cl
8.3876 total		

Produced a 1 phase system.

Run 76

Total Weight	Actual Weight	Weight %	
99.2360 gms	0.2985 gms	2.05	ϕSO_2Cl
98.9375 gms	2.2300 gms	14.58	$ClSO_3H$
96.7075 gms	12.7635 gms	83.47	CCl_4
83.9440 tare	15.2920 total		

Produced a 2 phase system.

Run 77

Added more ϕSO_2Cl to run 76.

Total Weight	Actual Weight	Weight %	
99.4133 gms	0.4758 gms	3.08	ϕSO_2Cl
	2.2300 gms	14.42	$ClSO_3H$
	12.7635 gms	82.51	CCl_4
	15.4693 total		

Equilibrium point - appearance of 1 phase.

Run 78

Added more CCl_4 to run 77.

Total Weight	Actual Weight	Weight %	
102.3615 gms	0.4758 gms	2.60	ϕSO_2Cl
	2.2300 gms	12.17	$ClSO_3H$
	15.6123 gms	85.23	CCl_4
	18.3181 total		

Produced 2 phases near equilibrium point.

Run 79

Added ϕSO_2Cl to run 78.

Total Weight	Actual Weight	Weight %	
102.3900 gms	0.4863 gms	2.65	ϕSO_2Cl
	2.2300 gms	12.17	$ClSO_3H$
	15.6123 gms	85.28	CCl_4
	18.3286 total		

Equilibrium point - appearance of 1 phase.

Run 80

Total Weight	Actual Weight	Weight %	
94.7819 gms	0.0912 gms	0.84	$ClSO_3H$
94.6907 gms	0.7505 gms	6.91	ϕSO_2Cl
93.9402 gms	10.0202 gms	92.25	CCl_4
83.9200 tare	10.8619 total		

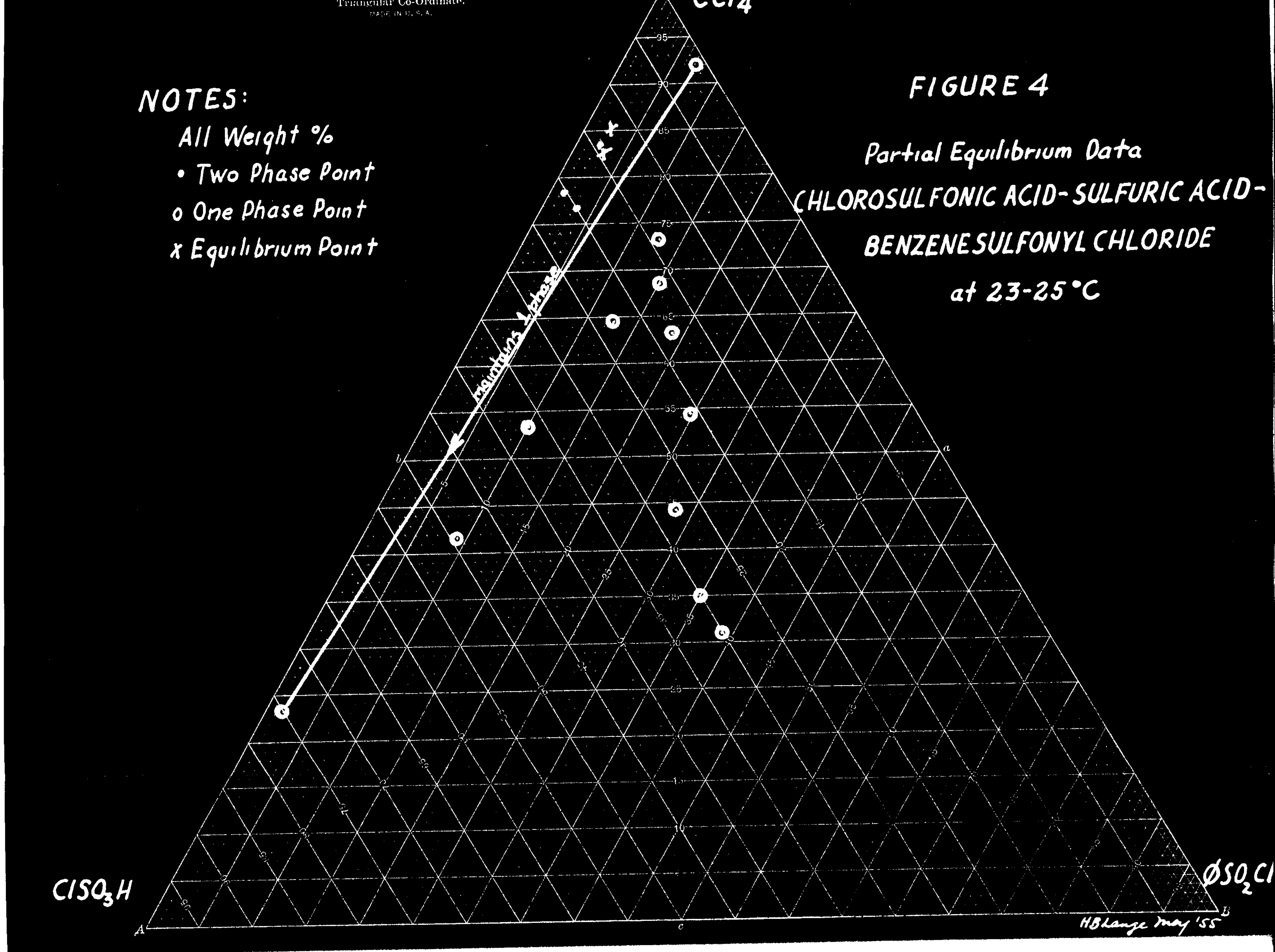
Produced a 1 phase system.

