PART I.

A SYSTEM OF ELEMENTAL ANALYSIS

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THE USE OF THIOACETAMIDE FOR THE HOMOGENEOUS PHASE PRECIPITATION OF INORGANIC SULFIDES

Thesis by

Eliot Andrew Butler

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1956

ACKNOWLEDGMENTS

I wish to express my appreciation to Professor Ernest H. Swift for his advice and guidance during the experimental work reported here. In particular I have appreciated the privilege of working with him in some of the developmental work on the system of elemental analysis.

I also wish to express my appreciation to Professor Norman Davidson for helpful discussions on the kinetics of the reactions of thioacetamide, to David F. Bowersox with whom the work reported in Part II was done, and to Fred Anson and Glenn Crabbs whose observations concerning the use of thioacetamide as a precipitant of inorganic sulfides led to the work reported in Part III.

I would like to express my appreciation to the California Institute of Technology for tuition scholarships and teaching assistantships during the academic years 1952-53 and 1953-54, to E. I. du Pont and Company for summer research grants during 1952, 1953 and 1954, and to the Corning Glass Works Foundation for a predoctoral fellowship during the academic year 1954-55.

I wish to express my appreciation to my wife, Ann, and to our children for patience, understanding and encouragement.

ABSTRACT

A system of elemental analysis for pedagogical use has been developed. Non-metallic solids are fused with sodium hydroxide, sodium carbonate and sodium nitrate and the melt is treated with water to give a residue of the basic element oxides, hydroxides and carbonates, and a solution containing the amphoteric and acidic elements. Metallic solids are dissolved in nitric acid and the hot solution is treated with sodium chlorate. The solution is made alkaline with sodium hydroxide and the separation into groups is the same as is obtained by the fusion treatment. The procedures are capable of yielding semi-quantitative results and thus they permit approximate estimation of the elements.

The standard potential of the iodine-iodine monocyanide half cell has been determined. Measurements were made through the concentration ranges 0.2 to 4 F $HClO_4$ and 0.06 to 0.3 F total cyanide and the value -0.6248 ± 0.0026 v was obtained for the potential. The constant for the disproportionation of iodine in hydrocyanic acid solutions was determined by solubility measurements to be 0.870 ± 0.009.

The hydrolysis of thioacetamide to acetamide and hydrogen sulfide in dilute acid solutions was found to be first order with respect to both thioacetamide and hydrogen ion concentrations; under the conditions of the experiments in this study only a small fraction of the acetamide formed was hydrolyzed to acetic acid and ammonia. The second order rate constant for the hydrolysis reaction was found to be 0.21 ± 0.02 liter/mole minute at 90° C. The energy of activiation was determined and is 19.1 kcal/mole through the temperature range from 60° to 90° C.

The precipitation of lead sulfide by thioacetamide was found to proceed through two distinct mechanisms depending upon the pH of the solution. At low pH the precipitation involves the hydrolysis of thioacetamide to give hydrogen sulfide which then reacts with the lead. At higher pH the rate of precipitation shows first order dependence upon both thioacetamide and lead ion concentrations and inverse half order dependence upon hydrogen ion concentration. The rate constant and energy of activation have been calculated to be $1.15 \pm 0.12 \times 10^{-3}$ liter$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ minute^{-1} and 15.5 kcal/mole respectively. A discussion of the analytical use of thioacetamide is presented.

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PART I. A SYSTEM OF ELEMENTAL ANALYSIS

Introduction

A system of elemental analysis for pedagogical use has been developed. The initial separation is made in an alkaline solution and is based on the acidic or basic properties of the elements. This work represents an adaptation of the principles used in a system of elementary analysis for chemical warfare agents (1,2) in which the initial separation is effected by fusion of the sample with sodium peroxide and sucrose followed by treatment of the melt with water. The elements are thereby separated into two broad subdivisions; (a) those elements which form oxides and hydroxides insoluble in alkaline solution (the basic element group) and (b) those elements which are soluble in such a solution (the acidic and amphoteric element groups).

The purposes and aims underlying the development of the present system of analysis are:

1. To provide much closer correlation with the acidic and basic properties of the elements than is possible by the usual hydrogen sulfide separations.

2. To use procedures which are capable of giving semi-quantitative results, thus providing the student with the opportunity to make approximate estimations and an acquaintance with procedures of practical usefulness.

3. To use samples of such size that good ma-

nipulative techniques can be learned and such that equilibrium principles will have meaning to the student.

4. To include elements which are of analytical interest and yet to keep the total number of elements small enough that the entire system can be covered adequately in a one semester course.

A considerable amount of experimental work was done in the development of procedures for the system of analysis; a tabulation of results of this work is presented in the following sections. The reference at the beginning of each section is to the Procedure being considered and to the Tabular Outline in which more detail is presented concerning the procedure. The numbering of Procedures and Tabular Outlines is that which is used in the March 1955 mimeographed edition of "Systematic Elemental Analysis" (3).

A. THE FUSION OF THE SAMPLE

1. CRUCIBLE MATERIAL. Tabular Outline II; Procedures 2 - 3.

In experiments made to determine the types of crucible which would serve satisfactorily for the fusion the following procedure was followed:

The crucible was cleaned thoroughly, scoured with cleansing powder and flamed in an oxidizing flame. It was then cooled and weighed. The fusion reagents were put into the crucible, heated until melted and maintained as a melt for just fifteen seconds. The melt was cooled and washed from the crucible which was then dried and weighed. The change in weight, ΔW_1, gave a measure of the quantity of fusion material introduced into the sample. In certain cases the crucible was then scoured with cleansing powder and reweighed. The change in weight ΔW_2, from the initial value indicated the extent of attack upon the crucible. In some cases the melt was analyzed for crucible material.

The fusion reagents used were: 1 g Na_2CO_3, 1 g NaOH, and 0.5 g Na_2O_2.

Crucible	ΔW_1	ΔW_2
Vycor	0.15 g	
	.13	
Nickel	.0001	0.0007 g
	.001	
	.0001	.0013
	.0002	.0007
	.0011	.0031
	.0014	.0030
Average of 30 fusions		.002*
Iron	.0191	.0199**
	.0100	.0103**
	.0077	.0085**
Porcelain	.168***	
Silver		.0008
		.0009

* The quantity of Ni(II) in the melt varied from a trace to 2 mg. A maximum of 1 mg Ni(II) was found in the melt after fusions in which the Na_2O_2 had been replaced by $NaNO_3$.

** A red-brown mixture was obtained when the melt was treated with water.

*** The porcelain crucible crumbled when it was being scoured after the fusion.

Nickel crucibles were found to be satisfactory except in the case that analysis was to be made for less than 2 mg of nickel. In this case silver crucibles can be used. Crucibles of porcelain, Vycor glass and iron were found to be unsatisfactory.

2. FUSION REAGENTS. Tabular Outline II; Procedures 2 - 3.

Sodium hydroxide and sodium carbonate were used in all fusion experiments. In early experiments sodium peroxide was added to make an oxidizing melt. This reagent was found to be satisfactory for the purposes of the fusion, but unsuited to use in student laboratories because of the rapidity of its decomposition when in contact with air and because of the fire hazard involved in its use.

Sodium nitrate was substituted for the sodium peroxide and fills the requirement that at the conclusion of the fusion of the sample the elements be in known oxidation states. Sodium nitrate has the disadvantage of introducing nitrite into the sample due to thermal decomposition as well as through reaction with reducing agents in the original unknown.

3. SEPARATIONS BY FUSION. Tabular Outline II; Procedures 2 - 3.

Comparison was made of the separations which could be obtained by (a) fusion with hydroxide, carbonate and peroxide or nitrate followed by treatment with water to give a residue of the basic elements and a solution of the acidic and amphoteric elements, and by (b) treatment with a hot solution which had the same composition as had the aqueous solution of the fusion melt. Thus, the final aqueous solutions were identical, but the histories of these were different, one having come from a fusion. The fusion reagents were 1 g NaOH, 1 g Na_2CO_3 and 0.5 g Na_2O_2 or $NaNO_3$. The melt was treated with water and diluted to 10 ml.

Aqueous Treatment.

Taken (mg) Zn	Ni	Mn	Zn found in solution after removal of precipitate.
1	100		Trace
2	100		0.5 mg
1		100	0
2		100	0
8		100	0
8*		100	0
32		100	Trace
64		100	1 mg
64*		100	1

* In these experiments 1 ml of 15 F NH_4OH was added to the solution before the precipitate was removed.

Fusion Followed by Aqueous Treatment.

Taken (mg) Zn	Ni	Mn	Zn found in solution after removal of precipitate.
1	100		0.5 mg
1		100	1

Taken (mg) Al	Zn	Cr	Mn	Ti	Ag	Elements in solution.
1		1	100			1 mg Al, 1 mg Cr
1	1	1		40		1 mg Al, 1 mg Cr, 1 mg Zn
1	1	1			100	1 mg Al, 1 mg Cr, 1 mg Zn, Trace Ag

The following salts were used in these experiments: $ZnCl_2$,

$MnSO_4 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$.

From these experiments it is apparent that the fusion greatly reduces the extent of the coprecipitation of amphoteric elements with basic oxides.

The effect of the fusion upon certain other elements was investigated:

Copper ($CuSO_4 \cdot 5H_2O$).

Only a small fraction of the copper taken was found to be present in the fusion solution after fusion with Na_2O_2. This, however, necessitates the analysis for copper in the amphoteric element group.

In fusions with $NaNO_3$ the following results were obtained:

Cu Taken	Cu found in fusion solution
50 mg	1 mg
25	0.5*

* Larger quantities of copper have frequently been found in the amphoteric group in student analyses; this is probably caused by fusion for an extended period of time.

Tin ($SnCl_2 \cdot 2H_2O$, II; or SnO_2, IV)

Sn taken mg	Oxidation state	Sn in fusion solution mg
100	II	80
100*	II	85
50	II	45
40	IV	30

20	IV	15
20**	IV	16
30	II	25
20***	IV	16

* The fusion mass was kept melted for 30 seconds.

** The amount of NaOH in the fusion was doubled in this case.

*** The fusion mass was kept melted for 2 minutes.

With large quantities of tin, the estimation tends to be 10 - 20% low. The tin which is carried into the residue is taken into the titanium group and does not interfere with the analysis for that group.

Lead ($Pb(NO_3)_2$,(a); or $Pb(CO_3)_2$,(b).)

Pb taken	Pb in residue (PbO_2)	Pb(IV) in fusion solution
100 (a)	3 - 5	10
20 (b)	1	*

* A total of 19 mg of lead were found in the fusion solution. The oxidation state was not determined.

The lead which is carried into the basic element group does not interfere with the analysis of that group.

Vanadium (NH_4VO_3).

V taken	V in fusion residue
100 mg	0

Alkaline Earth Elements ($BaCl_2 \cdot 2H_2O$, $CaCl_2$, $Mg(NO_3)_2 \cdot 6H_2O$).

Taken	Found in fusion solution
100 mg Ba	0

100 mg Ca	0
100 mg Mg	0

Nitrate

In connection with studies of the acidic element group it was of interest to determine the extent of thermal decomposition of sodium nitrate in the fusion process. The nitrite was estimated iodometrically.

Nitrate taken	Fusion period	Nitrite found
6 millimoles	60 seconds	0.6 millimoles

The fusion was extended to four times the usual period in order to determine an upper limit of the nitrite to be expected.

Perchlorate ($NaClO_4$).

Experiments were made to determine whether perchlorate is decomposed by the fusion.

Cl taken	Fusion period	Cl^- found
29 mg (as $NaClO_4$)	15 sec	2 mg
29 "	300	29

The rate of decomposition of $NaClO_4$ by the fusion is low and the fusion period must be extended if perchlorate is present.

4. SEPARATIONS BY AQUEOUS TREATMENT. Tabular Outline II a; Procedure 4.

The possibility of effecting separations by vigorous treatment in aqueous solution was investigated. Such a treatment would be of value in the analysis of samples already in solution, or in the analysis of metals which would first require solution in acid.

The procedure was as follows: Treat the sample with 3 ml of hot 16 F HNO_3, add excess $NaClO_3$, evaporate to 1 ml, cool and add NaOH to make the final solution 3 N in NaOH. Boil 3 - 4 minutes and centrifuge.

	Taken (mg)			Zn remaining in solution
	Zn(II)	Mn(II)	Ni(II)	
a	2	100		0*
b	2	50		0.5 - 1 mg**
c	1	50		1***
d	2		50	2
e	1		50	1

* Black MnO_2 changed to voluminous, hydrous appearing brown precipitate when the NaOH was added.

** After evaporation of the HNO_3 solution, three additional 1 ml portions of 16 N HNO_3 were added and evaporated similarly.

*** The procedure was amended as in experiment (b) and additional $NaClO_3$ was added with each portion of HNO_3.

Silver Chloride.

Since resistant alloys may require treatment with aqua regia, the action of silver in such conditions was investigated.

The indicated quantity of silver as $AgNO_3$ was treated with 4 ml of boiling aqua regia which was then fumed to drive off the hydrochloric acid. The procedure was continued as in experiment (c) above.

Ag taken	Ag found in solution	Ag as AgCl
50 mg	14 mg	36 mg
50	16	34
50*	0	50

* No $NaClO_3$ was added in this case. This indicates that the chlorate is effective in dissolving part of the AgCl.

These experiments show the necessity of special treatment in the case that the solution of an alloy containing silver is prepared by the use of hydrochloric acid. The precipitate of silver chloride will be carried into the titanium group, can be removed by centrifugation from the solution of the titanium group and then be dissolved in NH_4OH and treated by Procedure 31, Tabular Outline III.

B. THE BASIC ELEMENT GROUP

1. SUB-GROUP SEPARATIONS.

Nitric Acid---Chlorate Treatment. Tabular Outline III; Procedure 11.

Experiments were made on the separation of manganese from silver by treatment of 2 ml of a hot concentrated nitric acid solution with $KClO_3$. The silver and manganese were added as nitrates.

Taken (mg)		Observations
Ag(I)	Mn(II)	
	1	Mn completely precipitated
100		1 - 2 mg Ag as AgCl
100*		1 - 2 mg Ag as AgBr
	1*	Mn completely precipitated
50	50	About 5 mg Ag with MnO_2
5	50	1 mg Ag as AgCl
1	50	1/3 mg Ag as AgCl
50		1 mg Ag as AgCl
5**		2 - 3 mg Ag as AgCl did not dissolve

* $KClO_3$ replaced with $KBrO_3$.

** Added as freshly precipitated AgCl.

Only a small fraction of the silver present is precipitated as AgCl by the nitric acid - sodium chlorate treatment. However, even small amounts of AgCl are not completely dissolved by this treatment.

Basic Acetate Separation. Tabular Outline III; Procedure 11.

(a) Experiments were made to determine the effect of total concentration of acetate and acetic acid, and the effect of the ratio of acetate to acetic acid upon the precipitation of iron. The effect of added nickel and copper was also considered. The solution volume was 15 ml in each case. The ratio of acetate to acetic acid was 8 except where indicated otherwise.

	Taken (mg)			Total formal acetate moles/liter	Results
	Fe(III)	Ni(II)	Cu(II)		
a	7	12	6	0.6	Iron colloidal, did not coagulate
b	7	12	6	0.2	The precipitate coagulated well
c	10			0.6	As in b
d	7	12		0.6	The precipitate coagulated slowly but completely in 2 minutes
e	7		6	0.6	As in b
f	7	18		0.6	As in b
g	7		18	0.6	As in b
h	7	5	10	0.6	As in b
i	7	12	6	0.3*	The precipitate coagulated rapidly. 12 mg Ni and 6 mg Cu found in solution

* The ratio of acetate to acetic acid was 1.5 in this case.

Rapid coagulation of the basic acetate precipitate of iron is favored by decreased total formal concentration of acetate and decreased ratio of acetate to acetic acid. Experiments (a) and (h) indicate that the ratio of iron to nickel to copper strongly affects the coagulation of the precipitate.

(b) The extent of coprecipitation of copper with titanium and iron was investigated. The total formal acetate concentration was 0.3 moles/liter and the ratio of acetate to acetic acid was 1.5. The fourth column shows the quantity of copper found in the solution, after removal of the basic acetate precipitate.

Taken (mg)			Cu(II) in solution
Ti(IV)	Fe(III)	Cu(II)	
25		1	0.7
25		10	8 - 9
25		25	23 - 24
	25	1	0.7
	25	10	8
	25	25	23
10	10	10	8 - 10

These experiments show that copper is only slightly coprecipitated with titanium and iron in the basic acetate precipitation.

Basic Benzoate Separation. Tabular Outline III; Procedure 11.

The substitution of benzoate for acetate for the separation of the titanium group from the other basic group elements was considered. However, it was found that the precipitation of copper is essentially complete from a benzoic acid - benzoate buffer even in the absence of iron, so the system was not investigated further.

Precipitation of Alkaline Earth and Metal Ammine Groups. Tabular Outline III; Procedures 21, 31.

The separation of the alkaline earth group elements from the metal ammine group was studied. The quantities of the elements indicated were taken in 12 ml of a blank solution which was 0.8 F in NH_4NO_3, 0.06 M in $HC_2H_3O_2$, and 0.09 M in $NH_4C_2H_3O_2$. To this were added 2 ml of 15 N NH_4OH, 2 ml 6 N NaOH and 2 ml 3 N Na_2CO_3. The solution was agitated frequently over a period of 5 minutes and then filtered. The precipitate was washed with a solution consisting of 2 ml of 6 N NH_4OH, 0.2 ml of 6 N NaOH and 0.2 ml of 3 N Na_2CO_3. To the filtrate were added 2 ml of 6 N NaOH and the solution was boiled for three minutes after no more NH_3 could be detected, in order to precipitate the metal ammine group oxides.

Taken (mg)					Observations
Ba	Mg	Ag	Cu	Ni	
25		1			$BaCO_3$ colorless. 1 mg Ag found in filtrate.
25			1		As above; Cu not coprecipitated.
25				1	As above; Ni not coprecipitated.
	25	1			$Mg(OH)_2$ white but difficult to filter. No coprecipitation.
	25		1		$Mg(OH)_2$ pale blue after the washing. The color faded appreciably during the washing. 0.1 mg coprecipitated.
	25			1	$Mg(OH)_2$ white. No coprecipitation.
	10	10			No coprecipitation.
	10*		10		0.2 - 0.5 mg Cu coprecipitated.
	10*			10	No coprecipitation.

* In these two experiments 2 ml extra of 15 N NH_4OH were added before the precipitation of the alkaline earth group.

These experiments indicate that the only significant coprecipitation is of copper with magnesium. This is diminished by careful washing of the precipitate. Milligram quantities of any of the metal ammin elements are precipitated satisfactorily when the ammonia is removed from the alkaline solution.

2. TITANIUM GROUP.

Solution of Titanium Group Precipitate. Tabular Outlive IV; Procedure 12.

The solution of the basic acetate precipitate of titanium and iron was found to be accomplished satisfactorily in concentrated sulfuric acid to which had been added solid sodium sulfate. The mole ratio of H_2SO_4 to $Na_2SO_4 \cdot 10H_2O$ was four. In the absence of sodium sulfate, TiO_2 was not consistently dissolved by the treatment; moreover, anhydrous $Fe_2(SO_4)_3$ formed when sulfuric acid was fumed. This latter difficulty was not encountered when the additional sulfate was present.

Oxidation of Manganese (II) with (a) Lead Dioxide; (b) Sodium Bismuthate. Tabular Outline IV; Procedure 14.

(a) Attempts were made to oxidize Mn(II) to MnO_4^- in hot sulfuric acid by the addition of solid PbO_2. The concentration of sulfuric acid affected the results; the optimum concentration appeared to be from 0.5 to 3 N. However, even in this concentration range the oxidation was not quantitative.

(b) Oxidation of manganese (II) was accomplished by treatment of its 2 N H_2SO_4 solution with a slight excess of solid sodium bismuthate at room temperature:

Mn (II) taken	Mn (as MnO_4^-) obtained
0.1 mg	0.1 mg
0.5	0.5
2	2
10	8

The oxidation is satisfactory when 2 mg or less of Mn (II) are present. An aliquot of the solution must be taken when larger quantities are present.

Preparation of Titanium Known Solution.

The following procedure was used for the preparation of chloride free known solutions of titanium from $K_2TiO(C_2O_4)_2 \cdot 2H_2O$:

> To 740 mg $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ (100 mg Ti (IV)) add 5 ml 18 N H_2SO_4* and heat until no more CO_2 is evolved. Then add 3 g $Na_2SO_4 \cdot 10H_2O$ and dilute to 10 ml.
>
> * More concentrated acid causes charring of the mixture.

These solutions were found to be stable for periods of several months.

3. ALKALINE EARTH GROUP. Tabular Outline V; Procedures 22 - 27.

Interference of Metal Ammine Group Elements.

