POTENTIOMETRIC AND COULOMETRIC STUDIES AND THE MECHANISMS OF THE PRECIPITATION OF METAL SULFIDES FROM ACID SOLUTIONS BY THIOACETAMIDE

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Abstract

The standard potential of the half cell $I_{2(s)} + HCN = 2\ ICN + 2H^+ + 2e^-$ has been measured in cells with negligible liquid junction potentials. The value calculated at 25°C. in solutions 0.2 to 4.0 volume formal in perchloric acid is -0.711 volt; the value for a hypothetical half cell 1 molal in iodine is -0.625 volt. The constant for the reaction $I_2 + HCN = ICN + I^- + H^+$ was calculated from solubility measurements to be 0.87.

Conditions under which electrolytically generated chlorine can be employed for the coulometric titration of iodide to iodine monocyanide have been determined. Titrations in the presence of bromide were made. One to three mg. of iodide were determined with an accuracy of 0.1%.

The conditions were determined under which tetrapositive lead can be generated quantitatively. The determination of lead(IV) with electrolytically generated iron(II) was proved feasible. In confirmatory titrations with ferrous ion an accuracy of 0.1% was attained in the determination of quantities of lead(IV) in the range from 0.25 to 1.50 microgram. This showed the feasibility of alternately generating lead(IV) and iron(II) in a coulometric cell, that is, the use of the lead-iron system as dual intermediates.

Attempts to titrate glycols with excess lead(IV) were not successful because the reaction of glycols with lead(IV) was slow and incomplete when the reactants were present in

low concentrations.

The precipitation of cadmium as sulfide from acid solutions by thioacetamide has been studied. In solutions having pH values of 2 or less the rate of precipitation is controlled by the rate of hydrolysis of the thioacetamide to give hydrogen sulfide, and is first order with respect to the hydrogen ion and to the thioacetamide concentrations.

In solutions having pH values from 6.3 to 3.3 a direct reaction occurs in which the rate of cadmium sulfide precipitation is first order with respect to the hydrogen ion concentration. The velocity constant for the expression

$$-d[Cd(II)]/d\ t = k[Cd(II)]\ [CH_3CSNH_2]/[H^+]^{\frac{1}{2}}$$

is 8.1×10^{-4} liter$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$min^{-1} at 90°C. in 0.15 M sodium formate solution. The energy of activation for this reaction was calculated to be 20.8 kcal. per mole.

The rate of precipitation of cadmium as sulfide from acid solutions by thioacetamide in this pH range is slower in the presence of chloride. At a pH of 4.0 this effect has been quantitatively studied at 25° and 90°C. with chloride concentrations from 5×10^{-5} to 5×10^{-2} VF. The data obtained conforms to the rate expression

$$-d[Cd(II)]/d\ t = \left[k_1[Cd^{++}] + k_2[CdCl^+]\right] [CH_3CSNH_2]/[H^+]^{\frac{1}{2}},$$

where k_1 and k_2 are 8.1×10^{-4} and 4.6×10^{-4} liter$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$min^{-1}, respectively, at 90°C. The validity of these proposed constants was checked by the calculation of an equilibrium constant for the reaction

$$CdCl^{+} = Cd^{++} + Cl^{-}$$

at each chloride concentration by the use of these constants. The value of this constant is 2.0×10^{-3} mole per liter at 90°C.

The precipitation of nickel sulfide by thioacetamide has been studied in solutions in which the hydrogen ion concentration was maintained at values from 0.3 to 1×10^{-7} VM. Rate measurements have shown that the precipitation reaction conforms to the expression for the direct reaction

$$-d[Ni(II)]/d\ t = k[Ni(II)][CH_3CSNH_2]/[H^{+}]^{\frac{1}{2}},$$

where the velocity constant is 2.2×10^{-4} liter$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$min^{-1} at 90°C. Nickel sulfide was precipitated by the direct reaction with thioacetamide at hydrogen ion concentrations at which precipitation by hydrogen sulfide is not possible. The energy of activation for the reaction was calculated to be 20.8 kcal. per mole. Precipitation by the hydrolysis of thioacetamide was not observed.

The effectiveness of the separation of lead(II) and cadmium(II) from nickel(II) by the use of thioacetamide in solutions at 90°C. has also been studied. It was found that nickel sulfide was formed only by the direct reaction shown above. The precipitation of nickel sulfide was independent of the concentration of lead(II) or of cadmium(II), or of the amount of hydrogen sulfide in the reaction solution. It was found that the quantity of nickel sulfide which precipitated with the lead or cadmium sulfide was insignificant under certain conditions, and that an effective separation can be made.

Rate measurements were made to determine the mechanisms of the precipitation of zinc sulfide from acid solutions by thioacetamide. Two mechanisms, similar to those found for lead and cadmium, were observed.

In solutions having pH values of 1 or 2, the rate of precipitation of zinc sulfide is first order with respect to both the thioacetamide and hydrogen ion concentrations. The second order velocity constant for this reaction was found to be 0.21 liter mole^{-1}min^{-1} at 90°C., the same value as that reported for cadmium and lead.

In solutions having pH values from 6.3 to 2.5 the precipitation is first order with respect to both the thioacetamide and the zinc(II) concentrations and inversely half order with respect to the hydrogen ion concentration. The velocity constant for the expression

$$-d[Zn(II)]/d\ t = k[Zn(II)][CH_3CSNH_2]/[H^+]^{\frac{1}{2}}$$

was found to be 4.2×10^{-4} liter$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$min^{-1} at 90°C. in solutions 0.30 M in sodium formate, and the energy of activation for the reaction was calculated to be 20.1 kcal. per mole. This type of precipitation is similar to that observed for lead, cadmium, and nickel in the same pH range. The value of the energy of activation is almost equal to those calculated for the precipitation of cadmium and nickel.

Separations of lead(II) from zinc(II) by the precipitation of lead sulfide from solutions 0.3 M in hydrogen ion and 0.6 M in chloride were made with thioacetamide or hydrogen sulfide at 90°C. The two methods were comparable in effectiveness.

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Part I

The Standard Potential of the Iodine-Iodine Monocyanide Half Cell

Part I.

Standard Potential of Iodine-Iodine Monocyanide Half Cell*

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 volt is calculated for the half-cell reaction

$$I_2(1M) + 2HCN = 2ICN + 2H^+ + 2e^- \qquad (1)$$

However, from Kovach's data the iodine-iodide half-cell potential is calculated, with corrections for complex ion formation (4) to be -0.520 volt, 0.016 volt different from the

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*The material of this section was published by Bowersox, D. F., Butler, E. A., and Swift, E. H., Anal. Chem. 28, 221 (1956).

value given by Latimer (5). More recently Gaugin (6) reported an average value of -0.640 volt for the half cell of Equation 1. In his study, deviations from the mean were large, becoming 0.180 volt at pH 6.

In the present investigation potential measurements were made in solutions which ranged from 0.2 to 4 VF in perchloric acid and from 0.06 to 0.3 VF in total cyanide, and the value -0.625 ± 0.003 volt was obtained for this half cell. In the course of the potential measurements a re-evaluation of the equilibrium constant for the disproportionation reaction

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

was made by a study of the solubility of iodine in hydrocyanic acid solutions, and the value 0.870 ± 0.009 mole per 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, 0.6 VF, 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. of 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 1, consisted of three 200-ml. lipless beakers connected by glass tubing bridges to a single intermediate vessel. The bridges were prepared from 6-mm. outside diameter 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 $25.0^\circ \pm 0.5^\circ$C. by means of water baths.

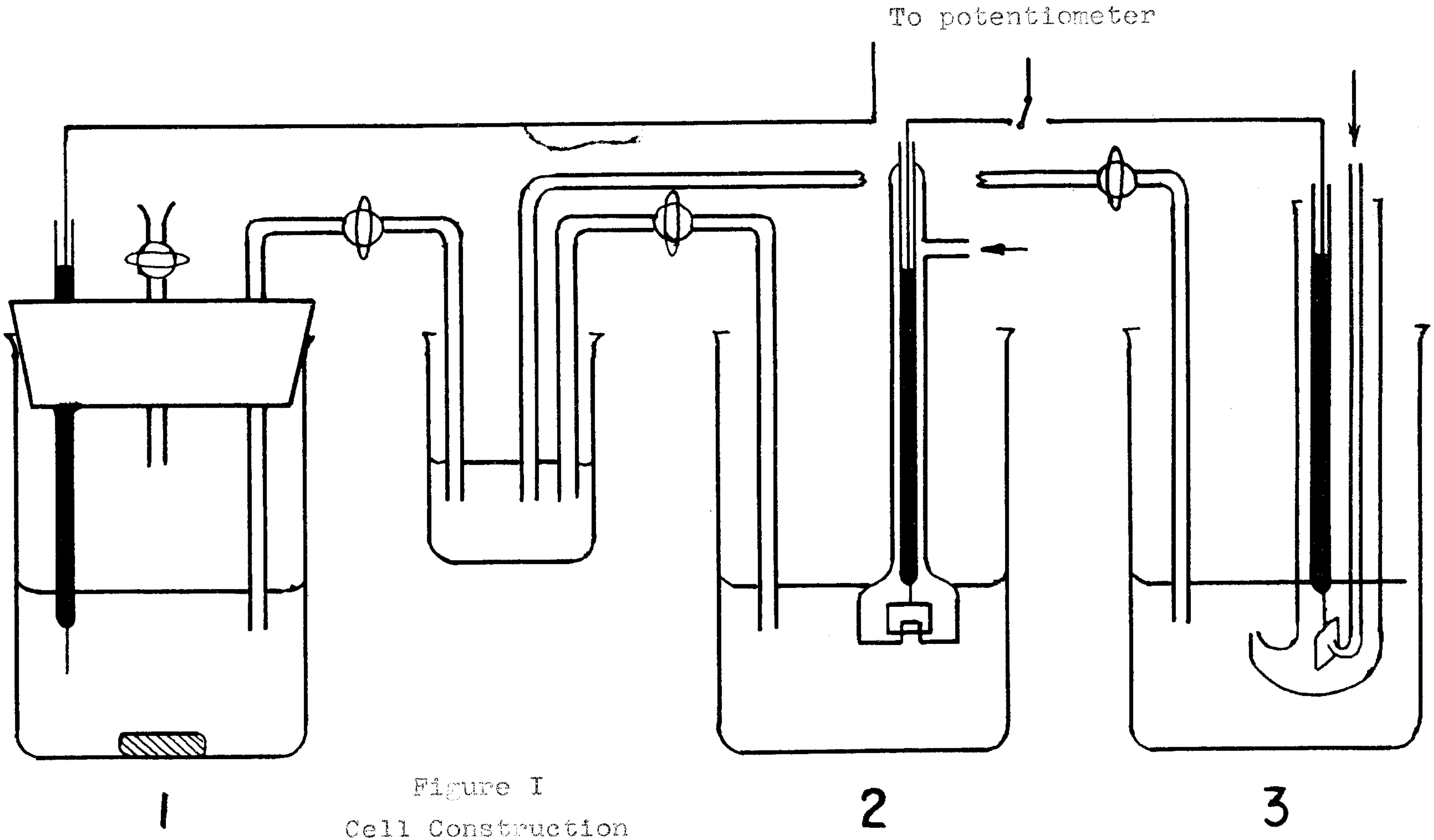


Figure I

Cell Construction

1. Iodine-iodine monocyanide half cell compartment.

2, 3. Hydrogen electrode compartments.

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 used (8,9); these are shown in Figure 1. 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 Co. Model E. potentiometer with a Leeds & 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 $25^\circ \pm 0.2^\circ$C. for periods of time up to 7 days. Samples were transferred by a 2.0-ml. pipet, using rubber bulbs for drawing the solution into the 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 partial pressure of the hydrogen cyanide above the pipetted solutions was less than that of water, therefore such solutions could be pipetted without significant change in concentration. 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 making 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 5- to 10-minute intervals until the readings remained constant within 0.1 mv. for at least 30 minutes. In preliminary experiments it was found that the cell potential remained constant to 0.1 mv. for 24 hours.

Discussion

<u>Disproportionation of Iodine in Hydrocyanic Acid Solutions</u>. The equilibrium constant for the disproportionation reaction (Equation 2) 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 this equation 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 under 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 $11.95 \pm 0.12 \times 10^{-4}$ VF. The sodium perchlorate was added in order to keep the ionic strengths in these and subsequent experiments constant.

In Table I are data and calculations from experiments made to determine the value of the disproportionation constant. The concentrations of iodine and triiodide ions were

Table I

Determination of Disproportionation Constant

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

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

Expt.	KIO_3 Required Mmole	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	0.0212	0.00703	0.00645	0.0135	0.0755	0.866
5	0.02141	0.00713	0.00654	0.0137	0.0753	0.894

Av. 0.870 ± 0.009

calculated from the solubility of iodine determined above, the volume of potassium iodide required for the titration of the sample, and the dissociation constant for the triiodide ion, K = 1.3×10^{-3} at 25°C. (12). The iodine monocyanide concentration is equal to the sum of the iodide ion and triiodide ion concentrations, while the hydrocyanic acid concentration is the difference between the initial formal sodium cyanide concentration and the iodine monocyanide concentration. The value obtained for the disproportionation constant 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 (7) 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 diiodocyanide 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 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 diiodocyanide complexes,

$K_1 = [I(CN)_2^-]/(ICN)(CN^-)$ and $K_2 = (I_2CN^-)/(ICN)(I^-)$, respectively. Hence, as the solutions used in the present investigation were acid and the iodide concentrations were low, these complexes were present only in small concentration. 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 diiodocyanide and iodine dicyanide are 2×10^{-4} and 1×10^{-11}, respectively. Less than 0.5% of the iodine monocyanide is complexed even to diiodocyanide.

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 20 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 because data for its activity are available (13) and it evidently has only very slight tendency to form complexes with the half-cell constituents.

Iodine-Iodine Monocyanide Half Cell. Analyses made over a 24-hour period of solutions at 25°C. and at the acid concentrations used showed no significant change in cyanide concentration. Therefore the half-cell reaction shown in Equation 1 was assumed to be the potential controlling reaction.

In preliminary experiments attempts were made to determine analytically the concentrations of iodide ion, iodine, and iodine monocyanide present in the cell solutions at the time of the potential measurements. However, the sampling technique did not entirely eliminate all the small particles of iodine that were present in the system; consequently this method did not yield satisfactory results. Therefore, the concentrations of species present at equilibrium were calculated in the following manner.

The concentration of iodine was determined from the solubility measurements discussed above. The concentration of iodine monocyanide was calculated from the volume of standard sodium iodate solution added, with the assumption that the reduction of iodate by iodine was quantitative. The difference between the total cyanide added and that present as iodine monocyanide gave the concentration of hydrocyanic acid. The hydrogen ion concentration was calculated from the quantities of perchloric acid and sodium iodate added, with correction for the hydrocyanic acid formed. Further refinement of the calculated concentration values was made by application of the disproportionation constant.

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 these calculations of the E^o value in order to simplify calculations involving unsaturated solutions. 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

$$E_{ref} = \frac{RT}{F} \ln \frac{(PH_2)^{\frac{1}{2}}}{(H^+)}$$

$$E^o = E_{cell} + \frac{RT}{F} \ln \frac{(ICN)}{(I_2)^{\frac{1}{2}}(HCN)} \qquad (4)$$

Table II

Standard Potential, E°, of Half Cell

$I_2(1M) + 2HCN = 2ICN + 2H^+ + 2e^-$

$HClO_4$, VF	ICN, VM	HCN, VM	$-E_{cell}$, Volt	-E°, Volt
4	0.050	0.150	0.6871	0.6288
			0.6840	0.6257
2	0.053	0.247	0.6695	0.6225
			0.6707	0.6237
	0.0515	0.148	0.6838	0.6223
			0.6838	0.6223
	0.050	0.050	0.7114	0.6249
			0.7126	0.6261
	0.0501	0.0099	0.7609	0.6327[a]
			0.7565	0.6293[a]
			0.7567	0.6295[a]
			0.7651	0.6368[a]
1	0.0539	0.252	0.6730	0.6263
			0.6710	0.6243
	0.0540	0.156	0.6820	0.6227
			0.6842	0.6249
	0.0513	0.0487	0.7119	0.6240
			0.7111	0.6232
	0.0481	0.0488	0.7103	0.6232
	0.0494	0.0126	0.7411	0.6196[a]
			0.7502	0.6287[a]
0.5	0.062	0.254	0.6625	0.6124[a]
	0.062	0.259	0.6740	0.6247
	0.061	0.239	0.6769	0.6255
			0.6762	0.6248
	0.058	0.152	0.6895	0.6278
			0.6870	0.6253
	0.0526	0.0474	0.7125	0.6235
			0.7124	0.6234
	0.0506	0.0094	0.7475	0.6178[a]
			0.7556	0.6259[a]
0.2	0.0725	0.2275	0.6840	0.6269
			0.6833	0.6262
	0.065	0.135	0.6945	0.6268
			0.6925	0.6248
			0.6950	0.6273
			0.7000	0.6323
	0.0558	0.0442	0.7195	0.6271
			0.7167	0.6243
	0.0513	0.0087	0.7614	0.6293[a]
			0.7610	0.6289[a]
			0.7627	0.6306[a]
			0.7600	0.6279[a]

Av. 0.6248 ± 0.0026 volt

[a] Not included in calculation of average.

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

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

in which solid iodine is taken as the reference state.

The calculated values of E^o are reproducible with a standard deviation of ± 0.0026 volt 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^o 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 = 0.15 VM; ICN = 0.05 VM
(B) HCN = 0.01 VM; ICN = 0.05 VM

If the concentration of hydrocyanic acid is changed by 0.003

mole per liter, the change in the calculated E° for case A is 0.0005 volt while that for case B is 0.0068 volt. 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:

$$
\begin{array}{rclr}
 & & & \Delta F \\
I_2(1M) + 2HCN & = & 2ICN + 2H^+ + 2e^- & 28846 \\
2I_2(1M) + 2HCN & = & 2ICN + 2H^+ + 2I^- & 165 \\
I_2(S) & = & I_2(1M) & 3918 \\
\hline
2I^- & = & I_2(S) + 2e^- & 24763
\end{array}
$$

or

$$E^\circ = -0.5366 \text{ volt}$$

This value for the iodine-iodide potential differs by just 0.0011 volt 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.