Run 81

Added $ClSO_3H$ to run 80.

Total Weight	Actual Weight	Weight %	
126.6202 gms	31.9295 gms	74.78	$ClSO_3H$
	0.7505 gms	1.75	ϕSO_2Cl
	10.0202 gms	23.47	CCl_4
	42.7002 total		

Remained a 1 phase system throughout addition.



Triangular Co-Ordinate.
MADE IN U.S.A.
CCl4
NOTES:
All Weight %
• Two Phase Point
o One Phase Point
x Equilibrium Point
FIGURE 4
Partial Equilibrium Data
CHLOROSULFONIC ACID-SULFURIC ACID-
BENZENESULFONYL CHLORIDE
at 23-25°C
maintains 1 phase
ClSO3H
ØSO2Cl
HBLange May '55

TABLE VII

Carbon Tetrachloride - Benzenesulfonyl Chloride - Sulfuric Acid - Chlorosulfonic Acid

Run 82

Total Weight	Actual Weight	Weight %	
97.5660 gms	2.9533 gms	31.00	H_2SO_4
94.6133 gms	1.9253 gms	20.22	$ClSO_3H$
92.6880 gms	2.3150 gms	24.38	CCl_4
90.3730 gms	2.3130 gms	24.30	ϕSO_2Cl
88.0600 tare	9.5066 total		

Bottom three components gave a 1 phase system. All four gave a 2 phase system. Total volume 6 c.c., bottom layer 4 c.c.

Run 83

Total Weight	Actual Weight	Weight %	
98.5120 gms	3.6626 gms	35.04	H_2SO_4
94.8494 gms	1.4082 gms	13.47	$ClSO_3H$
93.4412 gms	3.7028 gms	35.20	CCl_4
89.7384 gms	1.6804 gms	16.07	ϕSO_2Cl
88.0580 tare	10.4540 total		

Bottom three components gave a 1 phase system. Four components gave a 2 phase system. Total volume 6.7 c.c., bottom 3.5 c.c.

Run 84

Total Weight	Actual Weight	Weight %	
96.9456 gms	1.9176 gms	21.57	H_2SO_4
95.0280 gms	1.0035 gms	11.28	$ClSO_3H$
94.0245 gms	5.1245 gms	57.64	CCl_4
88.9000 gms	0.8454 gms	9.50	ϕSO_2Cl
88.0546 tare	8.8910 total		

Bottom three components produced a 1 phase system. All four gave a 2 phase system.