Experiments were made to indicate the effects caused by 5 mg quantities of the metal ammine group elements in the analysis for the alkaline earth group elements:

Taken	Observations
5 mg Cu(II)	Some Cu precipitated as chromate. The confirmatory test for Ba distinguishes Ba from Cu. No other interference.
5 mg Ag(I)	Precipitated as chromate. Ba confirmatory test distinguishes this. No other interference.
5 mg Ni(II)	No interference.

4. METAL AMMINE GROUP.

Copper Confirmatory Test. Tabular Outline VI; Procedure 35.

Experiments were made to determine if $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$ could be used to give confirmation of the presence of copper in the cuprous iodide precipitate obtained in the estimation of copper. The CuI precipitate was dissolved in 2 ml of 6 N NH_4OH, and the solution was diluted to 8 ml and halved. The portions were treated by reagents 1 and 2 below:

Taken	1) 1 ml 1 N $K_3Fe(CN)_6$ 1 ml 6 N HCl	2) 1 ml 1 N $K_4Fe(CN)_6$ 1 ml 6 N HCl
1 mg Cu	Red-brown precipitate when HCl added. I_2 color in solution.	As in 1, but no I_2 color.
5 mg Cu	As above.	As above.
25 mg Cu	Green-brown precipitate with $K_3Fe(CN)_6$; became red-brown with HCl. I_2 in solution.	As in 1, but no I_2.

The experiments show that $K_4Fe(CN)_6$ is preferable for the confirmatory test for Cu since there is not formation of iodine as there is when ferricyanide is used.

C. THE AMPHOTERIC ELEMENT GROUP

1. SULFIDE GROUP PRECIPITATION.

Use of Hydrogen Sulfide. Tabular Outline VIII; Procedure 51.

Experiments were made to determine suitable conditions for the separation of lead, copper, arsenic and tin from aluminum, zinc, vanadium and chromium by the use of hydrogen sulfide.

Arsenic, which is in the pentapositive state following the fusion, was found to be precipitated quantitatively as the sulfide from dilute acid only by the use of hydrogen sulfide under pressure. Reduction of As(V) to As(III) with iodide was tried; however the iodide interfered subsequently in the procedure when chromium and vanadium were reoxidized. The pressure treatment which was used was the following: The acid solution of the arsenic was saturated with hydrogen sulfide. If a precipitate formed the solution was heated to near boiling and again saturated with hydrogen sulfide. The flask containing the solution was then stoppered and heated in boiling water for 15 minutes. A tabulation of results follows. In each case the solution was 1 F in the sodium salt of the acid used. This salt concentration resulted from the neutralization of the alkaline fusion solution.

	Taken (mg)	Acid	Results
a	25 As(V)	0.37 M HNO_3	1 mg not precipitated.
b	50 As(V)	0.5 M HNO_3	5 mg precipitated.
c	50 As(V)	0.25 M HNO_3	Precipitation complete after second pressure treatment. Odor after first treatment indicated reduction of nitrate.
d	0.5 As(V)	0.25 M HNO_3	Precipitate easily detected.

e	50 As(V)	0.25 M HCl	Most of As precipitated before pressure treatment.
f	0.5 As(V)	0.25 M HCl	As in e.
g	0.5 Zn(II)	0.25 M HNO_3	No precipitate.
h	0.5 Zn(II) 50 As(V)	0.25 M HNO_3	As in c. Zn not coprecipitated.
i	0.5 Zn(II) 50 Sn(IV)	0.25 M HNO_3	Separation was satisfactory.
j	0.5 Zn(II) 50 Pb(II)	0.25 M HNO_3	Separation was satisfactory.
k	50 As(V)	0.5 M $HClO_4$	0.5 - 1 mg As not precipitated.
l	50 As(V)	1 M $HClO_4$	As in k.
m	50 As(V)	2 M $HClO_4$	As in k.
n	0.5 As(V)	0.75 M $HClO_4$	Trace unprecipitated.
o	0.5 Pb(II)	1 M $HClO_4$*	No PbS precipitated.
p	0.5 Pb(II)	0.5 M $HClO_4$*	As in o.
q	0.5 Pb(II)	0.4 M $HClO_4$*	Complete precipitation of Pb.
r	0.5 Sn(IV)	0.4 M $HClO_4$*	Complete precipitation of Sn.
s	0.5 Cu(II)	0.4 M $HClO_4$*	Complete and very rapid precipitation of Cu.

* No pressure treatment was used in these experiments.

From these experiments it appears that nitrate has an inhibiting effect upon the precipitation of arsenic sulfide by hydrogen sulfide and that chloride is not essential to prevent coprecipitation of zinc with the elements of the sulfide group under the conditions used.

Use of Thioacetamide. Tabular Outline VIII; Procedure 51.

(a) The use of thioacetamide (hereafter referred to as TAA) for precipitation of the sulfide group was investigated. The constituents were taken in 10 ml of solution of the composition shown and maintained just below boiling temperature for 2 minutes, or for the period of time indicated.

	Taken (mg)		[TAA] moles/liter	[HCl] moles/liter	Results
a	0.5	As(V)	0.07	6	Rapid and complete precipitation.
b	5	As(V)	.07	6	As in a.
c	50	As(V)	.2	6	As in a.
d	5	As(V)	.07	3	As in a.
e	5	As(V)	.07	1.5	Precipitation complete; slightly slower than a - d.
f	5	As(V)	.07	.6	3 minutes heating required to get complete precipitation.
g	0.5	As(V)	.07	.6	As in f.
h	50	As(V)	.25	.6	Precipitation complete in 4 minutes.
i	10	Pb(II)	.15	.6	No precipitate after 4 minutes.
j	10	Pb(II)	.15	.3	No precipitate after 3 minutes. Diluted to .15 N HCl, obtained rapid and complete precipitation.
k	10	Pb(II)	.15	.15	Fine granular precipitate formed slowly; about 1 mg Pb not precipitated after 4 minutes.
l	.5	As(V)	.2	.3	Precipitation complete in 1 minute.
m	10	As(V)	.2	.3	Precipitation complete in 2 - 3 minutes.
n	50	As(V)	.4	.3	Precipitation complete in 3 minutes.
o	10	Sn(IV)	.25	.3	Rapid and complete precipitation.
p	10	Sn(IV)	.25	.15	Precipitation was incomplete after 3 minutes.

q	2	Cu(II)	.25	.3	The solution became cloudy; when it was diluted to 0.15 N HCl there was rapid formation of black precipitate.
r	.5	Cu(II)	.25	.3	As in q.
s	.5	Sn(IV)	.25	.3	Precipitate formed rapidly when the solution was heated.
t	50	Sn(IV)	.25	.3	As in s. Precipitation complete.
u	50	Pb(II)	.25	.3	The solution was heated 1 minute, then diluted to .15 N HCl. Rapid precipitation, but not complete.
v	50	Pb(II)	.4	.3	Treated as in u. About 1 mg Pb not precipitated.
w	50	Pb(II)	.5	.3	Treated as in u. 1 mg Pb not precipitated.
x	50	Pb(II)			
	.5	Zn(II)	.5	.3	Treated as in u. 1 mg Pb not precipitated; Zn not coprecipitated.
y	50	As(V)			
	.5	Zn(II)	.5	.3	Treated as in u. As completely precipitated; Zn not coprecipitated.
z	50	Zn(II)	.5	.3	The solution was heated 1 minute, then diluted to 0.1 N HCl. No precipitate after 4 minutes.
a'	25	Pb(II)			
	1	Zn(II)	.5	.3	Treated as in z. Pb precipitated completely; Zn not coprecipitated.

These experiments show that As(V) can be precipitated much more quickly with thioacetamide than with H_2S. The precipitation of all members of the sulfide group can be effected by the use of thioacetamide. As(V) precipitates more rapidly from high acid concentrations; Pb(II) and Cu(II) precipitate satisfactorily from a solution 0.3 N in HCl which is heated and then diluted rapidly to 0.15 N HCl.

In student work the procedure followed in experiment (v) above did not give consistent results in the precipitation of lead sulfide. Because of this difficulty the procedure was amended in the following way: the solution, 12 ml in volume, 0.25 M in H^+, 0.5 M in Cl^- and 0.4 F in thioacetamide, and which contains the amphoteric group elements is heated almost to boiling and then placed in boiling water for 3 minutes. To this hot solution is added 1 ml of 3 F $(NH_4)_2SO_4$. This procedure reduces the possibility of H_2S being swept from the solution by accidental boiling of the solution, and also provides better control of the acid concentration for the precipitation of lead. The results of experiments in which this procedure was used are presented below.

	Taken (mg)		Observations
	Pb(II)	Zn(II)	
a	1		The precipitate formed rapidly when $(NH_4)_2SO_4$ was added. The precipitation was complete.
b		25	No precipitate was observed.
c	10	10	The lead precipitated completely. Zn was not coprecipitated.
d	25	1	As in c.

(b) Precipitation of zinc from alkaline solution with thioacetamide was investigated. The procedure followed was to treat the indicated amount of zinc (II) as in the precipitation of the sulfide group, experiment (v) above, and then add excess NaOH. Any precipitate obtained was removed and the solution was treated with NaHS.

Zn taken	Effect Observed	
(mg)	Alkaline TAA	NaHS
1	No precipitate	1 mg Zn as ZnS.

10	8 - 10 mg Zn as ZnS	0.5 - 1 mg Zn as ZnS.
50	Large white precipitate	1 - 2 mg Zn as ZnS.

These experiments indicate that ZnS can be precipitated in alkaline solution by means of thioacetamide if an acid solution of TAA and zinc is first heated and then made alkaline. It is probable that the precipitation is accomplished by the hydrogen sulfide produced in acid solution by hydrolysis of the thioacetamide.

2. ALUMINUM-CHROMIUM GROUP

Basic Benzoate Precipitation. Tabular Outline XII; Procedure 71.

Destruction of thioacetamide by oxidation subsequent to the precipitation of the sulfide group was attempted by use of Na_2O_2, Br_2, BrO_3^-, and ClO^-. In no case was the procedure satisfactory, so a procedure for the removal of the aluminum-chromium group from the thioacetamide solution was developed.

The practicability of precipitating aluminum, zinc, chromium (III) and vanadium (IV), following the thioacetamide treatment, by buffering the solution with benzoic acid - sodium benzoate was investigated.

The indicated constituent in 12 ml of a solution 0.25 F in HCl, 1 F in NaCl and 0.4 F in thioacetamide was heated almost to boiling for 3 minutes, then diluted to 20 ml and heated for 1 minute. Four milliliters of 1.5 F ammonium benzoate were added and the solution was swirled for 2 - 3 minutes.

	Taken (mg)	Observations
a	1 Zn(II)	No precipitate.* (ZnS precipitated readily with NaHS in alkaline solution).

b	10 Zn(II)	Zn completely precipitated.
c	50 Zn(II)	1 - 2 mg of Zn not precipitated. Large precipitate of benzoic acid.
d	1 V(IV)	0.7 - 1 mg V in precipitate.**
e	10 V(IV)	9 - 10 mg V in precipitate.
f	1 Al(III)	Completely precipitated. Voluminous white precipitate.
g	10 Al(III)	As in f.
h	25 Al(III)	As in f.
i	1 Cr(III)	Completely precipitated. Voluminous blue-gray precipitate.
j	10 Cr(III)	As in i.
k	25 Cr(III)	As in i.

* Experiments made in the subsequent study of thioacetamide make it appear probable that in experiment (a) the H_2S produced by hydrolysis of thioacetamide in acid solution was swept from the solution, thus preventing the precipitation of ZnS when the solution was made alkaline.

** This small amount of vanadium did not precipitate from the warm solution, but was carried down by the large amount of benzoic acid which precipitated as the solution cooled. When the benzoic acid was redissolved, the vanadium remained precipitated.

Thus, the basic benzoate precipitation is satisfactory for the precipitation of the aluminum - chromium group, if some sulfide is added (as NaHS) to insure the precipitation of zinc as sulfide.

Separation of Chromium and Vanadium. Tabular Outline XIV; Procedure 81.

The separation of chromium from vanadium by precipitation of lead chromate from dilute strong acid solution followed by precipitation of lead vanadate from acetic acid - sodium acetate buffer was investigated.

The indicated quantities of Cr(VI) and V(V) were taken in 6 ml of nitric acid of the concentration shown. Two milliliters of 1 N $Pb(NO_3)_2$

were added; any precipitate was removed, and sufficient 3 N $NH_4C_2H_3O_2$ was added to give a ratio of acetic acid to acetate of unity. The final volume was about 10 ml.

	Cr(VI) mg	V(V) mg	(H^+) (initial)	Observations
a	50	0	0.3 M	0.1 mg not precipitated from strong acid.
b	0.5	0	0.3	Precipitation complete.
c	0	50	0.3	2 - 3 mg precipitated from strong acid. Remainder precipitated completely from buffer.
d	0	25	0.3	No precipitate from strong acid. Quantitative precipitation from buffer.
e	0	0.5	0.3	As in d.
f	50	0	0.6	0.1 mg not precipitated from strong acid.
g	50	0	1.0	As in d.
h	0.5	0	1.0	As in d.
i	0	50	1.0	As in d.
j	0	25	0.6	As in d.
k	0	5	1.0	As in d.

Chromium can be separated from vanadium as lead chromate from solutions 0.3 to 1.0 M in HNO_3; however, a small quantity of chromium remains unprecipitated in 0.6 to 1.0 M HNO_3. Only with 50 mg of vanadium (two times the maximum provided for in the system) is some lead vanadate precipitated from 0.3 M HNO_3. The latter concentration was chosen as the most suitable for the separation.

Estimation of Vanadium. Tabular Outline XIV; Procedure 84.

Experiments were made to develop a suitable colorimetric estimation for vanadium by making use of the intense color of peroxyvanadate.

(a) Effect of initial oxidation state.

To the indicated amount of vanadium (IV) in 2 ml of 3 N H_2SO_4 was added 1 ml 3% H_2O_2. The color was compared with that obtained by identical treatment of the same quantity of vanadium (V).

	V(IV) mg	Color intensity, relative to same quantity of V(V)
a	1	Very slightly darker than with V(V).
b	10	Identical.
c	25	Just detectably lighter than with V(V).

It appears that the excess of hydrogen peroxide is large enough to obscure any effect of initial oxidation state of the vanadium.

(b) Effect of concentration of sulfuric acid.

Two sets of solutions were prepared: (1) Vanadium (V) in solution of 2 ml 6 N H_2SO_4 and 1 ml 3% H_2O_2, and (2) Vanadium (V) in solution of 2 ml 3 N H_2SO_4 and 1 ml 3% H_2O_2. The intensities of colors were compared.

V(V) taken (set 1)	The color corresponded to this quantity of V(V) in set 2
1 mg	1 mg
10	15
22	30

The intensity of color of the peroxyvanadate increases with the concentration of sulfuric acid; therefore control of the acid concentration is essential for satisfactory estimation of vanadium.

(c) Effect of concentration of hydrogen peroxide.

Three identical 3 ml portions (1, 2, 3) of 4 N H_2SO_4 were prepared and to each was added just 1.0 ml of 3% H_2O_2. To (1) was added 1/3 mg V(V), to (2) was added 2/3 mg V(V) and to (3) was added one mg of V(V). To a fourth 3 ml portion of 4 N H_2SO_4 **was added** 1.0 ml water, 1 mg V(V) and 1/30 ml of 3% H_2O_2. The color corresponded to that of solution (3) and showed no change when up to 1 ml of H_2O_2 was added. It is concluded that the intensity of the peroxyvanadate color is not critically dependent upon the concentration of hydrogen peroxide, so long as the peroxide is in excess of the vanadate.

D. THE ACIDIC ELEMENT GROUP

1. REMOVAL OF AMPHOTERIC ELEMENTS. Tabular Outline XV; Procedure 101.

Experiments were made to determine a suitable procedure for removal of certain amphoteric elements from the portion of the fusion solution which is to be analyzed for the acidic elements.

The Use of Ion Exchange Resin.

Solutions, 10 ml in volume, 0.6 N in HNO_3 and containing the constituents indicated were swirled 2 minutes with successive 2 g (moist weight) portions of acid charged Dowex 50 cation exchange resin, particle size 0.5 - 1.0 mm. The number of such treatments necessary to effect complete removal of the element in question is shown.

Taken (mg)	Treatments with resin for complete removal
25 Al(III)	2
25 V(IV)	4 (1 mg remained after 3 treatments.)
25 Cr(III)	5 - 8

It was concluded that removal of the amphoteric elements with this ion exchange resin was impractical for the system of analysis.

The Use of Monohydrogen Carbonate - Carbonic Acid Buffer.

Carbon dioxide was bubbled through a 10 ml portion of the fusion solution, which is about 2.5 F in NaOH and 1 F in Na_2CO_3, until a pH of 8 was obtained. The precipitate was removed by centrifugation.

	Taken (mg)	Observations
a	1 Si(IV)	Precipitate formed in 10 minutes;

		precipitation essentially complete.
b	1 Si(IV)*	Precipitation complete in 4 minutes.
c	10 Si(IV)	Precipitation complete in 8 minutes.
d	10 Si(IV)*	Precipitation complete in 6 minutes.
e	25 Si(IV)	Precipitation started in 5 minutes; complete in 8 - 10. Less than 1 mg not precipitated.
f	10 Al(III)	Precipitation complete in 5 minutes.
g	10 Zn(II)	Precipitation complete in 5 minutes.
h	25 Al(III)	
	4 P(V)	Only a trace of phosphate not coprecipitated.
i	25 Al(III)	
	4 As(V)	Arsenic not coprecipitated.
j	25 P(V)	
	25 Pb(II)	Precipitate formed, but almost all of this dissolved upon being washed with water. Most of Pb(II) in solution.

* Plus 20 mg Zn(II).

Added Zn(II) speeded the precipitation of Si(IV), particularly when the latter was present in small quantity. The precipitation of aluminum, zinc and silicon is satisfactory with these conditions.

2. INTRODUCTION OF SILICA INTO THE SAMPLE FROM GLASSWARE.

In the separation of the elements into groups, the fusion melt is treated with water and boiled for several minutes in a Pyrex beaker. The portion of the alkaline solution to be analyzed for the acidic group is stored in a Pyrex test tube until the time of its analysis. The relative amounts of silicon introduced into the sample by the boiling and by the extended period of contact with glass at room temperature were determined. The solution used in each case consisted of 1 g NaOH, 1 g Na_2CO_3 and 0.5 g $NaNO_3$ in 10 ml H_2O. The silicon was detected by treatment of the solution with fuming H_2SO_4.

(i) Comparison solution. The solution was prepared in a nickel crucible and stored in a carefully paraffined test tube. No silicon found in this case.

(ii) Contact with glass at room temperature. The solution was prepared and stored in a 15 x 125 mm Pyrex test tube. After 9 days the solution was tested for Si(IV). 0.2 mg Si(IV) in the solution.

(iii) Contact of boiling solution with glass. The solution was boiled 10 minutes in a 50 ml Pyrex flask. As a result of this treatment, 2 - 4 mg Si(IV) were in the solution.

These experiments show that the short treatment at boiling temperature causes much more silicon to be introduced into the sample than does contact with glass for an extended period at room temperature.

3. ESTIMATION OF IODINE AND BROMINE. Tabular Outline XVI; Procedures 106, 108.

Experiments showed that satisfactory estimation of iodine could be made by extraction into 2 - 5 ml of CCl_4 followed by addition of 2 ml of water and 0.5 mmole of HNO_3 and titration with $AgNO_3$. With similar conditions the estimation of bromine was unsatisfactory. If the bromine was first reduced, the estimation by titration with $AgNO_3$ gave good results.

Taken	Estimation
mg	mg
50 I	48
0.5 I	<1
10 Br	6 - 12 Endpoint very uncertain.
20 Br	12 (?) Endpoint very uncertain
20 Br*	18
30 Br**	28

* Before the titration, 1 ml H_2O, 0.5 ml C_2H_5OH and 0.5 mmole HNO_3 were added to the CCl_4 solution of the bromine.

** The bromine was reduced to bromide with KNO_2 - HNO_3. The bromide was then titrated with $AgNO_3$.

4. INTERFERENCE OF LEAD IN ANALYSIS OF PHOSPHORUS GROUP. Tabular Outline XVII; Procedures 113, 115.

It was observed that lead is only partially precipitated by the carbon dioxide treatment of the fusion solution. Therefore, experiments were made to determine if lead interferes with the analysis of the phosphorus group. The constituents shown were treated with excess $AgNO_3$ in an acetic acid-acetate buffer, the precipitate was separated, washed and treated with 6 N HCl. The filtrate from this treatment was made ammoniacal and treated with magnesium nitrate reagent which was 0.5 F in $Mg(NO_3)_2$, 3 F in NH_4NO_3 and 0.2 F in NH_4OH. The precipitate was dissolved in HNO_3 and treated with ammonium molybdate solution.

	Taken mg	Observations: Magnesium Nitrate Treatment	Observations: Ammonium Molybdate Treatment
a	2 P(V)	White crystalline precipitate.	Intense yellow precipitate.
b	2 P(V) 25 Pb(II)	As in a.	As in a.
c	25 P(V)	Large white crystalline precipitate.	Heavy yellow precipitate.
d	25 P(V) 25 Pb(II)	As in c.	As in c.