Analytical Application

By making use of this half-cell potential of -0.63 volt, one can calculate the potential required for the oxidation of any given quantity of iodine (or iodide) to iodine monocyanide under specified conditions. For example, assume that the solution is 1.0 molal in hydrogen ion, 0.1 molal in hydrocyanic acid, that the iodine monocyanide formed is 0.01 molal, and that the iodine at the end point is 10^{-6} molal; the iodine-iodine monocyanide potential in such a solution would be -0.74 volt. Considering only equilibrium conditions, this potential value indicates that the oxidation could be effected by electrolytically generated bromine, chlorine, or tetrapositive cerium; in addition, under similar conditions, quantitative oxidation of tripositive arsenic and antimony should be obtained. Qualitative experiments have indicated that these predictions can be realized and quantitative studies are in progress.

Part II

Coulometric Titrations

Part II A

Coulometric Titration of Iodide

Titration to Iodine Monocyanide by Chlorine with Use of an Amperometric End Point

Introduction

The titration of iodide to iodine monocyanide by means of an oxidizing agent such as nitrite, permanganate, bromate, or periodate, has been reported by Lang (14). The half cell reaction

$$I^- + HCN = ICN + H^+ + 2e^- \qquad (6)$$

goes to the right in the presence of chloride and a suitable oxidizing agent. The reaction is faster with chloride present; this effect is attributed by Oesper (1) to the rapid formation of iodine chloride followed by conversion into iodine monocyanide. Lang (14) reports that the oxidation is quantitative in 1 M hydrogen ion when iodate is employed as an oxidizing agent. Hydrolysis of iodine monocyanide to hypoiodous acid does not occur at room temperature unless the solution is basic (1), so that iodine monocyanide should be stable in acid solutions.

The feasibility of the titration of iodide by the reaction

$$I^- + Cl_2 + HCN = ICN + H^+ + 2\ Cl^- \qquad (7)$$

was shown by the investigation of the potential of the iodine-iodine monocyanide half cell (15) reported in Part I of this thesis. The study reported below was undertaken in the hope that such a titration would provide a simple and rapid method for the determination of milligram quantities of iodide in less acid solutions than those used for the titration to iodine monochloride (2).

Discussions of the advantages of the secondary type of coulometric process, in which an intermediate half-cell reaction is employed at an electrode, have been published (16,17). The intermediate reaction in the titration of iodide to iodine monocyanide is the oxidation of chloride to chlorine, which then reacts quantitatively with the iodide. One hundred per cent current efficiency at a known constant rate is attained in this way.

In this investigation a dual electrode amperometric end point was used which differed from those previously described (18) in that the indicator current decreased as the end point was approached and then remained constant. This type of end point is inconvenient because it requires that indicator readings be taken both before and after the end point. The simplicity of automation usually possible in coulometric titrations is lost, but such a method could be employed by means of a continuous recorder in the indicator circuit.

Experimental

Chemicals. All chemicals used were of reagent grade. A stock standard sodium iodide solution, 0.0100 VF (volume formal, formula weights per liter) was made by weight from dried salt, which was found to contain no iodate. This solution was made approximately 0.005 VF in sodium carbonate in order to minimize air oxidation of the iodide. Aliquots from this solution were diluted to appropriate volumes for use during the investigation.

Perchloric acid solutions were prepared by dilution of the 60% acid. Tests indicated that these solutions were free of impurities which would interfere in the subsequent determination.

Sodium cyanide solutions, approximately 2.0, 0.50, and 0.05 VF; 1.0 VF sodium chloride solutions; and sodium bromide solutions, 1.0 and 0.0100 VF, were prepared from the salts by weight. The latter solution was diluted for use in parts of this investigation.

Apparatus. The apparatus used was similar to that described by Ramsey, Farrington, and Swift (18). The cathode shield was filled with 2 VF perchloric acid to prevent diffusion from the titration cells into this shield during titrations.

Preliminary Adjustments. The current in the generation circuit was determined by measuring the drop in voltage across a standard resistance through which the generation current was passed. The rate of generation used in this investigation corresponded to 1.054×10^{-7} equivalent per second. The indicator potential scale was calibrated with a Gray Instrument Company Model E potentiometer.

When not in use, the indicator electrodes were shorted to the generator anode. Between titration series they were again shorted and stored in 0.20 VF sodium chloride. Before each set of determinations chlorine was generated in the shorted cell for 100 seconds.

The indicator electrodes were shorted to the generator anode and chlorine was generated for thirty seconds after each titration in order to maintain sensitivity. Whenever the sensitivity of the indicator electrodes was less than 0.1 mu a per three seconds generation during the approach to an end point, the electrodes were cleaned in aqua regia. This was usually necessary after from thirty to forty titrations.

Titration Procedure. Blanks. Blank solutions, that is solutions which contained all the constituents used in the titration except the iodide, which was replaced by an equal volume of distilled water, were titrated immediately before each series of titrations. The generator current was adjusted to the calibrated value, the blank cell was placed in position, and chlorine was generated for one second intervals. After each period of generation sixty seconds were allowed for equilibrium to be established and then both the generation time and the indicator current were recorded. The indicator current in these cells decreased upon generation of chlorine to a constant value.

The initial currents in blank solutions which were 2 VF in perchloric acid, 0.10 VF in chloride and 0.005 VF in sodium cyanide, were dependent upon the applied potential and ranged from 1.5 mu a at an applied potential of 140 mv. to 7.4 mu a at 400 mv. The decrease in the current upon generation of chlorine is very similar to that reported by Wooster, Farrington, and Swift (19). They reported that when bromine was generated in an acid chloride solution there was a short interval before the current began to rise. This interval, they claimed, was probably due to the presence of a small quantity of some substance capable of reducing bromine. A blank correction similar to the one employed in this investigation was used to correct for the small quantity of the reducing agent.

The amount of reducing agent present in the blank cells in this investigation was less than 10^{-6} equivalent. Attempts to determine what it might be were unsuccessful, but experiments demonstrated that no reducing substance capable of reducing chlorine was present in either the perchloric acid or the sodium chloride solutions that were used.

A blank correction of approximately three seconds was found when sodium cyanide was added to the other blank solution constituents. The use of this blank correction, although its cause was not clear, was adequate for the accurate determination of iodide in this study.

The constant current observed after the initial decrease in current could be due to disproportionation of the chlorine; that is, the reaction

$$Cl_2 + HCN = ClCN + Cl^- \qquad (8)$$

might proceed to the right. Qualitative experiments were made that showed that chloride formed when chlorine was placed in a solution 0.06 M in hydrogen cyanide and 1 M in perchloric acid. In a solution 1 M in perchloric acid and containing no cyanide, chloride was not formed. Similar tests indicated that bromide disproportionates in the same way. Lucas (20) reports that chlorine reacts with hydrogen cyanide according to reaction 8 and then that the reaction

$$ClCN + H_2O = HOCN + H^+ + Cl^- \qquad (9)$$

occurs. Both reactions 8 and 9 could be used to explain the constant current that was observed. In experiments in which chlorine was generated in a blank solution, it was found that the current did remain constant with increased time of generation over the potential range from 25 to 400 mv. The indicator current initially rose after the generation of chlorine, then fell to a constant value, from 1 to 2 mu a, within sixty seconds.

A blank correction was made by plotting the indicator current against the time of generation, and extrapolating the current line to the point of initial constant current. In this way, a pre-titration for any impurities in the cell was made. In general this correction ranged from one to five seconds.

If such a blank correction is undesirable, a titration of a known iodide could be used for the determination of a blank time correction. In such cases the blank correction would be the difference between the calculated and the observed end points.

Titrations. Titration solutions were prepared in 40 x 80 cm. weighing bottles. A sample of the iodide solution was pipetted into the weighing bottle and acid, chloride, cyanide, and water added to give 50 ml. of a solution 0.02 to 1.8 VF in perchloric acid, 0.01 to 0.40 VF in sodium cyanide, and 0.10 VF in sodium chloride.

The initial indicator current was first noted and recorded; then the indicator circuit was opened and generation of chlorine started. When the approximate iodide content was known, the indicator circuit was closed about 15 seconds before the calculated end point and readings taken at three second intervals. The determination of the end point was again made by graphing the indicator current against the generation time and extrapolating to the point of initial constant current.

Discussion

Potential Difference between Indicator Electrodes. In order to choose an applied potential such that the effects due to changes in the internal and external resistance of the indicator circuit would be minimized, a plot of the indicator current vs. the potential was made. The indicator current at various applied potentials was determined in both blank and titration solutions after chlorine was generated. These curves were flat in the range below 275 mv. An indicator potential of 250 mv. was chosen for most of this study.

Indicator Current Behavior. The indicator current at applied potentials of 140 to 400 mv. was determined for cells containing various concentrations of iodide, chloride, cyanide, and perchloric acid at timed intervals during the coulometric titration. In these cells an initial indicator current of three to ten mu a was observed. This current was slightly larger than that observed in the blank solutions.

Wooster, Farrington, and Swift (19) reported that an initial current was found in all the titration solutions used in their investigation of the coulometric determination of iodide by oxidation to iodine monochloride. They attributed this current to the air oxidation of the iodide. Relatively small indicator currents, (1 to 3 mu a), were reported when iodide solutions 0.005 to 0.01 VF in sodium carbonate were used, and when these solutions were not added to the acid titration solution until immediately before the titration. Their procedure was adopted for this investigation. In some cases the titration was not performed immediately after the iodide was added, and the initial current was as high as 15 mu a. In these cases the results were lower than the calculated value by 1 to 5%. If the initial current was greater than that of the blank by more than 3 mu a, the determination was discarded.

An iodine minimum in the amperometric current, such as that shown in Figure 2, was found when a cell containing 50 ml. of a solution 2.0 VF in perchloric acid, 0.005 VF in sodium cyanide, 0.10 VF sodium chloride, and 3.671×10^{-5} VF in iodide was titrated with chlorine at applied potentials of 250, and 300, and 400 mv. The minimum decreased with increased potential. This agrees with the results reported by Rowley (21) in a study of the behavior of the amperometric current during the oxidation of iodide to iodine monochloride. At 300 mv. no minimum occurred when the iodide concentration was increased to 9.178×10^{-5} VF, while the other concentrations were kept constant; as is shown in Figure 3.

In Figure 2 a qualitative picture of the stepwise oxidation of iodide with chlorine in acid cyanide solutions is given. Initially, the current was dependent upon the diffusion of iodine to the indicator anode and the current increased with the generation time. A maximum was attained when the iodine and iodide concentrations were electrolytically equivalent; then the current decreased to an "iodine

Figure 2.

Indicator Current Behavior

Solutions: 5 ml 3.671 x 10^{-4}VF NaI, in 50 ml of solution 1.8 VF in $HClO_4$, 0.005 VF NaCN,

○ 400 mv

□ 300 mv

△ 250 mv

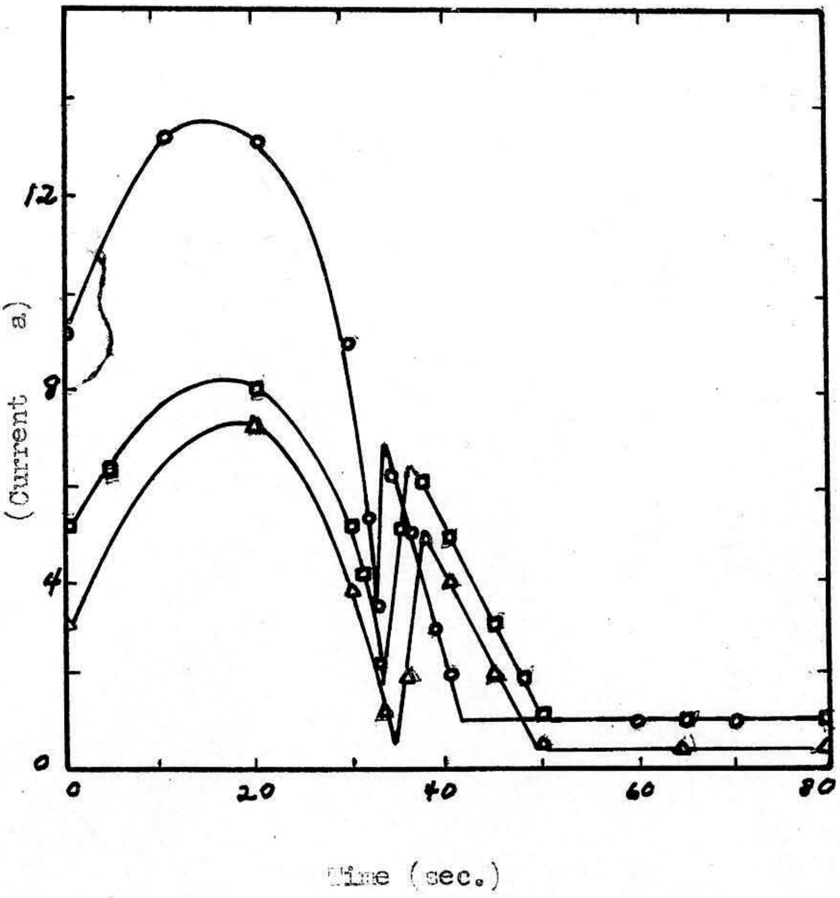


Figure 3.

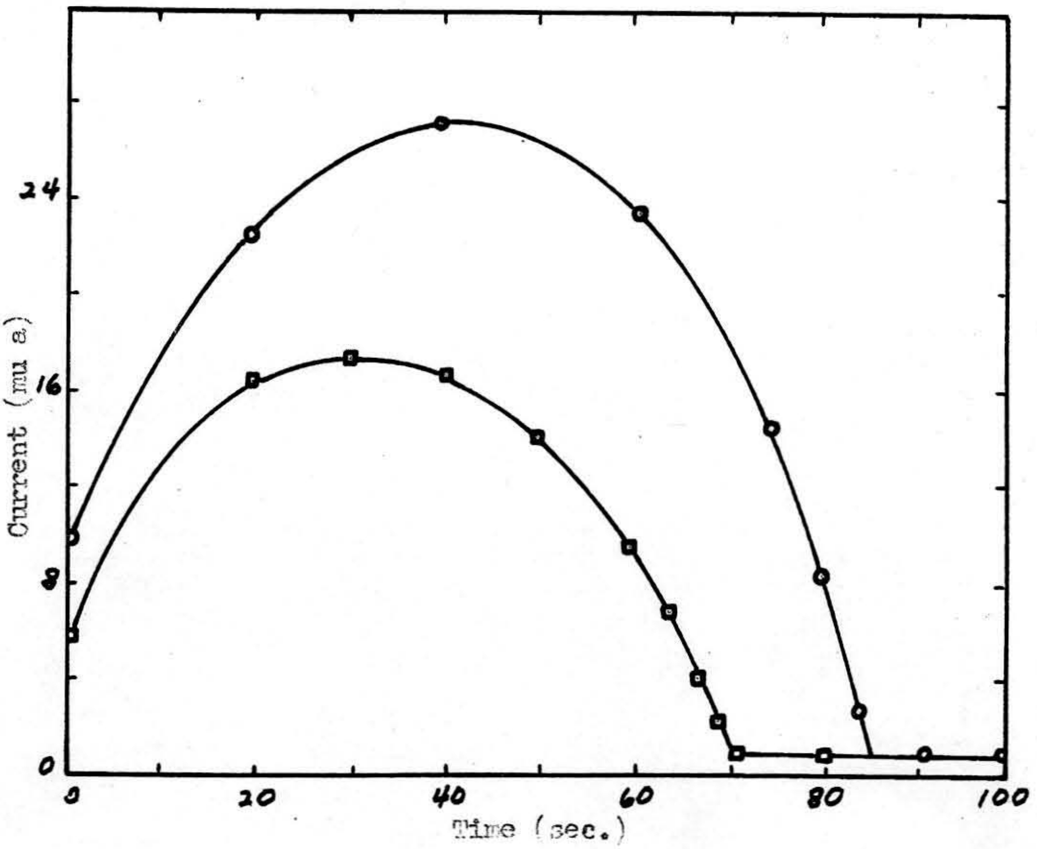
Indicator Current Behavior

Cell Solution: 1.8 VF in $HClO_4$, 0.005 VF NaCN,

and 0.20 VF NaCl in 50 ml solution.

○ 4.5×10^{-7} moles iodide

□ 3.6×10^{-7} moles iodide



minimum" as the iodide that diffused to the indicator cathode became current limiting. The current minimum would have been zero if only iodine was present; however, due to disproportionation of iodine the minimum was greater.

Upon further oxidation, iodine monocyanide was formed and the current increased to a maximum where the iodine and the iodine monocyanide concentrations were equivalent. With further oxidation the iodine concentration again was current limiting, and the current decreased to the constant value characteristic of the chlorine-chloride couple in acid cyanide solutions. The point of initial constant current was taken as the end point in all of these iodide titrations.

Elimination of Blank Correction. In an attempt to eliminate the necessity of a blank time correction, preliminary titrations of known amounts of iodide ion were made, and an additional quantity of iodide then added to the same cell. In those cases in which the additional iodide was added after the initial end point had been reached, no adequate generation time correction could be made. Evidently the reaction which caused the background current was not completely reversible. When the unknown was added before the initial end point, a blank correction was again necessary, and the procedure had no advantages.

Titrations. Oesper (1) reported that the ratio of hydrogen cyanide to hydrochloric acid must be controlled in the macro determination of iodide by oxidation to iodine monocyanide. This ratio probably is not as critical, however, as is the need to have sufficient hydrogen ion to prevent hydrolysis and to have cyanide present to form iodine monocyanide. If these conditions are met, iodide should be quantitatively oxidized to the unipositive state. The adjustment of the conditions in order to obtain satisfactory conditions for the coulometric determination are discussed below under separate headings.

Effect of Hydrogen Ion and Hydrogen Cyanide. The results of a series of analyses in which the hydrogen ion concentration was varied from 2.8×10^{-10} to 1.8 VF, and the cyanide concentration from 0.01 to 0.40 VF are given in Table III. The accuracy and precision of these titrations were at a maximum when the cyanide concentration was greater than 0.05 VF; and the hydrogen ion concentration was in the range 0.02 to 0.40 VF. At relatively high acid concentrations, 0.9 to 1.8 VF in perchloric acid, the results of the determinations were about 2% lower than calculated; this could be due to air oxidation of the iodide.