Extracted Layers

Acid Layer	G -	55.7984 gms
	T -	52.6655 gms
	N -	3.1329 gms
Solvent Layer	G -	60.1242 gms
	T -	54.6270 gms
	N -	5.4972 gms

Assay of Solvent Layer

Cold titration required 6.8 c.c. of 1 N NaOH. Added 10 c.c. of 1 N NaOH and heated to boiling for half hour. Back titration - 3.4 c.c. of 0.987 N H_2SO_4. Chloride assay required 49.0 c.c. of standard 3.59 mg Cl/ml solution.

Equilibrium Phases

Solvent Layer	Actual Weight	Weight %	
	0.095 gms	1.72	H_2SO_4
	0.187 gms	3.40	$ClSO_3H$
	0.593 gms	10.78	ϕSO_2Cl
	4.622 gms	84.00	CCl_4
	5.497 total		

Run 84 (continued)

Acid Layer	Actual Weight	Weight %	
	1.8226 gms	53.75	H_2SO_4
	0.8165 gms	24.00	$ClSO_3H$
	0.2524 gms	7.44	ϕSO_2Cl
	0.5025 gms	14.81	CCl_4
	3.3940 total		

Run 85

Total Weight	Actual Weight	Weight %	
92.4096 gms	1.0164 gms	10.80	H_2SO_4
91.3932 gms	2.5175 gms	26.77	$ClSO_3H$
88.8757 gms	2.6262 gms	27.93	CCl_4
86.2495 gms	3.2439 gms	34.49	ϕSO_2Cl
83.0056 tare	9.3040 total		

Produced a 1 phase system throughout.

Run 86

Added more H_2SO_4 to run 85.

Total Weight	Actual Weight	Weight %	
93.3138 gms	1.9206 gms	18.63	H_2SO_4
	2.5175 gms	24.42	$ClSO_3H$
	2.6262 gms	25.48	CCl_4
	3.2439 gms	31.47	ϕSO_2Cl
	10.3082 total		

Producod a 1 phase system.

Run 87

Added more H_2SO_4 to run 86.

Total Weight	Actual Weight	Weight %	
94.4015 gms	3.0083 gms	26.39	H_2SO_4
	2.5175 gms	22.10	$ClSO_3H$
	2.6262 gms	23.04	CCl_4
	3.2439 gms	28.46	ϕSO_2Cl
	11.3959 total		

Produced 2 phases. Total volume 7.4 c.c., bottom 4.75 c.c.

Extracted Layers

Acid Layer	G - 61.2240 gms	
	T - 53.7705 gms	
	N - 7.4535 gms	
Solvent Layer	G - 57.7115 gms	
	T - 53.9564 gms	
	N - 3.7551 gms	

Assay of Solvent Layer

Cold titration required 25.8 c.c. of 1 N NaOH. Added 30 c.c. of 1 N NaOH. Heated to boiling for twenty minutes. Back titration - 16.4 c.c. of 0.987 N H_2SO_4. Chloride assay 116.95 c.c. of standard 3.59 mg Cl/ml solution.

Equilibrium Phases

Solvent Layer	Actual Weight	Weight %	
	0.543 gms	14.47	H_2SO_4
	0.574 gms	15.28	$ClSO_3H$
	1.428 gms	38.02	CCl_4
	1.210 gms	32.22	ϕSO_2Cl
	3.755 total		

Run 87 (continued)

Acid Layer

Actual Weight	Weight %	
2.4653 gms	32.27	H_2SO_4
1.9435 gms	25.42	$ClSO_3H$
1.1981 gms	15.70	CCl_4
2.0339 gms	26.60	ϕSO_2Cl
7.6408 total		

Run 88

Total Weight	Actual Weight	Weight %	
89.8855 gms	0.3860 gms	5.60	H_2SO_4
89.4995 gms	2.0773 gms	41.74	$ClSO_3H$
86.6223 gms	2.8772 gms	30.14	CCl_4
84.5450 gms	1.5520 gms	22.52	ϕSO_2Cl
82.9930 tare	6.8925 total		

Produced a 1 phase system.

Run 89

Added more H_2SO_4 to run 88.