No effect of the lead was detected, either upon the size or appearance of the precipitates of phosphorus.

5. SEPARATION OF ARSENIC FROM PHOSPHORUS. Tabular Outline XVII; Procedure 114.

Thioacetamide was found to be satisfactory for use in effecting the separation of arsenic from phosphorus in 0.6 F HCl. No sulfur was observed to precipitate during subsequent treatment of the filtrate, and there was no interference with the precipitation of the phosphorus as ammonium molybdophosphate.

6. CONFIRMATORY TEST FOR SULFUR. Tabular Outline XVIII; Procedure 121.

Experiments were made in an effort to devise a confirmatory test for sulfur which would also permit its estimation. Sulfur is detected as $BaSO_4$, so the following experiments were made upon freshly precipitated $BaSO_4$: (i) Fusion with Na_2CO_3 (or NaOH) and paper pulp.

One milligram of $BaSO_4$ was mixed with about ten times its volume of paper pulp and fused as indicated; the melt was cooled, treated with water and tested for the presence of sulfide.

Fusion reagent	Results
0.5 g Na_2CO_3	Mass did not fuse; no sulfide detected.
0.5 g NaOH	Mass fused well; no sulfide detected.

No further experiments were made with this procedure.

(ii) Reduction of sulfur (VI) with HI and H_3PO_2.

The indicated quantity of sulfur as $BaSO_4$ was treated with a boiling solution which consisted of 0.2 ml of 50% H_3PO_2 and the quanity of 7 F HI shown. Air was drawn through the reaction solution and into an ammoniacal cadmium solution.

S(VI) (as $BaSO_4$)	HI (7 F)	Observations
2 mg	1 ml**	<0.5 mg S as CdS.
0.5*	1	CdS corresponded to 0.5 mg S.
2*	1	CdS corresponded to 2 mg S.
10*	1.5	CdS corresponded to 5 mg S.
20*	2	CdS corresponded to 8 - 10 mg S.

* A bath consisting of CaCl in water was used for heating the reaction mixture to 130° C. About 2 minutes were required to get the first CdS. The remainder precipitated in 5 - 10 minutes.

** 1 ml of 15 F H_3PO_4 added in this experinent.

This procedure was found to be satisfactory only for small quantities of sulfur, and even for such quantities the procedure required an excessive amount of time.

TABULAR OUTLINES

The following section shows in tabular form an outline of the procedures for detection and estimation of the elements included in the system of analysis. These Tabular Outlines are taken from "Systematic Elemental Analysis" and are designed to indicate as concisely as possible the steps involved in the making of analyses and the chemistry involved in each procedure. The designations P. 1, P. 2 etc. refer to the detailed procedures in the text, while the underlined portions indicate the treatment of the sample. (3)

Tabular Outline I

Behavior of the Elements of this System

upon

Fusion with NaOH, $NaNO_3$, and Na_2CO_3

Basic Elements	Amphoteric Elements	Acidic Elements
Fe_2O_3, Na_2TiO_3,	$Na_2Pb(OH)_4$, $NaCu(OH)_3$,[2]	NaI, NaBr, NaCl
MnO_2, Na_2MnO_4	Na_3AsO_4,[3] $Na_2Sn(OH)_6$	Na_3PO_4, Na_3AsO_4,[3]
$BaCO_3$, $CaCO_3$, $Mg(OH)_2$	$NaAl(OH)_4$, $Na_2Zn(OH)_4$	Na_2SO_4, NaF
Ag_2O, Ag, CuO, NiO	Na_2CrO_4, $NaVO_3$	
——		——
		$NaNO_3$,[4]
NaOH, Na_2CO_3,[1]		Na_4SiO_4, Na_2CO_3
KOH, K_2CO_3		

[1] Separate samples are analyzed for Na and K.

[2] A small quantity of copper will be found with the Amphoteric Elements.

[3] Arsenic will appear in the analysis of both the Amphoteric and Acidic Element Groups.

[4] Separate samples are analyzed for N and C.

Tabular Outline II

Behavior of the Elements after Treatment of the Fusion Product with Water.

Separation of the Basic Elements

P. 2 Fuse the sample with NaOH, $NaNO_3$, and Na_2CO_3

P. 3 Treat the melt with hot water.

Residue	Solution	
Basic Elements	Amphoteric Elements	Acidic Elements
Fe_2O_3, MnO_2, TiO_2	$Pb(OH)_4^{=}$, $Cu(OH)_3^{-}$,[3]	I^{-}, Br^{-}, Cl^{-}
$BaCO_3$, $CaCO_3$, $Mg(OH)_2$	$AsO_4^{\equiv}$,[4] $Sn(OH)_6^{=}$	$PO_4^{\equiv}$, $AsO_4^{\equiv}$, $SO_4^{=}$, F^{-}
Ag_2O, Ag, CuO, NiO	$Al(OH)_4^{-}$, $Zn(OH)_3^{-}$	———
[PbO_2, SnO_2][1]	$CrO_4^{=}$, VO_3^{-}	NO_3^{-}, $CO_3^{=}$,[5]
———	One half of the solution is used for the analysis of the amphoteric elements and the other half for the acidic elements.	
Separate Sample		
Alkali Metals[2]		
Na^{+}, K^{+}		

[1] Elements in brackets appear where indicated only when present in large quantities or as the result of imperfect separations.

[2] A separate sample is analyzed for sodium and potassium because their hydroxides and carbonates are soluble, and because sodium salts are used in the fusion.

[3] Only a small amount of copper is dissolved.

[4] Arsenic will appear with both the Amphoteric and Acidic Elements and may be detected in either group.

[5] Separate samples are analyzed for these elements.

Tabular Outline IIa

Treatment of Alloys

P. 4 Treat sample with HNO_3.

Solution: Mn^{++}, TiO^{++}, Fe^{+++}, Mg^{++}, Ag^{+}, Cu^{++}, Ni^{++}

Pb^{++}, Al^{+++}, Zn^{++}, Cr^{+++}, VO_2^{+}

Precipitate: $SnO_2 \cdot xH_2O$

(If necessary add HCl, then more HNO_3. Evaporate.

Add $NaClO_3$. Evaporate to 2 - 3 ml.

Solution: TiO^{++}, Fe^{+++}, Mg^{++}, Ag^{+}, Cu^{++}, Ni^{++}

Pb^{++}, Al^{+++}, $Cr_2O_7^{=}$, VO_2^{+}

Precipitate: MnO_2, $SnO_2 \cdot xH_2O$

Separation of the Basic Element Group

Neutralize with 6 N NaOH; add excess. Add 30% H_2O_2.

Add water. Heat (Treat by last part of P. 3)

Residue	Solution	
Basic Elements	Amphoteric Elements	Acidic Elements
MnO_2, TiO_2, Fe_2O_3	$Pb(OH)_4^{=}$, $Cu(OH)_3^{-}$	$SiO_3^{=}$, $AsO_4^{\equiv}$
$Mg(OH)_2$	$Sn(OH)_6^{=}$	$PO_4^{\equiv}$, $SO_4^{=}$
Ag_2O, $Ag_{(s)}$, CuO, $Ni(OH)_2$	$Al(OH)_4^{-}$, $Zn(OH)_3^{-}$	Usually present in small quantities and not included in this system of analysis for alloys.
To P. 11	$CrO_4^{=}$, VO_3^{-}	
	To P. 51	

Tabular Outline III

Separation of the Basic Element Group into Subgroups

Fusion Residue: Fe_2O_3, MnO_2, TiO_2. The Titanium Group.
$BaCO_3$, $CaCO_3$, $Mg(OH)_2$. The Alkaline Earth Group.
Ag_2O, Ag, CuO, NiO. The Metal Ammine Group. [PbO_2; SnO_2]

P. 11. Treat with HNO_3 and $KClO_3$.

Precipitate: MnO_2, PbO_2, SnO_2 . Gas: Cl_2, ClO_2.

Solution: TiO^{++}, Fe^{+++}, Ba^{++}, Ca^{++}, Mg^{++}, Ag^{+}, Cu^{++}, Ni^{++}, H^{+}.

Dilute, partly neutralize. Add $NH_4C_2H_3O_2$.

<table>
<tr><td rowspan="3">Precipitate:
Fe_2O_3, $FeOC_2H_3O_2$,
MnO_2, TiO_2.
PbO_2, SnO_2
The Titanium Group</td><td colspan="2">Solution: Ba^{++}, Ca^{++}, Mg^{++}, Ag^{+}, Cu^{++}, Ni^{++}; NH_4^{+}, $HC_2H_3O_2$, $C_2H_3O_2^{-}$.
P. 21 Add NH_4OH, NaOH and Na_2CO_3.</td></tr>
<tr><td rowspan="2">Precipitate:
$BaCO_3$,
$CaCO_3$,
$Mg(OH)_2$
The Alkaline Earth Group</td><td colspan="2">Solution: $Ag(NH_3)_2^{+}$, $Cu(NH_3)_4^{++}$; $Ni(NH_3)_4^{++}$;
$C_2H_3O_2^{-}$, OH^{-}, NH_4OH, $CO_3^{=}$.
P. 31 Add NaOH. Boil out NH_3.</td></tr>
<tr><td>Precipitate: Ag_2O, CuO, $Ni(OH)_2$
The Metal Ammine Group</td><td>Solution:
Discard.</td></tr>
</table>

Tabular Outline IV

Analysis of the Titanium Group

(See Tabular Outline III for the separation of the Titanium Group)

Precipitate: $Fe_2O_3 \cdot FeOC_2H_3O_2$, TiO_2, MnO_2.

P. 12 Treat with H_2SO_4, Na_2SO_4, and KNO_2. Boil out NO and NO_2.

($TiSO_4^{++}$, $FeSO_4^{+}$, Mn^{++})

Dilute to 10 ml. and analyze separate portions.

1 ml portion	1 ml portion	5 ml portion
Dilute. Add KSCN ($FeSCN^{++}$, red color) Match color with known ferric iron solution. P. 13	Dilute. Add $NaBiO_3$ (MnO_4^{-}, purple color) Match color with known permanganate solution. P. 14	Add H_3PO_4 and H_2O_2. (H_2TiO_4; orange color) Match color with known titanium solution. P. 15

Tabular Outline V

Analysis of the Alkaline Earth Group

Group Precipitate: $BaCO_3$, $CaCO_3$, $Mg(OH)_2$. (See Tabular Outline III)

P. 22 Dissolve with HNO_3. Add K_2CrO_4.

Neutralize with KOH.

Add HNO_3 and excess K_2CrO_4.

<table>
<tr>
<td rowspan="3">Precipitate:
$BaCrO_4$
P. 23 Dissolve in hot 12 N HCl.
(Ba^{++}, $CrCl^{++}$, Cl_2)
Dilute, add Na_2SO_4.
Ppt.: $BaSO_4$</td>
<td colspan="3">Solution: Ca^{++}, Mg^{++}, $Cr_2O_7^{=}$.
P. 24. Add $K_2C_2O_4$, then add excess NH_4OH.</td>
</tr>
<tr>
<td rowspan="2">Ppt: CaC_2O_4
P. 25. Add H_2SO_4.
(Ca^{++}, $H_2C_2O_4$)
Add $KMnO_4$
(Ca^{++}, Mn^{++}, CO_2)
Add C_2H_5OH.
Ppt. $CaSO_4$</td>
<td colspan="2">Solution:
$Mg(C_2O_4)_2^{=}$, $C_2O_4^{=}$, $CrO_4^{=}$
NH_4OH.
P. 26. Add KH_2PO_4.</td>
</tr>
<tr>
<td>Ppt. $MgNH_4PO_4$
P. 27 Dissolve in HCl.
Add NaOH and $C_{12}H_9N_3O_4$
$Mg(OH)_2$ - $C_{12}H_9N_3O_4$ lake (blue)</td>
<td>Solution:
Discard</td>
</tr>
</table>

Tabular Outline VI

Analysis of the Metal Ammine Group

Group Precipitate: Ag_2O, CuO, $Ni(OH)_2$ (See Tabular Outline III)

P. 32 Dissolve in HNO_3

(Ag^+, Cu^{++}, Ni^{++}, H^+, NO_3^-).

Add NH_4Cl.

<table>
<tr>
<td rowspan="2">Precipitate:
AgCl
P. 33 Dissolve in NH_4OH.
($Ag(NH_3)_2^+$, Cl^-)
Add KI
Precipitate: AgI
(yellow)</td>
<td colspan="2">Solution: Cu^{++}, Ni^{++}, NH_4^+, Cl^-, H^+.
P. 34 Neutralize with NH_4OH; add H_2SO_4.
Add KI
(CuI, I_2 and I_3^-)
Add Na_2SO_3.</td>
</tr>
<tr>
<td>Precipitate: CuI
P. 35 Add NH_4OH
($Cu(NH_3)_2^+$, I^-)
Add H_2O_2
$Cu(NH_3)_4^{++}$
(Blue)
Add $K_4Fe(CN)_6$
and $HC_2H_3O_2$
Precipitate:
$K_2CuFe(CN)_6$
(red-brown)</td>
<td>Solution: Ni^{++}, I^-, HSO_4^-, H_2SO_3
P. 36 Add excess NH_4OH
($Ni(NH_3)_4^{++}$, I^-, $SO_4^=$, $SO_3^=$)
Add $(CH_3)_2C_2(NOH)_2$
Precipitate:
$Ni[(CH_3)_2C_2NOH \cdot NO]_2$
(red)</td>
</tr>
</table>

Tabular Outline VII

Analysis for Sodium and Potassium

Preliminary Flame Tests

P. 41 Treat separate sample with 12 N HCl.

Moisten platinum wire. Heat wire in flame.

Yellow flame: presence of Na

Violet flame: presence of K

Detection and Estimation of Sodium and Potassium

P. 42 Treat separate sample with CaO and $(NH_4)_2CO_3$.

Boil until NH_3 expelled.

Solution: Na^+, K^+; I^-, Br^-, Cl^-, NO_3^-

Dilute to 5 ml. Take portions.

P. 43 Take 1 ml portion

Add $HC_2H_3O_2$ and $Na_3Co(NO_2)_6$.

Precipitate: $K_2NaCo(NO_2)_6$.

(yellow)

P. 44 Take 2 ml portion.

Add $HC_2H_3O_2$ and $Mg(ClO_4)_2$.

Precipitate: $KClO_4$

Discard

Solution: Add $Mg(C_2H_3O_2)_2$----$UO_2(C_2H_3O_2)_2$ reagent

Precipitate: $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$

(pale yellow crystals).

Residue: Mn_2O_3, TiO_2, FeO, Fe_2O_3, $BaCO_3$, $CaCO_3$, $MgCO_3$, Ag_2O, CuO, NiO, $PbCO_3$, $Ca(AsO_4)_2$, $Sn(OH)_4$, Al_2O_3, $ZnO \cdot ZnO_3$, $Cr(OH)_3$, $Ca(VO_3)_2$, $Ca_3(PO_4)_2$, CaF_2, $CaSiO_3$, $CaSO_4$

$CaCO_3$ and excess $Ca(OH)_2$

Discard

Tabular Outline VIII

Analysis of the Amphoteric Element Group

Separation of the Sulfide Group from the Alumium-Chromium Group.

Fusion Solution: Amphoteric Elements

$Pb(OH)_4^{=}$, $Cu(OH)_3^{-}$, $AsO_4^{\equiv}$, $Sn(OH)_6^{=}$, $Al(OH)_4^{-}$, $Zn(OH)_3^{-}$, $CrO_4^{=}$, VO_3^{-}

(also Na^{+}, K^{+}, and Acidic Elements; OH^{-}, NO_3^{-}, NO_2^{-}, $CO_3^{=}$)

P. 51 Partly neutralize portion with HCl; make 0.2 N in HNO_3. Heat (NO and NO_2).

Pb^{++}, Cu^{++}, H_3AsO_4, H_2SnCl_6

Al^{+++}, Zn^{++}, Cr^{+++}, $V(OH)_2^{++}$

Add CH_3CSNH_2. Heat. Add $(NH_4)_2SO_4$. Again heat.

Precipitate	Solution
PbS, CuS, As_2S_5, As_2S_3, SnS_2	Al^{+++}, Zn^{++}, Cr^{+++}, $V(OH)_2^{++}$
(S, H_2SiO_3)	(CH_3CSNH_2, CH_3CONH_2, H^{+}, Cl^{-} and Acidic Elements)
The Sulfide Group	The Alumimum-Chromium Group

Tabular Outline IX

Analysis of the Sulfide Group

Separation of the Lead Group from the Arsenic Group

Precipitate: PbS, CuS, As_2S_3, As_2S_5, SnS_2 (S, H_2SiO_3)

P. 52 Treat with $NaHS$ and $NaOH$.

Residue	Solution
Residue: CuS, PbS (H_2SiO_3) The Lead Group	Solution: $AsS_4^{\equiv}$, $SnS_3^{=}$, $S_2^{=}$ P. 61 Acidify with HCl. (As_2S_5, SnS_2, H_2S, S) The Arsenic Group

Tabular Outline X

Analysis of the Lead Group

Lead Group Precipitate: PbS, CuS.

P. 53 Treat with HNO_3

Residue	Solution
Residue: (S, H_2SiO_3)	Solution: Cu^{++}, Pb^{++} P. 54 Add $(NH_4)_2SO_4$

Precipitate	Solution
Precipitate: $PbSO_4$ P. 55 Add $NH_4C_2H_3O_2$. ($PbC_2H_3O_2^{+}$) Add K_2CrO_4. ($PbCrO_4$ - yellow)	Solution: Cu^{++}, HSO_4^{-}, $SO_4^{=}$ P. 56 Add $NH_4C_2H_3O_2$ and $K_4Fe(CN)_6$. ($Cu_2Fe(CN)_6$ - brown)

Tabular Outline XI

Analysis of the Arsenic Group

Sulfide Solution of the Arsenic Group from P. 52:

$AsS_4^{\equiv}$, $SnS_3^{=}$, $S_2^{=}$, $S^{=}$, OH^{-}

P. 61 Acidify with HCl.

Precipitate: As_2S_5, SnS_2, S

P. 62 Make solution 6 N in HCl. Heat. (H_2S)

Residue: As_2S_5, S.

P. 63 Treat with NaOH and H_2O_2. Heat.

($AsO_4^{\equiv}$, $SO_4^{=}$)

Neutralize with HNO_3. Add NH_4OH, NH_4NO_3, and $Mg(NO_3)_2$.

Precipitate: $MgNH_4AsO_4$

Treat with $AgNO_3$ and $HC_2H_3O_2$.

(Ag_3AsO_4 - red)

Solution: $SnCl_6^{=}$, Cl^{-}, H^{+}

P. 64 Neutralize with NH_4OH; heat

Precipitate: $SnO_2 \cdot H_2O_x$

P. 65 Dissolve in HCl

($SnCl_6^{=}$)

Add Pb metal; heat.

($SnCl_4^{=}$, $PbCl_3^{-}$)

Add $HgCl_2$

Precipitate: Hg_2Cl_2, Hg.

($SnCl_6^{=}$, $PbCl_3^{-}$)

Tabular Outline XII

Precipitation of the Aluminum-Chromium Group

Separation of the Aluminum Group from the Chromium Group

Solution (from P. 51): Al^{+++}, Zn^{++}, Cr^{+++}, $V(OH)_2^{++}$, CH_3CSNH_2, CH_3CONH_2, H^+, Cl^-

---

P. 71. Heat. Add $NH_4C_7H_5O_2$ (ammonium benzoate).

Precipitate: $Al(OH)_3$, $Al(OH)_2C_7H_5O_2$; $Cr(OH)_3$, $Cr(OH)_2C_7H_5C_2$; $VO(C_7H_5O_2)_2$

Add NaHS. Precipitate: ZnS

Precipitate: Aluminum-Chromium Group. (As above)

P. 72. Dissolve in HCl. Add HNO_3. Evaporate.

Solution: Al^{+++}, Cr^{+++}, $V(OH)_4^+$, Zn^{++}, $HC_7H_5O_2$, H^+.

Dilute. Add 30% H_2O_2. Add excess NaOH. Heat.

Solution: $Al(OH)_4^-$, $Zn(OH)_4^=$, $CrO_4^=$, VO_3^-, OH^-.

P. 73. Saturate with CO_2.

Solution: CH_3CSNH_2, CH_3CONH_2, $NH_4C_7H_5O_2$, $HC_7H_5O_2$, H_2S, Cl^-.

Discard.