Titration of Iodide Ion in the Presence of Sodium Bromide. The results of the titrations in which known amounts of iodide were determined in bromide concentrations from 1.8×10^{-4} to 0.2 VF are shown in Table IV. The accuracy and precision of the results were the same as those determinations made with similar amounts of iodide in which no bromide was

Table III

Effect of Hydrogen Ion and Hydrocyanic Acid Concentrations Upon the Determination of Iodide as Iodine Monocyanide

Iodide ion present, 1.164 mg.

Series	No. of Expts.	$[H^+]$(VM)	HCN(VM)	Iodide Found (mg.)	Ave. Error (%)	Ave. Dev. (%)
1	2	1.8	0.01	1.158	-0.47	0.125
2	12	0.9	0.01	1.167	0.25	0.38
3	3	0.9	0.01	2.945*	0.36	0.42
4	28	0.65	0.25	1.164	0.02	0.11
5	3	0.80	0.10	1.167	0.22	0.14
6	6	0.125	0.10	1.164	0.00	0.02
7	5	0.35	0.10	2.960*	0.87	0.17
8	4	0.10	0.05	1.164	0.00	0.00
9	7	0.02	0.05	1.155	-0.80	0.08
10	6	1.1×10^{-9}	0.035	1.161	-0.28	0.16
11	4	2.8×10^{-10}	0.035	1.153	-0.92	0.61
12	8	0.20	0.20	1.172	0.65	1.40
13	4	0.30	0.30	1.157	-0.58	0.06
14	4	0.40	0.40	1.165	0.05	0.17

*2.935 mg. iodide present.

Table IV

Titration of Iodide Ion in Presence of Bromide Ion

Iodide present, 1.164 mg.

Series	No. of Titrations	H^+(VM)	HCN(VM)	Br^-(VM)	Cl^-(VM)	% Error	Standard Dev.
D	4	0.04	0.10	0.00018	0.2	0.03	0.05
E 1	4	0.04	0.10	0.2	0.2	0.00	0.00
2	3	0.80	0.10	0.2	0.2	0.00	0.00
3	4	0.9	0.01	0.2	0.2	2.5	1.3
F 1	4	0.9	0.01	0.2	0.0	-1.7	0.2
2	4	0.09	0.05	0.2	0.0	-0.01	0.02

present. As can be predicted from the half-cell potentials, it was found that bromine can be used as a substitute for chlorine as the intermediate in the determination of iodide by oxidation to iodine monocyanide. The titration curves obtained by this substitution were similar to those obtained with electrolytically generated chlorine. Titrations in which only trace amounts of bromide were present were unchanged. Therefore, iodide could be determined in the presence of bromide with no additional difficulty.

Confirmatory Titrations. The results of the confirmatory analyses are given in Table V. In these determinations the hydrogen ion concentration was varied from 0.100 to 0.65 VM, and the cyanide concentration was varied from 0.05 to 0.25 VM. These analyses demonstrate that samples which contain milligram quantities of iodide can be determined with an accuracy greater than 0.2%. A wider range was not attempted because of the nature of the determination. Although the accuracy of the analyses tested was high, the sensitivity of the indicator system was quite low. The changes in the indicator current could be read more conveniently on a more sensitive meter. However, the confirmatory analyses do demonstrate that accurate, precise titrations are feasible with the equipment that was used in this investigation.

Table V

Confirmatory Titrations

Titration Solutions: 50 ml. of solution;

A is 0.65 VM in H^+, 0.25 VM in HCN;

B is 0.125 VM in H^+, 0.10 VM in HCN;

C is 0.10 VM in H^+, 0.05 VM in HCN.

Iodide present, 1.1640 mg.

Series		No. of Titrations	Iodide Found, mg.	% Error	Standard Dev.
A	1	5	1.1636	-0.04	0.13
	2	7	1.1653	0.11	0.05
	3	5	1.1659	0.16	0.12
	4	10	1.1638	-0.02	0.01
B		6	1.1640	0.00	0.03
C		4	1.1640	0.00	0.00

Recommended Procedure. In view of the results of this study, the following procedure is recommended for the titration of iodide to iodine monocyanide by means of electrolytically generated chlorine.

Blank titrations should be made at an applied potential of 250 mv. in cells which contain 50 ml. of a solution 0.09 VF in perchloric acid, 0.05 VF in sodium cyanide, and 0.20 VF in sodium chloride. An alternate blank solution would be the above plus a small known quantity of iodide. Blank titration times should agree within 0.2 second before analyses of unknown iodide solutions are made.

Determinations of the unknown should be made in cells which contain the same constituents as the blank solution in the same concentrations and a known volume of the iodide sample. The initial indicator current should be noted, and the indicator current recorded at intervals during the titration. It is recommended that the first determination be qualitative in order to determine the approximate end point. In subsequent determinations, indicator readings would be taken so as to bracket this end point. An analysis accurate to 0.2% is feasible by this method.

Part II B

The Generation and Determination of Lead(IV) and the Coulometric Titration of Glycols with Lead(IV)

Introduction

Lead tetraacetate is often used as an oxidizing agent for preparative organic synthesis (22). Its oxidizing properties are applicable for reactions involving dehydrogenation; substitutions of acetate for hydrogen in organic molecules; addition of two acetylated hydroxyl groups to a double bond; and for the cleavage of glycols.

Glycol cleavage by electrolytically generated lead(IV) was attempted in this investigation. It was hoped that the reaction would proceed quantitatively and rapidly and that an amperometric end point could be developed for the determination of glycols. It was hoped that such determinations would be simpler and faster than the methods now in use. Furthermore, it was believed that such an application would lead to a more widespread interest in and use of coulometric techniques in preparative and quantitative organic chemistry.

Experimental

Reagents. Reagent grade chemicals were used throughout this study.

A 0.4 VF (volume formal; formula weights per liter) ferric nitrate solution was prepared by weight.

Ferric acetate solution was made by dissolving ferric sulfate in 250 ml. of glacial acetic acid which was 1.0 VF in sodium acetate. A calculated excess of barium acetate was added, and the resulting barium sulfate removed by centrifugation. Tests showed that no sulfate remained in solution. The solution was then diluted to 500 ml. with water, thus making the final solution 1 VF in ferric acetate, 0.50 VF in sodium acetate, and 50% acetic acid.

Both 0.5 VF lead diacetate and 0.5 VF sodium acetate in glacial acetic acid were prepared by weight.

Standard ethylene glycol solutions were prepared by dilution. A standard propylene glycol solution was prepared in the same way.

Erythritol anhydride was prepared by refluxing erythritol with 50% sulfuric acid according to the method described by Henninger (23). The distillate was not checked for purity because the solution was used to determine only the general behavior of the product. This solution was approximately 0.001 VF in erythritol anhydride.

Apparatus. The coulometric apparatus that was built and described by G. M. Arcand (24), was used in this investigation. The generation rate was 1.0045×10^{-7} equivalents per second.

The external generator shield was filled with 0.5 VF sodium acetate in glacial acetic acid solution in order to prevent diffusion from the titration into the electrode compartment during titrations.

Blank Titrations. Blank solutions were prepared in 40 x 80 cm. weighing bottles by mixing appropriate quantities of lead diacetate, sodium acetate, and ferric acetate, or nitrate, solutions and then diluting the mixture to 50 ml. All these solutions had been checked and found free of oxidizing or reducing agents.

In one type of blank correction ferrous ion was generated for timed intervals and the indicator current was noted and recorded. In subsequent titrations it was found that if both this current and the current in the titration solution, as functions of the time of generation, were extrapolated to zero, or if the indicator current in the titrated solution were extrapolated to the initial current of the blank solution, equivalent corrections were made.

In the other type of correction, lead(IV) was generated for the period that it would be in the subsequent glycol titration, and then back-titrated with ferrous ion. In this type the indicator current was extrapolated to zero, and the blank time correction was the difference between this time and the total time of lead(IV) generation.

These blank corrections were equivalent for the subsequent titrations. However, since the last type was by a procedure similar to that used for the glycol titrations, it was adopted for most of the experimental glycol determinations.

Pre-titration of Solution. Attempts were made to pre-titrate solutions by means of the alternate electrolytic generation of lead(IV) and iron(II) in the same solution, that is, by use of the dual intermediate system. If successful, this would have eliminated the need for separate blank titrations.

Titrations were made in solutions 40 to 80% acetic acid, 0.04 to 0.10 VF in iron(III), 0.10 VF in lead(II), and 0.05 VF in sodium acetate. Lead(IV) was generated for intervals of 50 to 100 sec., then the generation polarity was reversed and iron(II) generated to beyond the end point. This procedure was repeated several times in each cell. In general, the first end point was within 0.2% of the calculated value; however, subsequent titrations were not as accurate.

Selection of the Indicator Potential. In a preliminary experiment ferrous ion was generated in a blank solution for timed intervals. The indicator current at selected applied potentials was plotted as a function of the potential. The indicator current at any potential from 150 to 400 mv. was satisfactorily constant for an amperometric end point; therefore, applied potentials of both 150 and 250 mv. were used in the indicator system for these titrations.

Data and Discussion

The Dual Intermediate. Preliminary experiments showed that the lead(II)-lead(IV) couple in acetate solution was not sufficiently electrode-reactive to give a current satisfactory for use in an amperometric end point. Furthermore, qualitative experiments showed that it would be desirable to have an excess of lead(IV) present in the glycol titrations. A study was initiated to find a dual intermediate system for which an amperometric end point would be feasible. It would then be possible to generate an excess of lead(IV), and to determine that excess by means of the second intermediate.

The cuprous-cupric, couple, which has been used with the bromide-bromine couple as a dual intermediate (26), was unsatisfactory. A halide was necessary to form a stable cuprous complex, but the halides also formed lead(II) salts which precipitated. These salts interfered with the operation of the generator and indicator systems.

The ferrous-ferric couple proved to be a satisfactory intermediate. Ferrous ion does not react with dipositive lead, and it was found that it could be generated with 100% current efficiency if the ferric ion concentration was approximately 0.05 VF or greater. The indicator current sensitivity, which varied from 0.25 to 1.0 ua per second of generation, was low, but adequate for this study.

Lead dioxide plated out on the generator electrode when the acetic acid concentration was less than 20%. This precipitation was prevented by increasing the acetic acid concentration.

Current Efficiency. In coulometric titrations, it is essential that the current efficiency be known, and it is preferable that it be 100% (25). In glacial acetic acid solutions, as determined qualitatively from readings of the generator ammeter, the current passing through the system when lead(IV) was generated was only one-third of the current found when the generator system had been calibrated in an aqueous system. The addition of sodium acetate to the solutions increased these readings to the calibrated value.

Several attempts were made to determine the current efficiency of the system quantitatively. Potassium iodide and a small excess of a standard solution of sodium thiosulfate were added to a cell in which tetrapositive lead had been generated for a known interval. Then iodine was generated to an amperometric end point. However, a precipitate of lead diiodide formed which caused erratic indicator currents and prevented the determination of an accurate end point.

Another method that was used in an attempt to determine the current efficiency was the generation of larger amounts of lead(IV). Potassium iodide was added to the solution and the iodine was titrated with standard sodium thiosulfate to an iodine-starch end point. Lead iodide masked the end point and may have adsorbed iodine. The results were approximately ten per cent lower than calculated.

After the ferrous-ferric couple had been adopted as the secondary intermediate, the current efficiency was checked by the generation of tetrapositive lead followed by the generation of ferrous ion to an amperometric end point. These titrations indicated a current efficiency of 100 ± 0.1%.

Determination of Tetrapositive Lead. Tetrapositive lead was generated for from 25 to 150 sec. in a cell which contained 50 ml. of a solution 0.05 VF in lead diacetate, 0.10 VF in ferric acetate, and 0.05 VF in sodium acetate. The polarity of the generator system was reversed and ferrous ion generated to the end point. The data from these experiments showed that the titration is accurate to 0.15%. The data are given in Table VI. The results also indicated that the lead-iron couples form a satisfactory dual intermediate system, and that titrations such as these would be satisfactory for the determination of unknown quantities of lead(IV).

The Titration of Glycols. Titrations were made with concentrations of acetic acid of from 20 to 80% in the 50 ml. solutions, with ferric ion concentrations from 0.04 to 0.3 VF, and with various glycol concentrations. It has been reported (27,28) that water increases the rate of the reaction of glycols with lead tetraacetate, and that in the presence of water the reaction results in quantitative

Table VI

The Determination of Lead(IV) by Ferrous Ion

Titration Solutions: Total volume 50 ml. 40% acetic acid, 0.05 VF in lead acetate, 0.10 VF in ferric acetate and 0.10 VF in sodium acetate.

Lead(IV) Generated (mu g)	Number of Determinations	Lead(IV) Found (mu g)	Average Dev. (Parts/1000)
26.01	4	26.22	1.0
52.02	10	52.02	1.4
104.04	2	103.99	0.5
156.06	2	156.48	0.7

oxidation of glycols to aldehydes; therefore, water was used in these titration solutions. The reactions for the titrations of glycols are:

$$2CH_3CO_2^- + Pb(C_2H_3O_2)_2 = Pb(C_2H_3O_2)_4 + 2e^- \qquad (10)$$

$$Pb(C_2H_3O_2)_4 + (ROH)_2 = 2RO + 2HC_2H_3O_2 + Pb(C_2H_3O_2)_2 \qquad (11)$$

$$e^- + Fe(III) = Fe(II) \qquad (12)$$

$$2Fe(II) + Pb(C_2H_3O_2)_4 = 2Fe(III) + Pb(C_2H_3O_2)_2 + 2CH_3O_2^- \quad , \qquad (13)$$

where $(ROH)_2$ is a glycol.

In most cases, after the blank correction had been determined, an excess of tetrapositive lead was generated in the titration solution, and then five to thirty minutes was allowed for reaction 11 to take place. The back titration with ferrous ion was then made.

Determination of Ethylene Glycol. Ethylene glycol was studied first. The ethylene glycol solution was standardized by macro determinations in which known volumes of the ethylene glycol solution were added to a standard solution of lead tetraacetate. Potassium iodide was added, and the iodine that was formed was titrated with standard thiosulfate to an amperometric end point. In other cases a potentiometric end point was used.

The titrations described above were then carried out with various amounts of ethylene glycol present. In all cases reaction 11 was slow and did not go to completion. The amount of ferrous ion required was dependent both upon the amount of lead(IV) generated and the time allowed for reaction 11 to take place. In some cases the cell was heated, but the results were similar. An equilibrium constant for reaction 11, based on the concentrations of the cell constituents before the generation of ferrous ion, was calculated for each titration. The values obtained ranged from 0.25 to 7.0, so that no constant can be reported.

Experiments that verify these conclusions were made over a ten-fold change in the ethylene glycol concentration. The effects of a twelve-fold change in the total quantity of lead(IV) generated was investigated. In some cases a large excess of lead(IV) was generated; in others, a large excess of ethylene glycol was present in the titration solution. The data from this work, shown in Table VII, were used to reach the above conclusions.

Determination of Propylene Glycol. It was hoped that the behavior of ethylene glycol, as the first member of the series, was anomalous to the glycol series. Therefore, propylene glycol was used for some titrations. In Table VIII the data from these determinations are given. The same type of equilibrium as was found in the ethylene glycol

Table VII

The Determination of Ethylene Glycol

Titration Solutions: Total volume 50 ml. of 40% acetic acid and 0.10 VF in lead acetate, 0.10 VF in sodium acetate, and 0.08 in ferric nitrate.

Ethylene Glycol Present (sec.)	Lead(IV) Generated (sec.)	Number of Trials	Ethylene Glycol Found (sec.)	K[a]
63.8	50.0	1	14.7	0.50
	75.0	2	27.0	1.7
	100.0	3	22.0	0.61
	150.0	1	35.3	2.7
	200.0	3	43.2	2.3
	300.0	2	68.5	---
127.6	100.0	1	22.7	0.25
	200.0	4	46.3	0.71
	250.0	2	64.5	1.4
	300.0	2	68.7	2.4
319.0	300.0	1	95.2	0.41
	400.0	3	139.0	1.6
	500.0	2	164.0	2.1
	600.0	2	208.2	4.0
638.0	225.0	7	184.3	7.0
	250.0	4	193.9	6.1
	300.0	4	222.0	6.0

[a] $K = (CH_2O)^2/[Pb(IV)][C_2H_4O_2H_2]$.

Table VIII

Titration of Propylene Glycol

Titration Solutions: 0.10 VF in lead acetate, 0.08 VF in ferric nitrate, total volume 50 ml. 40% acetic acid which contained 10.00 ml. of propylene glycol solution.

Pb (IV) Gen. (sec.)	Number of Trials	Pb (IV) Found (sec.)	Glycol Found (Calc.) (sec.)
150.0	1	90.6	59.4
200.0	2	125.3	74.7
250.0	1	161.9	88.1
300.0	2	191.2	108.8
400.0	2	238.7	161.3

titrations was observed. Evidently, reactions between lead(IV) and glycols are slow and not complete at low concentrations.

Determinations of Erythritol Anhydride. Reeves (29) reported that the direct titration of macro quantities of cis-glycols with lead tetraacetate is feasible. He claimed that this reaction is sufficiently rapid to be followed potentiometrically with both lead and platinum electrodes. He also reported that erythritol anhydride was determined in the same way. However, as is shown by the data tabulated in Table IX, such titrations of the anhydride were not successful at low concentrations of the reactants. Apparently the same type of equilibrium existed as in the cases cited previously.

Conclusions. The investigation was discontinued at this point. Although successful titrations of glycols have not been made, a method for the preparation of standard lead(IV) and a coulometric method of standardization have been developed. A glycol determination might be made by adding a known quantity of standard lead(IV) solution to a glycol in glacial acetic acid, and after sufficient time has been allowed for the reaction to occur, titrating the excess lead(IV) coulometrically with ferrous ion. Such a technique should be comparable to those now in use (2).

The lead(II)-lead(IV) couple, with the ferrous-ferric intermediate, should be useful in other redox systems. It would probably be necessary to investigate the possibilities

Table IX

Titration of Erythritol Anhydride

Titration Solutions: 0.10 VF in lead acetate, 0.20 VF in ferric acetate, total volume 50 ml. which is 40% acetic acid and contained 10.00 ml. of erythritol anhydride solution.