Total Weight	Actual Weight	Weight %	
90.2154 gms	0.7159 gms	9.91	H_2SO_4
	2.0773 gms	39.84	$ClSO_3H$
	2.8772 gms	28.76	CCl_4
	1.5520 gms	21.49	ϕSO_2Cl
	7.2224 total		

Produced a 1 phase system.

Run 90

Added more H_2SO_4 to run 89.

Total Weight	Actual Weight	Weight %	
90.6762 gms	1.1767 gms	15.31	H_2SO_4
	2.0773 gms	37.45	$ClSO_3H$
	2.8772 gms	27.04	CCl_4
	1.5520 gms	20.20	ϕSO_2Cl
	7.6832 total		

Produced a 1 phase system.

Run 91

Added more H_2SO_4 to run 89.

Total Weight	Actual Weight	Weight %	
91.4300 gms	1.9305 gms	22.88	H_2SO_4
	2.0773 gms	34.10	$ClSO_3H$
	2.8772 gms	24.62	CCl_4
	1.5520 gms	18.40	ϕSO_2Cl
	8.4370 total		

Produced a 2 phase system.

Extracted Layers

Acid Layer	G - 62.8047 gms	
	T - 55.5536 gms	
	N - 7.2511 gms	
Solvent Layer	G - 55.1210 gms	
	T - 54.1530 gms	
	N - 0.9680 gms	

Assay of Solvent Layer

Cold titration required 4.4 c.c. of 1 N NaOH. Added 15 c.c. 1 N NaOH. Heated to boiling for half hour. Back titration - 12.6 c.c. of 0.987 N H_2SO_4. Chloride assay - 21.4 ml of 3.59 mg Cl/ml solution.

Equilibrium Phases

Solvent Layer	Actual Weight	Weight %	
	0.573 gms	59.19	CCl_4
	0.066 gms	6.82	H_2SO_4
	0.226 gms	23.35	ϕSO_2Cl
	0.103 gms	10.64	$ClSO_3H$

Run 91 (continued)

Acid Layer	Actual Weight	Weight %	
	1.5043 gms	20.14	CCl_4
	1.8645 gms	24.96	H_2SO_4
	1.3260 gms	17.75	ϕSO_2Cl
	2.7742 gms	37.14	$ClSO_3H$

Run 92

Total Weight	Actual Weight	Weight %	
104.1853 gms	9.1283 gms	19.20	$ClSO_3H$
95.0570 gms	3.1428 gms	6.60	ϕSO_2Cl
91.9142 gms	10.4064 gms	21.85	H_2SO_4
81.5078 gms	24.8480 gms	52.25	CCl_4
56.6598 tare	47.5255 total		

Produced a 2 phase system.

DISCUSSION

In the initial phases of this work, two batch chlorosulfonations of benzene employing carbon tetrachloride as an inert solvent were made. The method of Gilman and Blatt (7) was employed. In the first run, the weight ratio of carbon tetrachloride to chlorosulfonic acid was 63%-37% respectively. The phase separation was rapid at the conclusion of the reaction period but the carbon tetrachloride layer was the same as the volume of solvent charged. It was suspected that, (a) benzenesulfonyl chloride was not in the organic layer, (b) the carbon tetrachloride had a high solubility in the acids or (c) a combination of both (a) and (b) existed. The second run was performed using a ratio of 54% chlorosulfonic acid to 46% carbon tetrachloride. In this case, phase separation was extremely slow and the carbon tetrachloride layer was again the same volume as that charged. These disturbing conditions prompted investigation into solvent systems and into an understanding of phase relationships. Some knowledge of liquid-liquid equilibria was necessary prior to a study of continuous operation.

A. Solvent Systems

A preliminary screening of possible solvents was undertaken. They were selected on the basis of density, relative inertness, availability and cost. However, the relative immiscibility with chlorosulfonic acid was the deciding factor in adoption of the solvent. Table III lists the solvent pairs in the ratios mixed and observed. Only carbon tetrachloride and cyclohexane showed some immiscibility. The commercial grade of cyclohexane which contains from 1% - 5% benzene was not acceptable because of the slow reaction with chlorosulfonic acid. Pure cyclohexane, spectrographic grade, behaved as the commercial grade but without the reaction. Due to the cost of this material, it was not considered further at this time. Carbon tetrachloride was adopted for further study.