Precipitate	Solution
$Al(OH)_3$, $ZnCO_3$	$CrO_4^=$, VO_3^-, HCO_3^-, H_2CO_3.
The Aluminum Group	The Chromium Group

Tabular Outline XIII

Analysis of the Aluminum Group

Precipitate from the CO_2 Treatment (P. 73): $Al(OH)_3$, $ZnCO_3$

P. 74. Dissolve in HCl. Add solid NH_4Cl, then NH_4OH.

<table>
<tr>
<td rowspan="2">Precipitate:
$Al(OH)_3$
P. 75. Dissolve in HCl.
Neutralize with NaOH and HCl.
Add $HC_2H_3O_2$, $NH_4C_2H_3O_2$, and "aluminon."
Add $(NH_4)_2CO_3$
($Al(OH)_3$. Red Lake)</td>
<td colspan="2">Solution: $Zn(NH_3)_4^{++}$
NH_4OH, NH_4^+, Cl^-.
P. 76. Add NaHS.</td>
</tr>
<tr>
<td>Ppt. ZnS.
P. 77. Dissolve in HCl. (Zn^{++}, H_2S)
Add $K_4Fe(CN)_6$.
($K_2Zn_3(Fe(CN)_6)_2$)
White Precipitate.</td>
<td>Solution: NH_4OH, NH_4^+
Cl^-, HS^-
Discard</td>
</tr>
</table>

Tabular Outline XIV

Analysis of the Chromium Group

Solution from the CO_2 treatment (P. 73): $CrO_4^{=}$, VO_3^{-}, HCO_3^{-}, H_2O_2.

P. 81. Add $KMnO_4$. Boil (O_2).

Solution: $CrO_4^{=}$, VO_3^{-}, $CO_3^{=}$. Add HNO_3	Precipitate: MnO_2 Discard.

($Cr_2O_7^{=}$, orange color; $V(OH)_4^{+}$, greenish-yellow color)

Add $Pb(NO_3)_2$.

Precipitate: $PbCrO_4$ P. 82. Add H_2SO_4	Solution: $V(OH)_4^{+}$, Pb^{++}, H^{+}, NO_3^{-}. P. 83. Add $NH_4C_2H_2O_2$ and $Pb(C_2H_3O_2)_2$.

Solution: $Cr_2O_7^{=}$, orange Add NaOH $CrO_4^{=}$, yellow.	Precipitate: $PbSO_4$ Discard

Ppt. $Pb(VO_3)_2$ P. 84. Add H_2SO_4 and Na_2SO_3	Solution: Discard.

Precipitate: $PbSO_4$	Solution: $V(OH)_2^{++}$ Boil out SO_2. Add H_2O_2. (HVO - orange).

Tabular Outline XV

Separation of the Acidic Elements into Groups

Fusion Solution: $SiO_3^=$; I^-, Br^-, Cl^-; $PO_4^{\equiv}$, $AsO_4^{\equiv}$, ($CrO_4^=$, VO_3^-); $SO_4^=$, F^-; NO_3^-, NO_2^-, $CO_3^=$.

(N and C detected in separate sample); also Alkali and Amphoteric elements, OH^-.

P. 101. Saturate with CO_2.

<table>
<tr>
<td rowspan="3">Precipitate:
H_2SiO_3
(also $SnO_2 \cdot H_2O_x$, $PbCO_3$, $CuCO_3$, $Al(OH)_3$, $ZnCO_3$)
P. 102. Heat with H_2SO_4
Add NaCl and H_2O.
Precipitate: $SiO_2 \cdot H_2O$
(Presence of Silicon)
Solution: $SnCl_6^=$, $PbCl_4^=$, $CuCl^+$, Al^{+++}
$ZnCl_4^=$. Discard.</td>
<td colspan="3">Solution: I^-, Br^-, Cl^-; $HPO_4^=$, $HAsO_4^=$ ($CrO_4^=$, VO_3^-); $SO_4^=$, F^-; NO_3^-, NO_2^-;
HCO_3^-, Alkali elements.
P. 103. Add HNO_3 and $AgNO_3$</td>
</tr>
<tr>
<td rowspan="2">Precipitate:
AgI
AgBr
AgCl
The Halogen Group</td>
<td colspan="2">Solution: H_3PO_4, H_3AsO_4, $Cr_2O_7^=$, $V(OH)_4^+$; HSO_4^-, HF_2^-; NO_3^-
H^+, Ag^+, and alkali elements.
P. 111. Neutralize with Na_2CO_3.
Add $HC_2H_3O_2$ and $NH_4C_2H_3O_2$. Add more $AgNO_3$.</td>
</tr>
<tr>
<td>Precipitate:
Ag_3PO_4, Ag_3AsO_4
(Ag_2CrO_4, $AgVO_3$)
The Phosphorus Group</td>
<td>Solution: HSO_4^+, HF_2^-, NO_3^-
H^+, Ag^+, and alkali elements
Analyze for Sulfur and Fluorine (see T.O. XVI)</td>
</tr>
</table>

Analyze separate samples for nitrogen and carbon.

Tabular Outline XVI

Analysis of the Halogen Group

Precipitate from P. 103. AgI, AgBr, AgCl.

P. 104. Add NH_4OH ($Ag(NH_3)_2^+$, Cl^-, Br^-). Add Zn.

Residue: Ag, excess Zn Discard	Solution: I^-, Br^-, Cl^-, $Zn(NH_3)_4^{++}$, NH_4OH P. 105. Add excess HNO_3. (Zn^{++}, NH_4^+, H^+, NO_3^-).

Add KNO_2. Shake with CCl_4. Separate Phases.

CCl_4 Phase: I_2 P. 106. Add H_2O and $AgNO_3$ ($AgI_{(s)}$, $AgIO_{3(s)}$)	Water Phase: Br^-, Cl^-, Zn^{++}, NO, NO_3^-, NH_4^+, H^+. P. 107. Boil out NO. Cool.

Add $KMnO_4$. Shake with CCl_4. Separate Phases.

CCl_4 Phase: Br_2 P. 108. Add H_2O, HNO_3 and KNO_2. Separate water phase. (Br^-, NO_3^-) Add $AgNO_3$. ($AgBr_{(s)}$)	Water Phase: Cl^-, Zn^{++}, NO_3^-, MnO_4^-, Mn^{++}, NH_4^+, H^+. P. 109. Add KNO_2 (Cl^-, Zn^{++}, NO_3^-, Mn^{++}, NH_4^+, H^+) Heat. Add $AgNO_3$. (Precipitate: AgCl)

Tabular Outline XVII

Analysis of the Phosphorus Group

Precipitate from P. 111: Ag_3PO_4, Ag_3AsO_4, (Ag_2CrO_4, $AgVO_3$).

P. 112. *Treat with HNO_3 and NH_4Cl.*

Precipitate: AgCl	Solution: H_3PO_4, H_3AsO_4, $Cr_2O_7^{=}$, $V(OH)_4^{+}$ *Add NH_4OH.* ($HPO_4^{=}$, $HAsO_4^{=}$, $CrO_4^{=}$, VO_3^{-}) P. 113. *Add $Mg(NO_3)_2$ and NH_4NO_3.*

Precipitate: $MgNH_4PO_4 \cdot 6H_2O$ $MgNH_4AsO_4 \cdot 6H_2O$	Solution: $CrO_4^{=}$, VO_3^{-}, Cl^{-}, NO_3^{-}, Mg^{++}, NH_4^{+}, NH_4OH *Discard or treat by P. 81.*

P. 114. *Dissolve in 9 N HCl.* (H_3PO_4, H_3AsO_4, Mg^{++}, NH_4^{+})

Heat. *Add CH_3CSNH_2*

<table>
<tr>
<td rowspan="2">Precipitate:
As_2S_5, As_2S_3, S
Discard or
treat by P. 63.</td>
<td colspan="2">Solution: H_3PO_4, Mg^{++}, NH_4^{+}, CH_3CSNH_2, H^{+}, Cl
P. 115. *Evaporate.* *Add HNO_3, Evaporate.*
Add $(NH_4)_2MoO_4$.</td>
</tr>
<tr>
<td>Precipitate: $(NH_4)_3PMo_{12}O_{40}$ (yellow).
P. 116. *Dissolve in NaOH.*
NH_4^{+}, HPO_4^{-}, $MoO_4^{=}$</td>
<td>Solution:
Discard</td>
</tr>
</table>

Tabular Outline XVIII

Analysis for Sulfur and Fluorine

Solution: $SO_4^{=}$, HF_2^{-}, Ag^{+}, NO_3^{-}, $C_2H_3O_2^{-}$, $HC_2H_3O_2$

P. 121. Add HNO_3 and $Ba(NO_3)_2$.

Precipitate: $BaSO_4$	Solution: HF_2^{-}, Ag^{+}, H^{+}, NO_3^{-}, Ba^{++}, $HC_2H_3O_2$ P. 122. Neutralize with Na_2CO_3. Add $HC_2H_3O_2$ and $Ca(NO_3)_2$.

Precipitate: CaF_2 P. 123. Dissolve in HNO_3 (Ca^{++}, HF_2^{-}) Add KSCN. Titrate with $Fe(NO_3)_3$ (FeF^{++}; with excess $Fe(NO_3)_3$ $FeSCN^{++}$, red.)	Solution: Discard

References

1. Swift, Ernest H., and Niemann, Carl, A System for the Ultimate Analysis of Chemical Warfare Agents, C.W.S. Field Lab Memo. 1-2-4 Revised, August 1944. (See reference 2).
2. Swift, Ernest H., and Niemann, Carl, Anal. Chem., 26, 538 (1954)
3. Swift, Ernest H., Systematic Elemental Analysis, Mimeographed Edition, California Institute of Technology, March 1955.

PART II. THE STANDARD POTENTIAL OF THE IODINE-IODINE MONOCYANIDE HALF CELL

Introduction

Titrations are in use which involve the oxidation of iodine to iodine monocyanide in acid cyanide solutions. (1). These titrations do not require such high acid concentrations as do the corresponding iodine monochloride titrations (2). The study of the iodine-iodine monocyanide half cell potential was made because of the use that this potential would have in the calculation of equilibria and end point conditions during iodine monocyanide titrations.

Earlier measurements have been made of the iodine-iodine monocyanide half cell potential, but the lack of consistency of the results leaves the data in question. In 1912 Kovach (3) studied the iodine-iodine monocyanide system and from her data the value -0.60 v is calculated for the reaction

$$I\ (1M) + 2HCN = 2ICN + 2H^{+} + 2e^{-} \qquad (1)$$

However, from Kovach's data the iodine-iodide half cell potential is calculated, with corrections for complex ion formation (4), to be -0.520 v; 0.016 v different from the value given by Latimer (5). More recently Gaugin (6) reported an average value of -0.640 v for reaction (1). In his study, deviations from the mean were large, becoming 0.180 v at pH 6.

In the present investigation potential measurements were made through the concentration ranges 0.2 to 4 F $HClO_4$ and 0.06 to 0.3 F total cyanide, and the value -0.625 ± 0.003 v was obtained for equation (1). In the course of the potential measurements a re-evaluation of the equilibrium constant for the expression

$$I_2 + HCN = ICN + I^{-} + H^{+} \qquad (2)$$

was made by a study of the solubility of iodine in HCN solutions, and the value 0. 870 ± 0.009 moles/liter was obtained.

EXPERIMENTAL

Reagents.

Reagent grade chemicals were used in all preparations. Volumetric apparatus was calibrated prior to its use.

A 6 VF perchloric acid solution was prepared from the 60% acid and was standardized against sodium hydroxide solution which had been standardized against potassium hydrogen phthalate.

Standard solutions of potassium iodate, approximately 0.1 and 0.002 VF, and of silver nitrate, 0.1 VF, were prepared by weight from the salts.

Sodium cyanide solutions, 0.6VF, were standardized by a modified Liebig titration just before each experiment. A 10.00 ml portion of the cyanide solution was mixed with 2 ml of 6 VF sodium hydroxide solution, 2 ml 6 VF ammonium hydroxide and 1 ml of 1.0 VF potassium iodide solution. This solution was diluted to 50 ml and titrated with silver nitrate solution to the appearance of the silver iodide precipitate.

The required quantity of resublimed iodine was ground in an agate mortar immediately before each experiment.

Commercial tank hydrogen was passed through a washing chain similar to that described by Kolthoff and Laitinen (7). In early experiments the potassium permanganate solution specified by these workers was troublesome because of the formation of large quantities of manganese dioxide, and was replaced by a solution 0.5 VF in chromic trioxide, 4 VF in phosphoric acid and 9 VF in sulfuric acid.

Apparatus.

The cell assembly, shown in Figure I, consisted of three 200 ml lip-

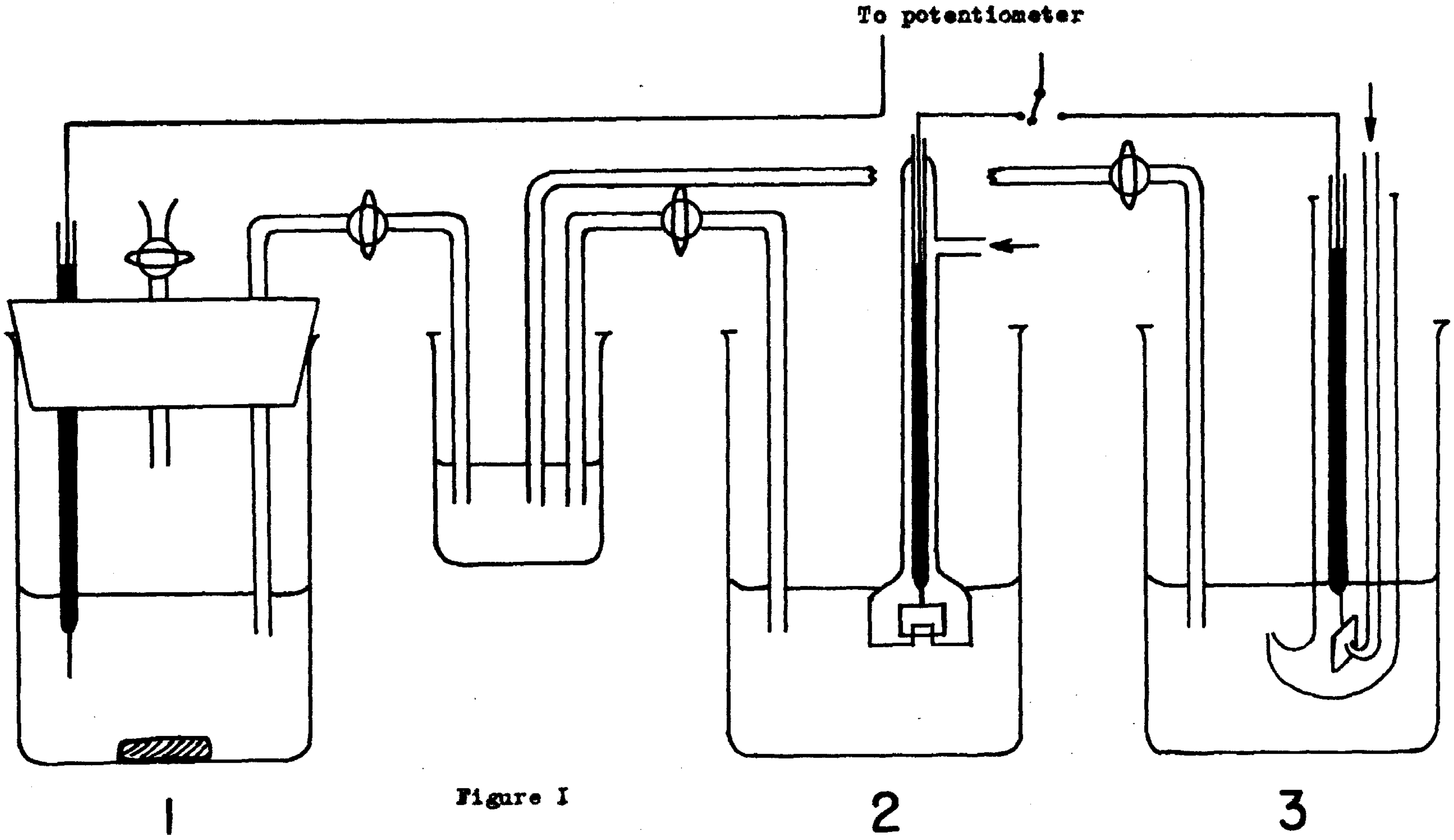

Figure I

Cell Construction

1. Iodine-iodine monocyanide half cell compartment.

2, 3. Hydrogen electrode compartments.

less beakers connected by glass tubing bridges to a single intermediate vessel. The bridges were prepared from 6 mm OD glass tubing and were fitted with ground glass stopcocks. One of the 200 ml beakers contained the iodine-iodine monocyanide half cell solution, and the other two contained hydrogen electrode assemblies. The temperature of the half cell solutions was maintained at $25.0 \pm 0.5^{\circ}$ C by means of water baths.

The beaker which contained the iodine-iodine monocyanide half cell solution had a tightly fitting stopper through which passed the bridge, a bright platinum wire electrode, mounted in 6 mm glass tubing, and an inlet tube which was flared and ground to fit the tip of the pipets used for adding the half cell solution components, thus permitting their addition without loss of hydrocyanic acid. A magnetic stirrer provided constant stirring throughout the measurements.

Two different types of hydrogen electrodes were prepared as shown in Figure I (8, 9). No significant advantage was found in one type over the other for the purposes of this study. The electrodes were platinized by the procedure of Lorch (10).

The potential measurements were made with a Gray Instrument Company Model E potentiometer with a Leeds and Northrup enclosed lamp and scale galvanometer.

Procedure.

In experiments made to determine the equilibrium constant for the disproportionation of iodine in the presence of hydrocyanic acid, two sets of solutions were prepared in glass stoppered flasks. One set was prepared by the addition of weighed portions of sodium perchlorate to standard perchloric acid; the other was prepared by mixing standard solutions of sodium cyanide and perchloric acid. The final perchloric acid concentration, sodium perchlorate concentration and ionic strength were the same in both sets of solutions. Finely ground iodine was added in excess to all solutions and the mixtures were maintained at 25 ± 0.2° C for periods of time up to seven days. Samples were transferred by a 25 ml pipet to 300 ml iodine flasks which contained 5 ml of carbon tetrachloride and sufficient hydrochloric acid to make its final concentration 4 VF. The solutions were then titrated with 0.002 VF potassium iodate by the procedure described by Swift (2). Titrations were repeated on successive days until the reproducibility of the results indicated that equilibrium had been achieved.

In the potential measurements, calculated volumes of water, potassium iodate solution, and perchloric acid were added to an excess of freshly ground iodine in the iodine-iodine monocyanide half cell beaker. The beaker was stoppered and standard sodium cyanide solution was added from a pipet through the inlet tube. The bridges, intermediate vessel and hydrogen electrode chambers were filled with perchloric acid of the same concentration as the final molal concentration of perchloric acid in the iodine-iodine monocyanide half cell. Potential measurements were made at five to ten minute intervals until the readings remained constant within 0.1 mv for at least thirty minutes. In preliminary experiments it was found that the cell potential remained constant to 0.1 mv for twenty four hours.

DISCUSSION

Disproportionation of iodine in hydrocyanic acid solutions.

The equilibrium constant for the disproportionation reaction must be known if the concentrations of the species present in the iodine monocyanide half cell are to be calculated. Earlier calculations of the equilibrium constant for equation (2) by Kovach (3) and by Lewis and Keyes (11) depended upon conductivity and vapor pressure measurements, respectively. In each case the acid concentrations at which the measurements were made were appreciably lower than those which were used in the present potential measurements. Therefore, it was concluded that a determination of the equilibrium constant should be made by an independent method with conditions comparable to those used in the potential measurements.

The solubility of iodine at 25° C in solutions 1.00 VF in perchloric acid and 0.089 VF in sodium perchlorate was found from a series of eight experiments to be $11.95 \pm 0.12 \times 10^{-4}$ F. By the use of this value for the solubility of iodine, the dissociation constant for the tri-iodide ion, $K = 1.3 \times 10^{-3}$ at 25° C (12), and the titer of the solutions which contained hydrocyanic acid, the equilibrium constant for equation (2) can be calculated. The concentrations of iodide and tri-iodide ions are calculated directly and the iodine monocyanide concentration is equal to their sum. The hydrocyanic acid concentration is the difference between the initial formal sodium cyanide concentration and the iodine monocyanide concentration. In Table I are shown the experimental data, the calculated concentrations of the various species, and the calculated disproportionation constant; the average value of the latter is 0.870 ± 0.009.

The values obtained for the constant by other methods are near this value. Calculations from the data of Lewis and Keyes (11) give values ranging from 0.91 to 1.67, with a "weighted mean" of 1.4. Kovach's values for the constant range from 1.17 to 1.50, with 1.38 as the average. Yost and Stone (4) have applied their formation constants for the iodine dicyanide and di-iodocyanide complexes to Kovach's data and obtained a corrected average value of 1.50.

In the present calculations of the standard iodine-iodine monocyanide half cell potential the value 0.87 was used for the disproportionation

Table I

Determination of the Disproportionation Constant,

$$K = \frac{(ICN)\ (I^-)\ (H^+)}{(I_2)\ (HCN)} \text{ at } 25^\circ \text{ C.}$$

Solutions were 1.00 VF in perchloric acid, 0.089 VF in hydrocyanic acid, and 0.089 VF in sodium perchlorate.

