A RE-CHECK OF DOUBTFUL POINTS ON THE HYDROCHLORIC ACID-SOLUBILITY CURVES OF CADMIUM AND LEAD SULFIDE

by

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Introduction

The present investigation is a part of a larger program of study dealing with solubilities and the solubility-product principle in acid solutions.

In particular, this thesis is prepared in an effort to check doubtful points on the unusual solubility curves of cadmium- and lead sulfide in hydrochloric acid solutions of varying normality. The solubility data on these two compounds over a wide range of acid normalities are meager, and the applicability of the solubility-product principle to them, with the possible exception of those in very low acid concentrations, is doubtful.

An investigation of the solubility of cadmium sulfide has been made recently by Mr. G. F. Kinney, with highly interesting results.[1] These findings indicate that cadmium sulfide does not conform entirely with the solubility product principle. Experiments made by Mr. C. H. Hale show a variance from the solubility product principle for lead sulphide as well as cadmium sulphide, and also show that the solubility curves for these sulfides cross twice in a narrow range of acid normality.[2]

The work instituted in this thesis is an attempt to verify or disprove the peculiar behavior of the sulfides of cadmium and lead, and if possible, suggest a cause for this behavior.

1 Kinney, Gilbert Ford-Thesis, The University of Tennessee(1930)

2 Hale, Charles H.-Thesis, The University of Tennessee(1930)

Concentrations in which the solubility measurements were made were:

3.6 Normal

2.5 Normal

0.42 Normal

0.316 Normal

0.28 Normal

The temperature was 25°C ± .01°C.

General Survey of the Field

From the beginnings of chemistry the phenomena of solubility have attracted interest and conjecture as to its mechanics, and many theories concerning solubility have been advanced.

One very important phenomenon of solubility is metabolism, indicating that the mere solution of a substance may so alter the state of that substance as to set energy free.[1] Various chemical reactions are dependent upon solution; it is an integral factor in the universal scheme.

The early theories of solubility, based upon the idea of molecules intruding the solute interstices,[2] gave rise to controversy and investigation, and with more accurate quantitative work, more tenable theories successively appeared.

The innumerable nooks and crannies of divers shapes necessary to satisfy the many combinations of solvent and solute soon proved the above theory to be inadequate.

Sir Isaac Newton then attempted to apply his newly developed gravitational theory to solutions.[3] He supposed a universal force acting between celestial bodies was also able to bind together different substances and cause their union to a new system. He reasoned that if water particles

1 Steel, Matthew-Physical Chemistry and Bio-Physics,106-John Wiley and Company(1928)

2-3 Arrhenius, Svante-Theories of Solutions, 6-7--Yale Press(1913)

exert a greater attraction on the salt particles than the salt particles exert on each other, the salt dissolves. This was more difficult to maintain, however, than the theory of gravitation, as gravitation is determined only by mass and distance, while solubility depends upon kinds of matter.

According to Nernst[1], the solution of a solid substance in any solvent is a process which has the greatest similarity to sublimation. In both cases the process is ended as soon as the expansive force of the evaporating or dissolving substance is held in equilibrium by the gas pressure of the vaporized molecules or by the osmotic pressure of the dissolved molecules, respectively. He therefore cites that the osmotic pressure of a saturated solution is called "solution pressure" of the dissolved substance in order to clarify the analogy to vapor pressure or sublimation pressure. Solubility varies very greatly with the nature of the solvent, the solvent having a much greater action on a solute of like structure.

Steel[2] describes the phenomena when sand, glucose, and water are brought into contact. The sand maintains with the water a two-phase relation, while the glucose and water merge into a single phase. When the glucose is brought into contact with the liquid some of the solid gradually disappears (dissolves) and a homogeneous system

1 Nernst, Walter-Theoretical Chemistry, 564-MacMillan(1923)

2 Steel, Matthew-Physical Chemistry and Bio-Physics, 110-John Wiley(1928)

is eventually obtained. Two forces work in establishing this homogeneous equilibrium, the kinetic energy of the molecules tending to fly off into space, and the attraction of the solvent molecules for those of the solute. The solvent attraction of molecules is more powerful, and the tendency is to pull the surface molecules of the solute away. Some of those pulled from the solute are, however, pulled back by the attraction the solute molecules have for each other. As the particles in solution increase, there is more chance of the molecules of the solution colliding with the solid, until finally a condition will result where as many molecules return to the solid as leave it.

By the phase rule Findlay[1] expresses the flexibility of solutions. Where P is the number of phases, F is the freedom of the system, and C is the number of components:

$$P + F = C + 2$$

That is, where the number of phases is one, greatest freedom is possible. In keeping with this rule, solubility is a function of temperature, pressure, size of solute crystals, etc.

There are many practical uses for solubility data, as in separation and purification processes with mixed salts,[2] and while the data are practically complete for the most common salts,[3] a great many compounds have not been closely investigated from a solubility standpoint.