Total time Lead(IV) Generated (sec.)	Erythritol Anhydride Found (sec.)	Time Waited for Equilibrium (min.)
200.0	75.3	0
	71.5	5
	71.8	5
	68.4	15
	69.8	30
	88.4	210
	91.7	240
250.0	96.7	30
300.0	111.8	0
	103.2	5
	104.4	5
	106.1	30
	106.2	30
500.0	187.2	0
	175.7	30

of this dual intermediate more closely. Particularly in the pre-titration of lead(IV) with iron(II), the effect of the exclusion of air should be checked. Although this was not of primary importance in the investigation above, since the results were low, the use of accurate pre-titration could well be an asset in other systems. The lead-iron system should be of value in cases where an excess of oxidant is required because of the slowness of the main reaction. It is hoped an application for the system will be found.

Part III

The Mechanism of the Precipitation of Metal Sulfides by Thioacetamide in Acid Solutions

Part III A

The Precipitation of Cadmium Sulfide from Acid Solutions by Thioacetamide*

Introduction

Swift and Butler (30) have studied the precipitation of lead sulfide from solutions similar to those used in this investigation. They found that at pH values less than approximately three the rate of precipitation was hydrolysis controlled and was first order with respect to both the thioacetamide and the hydrogen ion concentrations. The precipitation of lead sulfide at higher pH values was governed by a direct reaction which was dependent upon the lead ion and on the thioacetamide concentrations to the first order, and on the hydrogen ion to the inverse half order. In a subsequent investigation of the precipitation of tripositive arsenic (31) no evidence was found for other than the hydrolysis controlled reaction. Studies of the rates of precipitation of other metal sulfides are being made in the hope of obtaining a better understanding of the general principles governing these reactions and a rational basis for the analytical use of thioacetamide as a homogeneous phase precipitant for metal sulfides. Studies

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*Submitted to Anal. Chem.

of the coprecipitation effects resulting from such use of thioacetamide have been initiated.

Experimental

Reagents. Thioacetamide solutions, 1.00 VF (volume formal, formula weights per liter) were prepared from Baker's Lot No. 9260 Reagent Grade thioacetamide. This particular material gave clear, colorless solutions. These solutions were never kept more than two weeks.

Reagent grade chemicals were used throughout.

Standard 0.05 VF potassium iodate solution was prepared by weight. Sodium thiosulfate solutions, 0.05 VF, were standardized against this solution.

A 0.10 VF cadmium nitrate solution was used. Since the initial cadmium ion concentration was determined in each experiment, no standardization was made.

The 6 VF hydrochloric acid solution was prepared from a concentrated acid solution which was shown to be free from oxidizing agents.

The sodium formate-formic acid buffer solutions containing a constant sodium formate concentration were prepared from sodium hydroxide solutions and 90% formic acid. Solutions of various concentrations of formic acid were prepared and added to equal volumes of the sodium hydroxide solutions and then diluted to the same final volume. These buffers were used in the investigation of the rate of the direct reaction.

Apparatus. The apparatus used for the experiments at 90°C. was essentially that described by Swift and Butler (30). Nitrogen was not bubbled through the reaction solutions.

In the experiments at 25°C. the reaction solutions were placed in ground-glass stoppered flasks.

Procedure. The reaction solutions were prepared by the following method. Measured volumes of stock solutions of thioacetamide, cadmium nitrate, and acid or buffer were mixed and diluted to 100 ml. in the reaction vessel. The initial ionic strength was constant for each series of experiments. The reaction solution was then placed in a constant temperature bath.

At timed intervals approximately 12 ml. of the reaction solution were removed from the vessel, immediately cooled in an ice bath, and centrifuged to remove any cadmium sulfide. Duplicate 5.00 ml. portions of each sample were taken from the clear centrifugate and transferred to 15 x 125 mm. test tubes.

An excess of ammonium hydroxide was added to each test tube and the solution was placed in a bath of hot water in order to coagulate the cadmium sulfide precipitate. Then the mixture was cooled, the sample centrifuged, and the centrifugate carefully drawn off. The precipitate was washed with 2 ml. portions of 3 VF ammonium sulfate solution until the wash solution was sulfide free.

The precipitate was washed into a 100-ml. conical flask;

then water, potassium iodide, standard potassium iodate solution, and hydrochloric acid were added, and the solution titrated with standard sodium thiosulfate. This method was checked by the analysis of cadmium nitrate solutions with quantities of cadmium similar to those involved in the investigation. The average deviation in the results was less than one part per hundred.

Data and Discussion

Qualitative experiments indicated that the rate of precipitation of cadmium sulfide from acid solutions by thioacetamide reached a minimum at a pH of approximately 3. This indicated that as with lead(II) (30), two types of reactions were involved in the precipitation. Hereafter these two types will be designated as the hydrolysis controlled and the direct reaction precipitations.

Quantitative rate measurements were then made. The reactions were carried out at 90°C. in order to obtain an easily measurable rate of precipitation.

The Hydrolysis Controlled Precipitation. The rate of precipitation of cadmium sulfide from solutions of pH 1 and 2 was found to be independent of the cadmium ion concentration and was first order with respect to both the hydrogen ion and the thioacetamide concentrations. This indicates that the precipitation is controlled by the hydrolysis of the thioacetamide; also that there is rapid precipitation of the cadmium by the hydrogen sulfide thus formed. If this is true, the rate expression for the hydrolysis of thioacetamide

$$-\frac{d[CH_3CSNH_2]}{dt} = k[CH_3CSNH_2][H^+] \qquad (14)$$

where k has the value 0.21 liter $mole^{-1}min.^{-1}$ at 90°C. (30) should also be the rate expression for the precipitation of cadmium(II).

Table X shows a comparison of the measured cadmium(II) concentrations at various times with those calculated from expression 14; the assumption is made that all the hydrogen sulfide from the hydrolysis reacted rapidly with cadmium(II). The agreement between the experimental and the calculated values is well within that of the experimental errors. As in the case of lead(II) (30) no evidence was found of any catalysis or inhibition of the reaction by cadmium ion or by the cadmium sulfide precipitate.

Experiments at pH 1 and pH 5.7 with solutions containing the sodium formate-formic acid buffer constituents, were carried out at 90°C. These experiments were made to determine whether the presence of the buffer constituents would cause a change in the reaction mechanisms. No such change was observed; the rates of the precipitations conformed to the hydrolysis controlled mechanism at pH 1 and the direct reaction mechanism at pH 5.7 and with no change in the velocity constants for these reactions.

Table X

The Hydrolysis Controlled Precipitation of Cadmium Sulfide

Comparison of measured cadmium(II) concentration with that calculated from the expression $-\frac{d[Cd(II)]}{dt} = k[H^+][CH_3CSNH_2]$, where k = 0.21 liter $mole^{-1}$ min^{-1}.

Initial CH_3CSNH_2, 0.10 VF; temperature, 90°C.

Initial perchloric acid, 0.10 VF.

Time, Min.	Cadmium(II), Moles/Liter Found	Calculated
0.0	0.0062	---
0.75	0.0045	0.0046
1.75	0.0024	0.0024
2.42	0.0011	0.0010
Initial perchloric acid, 0.010 VF.		
0.0	0.0088	---
5.00	0.0071	0.0073
7.50	0.0064	0.0065
10.00	0.0058	0.0059
12.50	0.0049	0.0049
15.00	0.0038	0.0038

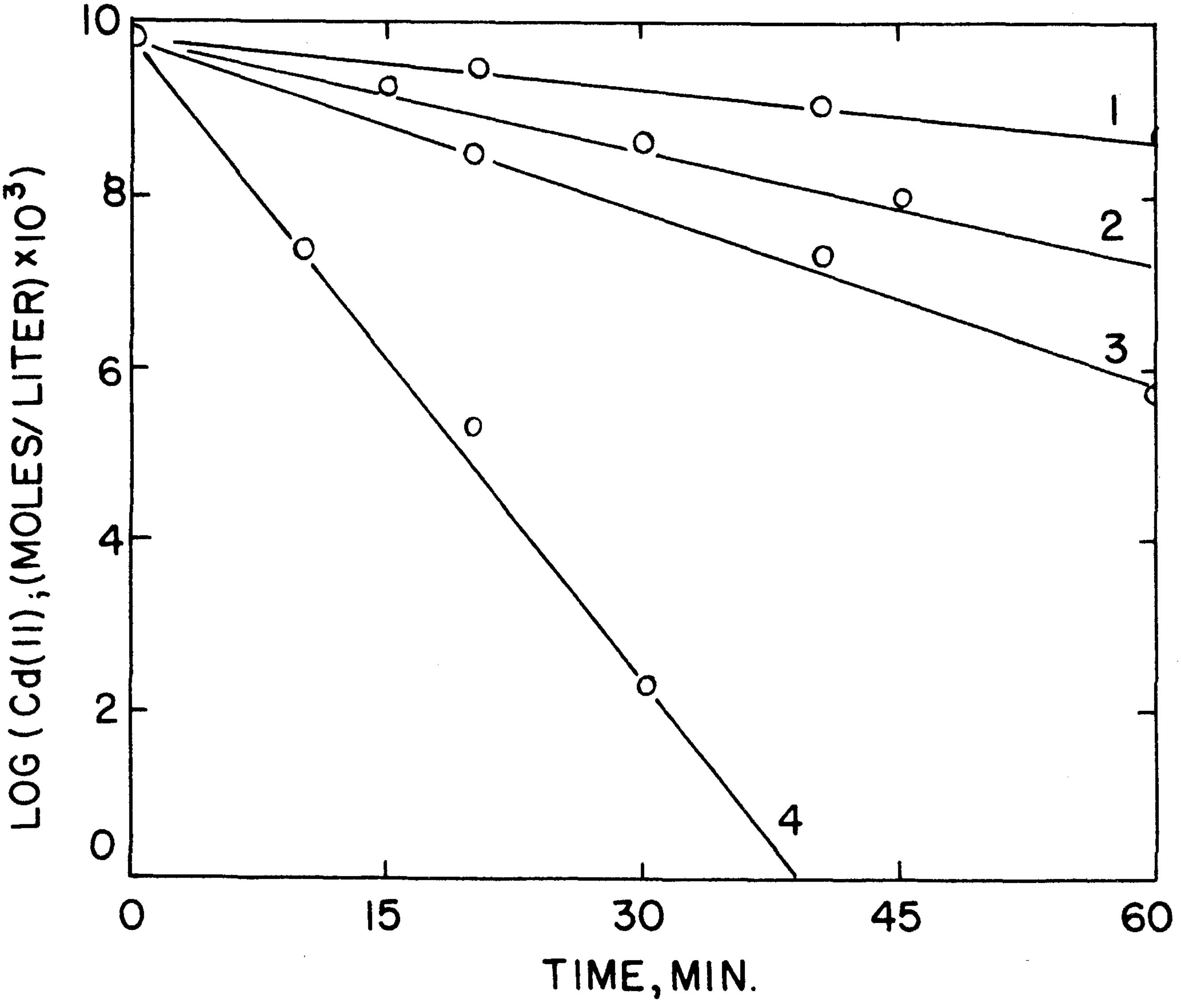
The Precipitation by the Direct Reaction. Formic acid-sodium formate buffers were used in experiments carried out in the pH range 6.3 to 3.3. These were designed to study any direct reaction similar to that found with lead(II) and to show the effect of the hydrogen ion concentration, the cadmium ion concentration, and the thioacetamide concentration upon such a reaction.

Effect of Cadmium Ion Concentration. The plots of the logarithm of the cadmium(II) concentration against the time for the various hydrogen ion concentrations were linear as shown in Figure 4; from this it was concluded that the reaction is first order with respect to the cadmium ion concentration.

Effect of Hydrogen Ion Concentration. The study of the effect of hydrogen ion was made with solutions in which the total ionic strength, the thioacetamide, and the cadmium ion concentrations were all initially constant while the hydrogen ion concentration was varied. The range of hydrogen ion concentrations investigated was from 5.0×10^{-4} to 5×10^{-7} VF. Rate constants calculated from the data obtained are shown in Table XI, and show that in this concentration range the rate of precipitation is dependent upon the inverse half power of the hydrogen ion concentration. This dependence is the same as that found previously for lead(II) (30).

Figure 4. Effect of the cadmium ion concentration upon the rate of precipitation of cadmium sulfide at 90°C.

Solutions initially 0.01 VF in cadmium(II); 0.10 VF in thioacetamide



1. pH 3.38
2. pH 3.92
3. pH 4.56
4. pH 5.70

Table XI

Effect of Hydrogen Ion Concentration upon the Rate of Precipitation of Cadmium Sulfide

Initial cadmium(II), 0.010 VF; thioacetamide, 0.10 VF

$[H^+]$	$-\frac{d[Cd(II)]}{dt} \cdot \frac{[H^+]}{[Cd(II)]}$		$-\frac{d[Cd(II)]}{dt} \frac{[H^+]^{1/2}}{[Cd(II)]}$	
	25°C.	90°C.	25°C.	90°C.
4.8×10^{-4}	35×10^{-10}	18×10^{-7}	1.6×10^{-7}	8.1×10^{-5}
1.2×10^{-4}	14×10^{-10}	9.1×10^{-7}	1.3×10^{-7}	8.4×10^{-5}
2.8×10^{-5}	6.1×10^{-10}	4.3×10^{-7}	1.2×10^{-7}	8.1×10^{-5}
2.0×10^{-6}	1.6×10^{-10}	1.1×10^{-7}	1.1×10^{-7}	7.8×10^{-5}
5.0×10^{-7}	--	0.6×10^{-7}	--	8.2×10^{-5}
		Average	$(1.3 \pm 0.2) \times 10^{-7}$	$(8.1 \pm 0.2) \times 10^{-5}$

Effect of Thioacetamide Concentration. The effect of the thioacetamide concentration upon the rate of the reaction was investigated over a range of thioacetamide concentrations of 0.05 to 0.30 VF. Rate constants calculated from the data obtained from these experiments are given in Table XII. The rate of precipitation is dependent upon the thioacetamide concentration to the first power.

Effect of Chloride Ion. It was found that chloride ion decreased the rate of the reaction. With the formal concentration of chloride five times that of the cadmium the rate found was only fifty per cent of that calculated. A quantitative investigation of this effect is now in progress.

Temperature Effect on the Direct Reaction. Experiments to determine the dependence of the rate upon the hydrogen ion and cadmium ion concentrations at 25°C. over the pH range from 5.7 to 3.3 were made. The results, which indicate first order dependence upon the cadmium ion concentration, and inverse half order dependence upon the hydrogen ion concentration are shown in Table XI. The rate of precipitation was so slow that the change in the cadmium ion concentration could not be measured with an accuracy greater than approximately ten per cent. Consequently, the calculated constants vary more than those for the experiments at 90°C. However, the data obtained clearly indicates that the mechanism of the reaction is similar to that at 90°C. in the same hydrogen ion concentration range. The calcu-

Table XII

Effect of Thioacetamide Concentration Upon the Rate of Precipitation of Cadmium Sulfide at 90°C.

Initial cadmium(II), 0.010 VF; hydrogen ion, 0.00012 M.

$[CH_3CSNH_2]$ Moles/liter	$-\frac{d[Cd(II)]}{dt}\frac{[H^+]^{1/2}}{[Cd(II)]}$	$-\frac{d[Cd(II)]}{dt}\frac{[H^+]^{1/2}}{[Cd(II)][CH_3CSNH_2]}$
0.050	3.65×10^{-5}	8.2×10^{-4}
0.10	8.3×10^{-5}	8.4×10^{-4}
0.15	10.9×10^{-5}	7.3×10^{-4}
0.20	16.5×10^{-5}	8.4×10^{-4}
0.25	20.2×10^{-5}	8.0×10^{-4}
0.30	23.9×10^{-5}	8.0×10^{-4}

Average $(8.07 \pm 0.3) \times 10^{-4}$

lated velocity constant is $1.3 \pm 0.2 \times 10^{-6}$ liter$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$ minute^{-1}.

The energy of activation for the direct reaction was calculated from data obtained at 25°, 70°, 90°C. A plot of log k versus 1/T was a straight line, thus showing a temperature dependence conforming to the Arrhenium equation. The activation energy was calculated to be 20.8 ± 1.2 kcal. per mole. This datum shows the analytical potentialities inherent in controlling the rate of formation of a cadmium sulfide precipitate by temperature control.

Analytical Considerations. Figure 5 shows the calculated rates of precipitation of cadmium sulfide by the hydrolysis controlled and by the direct reaction in solutions which are 0.10 VF in thioacetamide and 0.010 VF in cadmium(II) at 90°C. and which have the ranges of pH values shown. The direct reaction is dependent upon the cadmium ion concentration; therefore the direct reaction curve will be changed vertically by changes in the cadmium ion concentration.