It is of interest to note that the list of possible solvents is much larger than shown here. Selection of a more favorable solvent, from the liquid equilibria standpoint, may simplify any process. For a study in liquid-liquid equilibria other solvents are worth investigation. Trichloroethylene, perchloroethylene and fluorohydrocarbons are worthy of investigation.

B. Chlorosulfonic Acid - Sulfuric Acid - Carbon Tetrachloride System

The equilibrium relationships between chlorosulfonic acid, sulfuric acid and carbon tetrachloride are illustrated in Figures 1 and 2. The experimental runs are given in Table IV.

The data show that the ternary is binodal. One component is partially miscible in the other two. That is, carbon tetrachloride is partially miscible in sulfuric acid and partially in chlorosulfonic acid.

The small one phase region at high carbon tetrachloride concentrations was difficult to obtain with high accuracy. It is known to exist because of repeated experimental data showing some sulfuric acid and chlorosulfonic present in carbon tetrachloride. Practically, this region would be of little concern. Recovery of the acids from carbon tetrachloride would probably be uneconomical.

The large one phase region at high chlorosulfonic acid concentrations is very interesting. The shape of the equilibrium line between the one phase and two phase region is different from that usually observed for binodal systems. Of particular interest is the region between

65 - 70 weight per cent chlorosulfonic acid and 10 - 25 weight per cent sulfuric acid. Small changes in sulfuric acid concentration have a large influence on the concentration of carbon tetrachloride necessary to maintain the one phase region. Such a condition might be suspected since sulfuric acid and carbon tetrachloride are practically mutually insoluble. The experimental data in this region were carefully determined and checked. Three approaches were employed. Mixtures of carbon tetrachloride-chlorosulfonic acid were prepared and titrated slowly with sulfuric acid till the first appearance of the 2 phases. In Figure 1, it can be seen how well these points line up with the starting point and 100% sulfuric acid. The second approach was to start with the one phase mixtures of the acids and titrate with carbon tetrachloride. These points lie on the line contacting the starting point and 100% carbon tetrachloride. The final method was to use the tie line technique and analyze each phase of a two phase mixture.

These points fitted the expected curve. The fact that the experimental points plotted so well also indicates the reliability of the data under these experimental conditions. The small part of the one phase region lying along the 1% carbon tetrachloride line is to be expected from the rest of the curve. It is known that 2 phase points in the high sulfuric acid area must have an equilibrium point to match with that in the high carbon tetrachloride region. The equilibrium point at 53% chlorosulfonic acid, 45% sulfuric acid and 1% carbon tetrachloride indicates that the region above it may be very small. The data show this very small region. It is interesting to observe that runs 34 and 35 in Table IV show that no increase in the volume of the carbon tetrachloride was observed (in the high sulfuric acid area) as the sulfuric acid concentration was increased. This is what would happen with the equilibrium line as shown in Figure 2.

During the course of the experimental work, it was found that some of the sulfuric acid used was less than 99% acid. Fortunately no difference was observed in equilibrium points as a result of 98 or 99% sulfuric acid, (runs 25 - 38, Table IV). This may be due to the fact that carbon tetrachloride is equally insoluble in water or sulfuric acid-water mixtures.

C. Chlorosulfonic Acid - Sulfuric Acid - Benzenesulfonyl Chloride System

Table V and Figure 3 summarize the data obtained with this system. The first experiments (runs 39 - 49) were made with 98-98.5% sulfuric acid. This was not intentional and it was not discovered until the data shown in Figure 3 was obtained. It can be seen that with this small amount of water present a 2 phase region occurs. Changing to acid of 99+% assay, the 2 phase region almost disappeared (Figure 3). Actually it was found that the 2 phase region occurred at high concentrations of benzenesulfonyl chloride and that small amounts of chlorosulfonic acid (0.5-2.0% by weight) were sufficient to produce a 1 phase system.