Exp	KIO_3 required. (mmoles)	I^- (VM)	I_3^- (VM)	ICN (VM)	HCN (VM)	K
1	0.02105	0.00700	0.00643	0.0134	0.0756	0.854
2	0.02100	0.00698	0.00641	0.0134	0.0756	0.853
3	0.02136	0.00711	0.00653	0.0136	0.0754	0.884
4	0.02112	0.00703	0.00645	0.0135	0.0755	0.866
5	0.02141	0.00713	0.00654	0.0137	0.0753	0.894
			Ave.	0.870 ± 0.009		

constant. It was found that the use of 1.50 for the constant would change the calculated standard potential by only approximately 1 mv.

Complexes of iodine monocyanide.

Yost and Stone (4) obtained the values 1.17 and 2.50 for the association constants of the iodine dicyanide and di-iodocyanide complexes, $K_1 = (I(CN)_2^-)/(ICN)\ (CN^-)$ and $K_2 = (I_2CN^-)/(ICN)\ (I^-)$, respectively. Hence, since the solutions used in the present investigation were acid and the iodide concentrations were low, these complexes were present only in small concentrations. For example, in a solution approximately 0.5 VF in perchloric acid, 0.05 VF in hydrocyanic acid, 0.05 VF in iodine monocyanide, and which is saturated with iodine, the calculated molal concentrations of di-iodocyanide and iodine dicyanide are 2×10^{-4} and 1×10^{-11} respectively. Less than 0.5% of the iodine monocyanide is complexed even to di-iodocyanide.

Reference Electrodes.

Hydrogen electrodes had the major advantage over other common reference electrodes of permitting virtual elimination of liquid junctions from the cell. The electrodes were found to cause no difficulty either in their construction or operation. The special precaution was made of providing an intermediate vessel between half cells and ungreased stopcocks in the bridges. These stopcocks were opened briefly at the time of potential measurements. These steps were taken to minimize diffusion of components of the iodine-iodine monocyanide half cell into the hydrogen electrodes.

In general, about twenty potential measurements could be made with the two hydrogen electrodes before the potential readings obtained began to differ by more than 0.1 mv. When this occurred, the electrodes were replatinized.

Perchloric acid was chosen for use in this study since data for its activity are available (13) and since it evidently has only very slight tendency to form complexes with the half cell constituents.

The Iodine-Iodine Monocyanide Half Cell.

The concentrations of species in the iodine-iodine monocyanide half cell were calculated with the aid of the disproportionation constant of iodine as determined above and the assumption that the reduction of iodate by iodine was quantitative. Moreover, since over a twenty-four hour period there was no evidence of significant hydrolysis of hydrocyanic acid at 25° C at the acid concentrations used, the half cell reaction shown in equation (1) may be assumed to be the potential controlling reaction.

Calculations and Results.

In Table II are shown the cell concentrations, measured cell potentials (E_{cell}), and calculated standard half cell potentials (E^{o}) for equation (1). The calculations of the standard half cell potential were made with the assumption that the volume molal concentrations of iodine monocyanide and hydrocyanic acid are equal to their activities at the concentrations involved. The reference state for iodine is taken as 1.0 molal in the calculation of E^{o} in order to simplify calculations based on the use of the standard potential. The standard potential was calculated from the expression

$$E^{o} = E_{ref} + E_{cell} + \frac{RT}{F} \ln \frac{(H^{+})(ICN)}{(I_2)^{\frac{1}{2}}(HCN)} \qquad (3)$$

or, since $$E_{ref} = \frac{RT}{F} \ln \frac{(P_{H_2})^{\frac{1}{2}}}{(H^{+})},$$

$$E^{o} = E_{cell} + \frac{RT}{F} \ln \frac{(ICN)}{(I_2)^{\frac{1}{2}}(HCN)}$$

The addition of $\frac{RT}{F} \ln (s_{I_2})^{\frac{1}{2}}$, where s_{I_2} is the solubility of iodine, to the value of E^{o} gives the half cell potential for equation (5)

Table II

Standard Potential of the Iodine-Iodine Monocyanide Half Cell

$HClO_4$ (VF)	ICN (VM)	HCN (VM)	$-E_{cell}$ (v)	$-E^0$ (v)
4	0.050	0.150	0.6871	0.6288
			.6840	.6257
2	.053	.247	.6695	.6225
			.6707	.6237
	.0515	.148	.6838	.6223
			.6838	.6223
	.050	.050	.7114	.6249
			.7126	.6261
	.0501	.0099	.7609	.6327[1]
			.7565	.6293[1]
			.7567	.6295[1]
			.7651	.6368[1]
1	.0539	.252	.6730	.6263
			.6710	.6243
	.0540	.156	.6820	.6227
			.6842	.6249
	.0513	.0487	.7119	.6240
			.7111	.6232
	.0481	.0488	.7103	.6232
	.0494	.0126	.7411	.6196[1]
			.7502	.6287[1]

Table II (Cont.)

$HClO_4$ (VF)	ICN (VM)	HCN (VM)	$-E_{cell}$ (v)	$-E^\circ$ (v)
0.5	0.062	0.254	0.6625	0.6124[1]
	.062	.259	.6740	.6247
	.061	.239	.6769	.6255
			.6762	.6248
	.058	.152	.6895	.6278
			.6870	.6253
	.0526	.0474	.7125	.6235
			.7124	.6234
	.0506	.0094	.7475	.6178[1]
			.7556	.6259[1]
0.2	.0725	.2275	.6840	.6259
			.6833	.6262
	.065	.135	.6945	.6268
			.6925	.6248
			.6950	.6273
			.7000	.6323
	.0558	.0442	.7195	.6371
			.7167	.6243
	.0513	.0087	.7614	.6293[1]
			.7610	.6289[1]
			.7627	.6306[1]
			.7600	.6279[1]

Ave. = -0.6248 ± .0026 v

[1] Not included in calculation of the average.

$$I_2(s) + 2HCN = 2ICN + 2H^+ + 2e^- \qquad (5)$$

in which solid iodine is taken as the reference state.

The calculated values of E^0 are reproducible with a standard deviation of ± 0.0026 v through the range of concentrations studied, except at approximately 0.01 VM hydrocyanic acid, the lowest concentration of this species considered. A probable cause for the relatively large random errors at 0.01 VM hydrocyanic acid is that E^0 is dependent upon the ratio (ICN)/(HCN). The iodine monocyanide concentration is fixed by the quantity of iodate added, is approximately constant and is subject to errors of the same relative magnitude in every experiment. The concentration of hydrocyanic acid, however, depends upon the difference between the sodium cyanide added and the iodine monocyanide produced. Therefore, the absolute errors in the concentration of hydrocyanic acid remain about constant, but become much larger relatively as the concentration of hydrocyanic acid decreases. The effect of this is seen by the consideration of two cases:

(A) HCN = 0.15VM; ICN = 0.05VM

(B) HCN = 0.01VM; ICN = 0.05VM

If the concentration of hydrocyanic acid is changed by 0.003 mole/liter, the change in the calculated E^0 for case (A) is 0.0005 v while that for case (B) is 0.0068 v. Thus, the same absolute error in the concentration of hydrocyanic acid causes negligible error in the potential of case (A) and causes serious error in case (B). Because of the large random deviations of the potential values in solutions 0.01 VM in hydrocyanic acid, these potential values were not used in calculation of the average value.

A check upon the consistency of the data obtained can be made by the calculation of the iodine-iodide potential from the iodine-iodine monocyanide potential and the disproportionation constant for iodine in hydrocyanic acid. The following tabulation of equations indicates the calculation:

	ΔF
$I_2(1M) + 2HCN = 2ICN + 2H^+ + 2e^-$	28846
$2I_2(1M) + 2HCN = 2ICN + 2H^+ + 2I^-$	165
$I_2(s) = I_2(1M)$	3918
$2I^- = I_2(s) + 2e^-$	24763

or $E^0 = -0.5366$ v

This value for the iodine-iodide potential differs by just 0.0011 v from the value given by Latimer (5). Thus, the results of this study are found to be consistent with independent potential determinations of related systems.

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PART III. THE USE OF THIOACETAMIDE FOR THE HOMOGENEOUS PHASE PRECIPITATION OF INORGANIC SULFIDES

A. The Acid Catalyzed Hydrolysis of Thioacetamide.

Introduction

Thioacetamide was used as early as 1935 (1, 2) for the detection of certain elements, has found recent use in systems of qualitative analysis for the precipitation of the conventional hydrogen sulfide group elements (3, 4, 5, 6) and also has been proposed as a precipitant for the quantitative determination of certain metals (7). However, there does not appear to have been any critical investigation of the mechanism of the precipitation of sulfides by thioacetamide, of the conditions under which quantitative precipitations can be obtained, or of the relative advantages which might result from the use of thioacetamide for the homogeneous phase precipitation of sulfides.

In the course of experiments being made in this laboratory to determine the applicability of thioacetamide to a system of qualitative analysis it was noted that the precipitates so formed were better coagulated and more easily handled than were the corresponding precipitates obtained by the use of hydrogen sulfide. In certain cases the sulfide precipitate appeared to form much more rapidly with thioacetamide than with hydrogen sulfide, and in other cases the rates of precipitation of sulfides were appreciably faster than seemed compatible with the apparent rate of hydrolysis of thioacetamide. As a result of these observations an investigation was initiated of the mechanisms and rates of precipitation of sulfides by thioacetamide, and of the analytical use of the reagent as a means for the homogeneous phase precipitation of sulfides.

The results obtained from measurements of the rates of hydrolysis of thioacetamide in acid solutions are presented and discussed below.

EXPERIMENTAL

Reagents.

Thioacetamide solutions, 1.0 VF (volume formal, formula weights per liter), were prepared from Eastman White Label Reagent. The solid material was white and was found to have a melting point range of 109.5 to 110.6° C. The trace of white, insoluble matter was filtered from the solutions. The solutions were colorless and gave no indication of change over a period of two to three weeks. At no time was the odor of hydrogen sulfide detected above the solutions.

Hydrochloric acid solutions, 0.2 and 4 VF, were prepared from reagent grade concentrated acid and standardized against standard sodium hydroxide. These hydrochloric acid solutions were diluted appropriately to give the desired concentrations for specific experiments.

Collecting solutions for hydrogen sulfide were prepared by dissolving reagent grade cadmium chloride in 6 VF ammonium hydroxide to give solutions which were 0.4 VF in cadmium chloride.

Standard 0.01 VF potassium iodate and potassium dichromate solutions were prepared from analytical reagent salts.

A 0.1 VF sodium thiosulfate solution was prepared from reagent grade salt and standardized against the potassium iodate solution.

Reagent grade 90% formic acid and 6 VF sodium hydroxide solution were used for preparation of buffered solutions.

A 0.5 VF lead nitrate solution was prepared from reagent grade salt.

A 2 VF sodium hydrogen sulfide solution was prepared by saturating 4 VF sodium hydroxide with hydrogen sulfide and then diluting this with an equal volume of water.

Apparatus.

The apparatus is shown in Figure I. The reaction tube consisted of a stoppered 38 x 200 mm lipless test tube. Leading into and reaching to the bottom of the reaction tube was a sintered glass gas bubbling tube, through which nitrogen was passed. Attached vertically above the reaction tube was a 60 cm Liebig condenser. Tubing led from the condenser through a two-way stopcock to collecting tubes. The two-way stopcock permitted the changing of collecting tubes at will. The gas was led into the collecting tubes (22 x 175 mm test tubes) through drawn capillary tubing. A two-way stopcock on the nitrogen inlet tube permitted the reaction solution to be sampled by being forced back through the sintered glass bubbler.

The reaction tube was surrounded by a constant temperature bath which maintained the temperature of the reaction solution at $90 \pm 0.5^{\circ}$ C. Tests of the effluent gas showed that the collecting solutions effectively retained the hydrogen sulfide.

Procedure.

Forty milliliters of solution were prepared in the reaction tube from the standard stock solutions of hydrochloric acid and thioacetamide. The pH of the solution was determined before and after the hydrolysis with a Beckman Model G pH Meter in those cases in which the pH was 2 or greater. The reaction solution was heated to 90° C and the flow of nitrogen was started. Timed portions of the effluent gas were passed through successive collecting solutions.

Each collecting solution was added to a 200 ml flask containing a

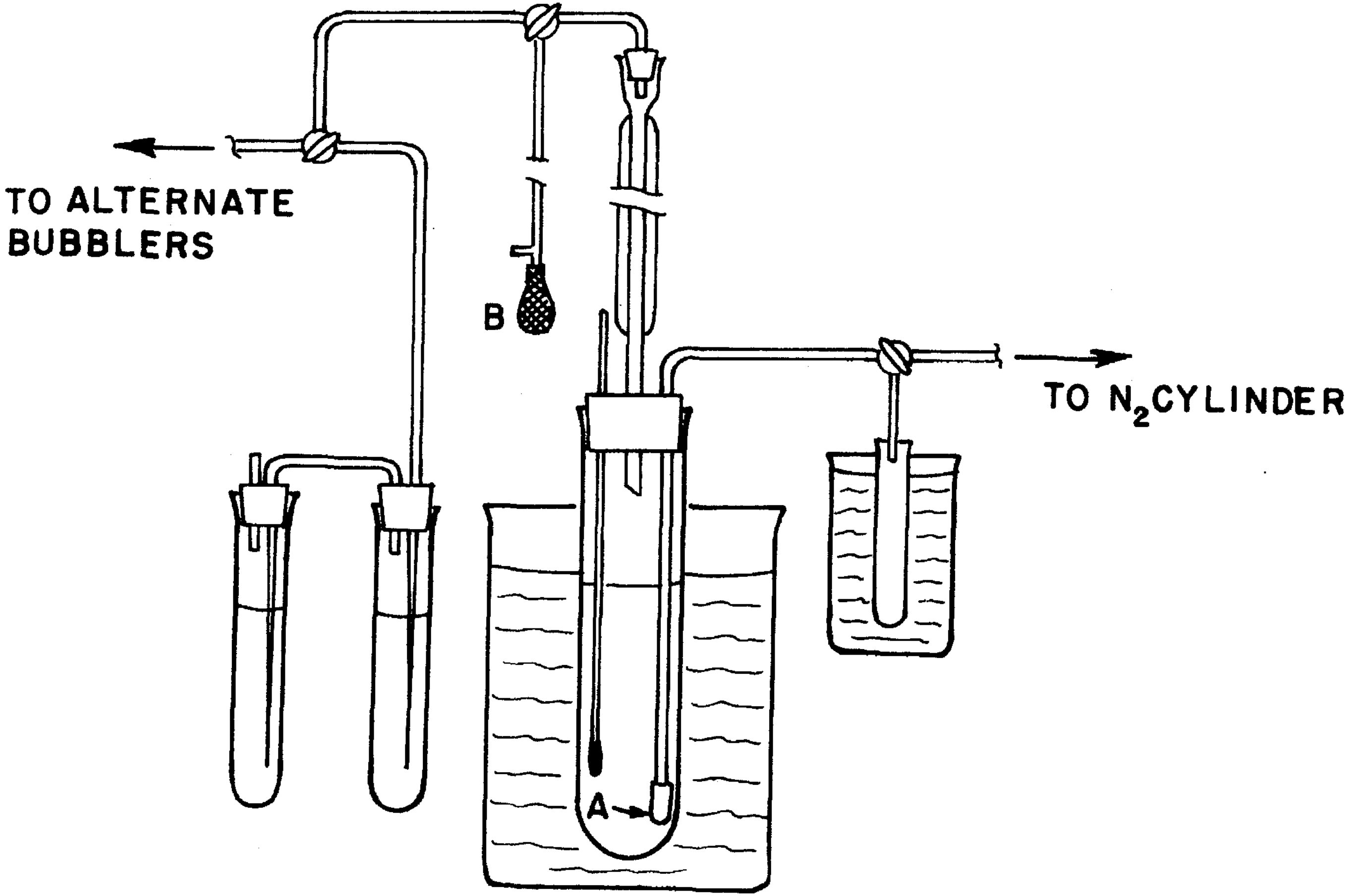

FIGURE I

A=SINTERED GLASS BUBBLER.
B=RUBBER PRESSURE BULB.

solution which consisted of approximately 0.5 g of potassium iodide dissolved in the appropriate volume of standard potassium iodate solution. An amount of 12 VF hydrochloric acid sufficient to neutralize the solution and make it 3 VF in excess hydrochloric acid was used to rinse the collecting tube and was then added to the solution in the flask. This relatively high acid concentration was used to insure the solution of all cadmium sulfide. The hydrogen sulfide is oxidized to sulfur. The excess of iodine in the resulting solution was titrated with standard sodium thiosulfate solution.

The velocity constant and order of the hydrolysis reaction of thioacetamide were calculated from data from series of such experiments.

Experiments to determine the effect of lead ion and lead sulfide upon the rate of hydrolysis of thioacetamide were conducted in the same manner as were the hydrolysis experiments with the modification that lead nitrate was added to the reaction solution. The precipitation of lead sulfide was prevented, in the cases in which the effect of lead ion was being studied, by the use of acid concentrations of 0.1 to 0.3 VF and lead nitrate concentrations of 0.001 to 0.01 VF. Higher lead nitrate concentrations or lower acid concentrations would have resulted in partial precipitation of the lead as sulfide.

When the effect of lead sulfide was under consideration the concentration of hydrogen ion was of the order of 10^{-3} VM. The thioacetamide concentration was 0.01 VF while the initial concentration of lead nitrate was only 10^{-4} VF. Thus, the concentration of thioacetamide was virtually unaffected by precipitation of all the lead as sulfide.

DISCUSSION AND RESULTS

The reactions were carried out at 90° C in order that the hydrolysis would proceed at a rate which could be followed readily. Initially, experiments were conducted in which the hydrolysis was continued until about 50% of the thioacetamide had reacted. It was found, however, that with an acid concentration of 10^{-4} to 10^{-1} VM the hydrolysis of thioacetamide required several hours and that the subsequent hydrolysis of acetamide took place to an appreciable extent in this time. Moreover, despite the use of a condenser, some loss of water by evaporation resulted. Because of these two factors there was an appreciable net change in the acid concentration. Since the rate of the thioacetamide hydrolysis is dependent upon hydrogen ion concentration, the decision was made to determine initial rates of hydrolysis from solutions of known concentration by continuing the reaction for a period of time sufficiently short that changes in concentrations of species present would be small with respect to experimental errors. In each experiment, with the exception indicated in Table II, the differences in the initial and final thioacetamide and hydrogen ion concentrations were less than five percent.

Velocity constant and order of reaction.

The data from series of experiments conducted at 90° C in 0.10 and 0.05 VF hydrochloric acid solutions with concentrations of thioacetamide ranging from 0.0063 to 0.20 VF are shown in Table I, together with the calculated first order velocity constants for the hydrolysis reaction of thioacetamide. Standard deviations are shown for the hydrogen sulfide analyses for each series and for the velocity constants.

The calculated velocity constant, k, for the first order expression

$$-\frac{d[CH_3CSNH_2]}{dt} = k[CH_3CSNH_2]$$

is seen to be constant. This is borne out by Figure II, in which

TABLE I. Rates of Evolution of Hydrogen Sulfide from Thioacetamide Solutions, and Calculated First Order Velocity Constants for the Hydrolysis of Thioacetamide at 90° C.