1 Findlay, Alex-The Phase Rule, 20-Longmans, Green-London(1906)

2 Robertson, G. R.-Trona Enterprise, 520-Ind. and Eng. Chem.(1929)

3 Teeple, J. E.-Industrial Development, Searles Lake Brines,-Chemical Catalog Company(1929)

It is apparent that unless complete data are accurately determined on all compounds, there is a possibility of erroneous conclusions being drawn from the results derived. For example, Berthollet observed that if mercury sulphate is dissolved in water real chemical changes take place[1], and he believed that these changes do not occur according to constant proportions. There was in his opinion only a difference of degree between a solution and a very well-defined chemical compound. Hence he denied the law of constant proportions in chemical compounds. Proust, however[2], cited that water might enter into combination with certain substances, such as salts. These compounds are known in crystalline state as crystal hydrates. Like other chemical compounds, they are of constant composition.

There are still possibilities in theory revision as new data are accumulated.

1-2
Arrhenius, Svante-Theories of Solutions,10-Yale Press (1913)

General Theory

From studies of Guldberg and Waage[1], which are the basis of the solubility product principle, it follows that the concentration of cadmium ions in solution in the presence of sulphide ions must be equal to a constant times the square of the concentration of ionic hydrogen:[2]

$$(Cd) = K(H)^2$$

() Indicates molecular concentration

This theory has proved to be generally true[3], and results from numerous experiments[4] have strengthened it materially.

Several methods of merit have been employed to measure solubilities, including the following:

Optical methods: These were employed by Stother and Mitchell,[5] using a Jamin interferometer with a mercury green light. Upon passing this light through a solution, and noting the interference caused by different concentrations of solution upon the light waves, the concentration of an unknown solution can be determined. This method is not subject to errors of handling the solution; however, colloidal particles may contribute to an error.

Refractometric methods:[6] These are dependent upon the

1 Guldberg and Waage-Jour. Am. Chem. Soc. A580(1879)

2 Kinney, G. F.-Thesis, The University of Tennessee(1930)

3-4 Taylor, Hugh S.-Treatise on Physical Chemistry, 454-5-6-7-D. Van Nostrand(1925)

5 Stother and Mitchell-Jour. Am. Chem. Soc. 1333-6(1926)

6 Taylor, Hugh S.-Treatise on Physical Chemistry,252-D. Van Nostrand(1925)

deviation in the refraction of a beam of light with changes in concentration of solute in the liquid. A scale of refraction can be set up for known concentrations, and the refraction of the unknown compared.

Conductance methods: These are based on the principle of increased conductance with increased dilution.[1] The electrical conductance (1/resistance) is easily determined, and assuming that very dilute solutions have the same conductance as their limiting value, infinite dilution, this method gives accurate results.

Chemical analysis generally consists in drawing off a portion of saturated solution, which has been allowed to reach equilibrium at a definite temperature with the solid phase, and after evaporation, determining the amount in solution gravimetrically.

[1] Schlesinger-Jour. Am. Chem. Soc., 41, 1923(1919)

Description of the Method and Apparatus Used

The procedure adopted was that employed by Hale[1] and Kinney.[2] It was as follows:

Two separate solutions of hydrochloric acid, 30cc each, were made approximately to 3.6 Normal. Two 300cc solutions of approximately 2.5 Normal hydrochloric acid were then prepared. In like manner, two 1250cc solutions of hydrochloric acid were prepared for each of the following normalities, approximately: 0.425 Normal, 0.316 Normal, and 0.28 Normal.

To these solutions was added an excess of cadmium chloride[3], and hydrogen sulfide gas bubbled through, forming the sulfide of cadmium. The bottles were then tightly stoppered, and placed in a constant temperature bath at $25^{\circ} \pm .010^{\circ}$ Centigrade. While in the bath the bottles were shaken daily, and after three days hydrogen sulfide was again bubbled through the samples.

In determining how long the samples should remain in the bath to reach equilibrium, the theory of solution velocity was considered. Noyes and Whitney,[4] in an investigation of simple cases of solubility, revolved cylinders made benzoic acid and lead chloride, respectively,

1 Hale, Charles H.-Thesis, The University of Tennessee(1930)

2 Kinney, G. F.-Thesis, The University of Tennessee(1930)

3 The same procedure was followed in the case of lead sulfide

4 Noyes and Whitney-Jour. Am. Chem. Soc.,Aii749(1897)

in water, measurements of velocities being made from time to time. They postulated that around the surface of the cylinders a film of saturated solution was continually present and that the solution process was achieved as result of diffusion of solute from this layer into the solvent medium.[1] Since rate of diffusion is alpha, according to Frick's law, to concentration gradient between the saturated layer and the surrounding solution, it follows that this rate, and consequently the rate of the solution process, must be determined by the difference in concentration between the saturated layer and the solvent. If S be the concentration of the saturated solution, and x the concentration of the bulk of the solution at time t, the rate of solution at time t is given by the equation:

$$dx/dt = Ck(S-x)$$

where C is area of solid exposed.