For solutions having the concentrations specified above the following calculations can be made:

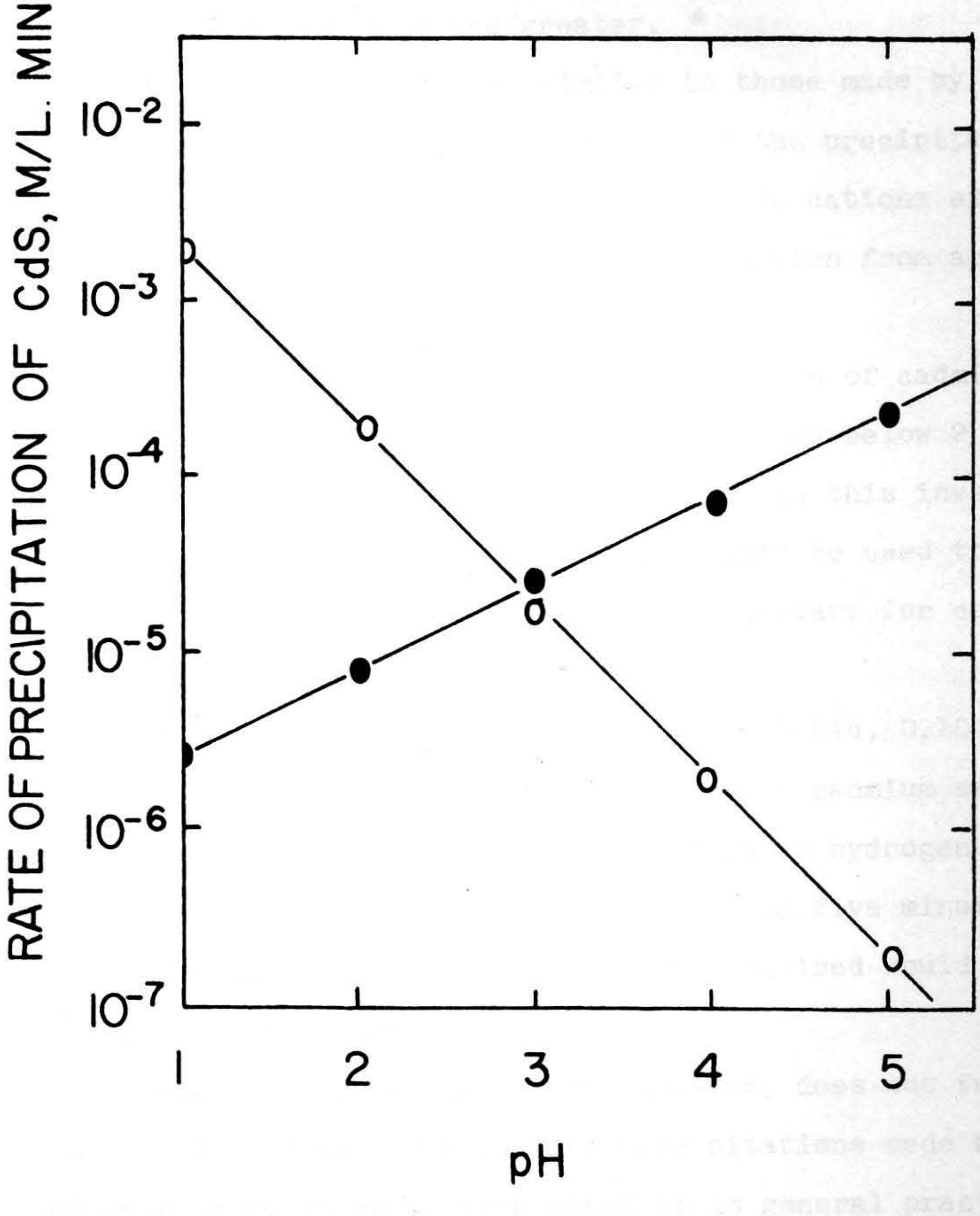
$R_d = R_h$ at pH 2.95, where R_d is the rate of precipitation by the direct reaction, and R_h is the rate by the hydrolysis controlled reaction.

$R_d = R_h/800$ at pH 1.

$R_d = 1250\ R_h$ at pH 5.

Figure 5. Rate of precipitation of cadmium sulfide by thioacetamide as functions of pH.

Solutions initially 0.01 VF in cadmium(II); 0.10 VF in thioacetamide; 90°C.



O Hydrolysis of thioacetamide

● Direct reaction

In solutions of pH 2 and lower precipitation of cadmium sulfide is primarily through hydrolysis. As the pH is raised the direct reaction becomes increasingly important until under the above specified conditions it is predominant at pH values of 4 and greater.

These observations are similar to those made by Swift and Butler (30) in the investigation of the precipitation of lead sulfide by thioacetamide. The two cations exhibit much the same behavior in their precipitation from acid solutions.

If it is assumed that the precipitation of cadmium as the sulfide by thioacetamide in the pH range below 2 is preceded by hydrolysis to hydrogen sulfide, as this investigation indicates, then the data obtained may be used to calculate the conditions which would be necessary for controlled homogeneous phase precipitations.

In a solution 0.1 VF in hydrochloric acid, 0.10 VF in thioacetamide, and initially 0.01 VF in cadmium salt, the time required for the hydrolysis to furnish hydrogen sulfide equivalent to the cadmium present would be five minutes at 90°C. At lower temperatures the time required would be correspondingly longer.

This type of precipitation, however, does not fulfill the conditions used for sulfide precipitations made by means of gaseous hydrogen sulfide since it is general practice to saturate the solution with the gas at atmospheric pressure; this provides an aqueous hydrogen sulfide concentration of approximately 0.1 VF. Complete hydrolysis of the thioacetamide under the above conditions would not saturate the solution; furthermore, at 90°C. the time required for half the thioacetamide to hydrolyze is calculated to be thirty-three minutes. This indicates that care should be exercised in replacing gaseous hydrogen sulfide with thioacetamide without careful investigation; especially is this true where only a "slight excess" of thioacetamide is added.

Barber and Taylor (32) have stated that "the hydrolysis is more rapid in an alkaline solution than in an acid solution of the same strength." It is interesting to note that in a solution having a pH of 6, and in which the initial cadmium ion concentration is 0.010 VF and the thioacetamide 0.10 VF, the time required for half of the cadmium to precipitate by the direct reaction is less than nine minutes at 90°C. In this time and under these conditions the cadmium sulfide precipitated by the hydrolysis controlled reaction would be less than 10^{-6} moles. This indicates that the more rapid precipitation that has been observed at higher pH values could be caused by the direct reaction mechanism rather than an increase in the rate of hydrolysis. An investigation of the hydrolysis of thioacetamide in alkaline solutions is now in progress in this laboratory.

The velocity constant for the precipitation of lead sulfide by thioacetamide in the pH range 5.1 to 3.5 was found by Swift and Butler (30) to be 1.15×10^{-3} liter$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ minute^{-1}, which is 42% higher than the constant for the precipitation of cadmium sulfide in the same pH range. The concentration of cadmium(II) in a saturated solution at a given sulfide concentration should be 52% greater than that of lead(II) in a similar solution (33). There may be some correlation between this increase in solubility and the decrease in the velocity constant. Any such relationship can only be postulated until further investigations in which the velocity constants for the rate of precipitation of other basic cations are determined.

Part III B

The Effect of Chloride on the Precipitation of Cadmium Sulfide from Acid Solutions by Thioacetamide

Introduction

In the experiments discussed in the preceding section of this thesis, it was found that chloride decreased the rate of the reaction of cadmium(II) with thioacetamide to form cadmium sulfide in the pH range 3 to 6. This inhibition could be caused by either no reaction or by a slower rate of reaction between the chloride complex and thioacetamide. Since the inhibition was observed only in the range in which the direct reaction is predominant, it was hoped that this study would provide a more satisfactory explanation of the mechanism of that reaction.

Experimental

Reagents. Thioacetamide solutions, 1.00 VF (volume formal, formula weights per liter), were prepared from Bakers Lot No. 1311 Reagent Grade thioacetamide. It was necessary to filter these solutions in order to remove a small amount of insoluble material. Because of possible decomposition, these solutions were not kept for more than two weeks.

Standard 0.05 VF potassium iodate solution was prepared by weight. Sodium thiosulfate solutions, 0.05 VF, were standardized against this solution.

A 0.10 VF cadmium nitrate solution was used; the initial cadmium concentration was determined in each experiment.

The 6 VF hydrochloric acid solution was prepared from a concentrated acid solution which had been found free of oxidizing agents.

A sodium chloride solution, 0.50 VF, was prepared from the Reagent Grade salt by weight; this solution was diluted as required.

Constant ionic strength was maintained by the addition of appropriate quantities of a 1.00 VF sodium perchlorate solution which had been prepared by weight from the salt.

The stock sodium formate-formic acid buffer solutions were prepared by mixing aliquots of a sodium hydroxide solution with known volumes of 90% formic acid, and then diluting the solution to such a volume that the total sodium formate concentration would be 0.15 VF in each experiment. The hydrogen ion concentration in these buffers was controlled by the amount of excess formic acid which was added.

Apparatus. The apparatus used for the experiments at 90°C. was similar to that described by Swift and Butler(30). Nitrogen was not bubbled through these reaction mixtures.

In the experiments carried out at 25°C., the reaction solutions were placed in ground glass stoppered flasks, then sealed, and placed in a constant temperature bath at 25° ± 1°C.

Procedure. One hundred milliliters of the reaction solution were prepared by mixing water and measured quantities of the stock solutions of cadmium nitrate, thioacetamide, buffer, sodium chloride and sodium perchlorate. All these solutions were initially 0.10 VF in thioacetamide, 0.010 VF in cadmium nitrate, and 0.00005-0.050 VF in sodium chloride. The reaction solution was then placed in a constant temperature bath and samples were removed at timed intervals. In the experiments at 25°C., duplicate 5-ml. samples were taken at intervals of forty-eight hours.

The method of analysis was that described in the preceding section of this thesis.

Data and Discussion

Preliminary experiments at 90°C. indicated that in solutions having a five-fold formal excess of chloride over the initial cadmium(II), the rate of formation of cadmium sulfide was decreased by almost one-half in the hydrogen ion concentration range in which the direct reaction is predominant. It was also found that a two-fold formal excess of chloride over cadmium(II) in the hydrolysis controlled reaction range, pH 1 to 2, did not alter the rate of precipitation of the sulfide. Since the rate of hydrolysis is independent of the cadmium(II) concentration, this result was as expected.

Quantitative rate measurements were made at hydrogen ion concentrations at which the direct reaction is predominant. The chloride ion concentration was kept lower than 0.05 VF because only the first cadmium chloride complex is formed in this concentration range at 25°C. (34), and it was assumed that this is also true at 90°C. Most of this study was done at 90°C. so that the precipitation would occur at an easily measured rate. The results from the preceding study at this temperature and at 25°C. on the direct reaction of cadmium ion with thioacetamide were applicable, so that no additional experiments were needed to determine the general rate expression for the reaction.

Experiments were made at 25°C. to recheck the effect of the chloride complex on the rate of precipitation. The equilibrium constants for the cadmium chloride complexes at 25°C. have been reported (35) so that the composition of the solution could be calculated. However, the rate of precipitation of cadmium sulfide was extremely slow and, hence, difficult to measure accurately. For this reason, the results obtained at 25°C. were used only to confirm those obtained at the higher temperature.

Discussion. An experimental velocity constant for each chloride concentration was calculated from the expression

$$-d[\mathrm{Cd(II)}]/dt = k_3[\mathrm{Cd(II)}][\mathrm{CH_3CSNH_2}]/[\mathrm{H^+}]^{\frac{1}{2}} \qquad (15)$$

The value of k_3 was calculated from the results of a series of at least four measurements at each chloride concentration.

It was assumed that k_3 is the summation of two velocity constants; the first is the constant for the reaction of cadmium ion with thioacetamide, the second is the constant for the reaction of the cadmium monochloride ion with thioacetamide. This can be expressed as

$$k_3[Cd(II)] = k_1[Cd^{++}] + k_2[CdCl^{+}] \quad . \qquad (16)$$

The measurements of k_3 were made at selected time intervals such that the ratio of the two cations had not shifted significantly; so that k_3 would not change.

The calculations at 90°C. will be discussed first. It was assumed that cadmium monochloride reacted very slowly, if at all, with thioacetamide to form cadmium sulfide so that k_1 is much greater than k_2. In the experiments discussed in the preceding section of this thesis, k_1 at 90°C. was found to be 8.1×10^{-4} $\text{liter}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{min}^{-1}$, so that, if this assumption is true, equation 16 may now be written as

$$k_3[Cd(II)] = 8.1 \times 10^{-4}[Cd^{++}] \qquad (17)$$

The assumption was checked by using the values of k_3 found at each chloride concentration to calculate the cadmium ion concentration, and from this value to calculate an equilibrium constant for the reaction

$$CdCl^{+} = Cd^{++} + Cl^{-} \quad , \qquad (18)$$

that is, to find K for the equation

$$\frac{(Cd^{++})(Cl^{-})}{(CdCl^{+})} = K \quad . \tag{19}$$

K has been calculated in this way at each chloride concentration. The results, shown under the heading K_a in Table XIII, varied over fifty fold, and the assumption that the monochloride complex reacts insignificantly appears to be false.

When k_2 is assumed to be significant, it can be calculated from equations 16 and 19, as is shown in the following specimen calculations:

Let x be the cadmium monochloride concentration in a solution which was made 0.0250 VF in chloride, and let y be the cadmium monochloride concentration in another solution which was made 0.050 VF in chloride. Then, 0.010 -x and 0.010-y are the molal cadmium ion concentrations, and 0.0250-x and 0.050-y are the molal chloride concentrations in the two solutions respectively. From equation 19, the equality

$$\frac{(0.01-x)(0.025-x)}{x} = \frac{(0.01-y)(0.05-y)}{y} \tag{20}$$

is derived; and from the data in Table II plus equation 17, two more equalities can be formulated;

$$0.01(4.7 \times 10^{-4}) = 8.1 \times 10^{-4}(0.01-y) + k_2\, y, \tag{21}$$

Table XIII

Calculated Equilibrium Constant for the Reaction

$$CdCl^+ = Cd^{++} + Cl^-$$

at 90°C. at Various Chloride Concentrations

Cl^-, VF	$k_3 \times 10^4$ [a]	K_a [b]	K_b [c]
0.00005	8.0	---	0.00190
0.00050	7.8	0.00303	0.00183
0.0100	5.8	0.183	0.00205
0.0200	5.1	0.0499	0.00203
0.0250	5.0	0.0617	0.00199
0.0500	4.7	0.0499	0.00191
		Ave.	0.00196

Initial cadmium(II), 0.01 VF; thioacetamide, 0.10 VF; pH 4.0.

[a] Calculated from the expression

$$-\frac{d[Cd(II)]}{dt} = k_3 \frac{[Cd(II)][CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}}$$

[b] Calculated by assuming that $k_3/k_1 = [Cd^{++}]/[Cd^{++}]_0$

[c] Calculated by assuming that $k_3[Cd(II)] = k_1[Cd^{++}]+k_2[CdCl^+]$, where k_1 is 8.1×10^{-4}, and k_2 is 4.6×10^{-4} $liter^{\frac{1}{2}}mole^{-\frac{1}{2}}min^{-1}$.

$$0.01(5.0 \times 10^{-4}) = 8.1 \times 10^{-4}(0.01-x) + k_2 x \ . \qquad (22)$$

The simultaneous solution of equations 20, 21, and 22 gave values of x to be 0.0089; y to be 0.00955; and k_2 to be 4.6×10^{-4}.

Values for the concentrations of cadmium ion and cadmium monochloride ion were then calculated at each chloride concentration by use of equation 16 and the calculated values for the constants k_1 and k_2, that is

$$k_3[\mathrm{Cd(II)}] = 8.1 \times 10^{-4}[\mathrm{Cd}^{++}] + 4.6 \times 10^{-4}[\mathrm{CdCl}^{+}] \ .(23)$$

From these values for K, the equilibrium constant for reaction 18, were obtained at each chloride concentration. The values obtained are shown under the heading K_b in Table XIII. The value for this constant, calculated thusly, varied less than five per cent over a thousand-fold change in the formal chloride concentration.

The value of this constant was checked through extrapolation of the data that has been reported for the complex at lower temperatures (34,35,36). Extrapolation of data at 25° and 47.5°C. (34) gave a value of 2.5×10^{-3} mole liter^{-1}; a value at 0°C. by King (34), plus those reported by Erikkson (35) and Leden (36) were used to obtain values of 1.8×10^{-3} and 2.2×10^{-3} mole liter^{-1}, respectively, at 90°C. Considering the large temperature changes involved in this extrapolation, these agree quite well with the value of 2.0×10^{-3} mole liter^{-1} found in this investigation.

As an additional confirmation that the rate of reaction can be expressed as the summation of the velocity constants of the two species, cadmium ion, and cadmium monochloride ion, experiments were carried out at 25°C. The chloride concentrations were varied so that 10, 30, 50, and 70% of the cadmium(II) would be complexed, according to the data of Erikkson (35). The value for k_1 at 25°C. calculated from the data discussed in the preceding section of this thesis, that is, 1.15×10^{-6} liter$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$min^{-1} and a value of 0.21×10^{-6} liter$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$min^{-1} for k_2, and a value of 2.86×10^{-2} liter^{-1} for K (35), were used to calculate values for the experimental velocity constant, k_3, at each chloride concentration. In Table XIV these calculated values are compared with those obtained experimentally. The agreement is surprisingly good.

The rate of the reaction of the cadmium ion with thioacetamide is apparently faster than that of the unipositively charged complex. Qualitative tests have indicated that the higher chloride complexes of cadmium(II) do not react with thioacetamide to form precipitates immediately. This would indicate that the uncharged and negative metallic complexes react even more slowly, if at all, with thioacetamide to form the sulfides. Butler and Swift (31), indeed, noted that no reaction other than hydrolysis occurred with arsenic(III), which would be present in an anionic form in solutions where the direct reactions of lead(II) (30), and

Table XIV

Calculated vs. Experimental Rate of the Precipitation of Cadmium as Sulfide from Acid Solutions by Thioacetamide at 25°C.

Cl^-, VF	$k_3 \times 10^6$	
	Calculated[a]	Experimental[b]
0.000	1.15	1.15
0.00417	1.10	1.10
0.0152	1.00	0.90
0.0336	0.68	0.68
0.0737	0.53	0.53

Initial cadmium, 0.01 VF; thioacetamide, 0.10 VF; pH 4.56.

[a] Calculated from the expression

$$k_3[Cd(II)] = k_1[Cd^{++}] + k_2[CdCl^+] \ ,$$

where k_1 is 1.15×10^{-6}, and k_2 is 0.21×10^{-6} liter$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$min.$^{-1}$, and $[Cd^{++}]/[CdCl^+]$ is 2.86×10^{-2} mole liter^{-1} (35).

[b] Calculated from the expression

$$-\frac{d[Cd(II)]}{dt} = k_3 \frac{[Cd(II)][CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}} \quad .$$

cadmium(II) have been observed.

Precipitations of cadmium as the sulfide are not of primary analytical importance in the pH range in which chloride slows the rate of the direct reaction with thioacetamide. However, the results of this study should be useful in the evaluation and prediction of the effects of anions present in the precipitation of other sulfides by thioacetamide in the hydrogen ion concentration range in which the direct reaction predominates. Quantitative studies of these effects on the rate, and perhaps the use of them in separations should be of interest in future investigations.

Part III C

The Precipitation of Nickel(II) as Sulfide from Acid Solution and the Separation of Cadmium(II) and Lead(II) from Nickel(II) by Thioacetamide

Introduction

The work reported in this paper is part of the general investigation of the use of thioacetamide as a precipitant for metal sulfides and as a means for effecting the precipitation of sulfides from homogeneous solutions. This process makes it possible to obtain dense precipitates which are easily separated from the solutions.