	0.10 VF HCl			0.05 VF HCl		
$[CH_3CSNH_2]$	Determinations made	$-\frac{d[CH_3CSNH_2]}{dt}$	k	Determinations made	$-\frac{d[CH_3CSNH_2]}{dt}$	k
VF		$\frac{\text{moles} \times 10^3}{\text{liter min}}$	min^{-1}		$\frac{\text{mole} \times 10^3}{\text{liter min}}$	min^{-1}
0.0063	4	0.12	0.019			
0.0125	4	0.24	0.019	3	0.11	0.0088
0.025	7	0.40	0.016	3	0.18	0.0072
0.050	5	0.78	0.016	4	0.40	0.0080
0.10	4	1.7	0.017	5	0.75	0.0075
0.20	2	3.2	0.016			
Average			0.017 ± 0.0015			0.0079 ± 0.0007

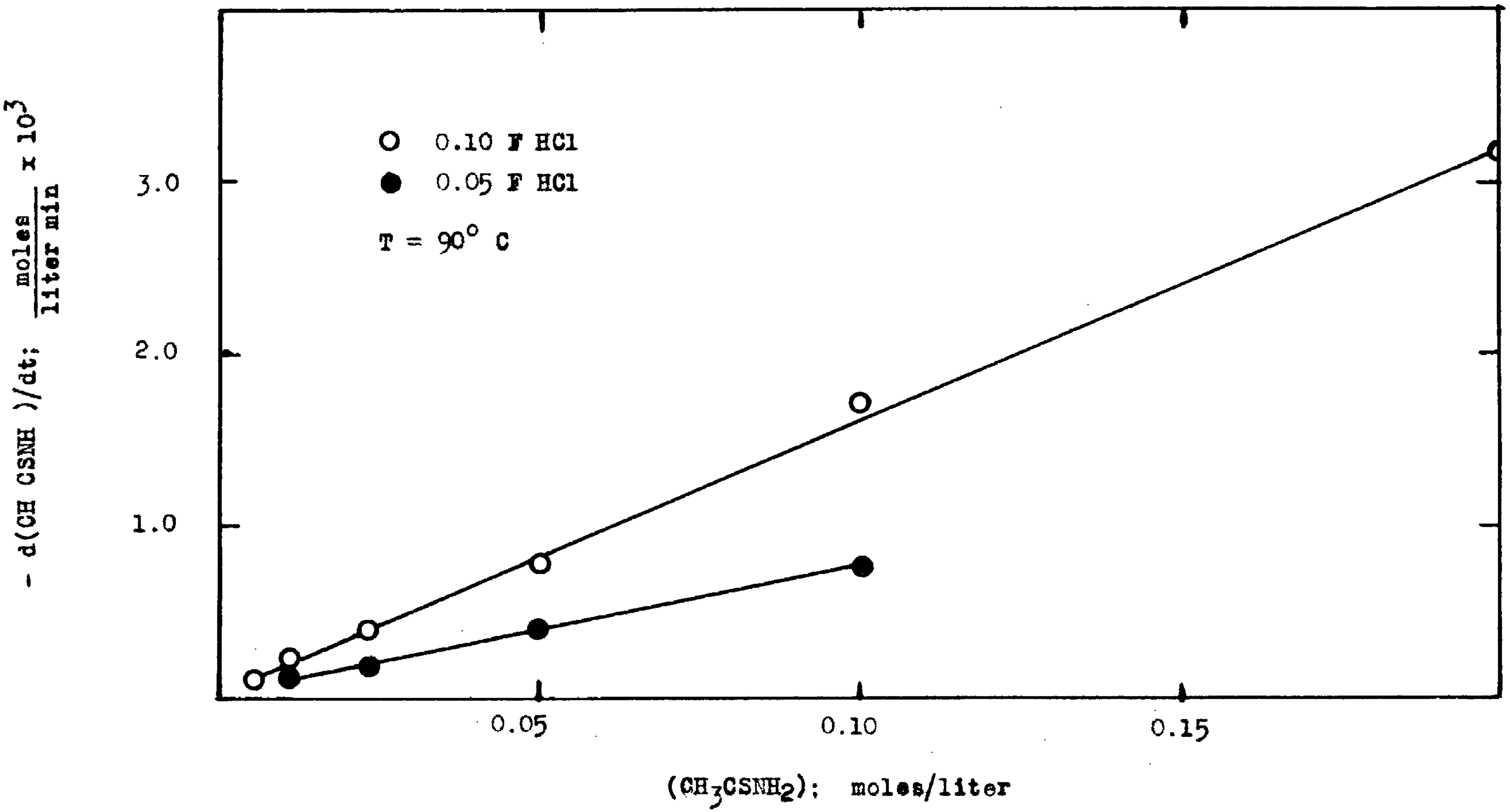

Figure II

Rate of hydrolysis of thioacetamide as a function of the thioacetamide concentration.

$-d[CH_3CSNH_2]/dt$ is plotted against the thioacetamide concentration.

From the data of Table I it can be seen that, for the two hydrochloric acid concentrations considered, the ratio $k/[H^+]$ is essentially constant, which implies that the hydrolysis is also first order with respect to hydrogen ion concentration. This effect was investigated with solutions ranging in hydrogen ion from 10^{-4} to 0.08 molal, and with the thioacetamide concentration kept constant at 0.100 VF. The data are assembled in Table II, where average values from a series of experiments are shown in each case.

As is seen in Table II the amount of hydrogen sulfide evolved in the experiments of Series 1 and 2 was small; as a result the reproducibility of the analyses is not better than 15-20%. In Series 5 and 6 the hydrogen ion activities were calculated from the formal hydrochloric acid concentrations by the use of the data of Randall and Young (8). In the other series a pH meter was used.

The ratio $k/[H^+]$ remains constant through the range of hydrogen ion activities considered, and the kinetic equation for the hydrolysis to acetamide may be expressed as

$$-\frac{d[CH_3CSNH_2]}{dt} = k'[H^+][CH_3CSNH_2]$$

where $k' = k/[H^+]$. Figure III shows the rate of hydrolysis of thioacetamide as a function of the pH.

Temperature dependence of the hydrolysis of thioacetamide.

The rates of hydrolysis of solutions 0.100 VF in thioacetamide and 0.100 VF in hydrochloric acid were determined through the temperature range from 60° C to 90° C. In Table III are values of k' for the various temperatures as calculated from the measurements. The activation energy

TABLE II. Data Showing the Effect of Hydrogen Ion upon the Hydrolysis of Thioacetamide.

Second Order Velocity Constant for the Hydrolysis.

The thioacetamide concentration was 0.10 VF in all experiments.

Series	Determinations made	a_{H^+}	$-\frac{d[CH_3CSNH_2]}{dt}$ $\frac{\text{moles} \times 10^4}{\text{liter min}}$	k^1 $\frac{\text{liter}}{\text{mole min}}$
1	2	8.0×10^{-5}*	0.018	0.23
2**	4	1.7×10^{-4}	0.041	0.24
3	5	1.1×10^{-3}	0.22	0.20
4	3	2.0×10^{-3}	0.38	0.19
5	5	4.1×10^{-2}	7.4	0.18
6	4	8.0×10^{-2}	17.	0.21
			Average	0.21 ± 0.023

* The change in hydrogen ion concentration in the experiments of this series amounted to approximately 12%.

** In experiments of series 2 a formic acid -- formate buffer was used. In other cases hydrochloric acid was used.

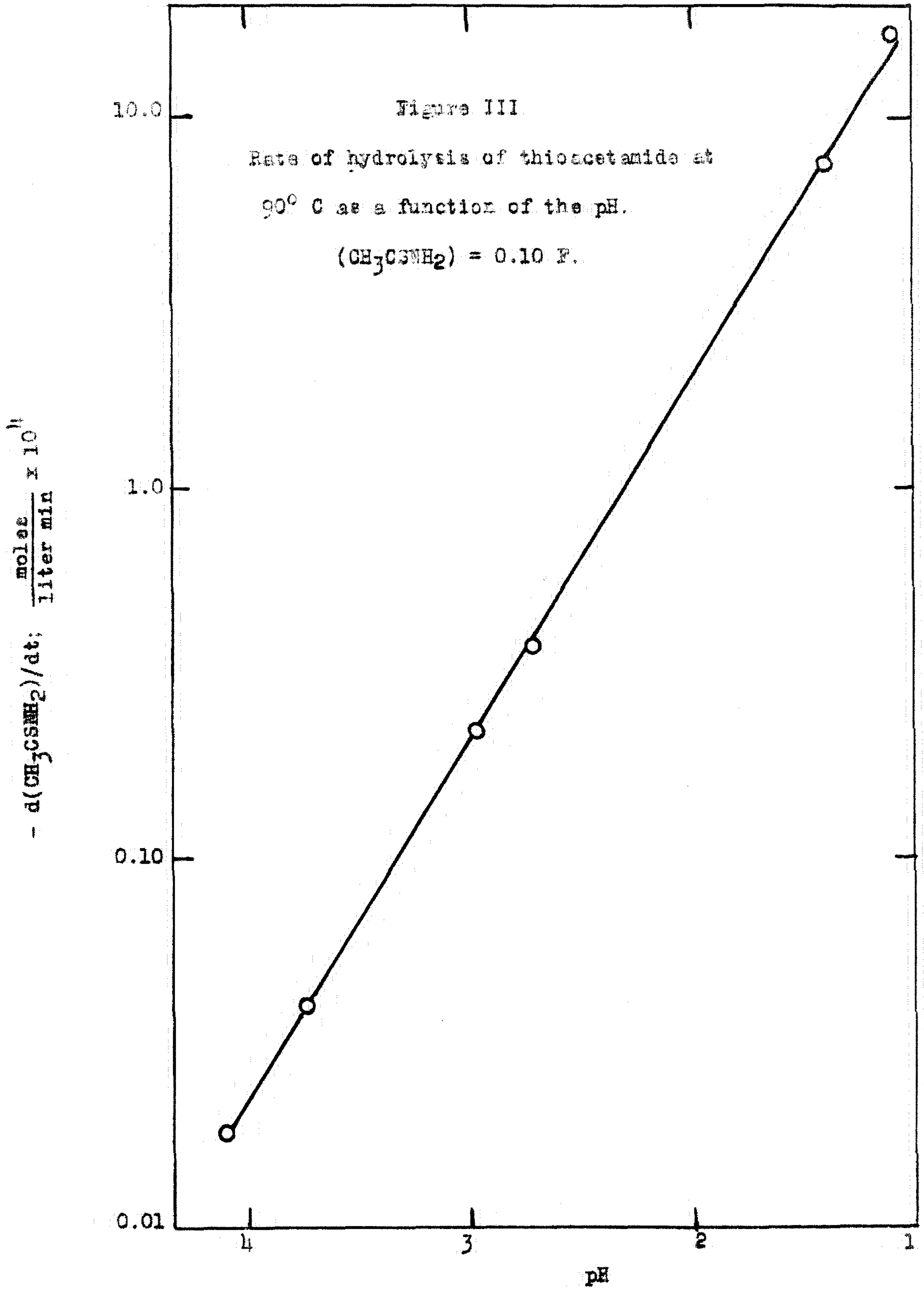

Figure III

Rate of hydrolysis of thioacetamide at

90° C as a function of the pH.

$(CH_3CSNH_2) = 0.10$ F.

is calculated from the slope of Figure IV, which is a plot of log k' against 1/T. The value obtained is 19.1 kcal/mole.

TABLE III

Variation of Second Order Hydrolysis Constant with Temperature

0.100 VF thioacetamide.

0.100 VF hydrochloric acid.

Temperature (°C)	90	80	70	60
k' (liter/mole min)	0.21	0.098	0.039	0.019

Hydrolysis of acetamide.

Analytical separations depending upon the use of thioacetamide would be considerably restricted in their application if, as has been assumed (4, 5, 6) the hydrolysis of acetamide were appreciable under the conditions and during the periods of time required for sulfide precipitations, since the ammonia produced by the acetamide hydrolysis would make uncertain the final acid concentration of the solution. Experiments were conducted in order to determine the extent of the acetamide hydrolysis.

In one such experiment, a solution 40 ml in volume and 0.10 VF in thioacetamide was maintained at 90° C for 180 minutes. The initial and final hydrogen ion activities were 2.0×10^{-3} and 1.7×10^{-3} respectively. The total hydrogen sulfide evolved was 0.24 millimole.

The change in total hydrogen ion is calculated to be 0.012 millimole. Thus, the results indicate that of the 0.24 millimole of acetamide formed only 0.012 millimole or 5% was hydrolyzed.

These results are in approximate agreement with the data given by Crocker (9). Extrapolation from Crocker's data gives a second order velocity constant of 0.2 liter/mole minute for the hydrolysis of acetamide

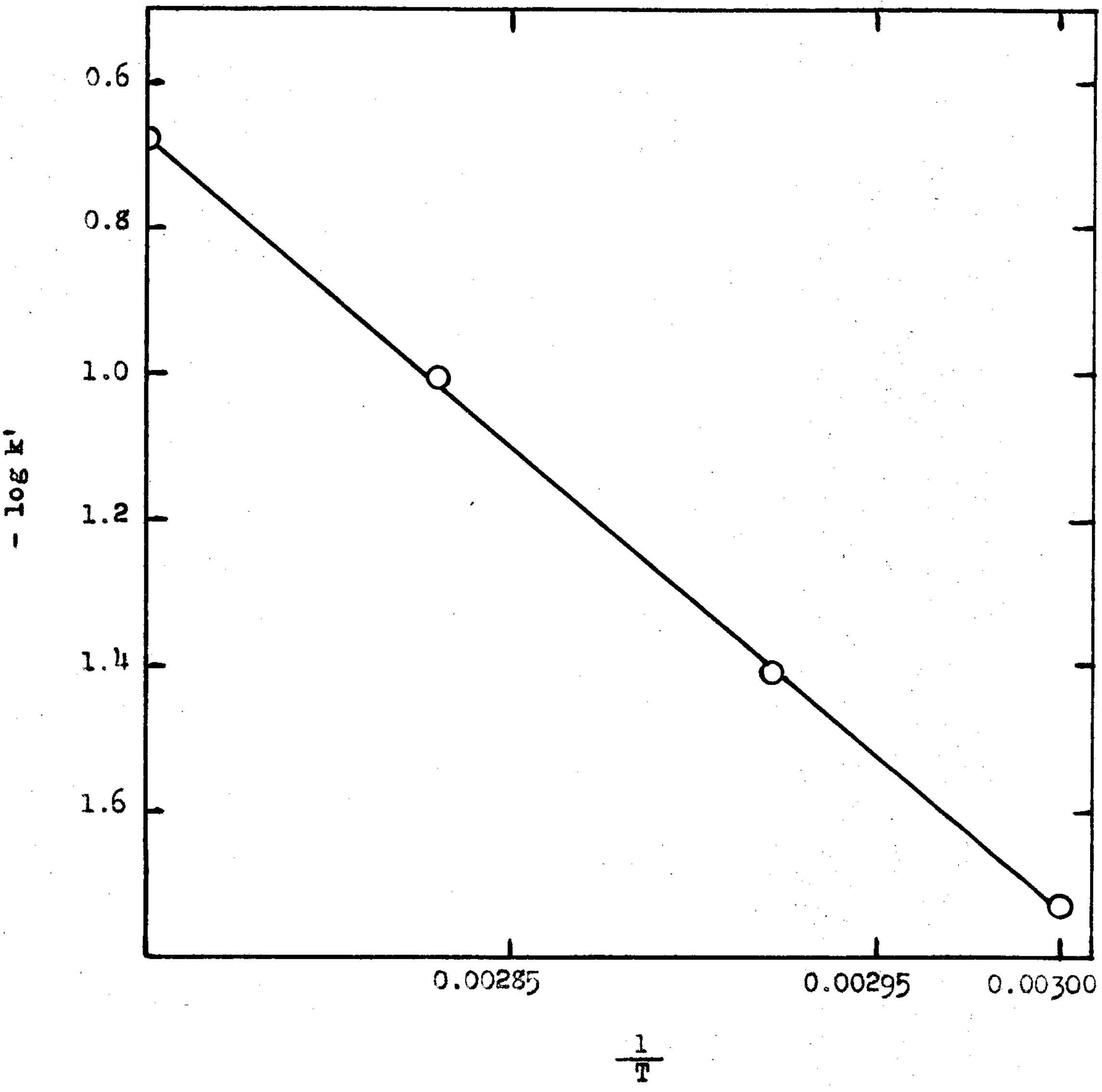

Figure IV

Rate of acid catalyzed hydrolysis of thioacetamide

as a function of the temperature.

at 90° C. If the average concentrations of acetamide and hydrogen ion in the above experiment are used, the value 0.3 liter/mole minute for the velocity constant is obtained. The difference from Crocker's value is of the magnitude to be expected from the approximations involved.

From the rate constants for the hydrolysis of thioacetamide and of acetamide it is possible to make approximate calculations of concentrations of various species after reaction for specified periods of time. If a solution 0.1 F in thioacetamide and 0.1 M in hydrogen ion is maintained at 90° for 30 minutes, the approximate concentrations of species will become 0.05 F thioacetamide, 0.04 F acetamide, 0.01 F acetic acid, 0.01 F ammonium chloride and 0.09 M hydrogen ion. With these initial concentrations and with 50% hydrolysis of the thioacetamide, the change in hydrogen ion concentration is just 10%.

If, however, a solution 0.5 F in thioacetamide and 0.1 M in hydrogen ion is maintained at 90° C for 60 minutes the approximate concentrations become 0.2 F thioacetamide, 0.2 F acetamide, 0.1 F acetic acid, 0.1 F ammonium chloride and 0.01 M hydrogen ion. In this case the hydrogen ion concentration has been reduced to one-tenth.

It is seen that the hydrolysis of acetamide does not cause serious variation of the hydrogen ion concentration if the initial concentrations of acid and thioacetamide are selected properly; however, if thioacetamide is in excess of hydrogen ion and if a large fraction of the thioacetamide is to be hydrolyzed, the reduction in the hydrogen ion concentration may become very appreciable. It should also be recognized that in work involving successive operations after the use of thioacetamide, there will be acetic acid and acetamide, as well as excess thioacetamide, in the solution.

Effect of lead sulfide on the rate of hydrolysis of thioacetamide.

Flaschka (7) has suggested that, in certain cases at least, the newly precipitated inorganic sulfide may catalyze the hydrolysis of thioacetamide. This possibility was investigated for the case of lead sulfide. In each experiment, a solution of 40 ml volume, 0.10 VF in thioacetamide, 10^{-4} VF in lead nitrate and with a hydrogen ion activity of 2×10^{-3} was maintained at 90° C and the rate of evolution of hydrogen sulfide was determined. In these experiments the lead precipitated rapidly as the sulfide as the reaction temperature was reached. The average rate of evolution of hydrogen sulfide from five experiments was 0.0015 ± 0.0002 millimole/minute. Comparison with Table II shows that the rate found here is the same as that calculated for the case in which no lead sulfide was present.

Effect of lead ion on the rate of hydrolysis of thioacetamide.

The effect of lead ion upon the hydrolysis of thioacetamide was also investigated in order to determine if it acts catalytically. Two similar experiments were made with solutions 0.05 VF in thioacetamide and 0.3 VF in hydrochloric acid. One solution was also 0.01 VF in lead nitrate. The data obtained are shown in Table IV. No lead sulfide precipitated in the solution containing lead nitrate. The close agreement of the data of the last three time periods indicates the absence of lead ion catalysis. The discrepancy in the first period is probably due to a slight difference in the rates at which the two solutions were heated.

Other experiments were made in which lead ion was in excess of the thioacetamide. Two solutions were maintained at 90° C and swept with nitrogen as in the hydrolysis experiments. Each was 40 ml in volume, 0.60 VF in hydrochloric acid and 0.05 VF in thioacetamide, and one was also 0.06 VF in lead nitrate. The rate of evolution of hydrogen sulfide

TABLE IV. Effect of Pb^{++} upon the Rate of hydrolysis of Thioacetamide.

Experiment	H_2S evolved in successive 3 min periods. $(\frac{\text{mmole}}{\text{min}})$			
	1	2	3	4
A	0.089	0.070	0.063	0.051
B	0.075	0.071	0.063	0.049

Solution A: 0.05 VF thioacetamide, 0.3 VF HCl.

Solution B: 0.05 VF thioacetamide, 0.3 VF HCl, 0.01 VF $Pb(NO_3)_2$.

as a function of the thioacetamide concentration is shown in Figure V. It is seen that there is no indication of a decrease in the rate of evolution of hydrogen sulfide from the solution which contains the lead nitrate such as would be expected if a stable complex of lead and thioacetamide were formed.

In a solution 0.05 VF in thioacetamide, 0.1 VF in hydrochloric acid and 0.001 VF in lead nitrate, the average rate of evolution of hydrogen sulfide was found to be 0.030 ± 0.002 millimole/minute from five determinations. This rate agrees within experimental error with the data shown in Table I for a similar solution with no lead ion.

It was concluded that under the conditions of these experiments neither lead sulfide nor lead ion catalyzes the hydrolysis of thioacetamide. The possibility of catalysis by other metal ions is not precluded by these experiments.

Analytical Considerations.

From the measurements which have been made it is possible to make calculations of conditions necessary for the use of thioacetamide as a source of hydrogen sulfide.

Published statements have inferred that thioacetamide can be used directly as a replacement for hydrogen sulfide. The following quotations are illustrative:

> "This compound (thioacetamide) hydrolyzes in water, particularly at higher temperatures, to give H_2S ... It therefore serves as a convenient source of H_2S. The hydrolysis is so slight at room temperature that an 8% solution of the compound ... undergoes very little deterioration. At temperatures of about 80° C the hydrolysis is sufficient so that an 8% thioacetamide solution yields a solution saturated with H_2S." (5).