Also, in experiments on calcium carbonate in sea water, Wells[2] found that after six or seven days solubility did not increase.

Therefore, after three days the samples of acid normality from 3.6 to 2.5 were pipetted quickly through a glass wool filter, ten ccs withdrawn, and this evaporated to dryness in a tared sillimanite evaporating dish with 2cc of sulfuric acid, ignited at low temperature, and the

[1] Taylor, Hugh S.-Treatise on Physical Chemistry, 942-D. Van Nostrand(1925)

[2] Wells, Roger Clark-Department of Marine Biology Papers, vol. ix, 317-398, Washington(1918)

residue weighed as cadmium sulfate. From the weight of cadmium sulfate the weight of cadmium sulfide dissolved in the solution was calculated.

The 1250cc samples, in which the acid normalities, and therefore the solubilities of the sulphide, were low, were allowed to remain in the bath for a week, after which time volumes of one liter each were drawn through glass wool filters by means of the constant temperature filtration apparatus shown in Fig. 5

The 1000cc drawn was evaporated to 50cc in liter beakers, then transferred quantitatively to tared sillimanite evaporating dishes, treated with 2cc of sulfuric acid, evaporated to dryness, and ignited at low temperature. The weight of cadmium sulfate obtained was calculated to cadmium sulfide.

As each sample was drawn, an additional sample was pipetted out and titrated with sodium hydroxide solutions which had been standardized against potassium acid phthalate, using methyl orange as an indicator. This gave the acid concentration of each solution.

Large samples were taken for doubtful points on the curves, thus diminishing chances of error. Close temperature control was maintained while the solutions were approaching equilibrium, and precautions taken to prevent change in temperature during filtration of the supernatant liquid from the solid phase. Two samples were not taken from the

same bottle, but checks were obtained from samples of the same acid normality in separate bottles.

The bottles were shaken from time to time, and hydrogen sulfide successively bubbled through them, to insure reaching equilibrium.

In removing the samples from the 1250cc bottles, cords were attached to the bottoms to prevent tilting when emptied. This tilting would have shaken up the precipitated sulfides on the bottom of the bottle, and rendered filtration more difficult.

Extreme care was necessary in evaporating the solutions of higher acid concentration, as spattering is evidenced when the hydrochloric acid is almost evaporated.

Some trouble was experienced in reading end-points on the higher normality solutions of lead sulfide, due to precipitation, but by holding the titration beaker off of the stand and looking against a filter paper, this difficulty was overcome.

Error may result from particles of glass wool coming into the filtrate. This was guarded against by packing the glass wool tightly into rubber tubing, but not crushing the wool into fine particles.

In evaporating, the burner was never allowed to stand directly under the dish until the SO_2 fumes poured off copiously; the burner was held in the hand and a small flame played carefully on the bottom of the dish.

Observations

Cadmium Sulfide Samples:

Determination of Acid Normality

No.	cc Solution	cc NaOH	cc Corrected	N Alkali	N Acid
1	(Water)				
2	(Water)				
3	5	65.1	64.98	.2280	2.94
4	5	67.0	67.06	.2280	3.05
5	5	41.6	41.65	.3104	2.58
6	5	48.8	48.85	.2280	2.26
7	10	13.9	13.90	.3104	0.431
8	10	13.9	13.90	.3104	0.431
9	10	10.7	10.69	.3104	0.332
10	10	10.7	10.69	.3104	0.332
11	10	9.5	9.48	.3104	0.294
12	10	9.5	9.48	.3104	0.294
Lead Sulfide Samples:					
1	(Water)				
2	(Water)				
3	5	67.7	67.74	.2280	3.09
4	5	58.0	58.00	.3104	3.51
5	5	48.6	48.65	.2280	2.22
6	5	39.0	38.95	.2280	1.78
7	10	13.9	13.90	.3104	0.431
8	10	14.1	14.09	.3104	0.437
9	10	10.5	10.49	.3104	0.326
10	10	10.5	10.49	.3104	0.326
11	10	9.5	9.48	.3104	0.294
12	10	9.4	9.39	.3104	0.291

Weight of Cadmium Sulfate:

(1)	Wt. Dish		33.6668 Gm.	(2)	Wt. Dish		33.4868 Gm.
	Wt. Dish + $CdSO_4$		33.6868		Wt. Dish + $CdSO_4$		33.4896
	Wt. $CdSO_4$		0.0200		Wt. $CdSO_4$		0.0028
	(Discarded)						
(3)	Wt. Dish		41.7010	(4)	Wt. Dish		40.4644
	Wt. Dish + $CdSO_4$		42.2138		Wt. Dish + $CdSO_4$		40.9890
	Wt. $CdSO_4$		.5128		Wt. $CdSO_4$		.5246
(5)	Wt. Dish		40.0303	(6)	Wt. Dish		40.5513
	Wt. Dish + $CdSO_4$		43.5920		Wt. Dish + $CdSO_4$		42.9890
	Wt. $CdSO_4$		3.5617		Wt. $CdSO_4$		2.3107
(7)	Wt. Dish		33.6668	(8)	Wt. Dish		33.4868
	Wt. Dish + $CdSO_4$		33.7080		Wt. Dish + $CdSO_4$		33.5170
	Wt. $CdSO_4$		.0312		Wt. $CdSO_4$		.0302
(9)	Wt. Dish		41.7010	(10)	Wt. Dish		40.4644
	Wt. Dish + $CdSO_4$		41.7250		Wt. Dish + $CdSO_4$		40.4880
	Wt. $CdSO_4$		.0240		Wt. $CdSO_4$		.0236
(11)	Wt. Dish		40.0303	(12)	Wt. Dish		40.5513
	Wt. Dish + $CdSO_4$		40.0556		Wt. Dish + $CdSO_4$		40.5770
	Wt. $CdSO_4$		.0253		Wt. $CdSO_4$		.0257

Weight of Lead Sulfate:

(1)	Wt. Dish		39.7113	(2)	Wt. Dish		39.8301
	Wt. Dish + $PbSO_4$		39.7122		Wt. Dish + $PbSO_4$		39.8310
	Wt. $PbSO_4$		.0009		Wt. $PbSO_4$		.0009
(3)	Wt. Dish		40.5054	(4)	Wt. Dish		42.5338
	Wt. Dish + $PbSO_4$		40.5342		Wt. Dish + $PbSO_4$		42.5660
	Wt. $PbSO_4$		.0288		Wt. $PbSO_4$		.0322
(5)	Wt. Dish		40.2177	(6)	Wt. Dish		38.0636
	Wt. Dish + $PbSO_4$		40.6570		Wt. Dish + $PbSO_4$		38.3014
	Wt. $PbSO_4$		.4394		Wt. $PbSO_4$		.2378
(7)	Wt. Dish		39.7113	(8)	Wt. Dish		39.8301
	Wt. Dish + $PbSO_4$		39.7300		Wt. Dish + $PbSO_4$		39.8490
	Wt. $PbSO_4$		.0187		Wt. $PbSO_4$		.0189
(9)	Wt. Dish		40.5054	(10)	Wt. Dish		42.5338
	Wt. Dish + $PbSO_4$		40.5270		Wt. Dish + $PbSO_4$		42.5550
	Wt. $PbSO_4$		.0216		Wt. $PbSO_4$		.0212
(11)	Wt. Dish		40.2190	(12)	Wt. Dish		38.0636
	Wt. Dish + $PbSO_4$		40.2352		Wt. Dish + $PbSO_4$		38.0786
	Wt. $PbSO_4$		.0142		Wt. $PbSO_4$		.0150

Calculations

No.	Wt. $CdSO_4$	Factor	Wt. CdS	Mols per Liter CdS
1	.0200 xx	.6932	.0138	.0096
2	.0028	.6932	.00191	.00132
3	.5128	.6932	.3555	.2440
4	.5246	.6932	.3637	.2518
5	3.5617	.6932	2.4689	.0624
6	2.3107	.6932	1.6018	.0444
7	.0312	.6932	.0216	.000149
8	.0302	.6932	.0209	.000145
9	.0240	.6932	.01663	.000115
10	.0236	.6932	.01636	.000113
11	.0253	.6932	.01750	.000121
12	.0257	.6932	.01781	.000123

No.	Wt. $PbSO_4$	Factor	Wt. PbS	Mols per Liter PbS
1	.0009	.7888	.00071	.00022
2	.0009	.7888	.00071	.00022
3	.0288	.9164	.0267	.0094
4	.0322	.9164	.0295	.0106
5	.4393	.9164	.4066	.00578
6	.2378	.9164	.2179	.00313
7	.0187	.7888	.0147	.0000615
8	.0189	.7888	.0149	.0000621
9	.0216	.7888	.0170	.0000710
10	.0212	.7888	.01669	.0000698
11	.0142	.7888	.01118	.0000467
12	.0150	.7888	.01183	.0000493

Rows 3–6 use $PbCl_2$ factors, Wt. PbS, and Mols per Liter PbS.