The mechanisms of the reactions of lead(II), arsenic(III) and (V), and cadmium(II) with thioacetamide and its products of hydrolysis have been the subjects of previous investigations in this laboratory (30, 31). Arsenic(III) and (V) were precipitated only in the tripositive form and by a hydrolysis reaction; that is, the rate of precipitation was dependent upon the thioacetamide and hydrogen ion concentrations each to the first power, and independent of the cation concentration. Both cadmium(II) and lead(II) are precipitated at hydrogen ion concentrations greater than 10^{-3} M by this hydrolysis reaction. This reaction has been proposed to consist of the attack of a hydrogen ion upon the thioacetamide molecule with the subsequent formation of hydrogen sulfide as the rate determining step, and then a fast reaction of the cation with the hydrogen sulfide to form the sulfide precipitate. At lower hydrogen ion concentrations this hydrolysis is replaced by a direct reaction, the rate of which is first order with respect to both the cation and the thioacetamide concentrations, and is inversely half order with respect to the hydrogen ion concentration.

This investigation of the rate of precipitation of nickel sulfide by thioacetamide, in conjunction with the evaluation of the separation of cadmium and lead from nickel by the use of thioacetamide, should be useful in the evaluation of the substitution of homogeneous phase precipitation of the sulfides by thioacetamide for the conventional hydrogen sulfide methods.

Experimental

Reagents. Reagent grade chemicals were used throughout this study.

Thioacetamide solutions, 1.00 VF (volume formal, formula weights per liter), were prepared from Arapahoe Lot No. 1402 material. These solutions were clear and colorless; however, they were not kept for more than two weeks.

Solutions of cadmium nitrate, lead nitrate and nickel(II) nitrate, each 0.100 VF, were prepared by weight.

The perchloric acid and the carbonate-free sodium hydroxide solutions which were used in this investigation were prepared by conventional methods. The 0.03 VF sodium hydroxide solution was standardized against potassium hydrogen phthalate.

Methyl red indicator, 0.0007 VF, was prepared by dissolving one gm. of the solid in 500 ml. of ethanol.

A 0.1 VF solution of dimetheylglyoxime was prepared by dissolving the solid in ethanol. The pH of this solution was six, and hence satisfactory for its later use.

The hydrogen phthalate-phthalate buffer solutions were made from equal volumes of a sodium hydroxide solution so that the concentration of phthalate ion would be constant. The pH of the buffer was controlled by the amount of potassium hydrogen phthalate that was added. These buffer solutions were then diluted to a given volume in order to form the stock buffer solutions. It was found that the buffer concentration did not affect the rate of reaction.

A solution of 0.10 VF sodium nitrate was prepared by weight and used in order to maintain an initial constant ionic strength in the reaction solutions in which a buffer solution was present.

Apparatus. The apparatus used for the quantitative study of the rate of precipitation of nickel sulfide was similar to that described by Swift and Butler (30). Most of these rate measurements were made at 90 ± 1°C.

The study of the effectiveness of the separation of cadmium and lead from nickel was carried out in 15 x 125 mm. test tubes. These were placed in a one liter water bath maintained at 90 ± 1°C.

Procedure. Two different procedures were used in this investigation. For quantitative studies in the pH range 5-7, the solutions were prepared by mixing measured amounts of the stock solutions of thioacetamide, nickel nitrate, buffer, and sodium nitrate in a reaction tube and diluting the solution to 100 ml. The sodium nitrate was added in order to attain an initial ionic strength of 0.40. The reaction tube was then placed in the constant temperature bath and approximately 12 ml. samples were removed at timed intervals. These samples were cooled in order to quench the reaction, and then centrifuged. Duplicate 5.00 ml. portions of the clear centrifugate were transferred to 15 x 125 mm. test tubes.

An excess of 6 VF ammonium hydroxide was added to each sample, and the sample tubes were then placed in a hot water bath in order to precipitate the nickel as sulfide. A coarse, easily separated precipitate was formed. The mixture was cooled and centrifuged. The centrifugate was drawn off and discarded.

In the qualitative study of the rate of nickel precipitation and its separation from cadmium and lead at low pH values, 10 ml. of reaction solution were prepared by mixing measured quantities of thioacetamide, nickel nitrate, perchloric acid, and, in the separation studies, cadmium or lead nitrate, solutions in each test tube. These tubes were then placed in a constant temperature bath, adjusted to $90^{o}C$. and removed at timed intervals. The reaction was quenched by cooling the reaction tube, and the precipitate separated by centrifuging the mixture. The clear centrifugate was discarded.

In all cases the precipitate was dissolved by the addition of 1 ml. of 9 VF perchloric acid and five drops of 6 VF nitric acid and heating the mixture in a hot water bath until no more precipitate dissolved. The mixture was then heated to fuming over an open flame until all the precipitate had dissolved. The oxides of nitrogen, which would interfere with the ensuing determination, were also expelled in this step. The resulting solution was cooled and then diluted to 2 ml. with water. Five drops of 0.007 VF methyl red indicator was added, and the solution adjusted to the methyl red transition color by the addition of 6 and 0.1 VF sodium hydroxide and 0.1 VF perchloric acid solutions. Comparison solutions were used in order to obtain this color more exactly. An excess of 0.1 VF dimethylglyoxime solution was added, and the mixture was centrifuged. The flocculent red precipitate that had formed was settled in this way.

If over two milligrams of nickel was calculated to be present in this precipitate, a titration with 0.030 VF sodium hydroxide solution was made to the methyl red transition color. The red precipitate interfered with the detection of this color, particularly near the end point unless the mixture was centrifuged at intervals during the titration. This method of analysis was checked with known quantities of nickel(II) similar to those which were present in this investigation, and the average deviation in the results was less than one per cent when comparison solutions were used.

In those cases where less than two mg. of nickel was calculated to be present, comparison solutions which contained known amounts of nickel(II) as the nickel dimethylglyoxime precipitate were used to make qualitative estimations of the amount of nickel in the samples. In determinations that were made with known amounts of nickel(II), and also quantities of lead(II) and cadmium(II) present similar to those in the studies, this estimation was superior in reproducibility and accuracy to the base titration if less than two mg. of nickel was present. These estimations with known quantities were well within ten per cent of the known value.

Data and Discussion

Rate of Nickel Sulfide Formation. In preliminary qualitative measurements, no formation of nickel sulfide was observed at $90^{\circ}C$. in solutions 0.01 VF in nickel(II) and 0.10 VF in thioacetamide in the hydrogen ion concentration range 0.3-0.01 VF. If the hydrolysis reaction caused precipitation at pH 1, calculations indicate that all the nickel present would have precipitated within ten minutes under the above conditions.

Quantitative Studies of the Rate of Precipitation. Quantitative measurements of the rate of precipitation were made in the pH range 5.0-7.1 at 90°C. At these hydrogen ion concentrations the precipitation took place at a conveniently measurable rate, and the results of this investigation could be conveniently compared with those found for the elements that have been previously studied.

The effects of the nickel(II), the thioacetamide, and the hydrogen ion concentrations upon the rate of precipitation were evaluated in order to determine the rate expression and to calculate a velocity constant.

Effect of the Nickel(II) Concentration. As is shown in Figure 6, the plots of the logarithm of the nickel(II) concentration versus the reaction time at various hydrogen ion concentrations were linear; thus it appears that the precipitation reaction is first order with respect to the nickel(II) concentration at 90°C.

Effect of the Thioacetamide Concentration. Table XV is a tabulation of the data from a series of experiments which were made to determine the effect of thioacetamide upon the reaction rate. In the range of concentrations studied, 0.050 to 0.30 VF in thioacetamide, the rate of reaction was first order with respect to the thioacetamide.

Effect of the Hydrogen Ion Concentration. The effect of the hydrogen ion concentration was studied quantitatively

Figure 6. Rate of precipitation of nickel sulfide by thioacetamide.

0.10 VF thioacetamide; 0.010 VF nickel(II); 90°C.

1. pH 5.0
2. pH 6.2
3. pH 6.5
4. pH 7.0

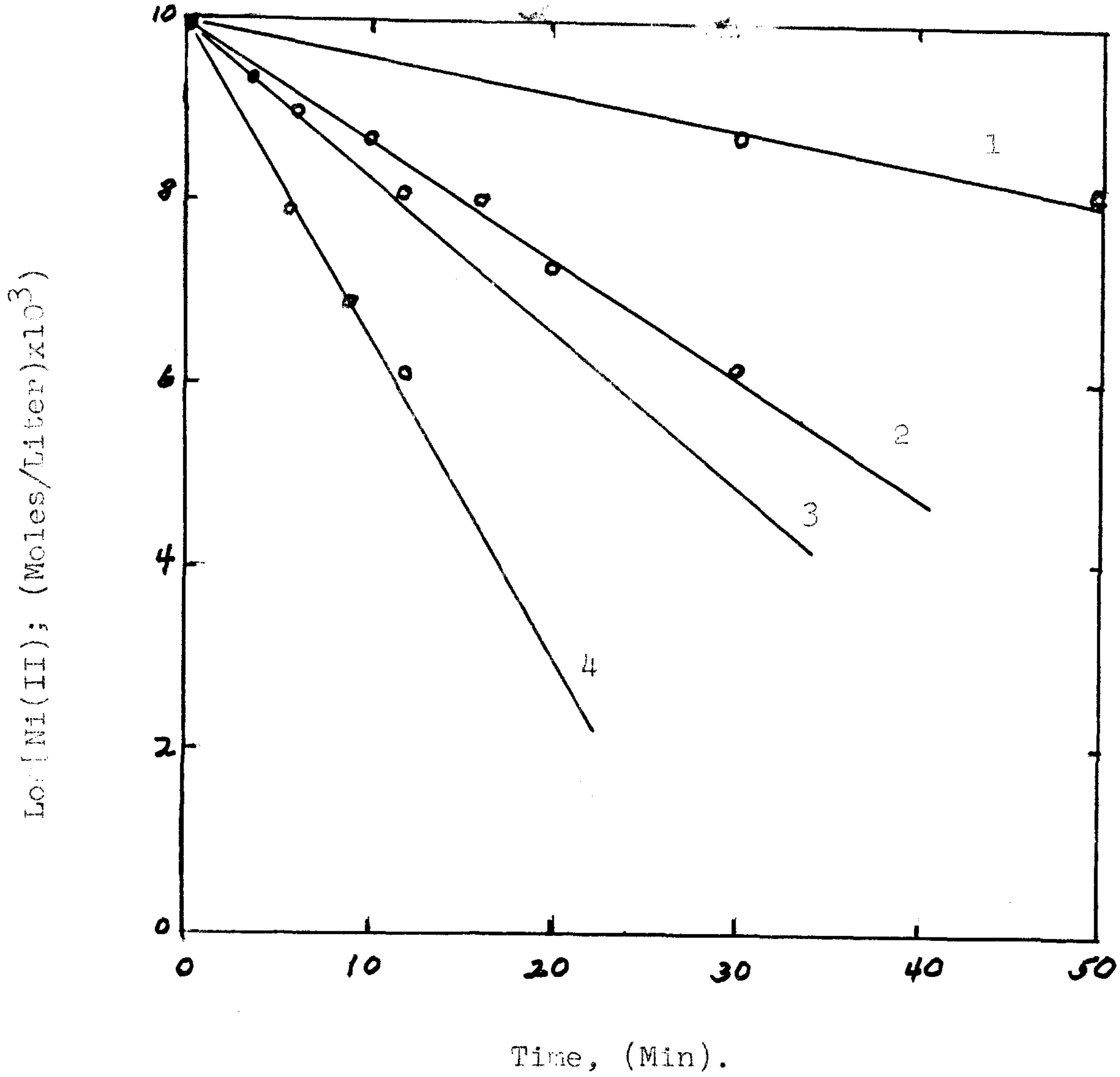


Table XV

Effect of Thioacetamide on the Precipitation of Nickel

(CH_3CSNH_2), VM	k_1 [a]	$k_2 \times 10^4$ [b] ($\text{liter}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{min.}^{-1}$)
0.050	0.0177	2.25
0.100	0.0342	2.21
0.150	0.0553	2.31
0.200	0.0733	2.31
0.250[c]	0.0774	2.19
0.300	0.1068	2.26

Average $(2.25 \pm 0.05) \times 10^{-4}$

Initially 0.010 VF in nickel(II); pH 6.4; 90°C.

[a] Calculated from the expression

$$-\frac{d[Ni(II)]}{dt} = k_1[Ni(II)] .$$

[b] Calculated from the expression

$$-\frac{[Ni(II)]}{dt} = k_2 \frac{[Ni(II)][CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}} .$$

[c] Measurements at pH 6.3.

over the range from 1 x 10^{-5} to 10^{-7} VF. Haring and Westfall (37) reported that quantitative precipitation of nickel as sulfide is possible in this pH range with hydrogen sulfide. Nitrogen was bubbled through the reaction solution in some experiments in order to eliminate this type of precipitation. The rate of precipitation was unchanged and there was no evidence of precipitation through hydrolysis of thioacetamide. The data from this study are given in Table XVI and showed that the reaction has an inverse half order dependency upon the hydrogen ion concentration.

This investigation demonstrated that the precipitation under the conditions that were quantitatively studied is by a direct reaction similar to those reported for lead (30) and cadmium at pH values greater than 3. This direct reaction is first order with respect to both the cation, nickel(II), and thioacetamide concentrations, and is inversely half order with respect to the hydrogen ion concentration; that is

$$-d[\mathrm{Ni(II)}]/dt = k\,[\mathrm{Ni(II)}][\mathrm{CH_3CSNH_2}]/[\mathrm{H^+}]^{\frac{1}{2}}\ , \qquad (24)$$

where the velocity constant, k, is 2.2 x 10^{-4} at 90°C.

<u>The Energy of Activation</u>. The velocity constant for this direct reaction was determined at 70° and 80°C. in order to calculate the energy of activation. The constants were 8.95 x 10^{-5} and 1.45 x 10^{-4} liter$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$min.$^{-1}$, respectively.

Table XVI

Effect of Hydrogen Ion on the Precipitation of Nickel by Thioacetamide

pH	k_1[a]	$k_2 \times 10^5$[b]
7.1	0.078	2.21
6.5	0.039	2.23
6.4	0.034	2.21
6.2	0.029	2.30
5.0	0.006	2.14
		Average $(2.22 \pm 0.05) \times 10^{-5}$

Initially 0.01 VF in nickel(II); 0.10 VF in thioacetamide; 90°C.

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = k_1[\mathrm{Ni(II)}] \quad .$$

[b] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = k_2 \frac{[\mathrm{Ni(II)}]}{[\mathrm{H}^+]^{\frac{1}{2}}} \quad .$$

From these values and that determined at 90°C., the energy of activation was calculated to be 20.8 ± 0.8 kcal. per mole. This is approximately the same as the value calculated for cadmium, and indicates that the two reactions are quite similar.

Qualitative Measurements of the Precipitation. The direct reaction has not been observed at pH 1 and 2 in previous investigations with thioacetamide because any such reaction would be masked by the predominant hydrolysis reaction. However, since the hydrolysis reaction did not cause precipitation of nickel(II), a check for the direct reaction was made at these hydrogen ion concentrations.

It was found that no precipitate was formed when a solution 0.040 VF in nickel(II) at pH 1 or 2 was saturated with hydrogen sulfide and maintained at 90°C. for one hour. When solutions 0.040 VF in nickel(II) and 0.40 VF in thioacetamide at the same pH values were maintained at 90°C., nickel sulfide was slowly formed. In other cases when hydrogen sulfide was added to the above solutions, no change was observed in the rate of precipitation. Comparisons of the amount of nickel(II) found in the precipitates and that calculated by expression 24 are given in Table XVII. The agreement is well within the limits of the accuracy of the estimation. Experiments in which cadmium or lead sulfide was present showed that these did not alter the rate of nickel sulfide precipitation. It was concluded that the

Table XVII

Experimental vs. Calculated Weight of Nickel Sulfide Formed by Direct Reaction at pH 1 and 2 at 90°C.

Time (Min.)	Mg. Nickel Precipitated as NiS	
	Found	Calculated[a]
pH 1		
5	0.04	0.04
12	0.15	0.09
pH 2		
12	0.16	0.24
24	0.46	0.48
28	0.58	0.56
60	1.35	1.2
120	2.15	2.1

Initially 0.04 VF $Ni(NO_3)_2$; 0.40 VF CH_3CSNH_2.

[a] Calculated from the expression

$$-\frac{d[Ni(II)]}{dt} = 2.2 \times 10^{-4} \frac{[Ni(II)][CH_3CSNH_2]}{[H^+]^{\frac{1}{2}}} .$$

direct reaction occurred at these hydrogen ion concentrations.

Nickel sulfide, according to Haring and Westfall (37), does not precipitate from solutions saturated with hydrogen sulfide at pH 1. In general, nickel sulfide does not dissolve readily in solutions 1 N in cold hydrochloric acid (38). This phenomenon is usually attributed to the existence of several allotropic forms of nickel sulfide. Ringhom (39) reports three such forms, α, β, and γ, with solubility products of 3×10^{-19}, 1×10^{-24}, and 2×10^{-26}, respectively. The more soluble forms evidently precipitate from hydrogen sulfide solutions and then change into the less soluble type. Swift (38) reports that this transformation seems to be favored by heat and by acid.

It is also possible that the phenomenon may be explained by a slow rate of solution. Such an explanation would mean that if sufficient time were allowed, the sulfide would redissolve. It was necessary in this study to use both an acid and an oxidizing agent to dissolve the nickel sulfide that had precipitated.

It was believed that the γ-form of nickel sulfide was formed by the direct reaction. This would explain the precipitation at pH 1 and 2 that has not been observed with hydrogen sulfide.

Qualitative observations were also made in 50 ml. of a solution 0.4 VF in nickel(II), 0.40 VF in thioacetamide, and 0.3 VF in perchloric acid. At this hydrogen ion concentration the thioacetamide concentration is reduced very rapidly by hydrolysis; in fact, it is reduced to one-half the initial concentration within ten minutes. The calculated rate of the direct reaction is approximately half that at pH 1 under the same initial conditions, so that no quantitative measurements were made. The estimated quantity of nickel precipitated under these conditions in twenty minutes was 7 mg., which is close to the calculated value of 5 mg.