> "The use of thioacetamide introduces no fundamental changes in the usual theoretical treatment of the precipitation of the sulfides because the thioacetamide is es-

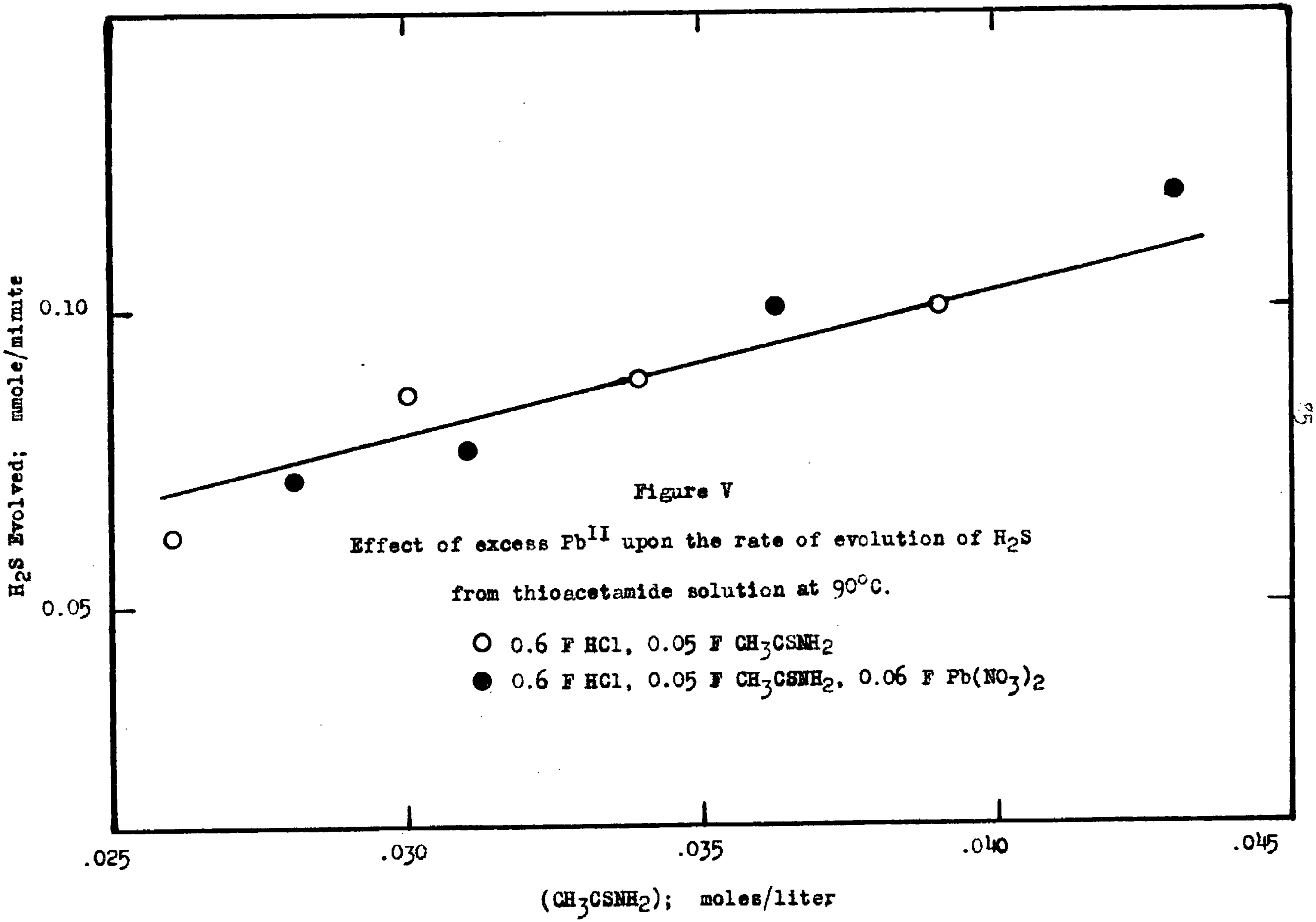

Figure V

Effect of excess Pb^{II} upon the rate of evolution of H_2S from thioacetamide solution at 90°C.

sentially a source of H_2S." (4).

> "... techniques based on the empirical use of hydrogen sulfide as a precipitant are in no way disturbed. Techniques for detection of metallic unknowns are carried out with no deviations whatever in theory .... The only point of departure is in the introduction of Sulfi-Down (thioacetamide) in place of free H_2S.... Upon heating, exactly the same result is achieved as would be achieved with hydrogen sulfide gas." (10).

> "In the use of thioacetamide as a substitute for hydrogen sulfide in precipitating Group II and Group III sulfides, no basic change in analytical procedure is required." (11).

From such statements one would suppose that a solution which is treated with thioacetamide at above 80° C would become saturated with hydrogen sulfide, that is, reach a concentration of 0.1 M, in the time of the treatment. Consideration of the second order rate constant for the hydrolysis of thioacetamide makes it evident that the concentration of thioacetamide must be appreciably greater than 0.1 F if the solution is to become saturated with H_2S in a reasonable period of time. A solution 0.1 F in hydrochloric acid and 0.2 F in thioacetamide would become saturated with H_2S only after about 25 minutes at 90° C, provided that no hydrogen sulfide was lost from the solution. The time could be reduced to 5 minutes by the use of a 1 F thioacetamide solution; however, the cost of the reagent precludes this for student laboratory use, in general.

Precipitations at lower hydrogen ion concentrations require special consideration. To precipitate 6 mg of copper from 100 ml of solution 0.1 F in thioacetamide and buffered at pH 3 would require approximately 8 hours if all the hydrogen sulfide produced by hydrolysis reacts rapidly with the copper, and if copper is precipitated only by hydrogen sulfide from hydrolysis.

Thus, the substitution of thioacetamide for hydrogen sulfide must be made with considerable caution. On the other hand, the use of thioacetamide makes possible the production of hydrogen sulfide in solution at a controlled rate, which offers particular advantages in studies of precipitation and coprecipitation phenomena.

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B. Precipitation of Lead Sulfide by Thioacetamide.

Introduction

In the preceding section the results of a study of the acid catalyzed hydrolysis of thioacetamide are presented. The work reported here is a continuation of the investigation of the reactions of thioacetamide and its applications to chemical analysis. In the earlier study it was shown that neither lead ion nor lead sulfide catalyzes the hydrolysis of thioacetamide in acid solutions. This section presents the results of a study of the precipitation of lead sulfide by thioacetamide in acid solutions.

EXPERIMENTAL

Reagents.

Standard solutions of potassium dichromate were prepared by weight and sodium thiosulfate solutions were standardized against these.

A standard solution of sodium perchlorate for control of the ionic strength of solutions was prepared by the neutralization of a measured solume of standard perchloric acid with sodium hydroxide to pH 7.0, measured with a pH meter. The neutral solution was then diluted to a known volume.

Solutions of thioacetamide, lead nitrate and sodium hydrogen sulfide were prepared as is described in the preceding section. Eastman White Label thioacetamide, lot #34, and Matheson, Coleman & Bell thioacetamide, lot #209518, were used in the experiments and were found to give identical results.

Sodium formate -- formic acid buffer solutions with constant sodium formate concentration were prepared from sodium hydroxide solution and 90% formic acid. Solutions of formic acid of various concentrations were prepared and to each of these was added the same amount of sodium hydroxide solution. The solutions were adjusted by addition of water to the same final volume.

Apparatus.

The reaction apparatus and sampling device were the same as were used in the hydrolysis study.

Procedure.

The reaction solutions were prepared by mixing measured volumes of stock solutions of thioacetamide, buffer, sodium perchlorate and lead nitrate and diluting to 100 ml. The reaction solution was placed in the constant temperature bath, and when measurements of the direct reaction were being made, a slow stream (one to two bubbles a second) of nitrogen was passed through the solution. The nitrogen served to keep the reaction solution stirred, and to force solution from the sampling outlet tube after a sample had been taken.

At timed intervals about ten ml of solution were forced through the sintered glass bubbler from the reaction tube into a sample tube surrounded by a cooling bath which served to quench the reaction.

The sample was left in the cooling bath for one to two minutes, by which time it had reached room temperature, then was centrifuged to remove the small amount of lead sulfide which passed through the sintered glass. A 5.00 ml portion of the sample was taken from the centrifugate by pipet and transferred to a 15 x 125 mm test tube which contained 1.5 millimoles of sodium hydroxide. The lead in solution was rapidly and quantitatively precipitated in the alkaline solution by the thioacetamide. In experiments in which equivalent amounts of lead and thioacetamide were present, 0.2 millimole of sodium hydrogen sulfide was added to insure that the lead was completely precipitated. The precipitate of lead sulfide was removed by centrifugation and washed twice with 2 ml portions of hot water which contained 0.1 millimole of sodium hydrogen sulfide.

The lead sulfide was then treated with 1.5 ml of 2 F nitric acid and the mixture was heated in boiling water. If, after five minutes, any black residue remained, the mixture was heated over a direct flame until the residue dissolved. Dilute nitric acid and moderate heating in a water bath were used in order to lessen danger of oxidation of sulfide to sulfate, which takes place in hot concentrated nitric acid. There was occasionally evidence of some sulfur formation.

The nitric acid solution of the lead was treated with 6 milliequivalents of ammonium acetate, heated in boiling water for one to two minutes to dissolve any lead sulfate which may have formed, and then was transferred to a 125 ml conical flask. Standard potassium dichromate in slight excess was added by pipet and the mixture was heated to boiling to coagulate the lead chromate. The mixture then was cooled, filtered, and the filtrate was titrated with standard sodium thiosulfate from a microburet.

Experiments to determine the extent of complex formation by lead and formate were made by adding excess solid lead chloride to solutions which had constant pH and ionic strenght values, but had various sodium formate concentrations. The mixtures were rotated in a constant temperature bath until equilibrium was reached (equilibrium was approached from both above and below saturation); then the lead concentration was determined by precipitation of the lead with excess standard potassium dichromate and iodometric titration of the excess with sodium thiosulfate.

DISCUSSION AND RESULTS

a. Precipitation of Lead by Hydrolysis of Thioacetamide.

Semiquantitative experiments indicated that in acid concentrations of the order of 0.01 M the rate of precipitation of lead by thioacetamide corresponded to the rate of hydrolysis of thioacetamide, but that at a pH of 4 the precipitation proceeded much faster than does the hydrolysis.

Quantitative measurements supported these observations. It was found to be possible to follow the rate of hydrolysis of thioacetamide in 0.01 F hydrochloric acid by observing the change in concentration of lead (II). In a solution 0.10 F in thioacetamide, 0.01 F in hydrochloric acid and 0.01 F in lead nitrate maintained at 90° C the results shown in Table I were obtained. No nitrogen was bubbled through the solution in this case. The values in the last row in the table were calculated, by use of the second order hydrolysis constant for thioacetamide, from the concentration of Pb(II) found at time = 0 upon the assumption that all hydrogen sulfide would react rapidly with Pb(II). The rate of precipitation of lead sulfide is seen to agree, within the limits of experimental accuracy, with the rate of hydrolysis of thioacetamide.

TABLE I

Precipitation of PbS by H_2S from Hydrolysis of Thioacetamide

0.10 F CH_3CSNH_2; 0.01 F HCl; 90° C.

Time (min)	0	3	6	18
$[Pb^{II}]$ found, moles/liter	0.0088	0.0083	0.0077	0.0051
$[Pb^{II}]$ calculated, " "		.0082	.0076	.0051

These data support the results obtained in the study of the hydrolysis of thioacetamide that neither lead ion nor lead sulfide catalyzes the hydrolysis and that lead ion does not inhibit the hydrolysis. Thus, there is no evidence for the formation of a stable intermediate between lead and thioacetamide.

b. Precipitation of Lead by Direct Reaction with Thioacetamide.

Subsequent experiments were made in solutions of lower hydrogen ion concentration, where the rate of precipitation of lead is much greater than is the rate of hydrolysis of thioacetamide.

Effect of Formate Concentration.

In preliminary experiments made to determine a suitable analytical procedure, it was noted that the rate of precipitation of lead sulfide by thioacetamide was dependent upon the total concentration of the formic acid - sodium formate buffer used. When the sodium formate concentration was doubled and the pH kept constant, the rate of precipitation was reduced by about 50%. Experiments on the solubility of lead chloride in solutions buffered with formic acid -sodium formate indicated that lead and formate ions complex significantly and that the effects noted in the precipitation rate experiments were of the order of magnitude to be expected from the strength of the complex. Throughout the experiments reported, the sodium formate concentration was kept constant at 0.081 M.

Effect of Surface.

Increase of the glass surface by about 500% by the addition of 0.275 gram of dry Pyrex glass wool did not have a measurable effect upon the rate of precipitation. The surface area of the reaction vessel, bubbling tube and thermometer in contact with the solution was about 125 cm^2. The surface area of the glass wool was estimated from the diameter of the fibers (8×10^{-4}cm) and the density of glass (2.2 g/cm^3) to be 630 cm^2. Figure I shows the agreement of experimental determinations of the rate of precipitation of lead sulfide with and without the presence of the glass wool. The concentrations of all species were identical in the two experiments. It is concluded that the precipitation reaction is not surface catalyzed.

Effect of Thioacetamide Concentration.

Experiments demonstrated that the precipitation reaction is first order with respect to the concentrations of both thioacetamide and lead (II). Experiments were made at constant initial concentrations of lead nitrate and formic acid - sodium formate buffer, but with various initial thioacetamide concentrations. The experiments were so designed that in no case had more than 8% of the thioacetamide reacted by the end of the run. At the pH which obtained the hydrolysis of thioacetamide proceeded to the extent of only 0.2% an hour, so changes in concentration due to this effect may be disregarded.

In Figure II are shown plots of log $[Pb^{II}]$ vs time for various thioacetamide concentrations. The plots are seen to be linear which indicates that the reaction is first order with respect to the concentration of lead (II). In Table II are calculations, from the slopes, of the second order velocity constant for the expression

$$-\frac{d\,[Pb^{II}]}{dt} = k_1\,[Pb^{II}][CH_3CSNH_2].$$

The consistency of the calculated rate constants indicates that the effect of thioacetamide is first order.

Experiments at constant ionic strength in which the initial lead concentration was varied showed, as does the linearity of the curves in Figure II, the first order dependence upon lead.

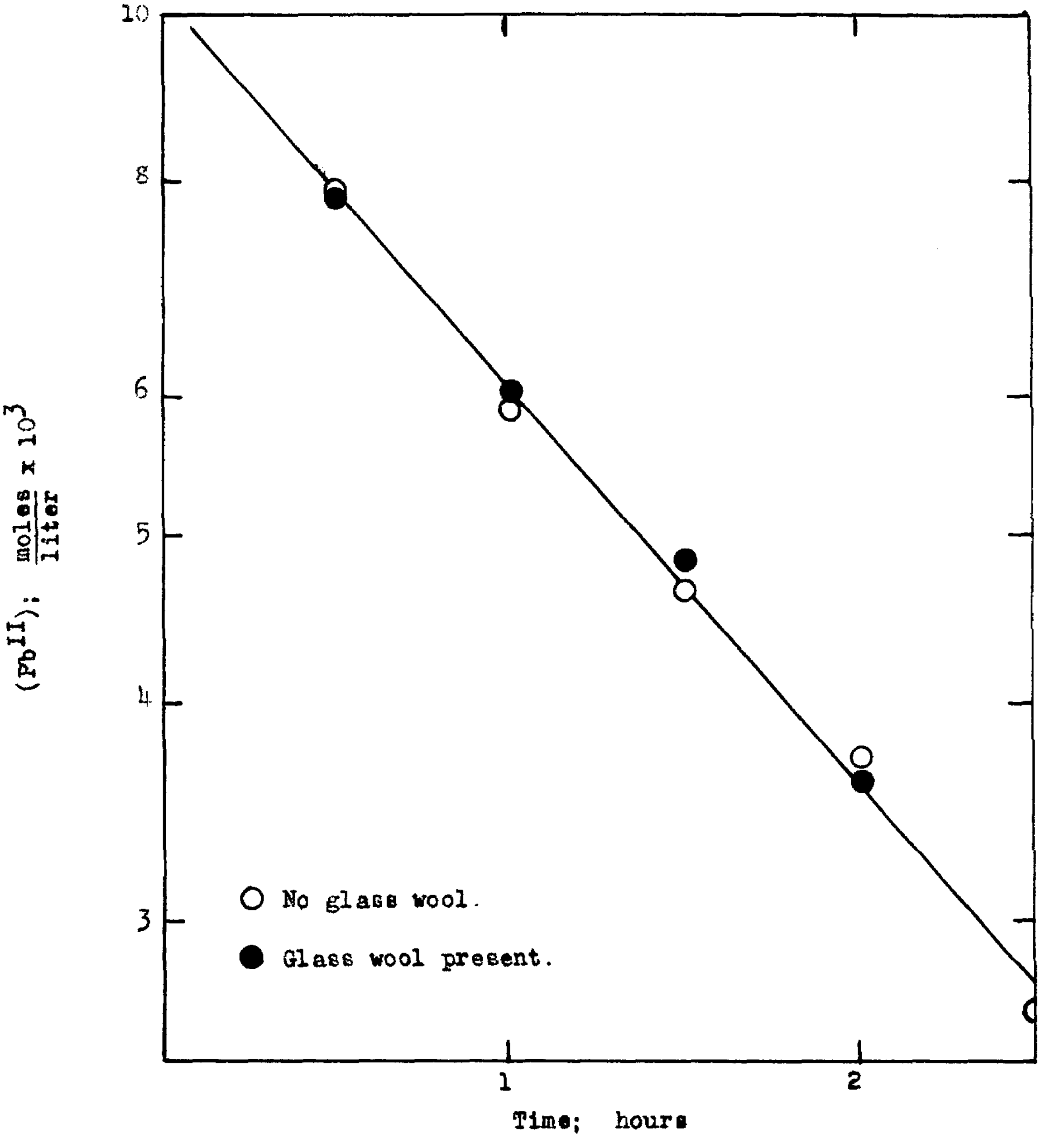

Figure I

Effect of surface upon the rate of precipitation of PbS by thioacetamide at 90° C.

0.10 F CH_3CSNH_2

1.6×10^{-4} M H^+

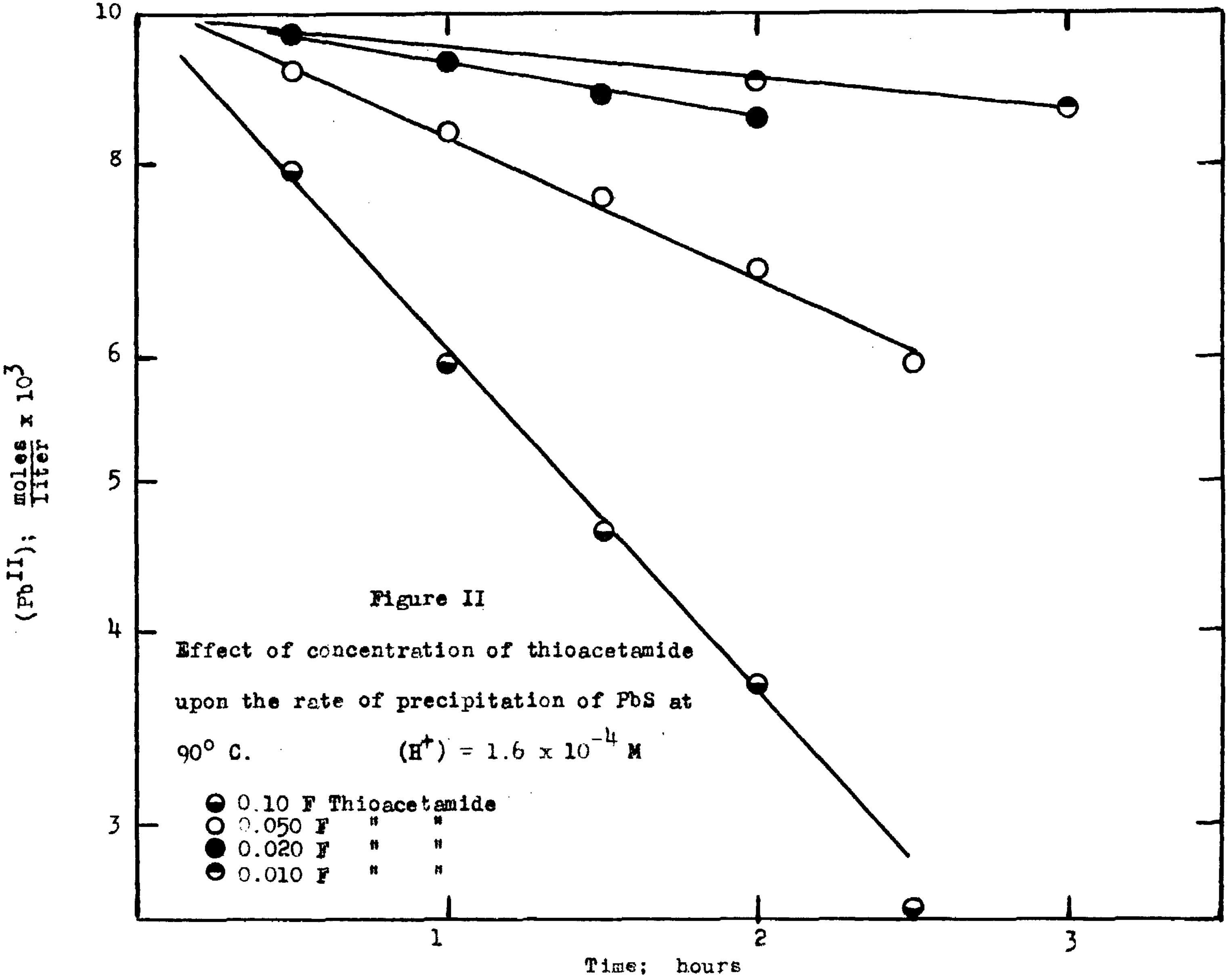

Figure II

Effect of concentration of thioacetamide upon the rate of precipitation of PbS at 90° C. $(H^+) = 1.6 \times 10^{-4}$ M

TABLE II

Effect of Concentration of Thioacetamide Upon the Rate of Precipitation of PbS

Calculated constant for the expression $-\frac{d[Pb^{II}]}{dt} = k_1[Pb^{II}][CH_3CSNH_2]$

Initial $[Pb^{II}] = 0.010$ F; $[H^+] = 1.6 \times 10^{-4}$ M; T = 90° C.