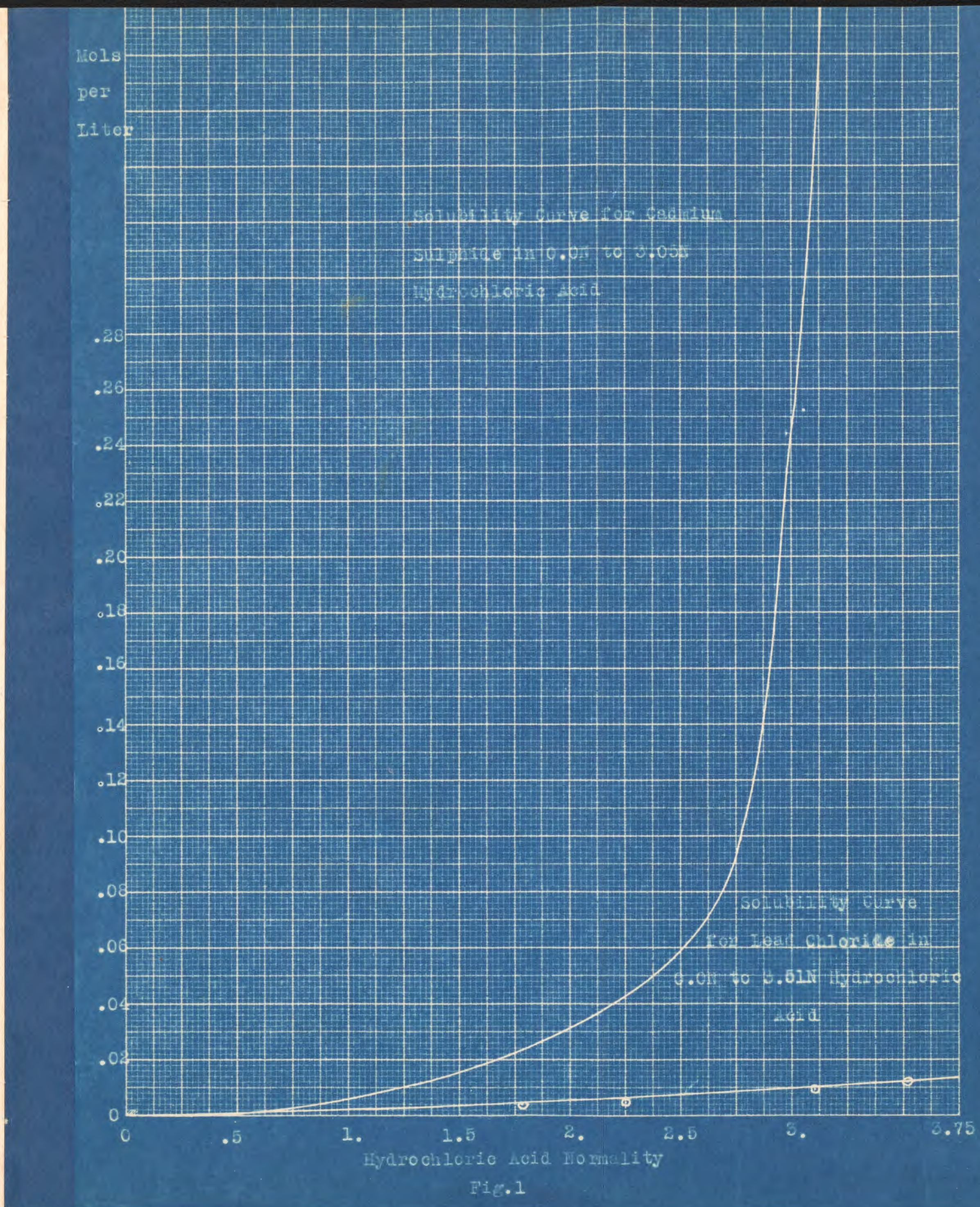

Mols per Liter
.28
.26
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
0
Solubility Curve for Cadmium Sulphide in 0.0N to 3.0N Hydrochloric Acid
Solubility Curve for Lead Chloride in 0.0N to 3.51N Hydrochloric Acid
0
.5
1.
1.5
2.
2.5
3.
3.75
Hydrochloric Acid Normality
KEUFFEL & ESSER CO.

Fig.1

KEUFFEL & ESSER CO N.Y.

.040
per
.038
Liter
.036
.034
.032
.030
.028
.026
.024
.022
.020
.018
.016
.014
.012
.010
.008
.006
.004
.002
0

Solubility Curve for Cadmium Sulphite in 0.0N to 3.5N Hydrochloric Acid

Solubility Curve for Lead Chloride in 0.0N Hydrochloric Acid to 5.51N Hydrochloric Acid

Pbs

0 .5 1. 1.5 2. 2.5 3. 3.75

Hodrochloric Acid Normality

.00040

per

.00038

Liter

.00036

.00034

Solubility Curve

.00032

for Cadmium Sulphide

.00030

in 0.0N to 0.45N

Hydrochloric Acid

.00028

.00026

.00024

.00022

.00020

.00018

.00016

.00014

.00012

.00010

.00008

.00006

.00004

.00002

0

0 .25 .5 1. 1.5 2.

Hydrochloric Acid Normality

Solubility Curve for

Lead Chloride in 1.0N to

1.76N Hydrochloric Acid

Solubility Curve for

Lead Sulphide in 0.0N to

1.0N Hydrochloric Acid

KEUFFEL & ESSER CO. N.Y.

cos

Correction

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50

.10
.09
.08
.07
.06
.05
.04
.03
.02
.01
0
.01
.02
.03
.04
.05
.06
.07
.08
.09
.10

Calibration Curve for Lorette

Fig. 4

KEUFFEL & ESSER CO. N.Y.

per

Li ter

.255

.240

.225

.210

.195

.180

.165

.150

.135

.120

.105

.090

.075

.060

.045

.030

.015

0 .30 .60 .90 1.2 1.5 1.8 2.1

$(\frac{1}{H}$ Ion Concentration$)^2$ -

Mole per Liter Solubility

Curve for Cadmium Sulphide

in 0.0M to 5.05M Hydrochloric

Acid

$(\frac{1}{H}$ Concentration$)^2$

Fig. 6

KEUFFEL & ESSER CO. N. Y.