Further experiments showed that chloride ion, in concentrations up to 0.6 VF, had no effect upon the rate of the direct reaction. This indicates that nickel(II) does not form a stable chloride complex in aqueous solution, since chloride inhibited the direct reaction of cadmium.

An empirical correlation between the velocity constants for the direct reactions and the solubility products for the sulfides of lead(II), cadmium(II), and nickel(II) has been found. Many conflicting values for the solubility products have been reported, so that only one source, Ringhom (39), was used for this comparison. Ringhom has listed the various values that he found in the literature and reported the probable value for the solubility product of each sulfide from considerations of ΔF^{o} for formation of the metal sulfide, hydrogen sulfide, and the metallic cation.

The correlation can be shown by the empirical relation

$$K \times 10^{23} = -1.9\ k + 24.2 \times 10^{-4} \tag{25}$$

where K is the solubility product constant at 25°C., and k is the direct reaction constant at 90°C. The reported values of K, and the values calculated in this way are compared in Table XVIII. Perhaps a more understandable type of correlation is that obtained by the ratio of the change in the direct reaction to the change in the solubility constant. This ratio averages -0.55×10^{-23}, which would indicate that the solubility product decreases at approximately twice the rate that the rate of the direct reaction increases. Any such relationship can only be postulated until more data are available.

The Separation of Cadmium(II) and Lead(II) from Nickel(II).

In most conventional schemes of analysis lead and cadmium are separated as members of the Hydrogen Sulfide Group from the other common elements, such as nickel, by precipitation from solutions which are saturated with hydrogen sulfide and in which the hydrogen ion concentration is usually about 0.1 to 0.3 molal. For quantitative purposes this separation can be made with the hydrogen ion concentration as low as 10^{-2} molal in the absence of zinc.

The effectiveness of the separation of cadmium(II) and lead(II) from nickel(II) by the precipitation of the sulfides of the first two cations from thioacetamide solutions was checked by varying the concentrations of the constituents in the separations. The studies of the formation of lead and cadmium sulfides (30) have shown that the rate of sulfide

Table XVIII

Correlation of Velocity Constant for the Direct Reaction and the Solubility Constant

Cation	$k \times 10^4$	$K \times 10^{27}$	
		Reported[a]	Calculated[b]
Pb^H	11.5	2.5	2.2
Cd^H	8.1	8	8.8
Zn^H	2.2	20	20

[a] From Ringbom, The Solubilities of the Sulfides (39).

[b] Calculated by the equation

$$K \times 10^{23} = 1.9k + 24.2 \times 10^{-4}$$

formation in thioacetamide solutions at hydrogen ion concentrations of 0.010 and 0.100 VF is primarily governed by the hydrolysis, and is independent of the cation concentration. The rate of the formation of these sulfides at 90°C. and at these hydrogen ion concentrations can be calculated from the expression

$$-\frac{d[M(II)]}{dt} = 0.21\ [H^+][CH_3CSNH_2]\ , \qquad (26)$$

where M(II) is the concentration of the cation.

Nickel(II), as has been shown above, does not precipitate at a rate controlled by this reaction. The expected rate of its sulfide precipitation can be calculated from expression 24, if it is assumed that no coprecipitation occurs.

In this investigation the thioacetamide concentration was varied from 0.10 to 0.40 VF. At the latter concentration precipitation of all the cations was faster and the rapid formation of hydrogen sulfide by hydrolysis could be utilized in order to simulate the conditions of a hydrogen sulfide type of separation.

The lead(II), cadmium(II), and nickel(II) concentrations were also varied in order to find the effect of each upon the separation.

The initial experiments were carried out at pH 2 so that the direct reaction of nickel would be faster, and hence more conveniently measured than at the lower pH values. At pH 2 the rate of precipitation of nickel should be three times as fast as at pH 1 under the same conditions.

Data tabulated in Table XIX show that the amount of nickel sulfide formed is not a function of the type of cation present. The agreement between the amounts of nickel sulfide formed, and the quantities calculated by expression 24 is good.

In Table XX it is shown that the quantity of nickel sulfide formed is independent of the concentration of the other cation, and, in conjunction with the data in Table XIX, it is shown that the formation of nickel sulfide is first order with respect to the nickel(II) concentration. In order to verify these results, reaction tubes containing nickel and cadmium, or lead, were treated simultaneously in order to insure that both the reactions and the analytical determinations were done under the same conditions. The data, which is tabulated in Table XXI, showed that the reaction at this pH to form nickel sulfide corresponds to the direct reaction of expression 24, and that the foreign cation did not affect the rate of this reaction.

Data were also taken at pH 1, which is a more practical hydrogen ion concentration than pH 2 to use in analytical separations of this type because the rate of the precipitation of cadmium and lead as sulfides is faster by a factor of ten, and the rate of the direct reaction to form the nickel sulfide precipitate is slower. In Table XXII the data from a series of these experiments at pH 1 are given.

Table XIX

Precipitation of Nickel Sulfide in the Separation of Lead and Cadmium from Nickel at pH 2

Time (Min.)	Ni(II) precipitated as NiS (mg.)		
	A.[a]	B.[b]	C.[c]
4	0.09	0.09	0.08
8	0.14	0.16	0.16
12	0.21	0.25	0.24
16	0.29	0.31	0.32
20	0.40	0.38	0.40
24	0.47	0.47	0.48
28	0.54	0.60	0.56
60	1.3	1.1	1.2
90	1.5	1.5	1.6
120	2.2	2.0	2.1

Initially 0.40 VF thioacetamide; 20 mg. nickel(II), 90°C.

[a] Initially 11 mg. Cd(II).

[b] Initially 21 mg. Pb(II).

[c] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}} .$$

Table XX

Precipitation of Nickel Sulfide at pH 2

Time (Min.)	Ni(II) precipitated as NiS (mg.)				
	A[a]	B[b]	D[d]	E[e]	C[c]
4	0.04	0.04	0.06	0.06	0.04
8	0.06	0.07	0.10	0.08	0.08
12	0.12	0.10	0.12	0.10	0.12
16	0.15	0.13	0.18	0.16	0.16
20	0.19	0.16	0.23	0.21	0.20
24	0.23	0.19	0.26	0.25	0.24
28	----	0.24	0.30	0.30	0.28

Initially 0.40 VF thioacetamide; 10 mg. nickel(II), 90°C.

[a] Initially 11 mg. Cd(II).

[b] Initially 22 mg. Cd(II).

[d] Initially 21 mg. Pb(V).

[e] Initially 42 mg. Pb(II).

[c] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = 2.2 \times 10^{-4}\ \frac{[\mathrm{Ni(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}} .$$

Table XXI

Precipitation of Nickel Sulfide at pH 2 in the Separation of Nickel from Lead and Cadmium Under Similar Conditions

Time (Min.)	Nickel precipitated as nickel sulfide (mg.)		
	A.[a]	B.[b]	C.[c]
5	0.08	0.09	0.10
10	0.18	0.18	0.20
15	0.30	0.30	0.30
20	0.45	0.40	0.40

Initially 0.40 VF thioacetamide; 20 mg. nickel(II); 90°C.

[a] Initially 11 mg. Cd(II).

[b] Initially 21 mg. Pb(II).

[c] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}} \quad .$$

Table XXII

Precipitation of Nickel Sulfide at pH 1 in the Separation of Cadmium and Lead from Nickel

Time (Min.)	Nickel precipitated as nickel sulfide (mg.)		
	A.[a]	B.[b]	C.[c]
2	0.02	0.02	0.01
4	0.03	0.05	0.03
6	0.05	0.08	0.04
8	0.07	0.11	0.05
10	0.08	0.13	0.07
12	0.14	0.15	0.09

Initially 0.40 VF thioacetamide; 20 mg. nickel(II); 90°C.

[a] Initially 11 mg. Cd(II).

[b] Initially 21 mg. Pb(II).

[c] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}} .$$

It should be noted that some precipitation occurred during the heating of the solutions to 90°C.; since no correction *has been made for this in the data, the change in the weight* of the nickel in the precipitate is more indicative that the rate of formation of nickel sulfide is controlled by the direct reaction than the untreated data. The results of subsequent experiments, shown in Table XXIII, in which the two separations were performed simultaneously as was done previously at pH 2, agree excellently with those values calculated by expression 24.

It should be noted that the precipitation of nickel sulfide *observed in this study is not coprecipitation,* but is due strictly to chemical precipitation.

Analytical Application. This investigation has shown that the hydrogen ion concentration is of primary importance in the separation of cadmium(II) and lead(II) from nickel(II) by sulfide precipitations from thioacetamide solutions. In order to illustrate how effective such a separation can be made, the following conditions have been assumed.

In 250 ml. of solution *initially* 0.1 VF in thioacetamide and 0.10 VF in hydrogen ion, and containing 250 mg. each of cadmium(II) and nickel(II), at 90°C., it is calculated that *the cadmium(II) would be precipitated quantitatively within* ten minutes. In this time less than 0.25 mg. of nickel sulfide would be precipitated, according to the calculations made on the basis of the direct reaction. A similar set of

Table XXIII

Precipitation of Nickel Sulfide at pH 1 in the Separation of Nickel from Lead and Cadmium Under Identical Conditions

Time (Min.)	Nickel precipitated as nickel sulfide (mg.)		
	A.[a]	B.[b]	C.[c]
5	0.04	0.04	0.03
10	0.07	0.07	0.06
15	0.11	0.11	0.10
20	0.15	0.15	0.13

Initially 0.40 VF thioacetamide; 20 mg. nickel(II); 90°C.

[a] Initially 11 mg. Cd(II).

[b] Initially 21 mg. Pb(II).

[c] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}} .$$

conditions is adequate for considering the effectiveness of the separation of lead from nickel. These have been checked with solutions containing 10 mg. of either lead or cadmium and 10 mg. of nickel in ten ml. of solution. The results, shown in Table XXIV, are in close agreement with the calculated values.

Decreasing the concentration of cadmium(II) or lead(II) would, of course, decrease the amount of time required for quantitative precipitation, and thus the amount of nickel sulfide contaminant. A decrease in the amount of nickel(II) will decrease the rate of the direct reaction, and therefore, the amount of contamination proportionately.

At pH 2 the above solution would require almost one hundred minutes for quantitative precipitation of the cadmium(II). In this time over 6 mg. of nickel(II) will precipitate. Therefore the separation should be carried out at the lower pH, in consideration for the time involved and of the effectiveness of the separation.

This investigation has demonstrated the need for caution in the substitution of thioacetamide for hydrogen sulfide in analytical separations. It is hoped that further investigations will be made into other similar procedures.

Table XXIV

Effectiveness of the Separation of Cadmium(II) and Lead(II) from Nickel(II) at pH 1

Time (Min.)	Nickel precipitated as nickel sulfide		
	A.[a]	B.[b]	C.[c]
5	0.01	0.01	0.004
10[d]	0.02	0.02	0.01
15	0.04	0.04	0.015
20	0.08	0.05	0.02

Initially 0.10 VF thioacetamide; 10 mg. Ni(II); 10 ml; 90°C.

[a] Initially 10 mg. Cd(II).

[b] Initially 10 mg. Pb(II).

[c] Calculated from the expression

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni(II)}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}} .$$

[d] Precipitation of cadmium and lead complete.

Part III D

Precipitation of Zinc Sulfide from Acid Solutions by Thioacetamide

Introduction

This investigation is an extension of the general study of the precipitation of metal sulfides by thioacetamide to include zinc(II). In previous investigations the mechanisms of the reactions of lead(II) (30), arsenic(III) and (V) (31), cadmium(II), and nickel(II) have been studied in this laboratory. The separation of cadmium(II) and lead(II) from nickel(II) by means of homogeneous phase precipitation in acid solutions of thioacetamide was discussed in the preceding section of this thesis.

The precipitation of zinc(II) by thioacetamide is of particular interest because of the results of the previous investigations. In solutions having pH values less than three, it has been found that lead(II) (30) and cadmium(II) sulfides precipitate at 90°C. through the hydrolysis of thioacetamide; that is, the rate of precipitation quantitatively follows the rate of hydrolysis of thioacetamide, which is first order with respect to both the thioacetamide and hydrogen ion concentrations. Lead(II) and cadmium(II) sulfides precipitate primarily by a direct reaction at 90°C. in solutions having pH values from 3 to 7; that is, the precipitation is first order with respect to both the thioacetamide and metallic cation concentrations and inversely half order with respect to the hydrogen ion concentration. Nickel sulfide does not precipitate in solutions saturated with hydrogen sulfide at pH 1 or 2 (37), and no hydrolysis precipitation was observed at 90°C. with nickel(II) in thioacetamide solutions. The direct reaction of nickel(II) was observed in solutions 0.3 to 10^{-7} M in hydrogen ion.

The transition between the hydrolysis and direct mechanisms of sulfide precipitation has been at approximately pH 3 in solutions 0.01 VF in lead(II) or cadmium(II) and 0.10 VF in thioacetamide at 90°C. This is about at the pH range (2-3) reported by Fales and Ware (40) as most favorable for quantitative precipitationof zinc sulfide from solutions which contain hydrogen sulfide. It is, therefore, of considerable interest to determine the mechanisms of zinc sulfide precipitation from solutions which contain thioacetamide in this pH range.

Experimental

Reagents. Reagent grade chemicals were used throughout this investigation.

Arapahoe thioacetamide, Lot No. 1402, was used to prepare 1.00 VF stock solutions by weight. These freshly prepared solutions were clear, colorless, and approximately the pH of the distilled water that was used in their preparation.

Stock solutions of 0.10 VF zinc nitrate, which was later standardized, of 0.10 VF lead nitrate, and of 3.0 VF ammonium chloride were prepared by weight.

Hydrochloric acid solutions, 3.0 and 6 VF, prepared from the concentrated acid, were found free from oxidizing agents. Both 1.0 and 0.10 VF perchloric acid solutions were prepared from the commercial acid.

Standard 0.05 VF potassium iodate solution was prepared by weight. Sodium thiosulfate solutions, approximately 0.05 VF, were standardized against the potassium iodate solution.

The following solutions were prepared for use in the colorimetric determination of zinc(II):

A 0.001% (weight/volume) dithizone solution was prepared in carbon tetrachloride.

An acetate buffer solution, pH 4.8, was made by mixing equal volumes of 2 VF sodium acetate and 2 VF acetic acid.

A sodium thiosulfate solution was prepared by dissolving 25 g. of the hydrated salt in 100 ml. of water.

Standard zinc(II) solutions were prepared by dilution of the stock 0.10 VF zinc nitrate solution that had been previously standardized.

For the study of the rate of precipitation of zinc(II) in the pH range 3 to 7, sodium formate-formic acid buffer solutions were prepared from sodium hydroxide and 90% formic acid solutions. These buffer solutions, which contained a constant sodium formate concentration, were prepared by mixing various quantities of formic acid with equal volumes of a 6 VF sodium hydroxide solution and then diluting each solution to the same final volume.

Apparatus. The apparatus used for the study of the mechanisms of the precipitation of zinc sulfide was essentially that described by Swift and Butler (30). In the study of the separation of lead(II) from zinc(II) solutions 15 x 25 mm. test tubes which contained the reaction solutions were immersed in a constant temperature bath.

Procedures. In the rate studies, measured volumes of the stock zinc nitrate and hydrochloric, or perchloric acid, or the sodium formate-formic acid buffer solutions were mixed and diluted to 100 ml. in the reaction tube. The reaction tube was then placed in the constant temperature bath.

At timed intervals approximately 12 ml. of solution were removed from the reaction tube, immediately cooled to quench the reaction, and centrifuged to coagulate any zinc sulfide. Duplicate 5.00 ml. portions of each sample were pipetted from the clear centrifugate into 15 x 125 mm. test tubes.

An excess of ammonium hydroxide was added to each test tube, and the solutions were placed in a bath of hot water in order to speed precipitation. The mixtures were cooled, centrifuged, and the centrifugate drawn off and discarded. The precipitate was washed with 2 ml. portions of pH 5.4

sodium formate-formic acid buffer until the wash solution was free of zinc(II). The precipitate was washed into a 100 ml. conical flask; then potassium iodide, standard potassium iodate solution, and 6 VF hydrochloric acid were added in the order listed. The solution was titrated with standard sodium thiosulfate.

In confirmatory analyses of the zinc nitrate solution by the procedure outlined above, the average deviation was less than one part per hundred. The procedure was adopted for the measurement of the rate of precipitation in the pH range 2 to 7.

A colorimetric method was used to determine the quantities of zinc that precipitated with the lead sulfide in the study of the separation of lead(II) from zinc(II) when either thioacetamide or hydrogen sulfide were used as a precipitant. Reaction solutions were prepared by mixing measured quantities of zinc(II), lead(II), hydrochloric acid, and ammonium chloride solutions in 15 x 125 mm. test tubes. Water and hydrogen sulfide gas were added to some solutions; thioacetamide was added to others. The test tubes were placed in a bath at 90 ± 1°C. for timed intervals, and then cooled in an ice bath. After centrifugation, the precipitate was washed with 2 ml. portions of pH 5.4 buffer until the wash solution was free of zinc(II), and then dissolved in a mixture of perchloric and nitric acids.

The solution was diluted to 100 ml. in a volumetric flask, and one ml. samples were used for the colorimetric determination of zinc(II) by means of dithizone reagent as described by Sandell (41). The sample of unknown was diluted to 10 ml. in a separatory funnel; 5 ml. of acetate buffer were added to adjust the pH; and 1.00 ml. of the sodium thiosulfate solution was added in order to complex the lead(II). This solution was shaken with 5.0 ml. of the dithizone solution. The colored carbon tetrachloride phase was run into a Klett test tube and the transmittancy of the solution was determined in a Klett-Summerson photoelectric colorimeter equipped with a green filter.

Solutions which contained known amounts of zinc(II) and lead(II) were used in order to obtain a standardization curve for this method. The procedure was adopted for the estimation of the quantity of zinc(II) that precipitated with lead(II) in the sulfide separations.

Data and Discussion

In qualitative experiments it was found that the initial rate of formation of zinc sulfide from thioacetamide solutions increased with pH in the pH range 1 to 7. In solutions at pH 1 and 2 the rate of sulfide formation at 90°C. increased rapidly after from six to eight minutes.