The only apparent reason for the difference in the equilibrium curves is in the acid strength. This may be explained by the fact that benzenesulfonyl chloride is insoluble in the sulfuric acid-water-hydrate and enough was present to upset the normal equilibria or to act as a fourth component. When sulfuric acid and the benzenesulfonyl chloride are mixed prior to the addition of chlorosulfonic acid the presence of water tended toward the immiscibility condition. However, if chlorosulfonic acid was added before the benzenesulfonyl chloride, it would react with the water and form sulfuric and hydrochloric acids. The data with 99+% acid tends toward a completely miscible three component system.

D. Chlorosulfonic Acid - Carbon Tetrachloride - Benzenesulfonyl Chloride System

Table VI and Figure 4 contain the data for this ternary. Although the study is not extensive, some conclusions may be drawn.

It is known that benzenesulfonyl chloride is miscible in carbon tetrachloride and in chlorosulfonic acid. However, it has been shown that carbon tetrachloride and chlorosulfonic acid form a partially miscible pair. Hence, it is anticipated that this ternary would contain a 2 phase region. This is demonstrated (in part) by the data. It is also conceivable that this two phase region would lie near the high carbon tetrachloride concentrations. This too is shown (in part) by the data. The 2 phase region cannot cover much of the area, high carbon tetrachloride - low chlorosulfonic acid. Runs 80 and 81, Table VI, illustrate that a one phase region is maintained, going from 1 weight per cent acid to 75 weight per cent along the line to 100% chlorosulfonic acid (Figure 4).

E. Carbon Tetrachloride - Benzenesulfonyl Chloride - Sulfuric Acid - Chlorosulfonic Acid System

Analysis of a four component system requires extensive data. The data assembled here can serve only as a first approximation of the entire system.

The first factor that appears important is the sulfuric acid concentration. In all experiments where a 2 phase region was obtained, the sulfuric acid concentration was over 20 weight per cent. The concentration was also greater than that of chlorosulfonic acid (except run 91, Table VII). Run 91, which had a higher chlorosulfonic acid concentration than sulfuric acid, gave a phase separation but an unfavorable distribution of sulfonyl chloride. The solvent layer retained only 15 weight per cent of the sulfonyl chloride charged.

The second factor is the solvent concentration. No direction is apparent from the limited number of runs reported here. However, a high recovery of benzenesulfonyl chloride in the organic layer was obtained in run 84, Table VII. Here the organic solvent retained 70% weight of the initial sulfonyl chloride. The initial mixture contained 58 weight per cent solvent. Conditions of this experiment gave a more favorable distribution of sulfonyl chloride than run 87, Table VII. Under conditions of the latter only a 37 weight per cent recovery of the chloride compound was in the organic stream. The evidence from these experiments is, that an interaction exists between sulfuric acid and carbon tetrachloride concentration for maximum chloride recovery. It is conceivable that conditions such as 50-60% carbon tetrachloride, 15-20% sulfuric acid, 10-15% chlorosulfonic acid and 5-10% sulfonyl chloride would give a favorable distribution of all materials.

CONCLUSIONS

In an effort to develop a process for the continuous chlorosulfonation of benzene, liquid-liquid equilibria data for a proposed system were studied. Ternary data for chlorosulfonic acid - sulfuric acid - carbon tetrachloride were developed at 23-25°C. The system is composed of two single phase regions and a two phase region. The ternary chlorosulfonic acid - sulfuric acid - benzenesulfonyl chloride is mostly a single phase system. A very small two phase region was found, the size of which is determined by the purity of sulfuric acid. The ternary, chlorosulfonic acid - carbon tetrachloride - benzenesulfonyl chloride has a small two phase region. However, this system was not completely developed. The quaternary, carbon tetrachloride - benzenesulfonyl chloride - sulfuric acid - chlorosulfonic acid shows that high concentrations of sulfuric acid are necessary for a favorable distribution of benzenesulfonyl chloride in the solvent layer.

The work herein can serve as a basis for the study of continuous chlorosulfonation of benzene.

RECOMMENDATIONS

It is recommended that further work be carried out to complete the quaternary system study begun here and to develop the continuous chlorosulfonation process.

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