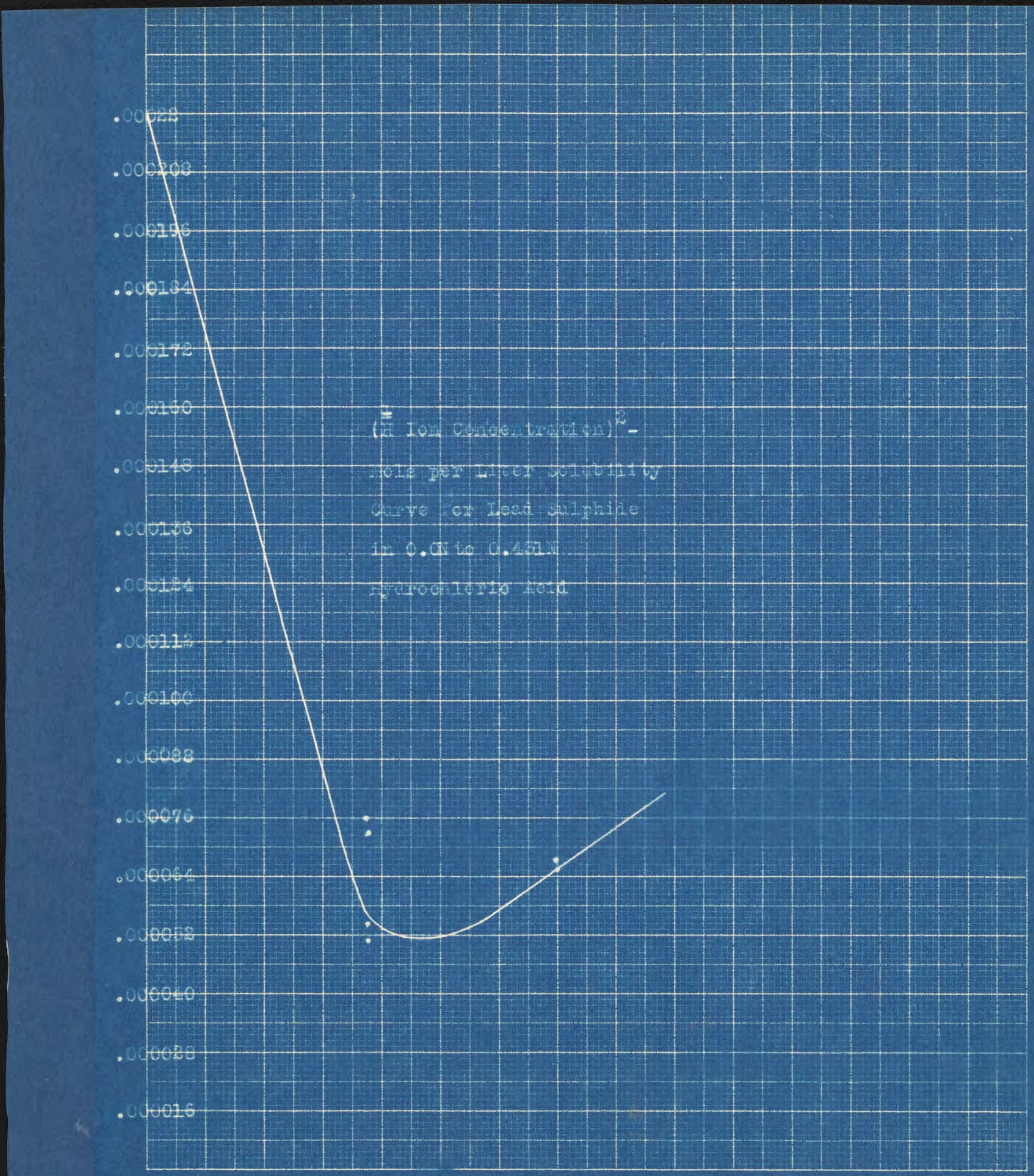


Fig. 7

KEUFFEL & ESSER CO. N.

per Liter

.255
.240
.225
.210
.195
.180
.165
.150
.135
.120
.105
.090
.075
.060
.045
.030

Solubility Product Constant-
Mols per Liter Solubility
Curve for Cadmium Sulphide
in 0.0N to 3.0N Hydrochloric
Acid