The Precipitation by the Hydrolysis Reaction. Quantitative measurements of the rate of precipitation were made at pH 1 and 2 at 90°C. in solutions initially 0.10 VF in thioacetamide and 0.01 VF in zinc(II). The measurements indicated that the sulfide precipitated by the hydrolysis mechanism, that is, that the rate of precipitation was independent of the zinc(II) concentration and first order with respect to both the hydrogen ion and the thioacetamide concentrations. The velocity constant for the expression

$$-\frac{d[Zn(II)]}{dt} = k[H^+][CH_3CSNH_2] \qquad (27)$$

was 0.21 liter mole^{-1} at 90°C. This is the same expression as that found for lead(II) (30) and cadmium(II) at these hydrogen ion concentrations. In this case, however, there was an initial interval in which the zinc(II) did not precipitate; evidently the hydrogen sulfide concentration was at a certain level before precipitation occurred.

In solutions 0.3 M in hydrogen ion, 0.6 M in chloride ion, and 0.04 M in zinc(II), no observable precipitation occurred within one hour at 90°C. when either hydrogen sulfide or thioacetamide was present.

<u>The Precipitation by the Direct Reaction</u>. Formic acid-sodium formate buffer solutions were used to control the hydrogen ion concentration in solutions in the pH range 6.3 to 4.5. In this range it was possible to study the effects of the hydrogen ion, zinc ion, and thioacetamide upon the rate of precipitation.

Effect of Zinc Ion Concentration. The plots of the logarithm of the zinc ion concentration against time for the pH range 6.3 to 4.5 were linear as is shown in Figure 7. It was concluded that the reaction is first order with respect to the zinc ion concentration.

Effect of the Hydrogen Ion Concentration. The range of hydrogen ion concentrations considered in the study of the rate of precipitation was from 3.2×10^{-3} to 5×10^{-7} VM. Rate constants calculated from this datum are tabulated in Table XXV, and show that the rate of precipitation is dependent upon the inverse half power of the hydrogen ion concentration. This dependency upon hydrogen ion is the same as that reported in the previous investigations of cadmium(II) and lead(II) (30).

Rate measurements were made in solutions 3.2×10^{-3} VM in hydrogen ion while nitrogen was bubbled through the solution to prevent any reaction of zinc(II) with the hydrogen sulfide formed by hydrolysis of thioacetamide at this pH. The expression for the rate of precipitation conformed to that found in the pH range 6.3 to 4.5. Qualitative experiments at pH 1, in which nitrogen was bubbled through the reaction solution, indicated that precipitation by the same reaction occurred.

Effect of Thioacetamide Concentration. The effect of the thioacetamide concentration was investigated over the range of thioacetamide concentrations from 0.05 to 0.03 VF

Figure 7. Rate of precipitation of zinc sulfide by thioacetamide.

Initial zinc, 0.01 VF; thioacetamide, 0.10 VF; 90°C.

1. pH 5.4
2. pH 5.7
3. pH 6.4

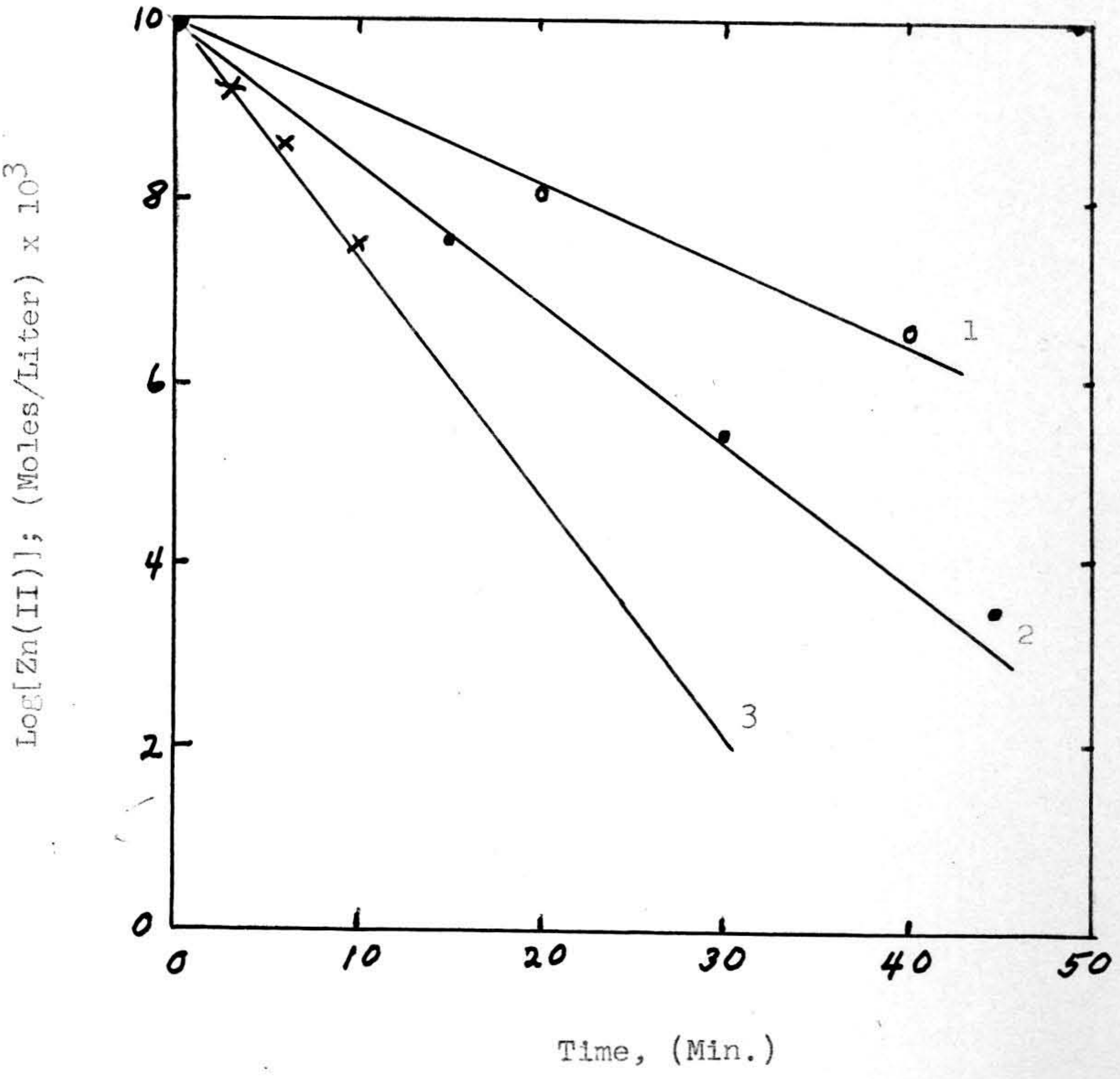


Table XXV

Effect of Hydrogen Ion Concentration upon the Rate of Precipitation of Zinc Sulfide at 90°C.

Initial zinc(II), 0.011 VF; thioacetamide, 0.10 VF.

(H^+)	$k_1 \times 10^8$ [a]	$k_2 \times 10^4$ [b]
3.0×10^{-3}	200	4.3
2.8×10^{-5}	21	4.0
4.0×10^{-6}	8	4.3
2.0×10^{-6}	6	4.2
5.0×10^{-7}	3	4.2
		Ave. = $(4.2 \pm 0.1) \times 10^{-5}$

[a] Calculated from the expression

$$-d[Zn(II)]/dt = k_1 \frac{[Zn(II)]}{[H^+]} .$$

[b] Calculated from the expression

$$-d[Zn(II)]/dt = k_2 \, [Zn(II)]/[H^+]^{\frac{1}{2}} .$$

at pH 5.7. Rate constants from the data obtained are given in Table XXVI; these show that the rate of precipitation is dependent upon the thioacetamide concentration to the first power.

Therefore, it has been shown that the precipitation of zinc(II) by thioacetamide is by a mechanism similar to that found for cadmium, lead, and nickel at pH values greater than 3. Precipitation is by the so-called direct reaction; that is, a reaction that is first order with respect to both the thioacetamide and the zinc(II) concentrations, and is inversely half order with respect to the hydrogen ion concentration. The rate of precipitation corresponds to the expression

$$-d[Zn(II)]/d\ t = k[Zn(II)][CH_3CSNH_2]/[H^+]^{\frac{1}{2}} \qquad (28)$$

where k is 4.2×10^{-4} $liter^{\frac{1}{2}}mole^{-\frac{1}{2}}min^{-1}$ at 90°C.

Temperature Effect on the Direct Reaction. The rates of the direct reaction in solutions initially 0.01 VF in zinc nitrate and 0.10 VF in thioacetamide at pH 5.70 were determined at 70°, 80°, and 90°C. The energy of activation, calculated from the slope of a plot of the logarithm of the rate vs. 1/T, was 20.1 ± 0.8 kcal./mole. This value is similar to those previously reported in this thesis for the direct reactions of cadmium(II) and nickel(II), which were both 20.8 kcal./mole. Evidently the energy of activation is equivalent for these reactions.

Table XXVI

Effect of Thioacetamide Concentration Upon the Rate of Precipitation of Zinc Sulfide at 90°C.

Initial zinc(II), 0.011 VF; hydrogen ion, 2.0×10^{-6} M.

(CH_3CSNH_2) Moles/liter	$k_1 \times 10^5$ [a]	$k_2 \times 10^4$ [b]
0.050	2.1	4.2
0.100	4.2	4.2
0.200	8.4	4.2
0.300	13.2	4.4

[a] Calculated from the expression

$$-d[Zn(II)]/dt = k_1[Zn(II)]/[H^+]^{\frac{1}{2}} \quad .$$

[b] Calculated from the expression

$$-d[Zn(II)]/dt = k_2[Zn(II)][CH_3CSNH_2]/[H^+]^{\frac{1}{2}} \quad .$$

Correlation of the Velocity Constants of the Direct Reactions. In the preceding section of this thesis it was shown that the solubility product constants of the sulfides and the velocity constants for the direct reaction in the cases of nickel(II), cadmium(II), and lead(II) could be correlated by the emperical equation

$$K \times 10^{23} = -1.9 \; k + 24.2 \times 10^{-4} \qquad (29)$$

where K is the solubility product constant, and k is the velocity constant for the direct reaction. If the solubility product constant for the most insoluble form of zinc sulfide, sphalerite, 1.5×10^{-24} (39), is used to solve equation 29, a value of 0.08 is calculated for k. It is obvious that the correlation can not be extended to include zinc(II).

A correlation between the radii of the cations and the velocity constants was obtained by plotting the radii as a function of the velocity constants. The empirical equation

$$r = 600 \; k + 0.52 \; , \qquad (30)$$

where r is the radius in angstroms, and k is the constant for the direct reaction, fits the data. The values of r reported by Pauling (42) are compared with those calculated by this equation in Table XXVII. The agreement is surprisingly good. It should be obvious that this correlation is not due to any properties of the direct react; it is only an interesting side light.

Table XXVII

Correlation of Cation Size and Velocity Constant

Cation	$k \times 10^4$	Cation Size (Å) Calculated[a]	Reported (42)
Pb^{++}	11.5	1.18	1.21
Cd^{++}	8.1	1.00	0.97
Zn^{++}	4.2	0.77	0.74
Ni^{++}	2.1	0.64	0.69

[a] Calculated from the equation

$$r = 600\ k + 0.52,$$

where r is the radius in angstrom, and k is the velocity constant for the direct reaction at 90°C.

Separation of Lead(II) from Zinc(II). Using the value 1×10^{-24} for the solubility product of zinc sulfide, it is calculated that, in order to hold 100 mg. of zinc in 100 ml. of solution saturated with hydrogen sulfide, the hydrogen ion concentration must be greater than approximately 0.4 M Experimentally more than 250 mg. of zinc were held in 100 ml. of a solution 0.3 M in hydrogen ion and 0.6 M in chloride for over one hour at 90°C. when the solution initially contained either thioacetamide or hydrogen sulfide.

At a pH of 1.2 precipitation of zinc sulfide has been reported (40) in hydrogen sulfide solutions, and was found in this study to occur in thioacetamide solutions by the hydrolysis mechanism at both pH 1 and 2.

A series of experiments was made to determine whether thioacetamide can be substituted for hydrogen sulfide in the separation of lead(II) from zinc(II) without modification of procedure. Because zinc sulfide would form at pH 1 in either case, these experiments were made in solutions 0.3 M in hydrogen ion and 0.6 M in chloride. It was found, as shown by the data in Table XXVIII, that the separation is as effective with thioacetamide as with hydrogen sulfide. Therefore, the separation by thioacetamide differs from that of the classical hydrogen sulfide separation only in that the gas is generated by hydrolysis of thioacetamide within the solution,thus eliminating the need for equipment for gas generation. The precipitation of zinc sulfide by the direct reaction is not a serious cause of contamination

Table XXVIII

Comparison of the Effectiveness of the Separation of Lead(II) from Zinc(II) by Thioacetamide and Hydrogen Sulfide at 90°C.

Solutions: 10 ml., 0.6 M in chloride, 0.3 M in hydrogen ion, initially 20 mg. lead(II), and saturated in hydrogen sulfide at 0.40 VF in thioacetamide. Samples taken after 20 min. at 90°C.

Initial Zn(II), mg.	Zn(II) in precipitate, mg.	
	Thioacetamide Solution	Hydrogen Sulfide Solution
120	0.4	0.4
60	0.3	0.3
14	0.02	0.02
7	0.01	0.01

because the time required for one-half the thioacetamide to hydrolyze is nine to ten minutes at this pH and temperature and thus the rate of the direct reaction is reduced by a half. At a hydrogen ion concentration of 0.3 M and a thioacetamide concentration of 0.50 or less the precipitation by this reaction would be negligible.

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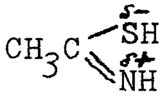
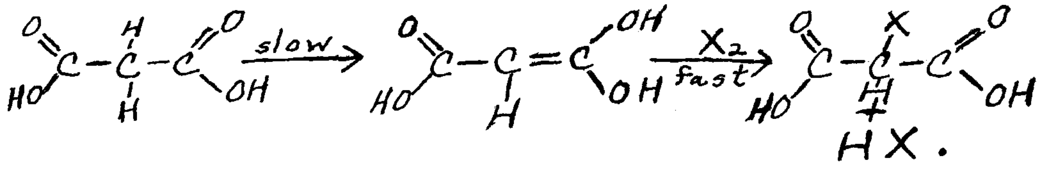
Propositions

1. In Part III B of this thesis it was shown that the rate of precipitation of cadmium as sulfide in the pH range 3 to 6 by thioacetamide is slower in the presence of chloride. It is proposed that this is due to an active state of thioacetamide such as  $\mathrm{CH_3C}{\overset{\delta-}{\diagup \mathrm{SH}} \atop \overset{\delta+}{\diagdown\!\!\diagdown \mathrm{NH}}}$. Such a state can be used to explain several facets of the mechanisms of the precipitation of metal sulfides by thioacetamide (1,2,3,4).

2. The use of either borax or sodium acetate as a replacement *for the Zimmerman-Reinhardt reagent in the* titration of iron(II) by permanganate has been reported (5). However, the titre values of iron(II) decreased with increased concentration of these substances. Any effects of borax could be due to a pH change; sodium acetate could cause either a pH change or the formation of a ferric acetate complex. The data are not conclusive particularly because an excess of acid was present. In order to evaluate the effectiveness of these materials, a systematic study should be made.

3. The reactions of malonic acid with bromine and iodine probably proceed by the same reaction mechanism, although contradictory reports have been published (6,7).

It is believed that spectrophotometric measurements would prove that the mechanism of the reaction is



In excess halogen, or at higher temperatures, the dihalomalonic acid would be formed through a second, similar reaction.

4. Stone and Finston (8) reported the successful separation of bismuth as the sulfide from uranium in 2N nitric acid by thioacetamide. Their study would be more convincing if the amount of uranium in the precipitate, and the bismuth left in solution had been checked. However, counting techniques similar to the one used should afford an excellent method to study the rates of reaction in studies of precipitation from homogeneous solutions.

5. Quite often it is impossible to determine the basis chemists have used for the rejection of data. Some standardized procedure, one which is based on statistics, should be adopted by the scientific societies. Any deviations from this procedure in any report should be fully justified by the author.

6. The rates of reaction of olefins with halogens might be measured conveniently in a coulometric cell in which the halogen is electrolytically generated (9,10,11,12).

7. It is proposed that a study of the mechanisms of the precipitation of Sb(V) and Sb(III) as sulfides from acid solutions by thioacetamide be initiated. If an apparently direct reaction of thioacetamide with Sb(V), similar to that reported for As(V) (1), is observed, spectrophotometric studies of the rate of the disappearance of thioacetamide should be made.

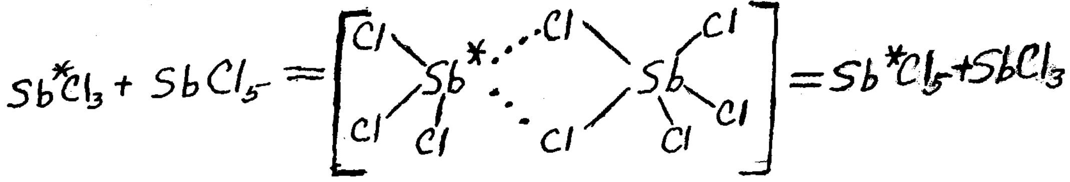
8. Barker and Kahn (13) reported that the rate of exchange of radioactive antimony between Sb(III) and Sb(V) can be calculated from the expression

$$R = 1 \times 10^{6} e^{-\frac{19000}{RT}} (SbCl_5) + 4 \times 10^{6} e^{-\frac{15000}{RT}} (SbCl_3)(SbCl_5)^2 .$$

Calculations from their data show that the expression

$$R = 1.1 \times 10^{12} e^{-\frac{28900}{RT}} (SbCl_3)(SbCl_5)$$

is valid, and a mechanism such as



might be proposed. The latter is a more defensible mechanism for the exchange reaction than that proposed by these authors.

9. Evidence cited for the existence of stable nickel chloride complexes in aqueous solution is not convincing (14,15,16) and is contrary to other work. Additional data should be obtained.

10. Several items to be included in a more extensive program for the orientation of graduate students in the chemistry department are proposed.

11. An efficient air conditioning system, as regards to both heating and cooling, should be installed in the chemistry building.

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