$[CH_3CSNH_2]$ moles/liter	$[Pb_i^{II}]/[Pb_f^{II}]$ *	Total time min	k_1 $\frac{\text{liter}}{\text{mole min}}$
0.10	3.50	150	0.083
0.05	1.69	150	0.070
0.02	1.18	120	0.069
0.01	1.14	180	0.073
		Average	0.074 ± 0.006

* Subscripts <u>i</u> and <u>f</u> refer to initial and final, respectively.

Effect of Hydrogen Ion Concentration.

The effect of the concentration of hydrogen ion was studied in solutions of constant initial concentrations of lead ion, thioacetamide, sodium perchlorate and sodium formate. Hydrogen ion was found to have a half order inhibition effect upon the rate of precipitation of lead sulfide. In Figure III are shown the results of experiments in which the hydrogen ion concentration was maintained at from 8 x 10^{-6} to 3.1 x 10^{-4} M. At the lower limit the ratio of lead ion to lead monohydroxide ion is approximately 10. (1). The concentrations of such proposed polynuclear species as Pb_2OH^{+++} and $Pb_4(OH)_4^{++++}$ (2) are such that less than 0.1% of the total lead is in such forms. At the upper hydrogen ion concentration the ratio of the rate of hydrolysis of thioacetamide to the rate of precipitation of lead sulfide by the direct interaction is 0.05. Thus, through the range of hydrogen ion concentrations studied these extraneous effects were of minor importance. In Table III are calculated velocity constants for the expression

$$-\frac{d[Pb^{II}]}{dt} = k\ \frac{[Pb^{II}][CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}} .$$

The agreement of the values of the calculated constant over the forty fold change in hydrogen ion concentration is seen to be within the limits of the experimental accuracy.

Temperature Effect.

Knowledge of the effect of temperature upon the rate of precipitation of lead sulfide is of value in the calculation of suitable conditions for obtaining complete precipitation of lead and for effecting quantitative separations from other elements. The rate of precipitation was found to vary by a factor of approximately two for a ten degree change in

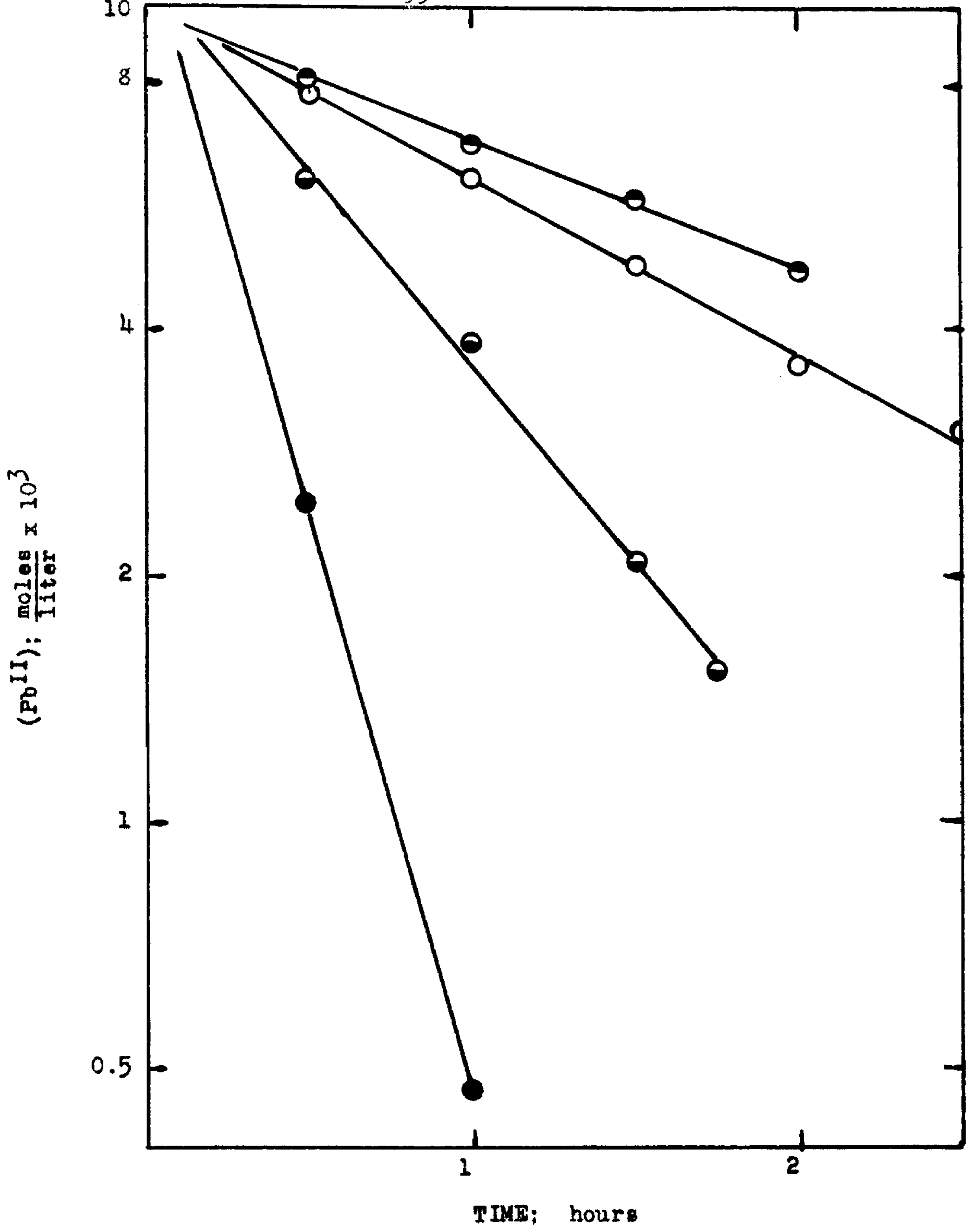

Figure III

Effect of hydrogen ion concentration upon the rate of precipitation of PbS at 90° C.

● (H^+) = 8.0 x 10^{-6}
◓ " 4.0 x 10^{-5}
○ " 1.6 x 10^{-4}
◒ " 3.1 x 10^{-4}

TABLE III

Effect of Concentration of H^+ Upon the Rate of Precipitation of PbS

Calculated constant for the expression $-\frac{d[Pb^{II}]}{dt} = k\,\frac{[Pb^{II}][CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}}$

Initial $[Pb^{II}] = 0.010$ F; $[CH_3CSNH_2] = 0.10$ F; T = 90° C.

$[H^+]$ moles/ liter	$[Pb_i^{II}] / [Pb_f^{II}]$	Total time min	$k \times 10^3$ liter $mole^{-}$ min^{-1}
3.1×10^{-4}	2.15	120	1.12
1.6×10^{-4}	3.50	150	1.05
4.0×10^{-5}	6.25	105	1.10
8×10^{-6}	4.06	30*	1.32
		Average	1.15 ± 0.12

* The point at 30 minutes was used because of the uncertainties involved in the determination of the very low concentration of lead after 60 minutes.

temperature through the range from 60° to 90° C. Figure IV is a plot of log k vs 1/T and the plot is seen to show an Arrhenius temperature dependence. The activation energy is calculated from the slope to be 15.5 kcal/mole.

It was noted that the lead sulfide precipitate obtained at the very slow rate at 60° C was finely granular in appearance. Microscopic examination of the precipitates obtained at 60° C and at 90° C showed that discrete and regular shaped particles could be detected in the former case but not in the latter. This emphasizes a potential analytical advantage in the use of thioacetamide; namely, the possibility of control of the rate of formation, and hence of the physical characteristics of the sulfide being precipitated.

Ionic Strength Effect.

The Bronsted-Bjerrum-Christiansen equation (3)

$$\ln k = \ln k_o + 2\ Z_a Z_b \alpha \sqrt{\mu}$$

predicts that the effect of ionic strength upon the rates of hydrolysis of thioacetamide and of direct reaction of lead and thioacetamide will be small except at high ionic strengths, since presumably one of the reactants in each of the reactions is a neutral molecule.

No measurable effect upon the rate of direct reaction resulted from decreasing the ionic strength from 0.14 to 0.11; however, the effect of larger variations in ionic strength was not investigated.

Analytical Considerations.

Figure V shows the rates of precipitation of lead sulfide by thioacetamide by hydrolysis of the latter and by direct reaction as calculated from the rate constants. It should be noted that only the rate of the direct reaction depends upon the concentration of lead; a change in

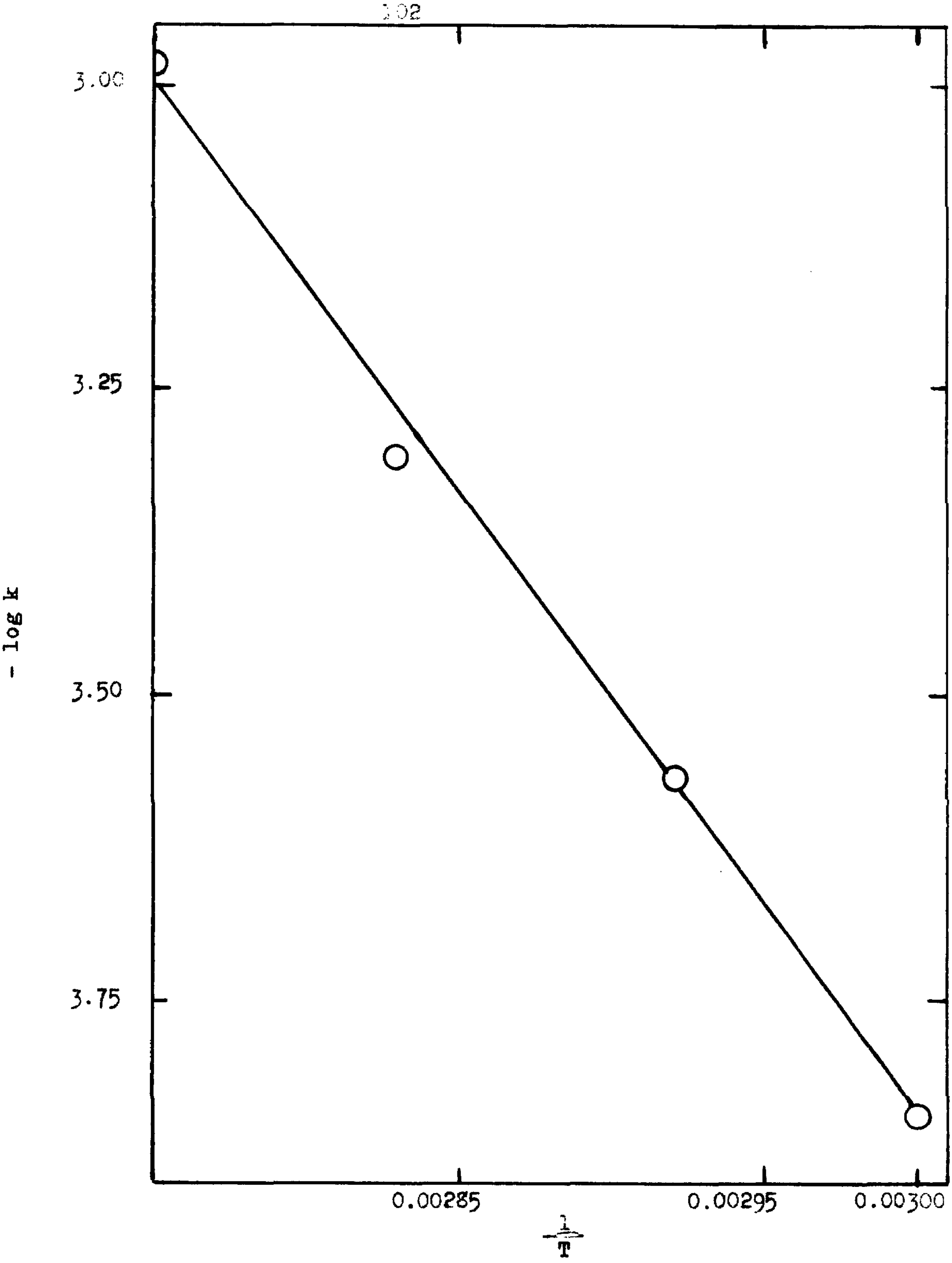

Figure IV

Rate of precipitation of PbS as a function of the temperature.

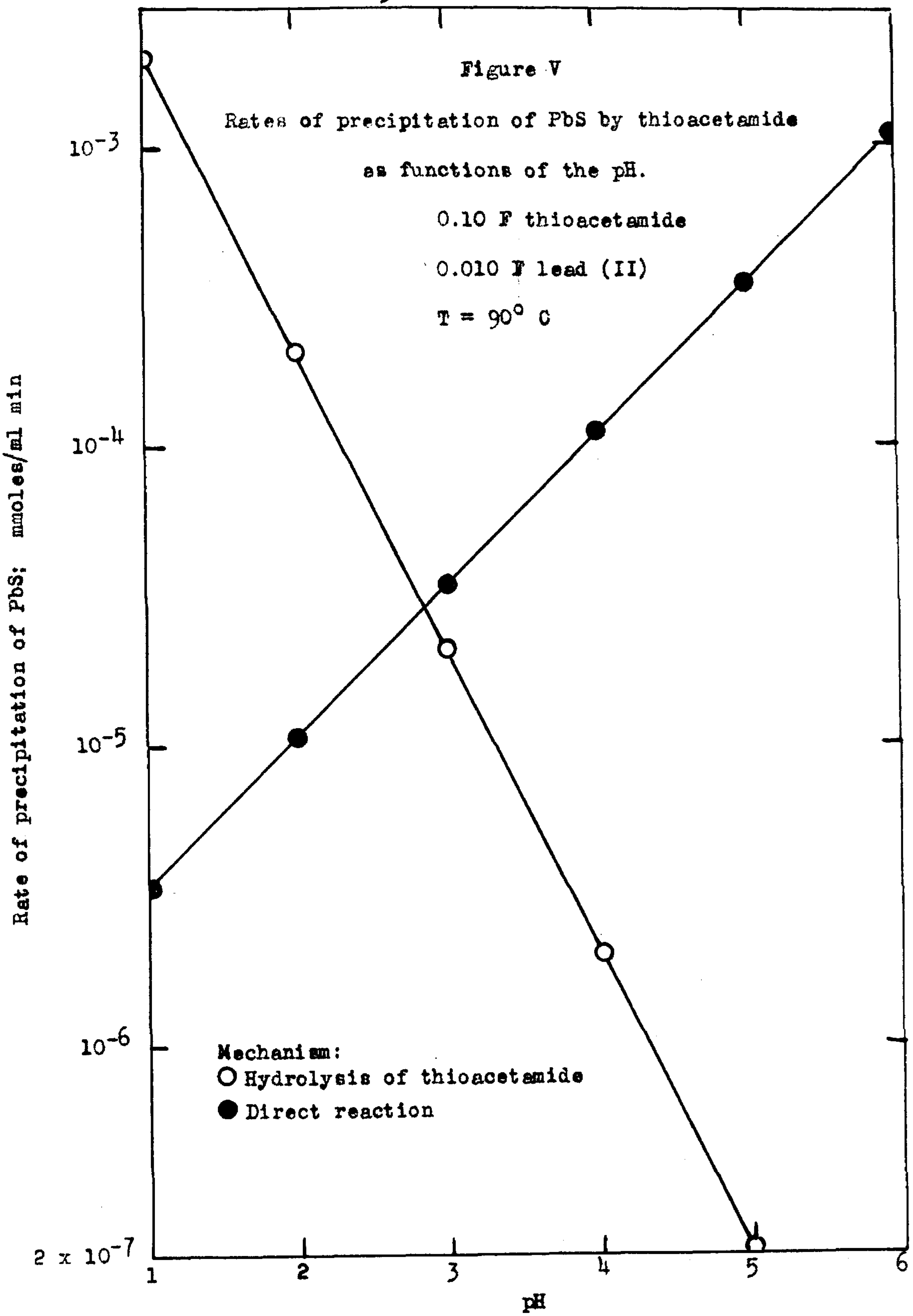

Figure V

Rates of precipitation of PbS by thioacetamide as functions of the pH.

0.10 F thioacetamide

0.010 F lead (II)

T = 90° C

lead concentration results in vertical displacement of this curve.

The following observations are significant concerning a 0.01 F lead (II) solution;

(A) $R_d = R_h$ at pH 2.8

where R_d is the rate of direct reaction and R_h is the rate of precipitation of lead sulfide by hydrogen sulfide from hydrolysis.

(B) $R_d = R_h/600$ at pH 1

(C) $R_d = 1000R_h$ at pH 5.

Thus, in solutions of pH 2 and lower the precipitation of lead by thioacetamide takes place almost exclusively through hydrolysis of the latter. As the pH is raised the direct reaction becomes increasingly important until at pH 4 and above (for 0.01 F Pb(II)) the hydrolysis reaction is obscured by the much faster direct reaction. Barber and Taylor (4) state that "the hydrolysis (of thioacetamide) is more rapid in an alkaline solution than in an acid solution of the same strength". Preliminary experiments on the hydrolysis of thioacetamide in alkaline solutions, suggest that what was actually observed was more rapid precipitation of metal sulfides because of a change of mechanism from hydrolysis to direct reaction such as has been observed for the case of lead.

This investigation has illustrated that the indiscriminate use of thioacetamide as a substitute for hydrogen sulfide is not justified since, in certain cases the reactions involved in its use are complicated by mechanisms which change with the pH of the solution. New uses for thioacetamide are indicated. The controlled rate of precipitation which can be achieved by its use should be of value in studies of precipitation and coprecipitation mechanisms. Moreover, separations may be possible which depend upon variations in the rates of the direct reaction between thioacetamide and metal ions. However, there must first be a thorough investigation of the precipitation of other sulfides by thioacetamide.

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PROPOSITIONS

1. It has been suggested (1) that the hydrolysis of thioacetamide proceeds through the thioenol form.

a. Measurements of the rate of hydrolysis of N, N-dimethylthioacetamide will show whether or not the thioenol form is necessary.

b. The necessity of the existence of the thioenol form in the case of direct reaction of lead and thioacetamide should also be investigated.

2. Heidt and Berestecki (2) claim, on the basis of a spectrophotometric study, to have demonstrated the existence of a cerium (III) perchlorate complex. The evidence is insufficient, since an earlier investigation (3) indicated that the ionic strength and not the perchlorate concentration affected the absorption coefficients at the wavelength which was used.

3. It is proposed that the method of anion exchange equilibria which has been used in the case of lead(II) chloride complexes (4) be applied to the ferric thiocyanate system in order to determine the conditions under which negatively charged complexes become predominant. This information, together with spectrophotometric and distribution data should permit the classification of the system.

4. A coulometric titration of microgram quantities of sulfide with hypochlorite is proposed.

5. It is proposed that Flaschka's (5) failure to get formation of sulfo-salts of arsenic and molybdenum with thioacetamide in ammonium hydroxide solutions could be overcome by a slight increase in the alkalin-

ity of the solutions.

6. Gordon, Teicher and Burtt (6) commenced a study of coprecipitation of manganese during the precipitation of basic stannic sulfate by homogeneous phase precipitation involving the hydrolysis of urea. However, the results are in question because during the course of the experiments there was appreciable increase in the pH, and thus increase in the tendency for the manganese to coprecipitate. It is proposed that a more meaningful study of coprecipitation could be made by the use of thioacetamide and acetamide in such concentrations that their hydrolysis would result in no net change in the pH.

7. It has been reported (7) that the color intensity of the titanium (IV) thiocyanate complex in acetone-aqueous solutions is a function of time when either sulfuric or hydrochloric acid is present. These effects are attributed to strong complexing of titanium(IV) with sulfate and only slight complexing with hydrochloric acid. However, the data upon which this assumption is made can also be interpreted to mean that the relative strengths of the complexes are reversed. A determination of the effect of perchloric acid should be made to resolve this question.

8. A method for the standardization of vanadate solutions against sodium oxalate as the primary standard has been published by West and Skoog (8). In this procedure sodium oxalate is not a true primary standard; moreover, the procedure would be improved by the omission of the sodium oxalate.

9. It is proposed that the practicability of a coulometric determination of aldehydes by electrolytically generated silver(I) in ammonium

hydroxide solution be investigated.

10. It is proposed that the study of weak complexes be carried out in non-aqueous solvents. This should prove to be particularly useful in the case of complexes whose existence is in question.

11. It is proposed that the evidence presented by Barton (9) in the second color plate, page 69, is atypical. A statistical study of the situation would reveal the misleading nature of the results presented in the photograph.

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