$1x10^{-28}$ $1x10^{-27}$ $1x10^{-26}$ $1x10^{-25}$ $1x10^{-24}$

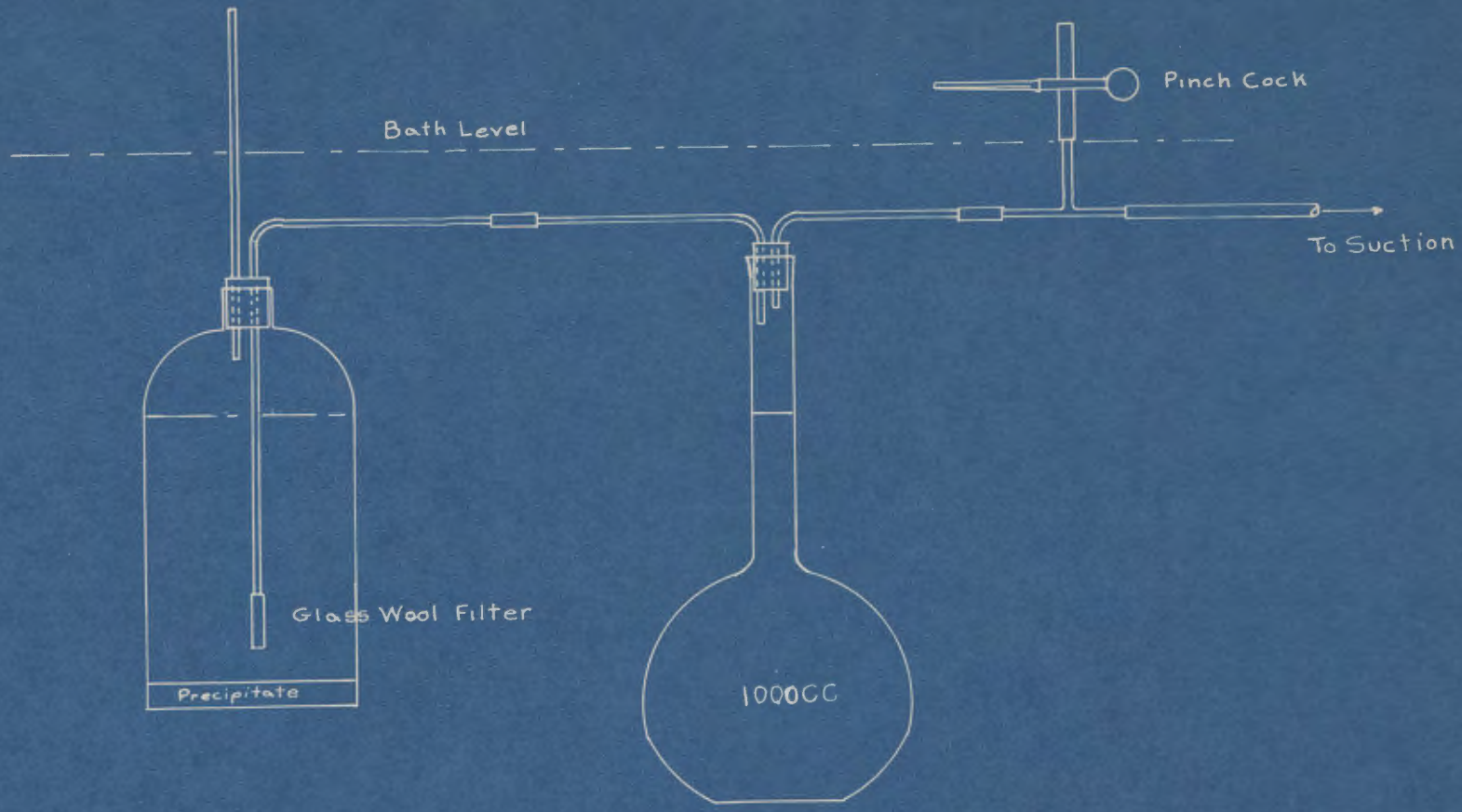
K_{sp}

Fig. 8

KEUFFEL & ESSER CO N.Y.

No.	Normality	$\pm$ H Ion Conc.	Solubility Product Const.	$(\pm$ H Ion Conc.$)^2$	$-$ S Ion Conc.
			CdS		
1	Water		(3.6×10^{-29}) [1]		
2	Water		4.2×10^{-7}		
3	2.94	1.47	1.2×10^{-24}	2.16	5.1×10^{-24}
4	3.05	1.49	1.3×10^{-24}	2.22	5.0×10^{-24}
5	2.58	1.41	3.4×10^{-25}	1.98	5.5×10^{-24}
6	2.26	1.34	2.7×10^{-25}	1.795	6.1×10^{-24}
7	0.431	0.373	1.2×10^{-27}	0.139	7.8×10^{-24}
8	0.431	0.373	1.2×10^{-27}	0.139	7.8×10^{-24}
9	0.332	0.28	1.1×10^{-27}	0.118	9.3×10^{-24}
10	0.332	0.28	1.1×10^{-27}	0.118	9.3×10^{-24}
11	0.294	0.274	1.8×10^{-27}	0.075	14.6×10^{-24}
12	0.294	0.274	1.8×10^{-27}	0.075	14.6×10^{-24}
			PbS		
1	Water		(3.4×10^{-28}) [2]		
2	Water		4.8×10^{-8}		
3	3.09		$PbCl_2$		
4	3.51		$PbCl_2$		
5	2.22		$PbCl_2$		
6	1.78		$PbCl_2$		
7	0.431	0.373	4.8×10^{-28}	0.139	7.8×10^{-24}
8	0.437	0.373	4.8×10^{-28}	0.139	7.8×10^{-24}
9	0.326	0.28	1.0×10^{-27}	0.075	14.6×10^{-24}
10	0.326	0.28	1.0×10^{-27}	0.075	14.6×10^{-24}
11	0.294	0.274	7.0×10^{-28}	0.075	14.6×10^{-24}
12	0.291	0.274	7.0×10^{-28}	0.075	14.6×10^{-24}

1-2 Olsen-D. Van Nostrand's Chemical Annual(1926)



CONSTANT TEMPERATURE SUCTION FILTER

FIG. 5

Discussion of Results

From the tabulated results the solubility in mols per liter of the cadmium sulfide, lead sulfide, and lead chloride were calculated for the the various acid concentrations, and curves plotted for each of the three with acid normality of the solution as abscissae, and solubility in mols per liter as ordinates.

The cadmium sulfide solubility curve came almost straight down between acid concentrations of 3.05N and 2.75N, then curved sharply , showing that from 2.75N to 0.0N the solubility does not differ as greatly with acid concentration as it does from 2.75N to 3.05N. (Fig. 1) From an acid concentration of 0.3N to 0.0N, the solubility curve takes an upward turn, the cadmium sulfide being .00002 mols per liter more soluble in water than 0.3N hydrochloric acid. (Fig. 3).

From acid concentration of about 1.0N upward the solute resulting from the treatment of lead chloride in acid solution with hydrogen sulfide was lead chloride. (Figs. 2-3). The solubility of the lead chloride over the range of acid concentrations from 1.0N to 3.51N increased uniformly with the acid concentration, the solubility curve being almost a straight line.

The solubility of the lead sulfide resulting from the treatment of lead chloride in 0.0N to 1.0N hydrochloric acid solution with hydrogen sulfide decreased from .00014 mols per liter in a 1.0N acid concentration, to .000056 mols per liter in 0.3N acid concentration; then increased

to .00022 mols per liter at 0.0N acid concentration. (Fig. 3)

The solubility of the lead sulfide was less than that of the cadmium sulfide from 0.14N acid concentration upward, however, at 0.14N the lead sulfide solubility curve crossed the cadmium sulfide solubility curve, showing a more rapid increase in solubility with decreased acid concentration. Both the cadmium- and lead sulfide showed minimum solubility at 0.3N acid concentration. (Fig. 3)

To test the validity of the solubility product principle with reference to cadmium sulfide in solutions from 0.0N to 3.05N hydrochloric acid concentration, a curve was plotted with the square of the hydrogen ion concentration as abscissa, and mols per liter solubility as ordinate. The values of the hydrogen ion concentration for the normalities used were obtained from Olsen.[1] This curve (Fig. 6) showed that for acid concentrations from 1.8N upward, the solubility product principle does not hold, however, from 1.8N acid concentration downward the curve is more nearly straight.

A similar curve was plotted for lead sulfide (Fig. 7), but because of limited values, very little can be determined from it.

A varying solubility product "constant" has been suggested,[2] therefore the "constant" for each of the cadmium sulfide samples was calculated. Since the solubility product constant for hydrosulphuric acid is 1.1×10^{-22}, and

[1] Olsen-Van Nostrand's Chemical Annual(1926)

[2] Kinney, G. F.-Thesis, The University of Tennessee(1930)

the concentration of hydrogen sulfide in a saturated solution is 0.1 molar, the value for the concentration of the sulfide ion may be calculated by dividing 1.1×10^{-23} by the square of the hydrogen ion concentration. Assuming that the concentration of the cadmium ion is the same as that of the cadmium salt, the solubility constant may be calculated by multiplying the concentration of cadmium in mols per liter by the concentration of the sulfide ion calculated as described.

A curve was plotted using values of the solubility product "constant" of the cadmium sulfide samples as abscissa, and mols per liter of cadmium sulfide dissolved as ordinate. This curve also showed that the solubility product "constant" is a variable at higher acid concentrations. (See Fig. 8)

Conclusions

1. The unusual curves obtained by previous experiment are essentially correct; however, the solubility curves cross only once.
2. The sulfides of cadmium and lead do not adhere to the solubility product principle in higher acid concentrations.
3. There is a change in the nature of the solvent at approximately 0.3N acid concentration, as evidenced by increasing solubility of both lead- and cadmium sulfide from that concentration to 0.0N acid concentration.

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APPROVAL.

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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