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Anodic dissolution and disintegration of indium, thallium, and indium-cadmium solid solutions and valency of the ions going into solution.

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ANODIC DISSOLUTION AND DISINTEGRATION OF INDIUM, THALLIUM, AND INDIUM-CADMIUM SOLID SOLUTIONS AND VALENCY OF THE IONS GOING INTO SOLUTION

BY

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A

THESIS

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ABSTRACT

Indium was found to form only In^{+3} ions when dissolving anodically in aqueous acid solutions. Thallium dissolves anodically in acid solutions giving Tl^{+1} ions only. The reason why Faraday's law is not being formed is that the anode undergoes partial disintegration producing small metallic particles.

Disintegration of these anodes depends on several factors: the nature and concentration of the corrosive medium, the surface condition of the anode, the current density, and the temperature of the corrosive solution. Disintegration may be due to different mechanisms depending on the nature of the electrolyte.

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I INTRODUCTION

In the past few years indium has found increasing industrial application. One of the properties of indium responsible for this increased use is its good resistance to corrosion. In its pure form it is highly resistant to acids and alkalis and remains untarnished during exposure to most atmospheres. Of the common acids and bases indium is susceptible only to fairly concentrated perchloric acid. As a result of this high resistance it is alloyed in small amounts with steels and solders to improve their corrosion properties.

Pure indium is plated on engine bearing surfaces since its soft "oily" physical nature gives low friction and it has high resistance to corrosive attack by lubricants and combustion products. Indium is also used in nuclear applications because of its unique combination of nuclear and anti-corrosive properties. Due to low melting points and high wetability, indium and indium-silver alloys are used for bonding metals, and metals to non-metals especially in specialized electrical applications.

Metallic thallium has not been available in sufficient quantities to allow appreciable industrial application. It is less resistant to corrosive attack than indium but does exhibit relatively good resistance to corrosion.

Thallium tarnishes on contact with air to form a black product. Compounds of thallium are quite toxic and are sometimes used as pesticides.

The purpose of this study was to observe the behavior of indium and thallium during their anodic dissolution in aqueous solutions. It has been reported in the literature that these metals show deviations from Faraday's law when undergoing anodic dissolution in serveral media.(10,11,17) This investigation was aimed at studying these deviations and attempting to present a mechanism for their occurence.

II LITERATURE REVIEW

The fact that some metals do not appear to obey Faraday's law during anodic dissolution has been known for more than a century. Beetz (1) observed "reversed electrolysis" in the case of a magnesium anode which resulted in greater than 100% current efficiency during dissolution. He also observed darkening of the anode surface, the evolution of hydrogen from the anode, and a suspension of small magnesium particles in the anolyte. Wöhler and Buff (2) reported a similar occurrence for an aluminum anode undergoing electrolysis. As the least likely of several possibilities, they suggested the possibility of the formation of low valent ions.

Turrentine (3) studied the behavior of anodes of magnesium and aluminum. He explained the experimental results by proposing that dissolution took place partially as univalent ions. Later work by Epelboin (4) on zinc anodes supported the low valent ion proposal. In recent years greater than 100% current efficiency for anodic dissolution has been observed and studied for beryllium, iron, indium, gallium, zinc, thallium, aluminum, cadmium, magnesium, and titanium.

Del Boca (5) proposed a mechanism for the anodic behavior of cadmium, zinc and aluminum which involved either the production of a colloidal suspension or the formation of complex ions such as $Cd \cdot Cd^{++}$, $Zn \cdot Zn^{++}$, or $Al_2 \cdot Al^{+++}$. In partial agreement Marsh and Schachl (6) suggested a "chunk effect" for anodic dissolution of steels at fairly high rates. They maintained that oxidation at the anode surface is accompanied by the expulsion of chunks of metallic iron containing several atoms. Other investigations (7,8,9) have suggested the probability that under certain conditions anodic dissolution is film controlled; the spalling of the surface film carries away small metallic particles which go into solution outside the electrical circuit.

Davidson, Kleinberg, and co-workers (10,11,12,13,14, 15,16,17) favor the uncommon valency theory as a mechanism. McElroy, Kleinberg, and Davidson (10) studied the dissolution of the higher members of the aluminum family in liquid ammonia solutions of NH_4Br and obtained initial valencies ranging from 2.01 to 4.72. They account for valencies below 3.00 as In going into solution along with the In and valencies above 3.00 as due to passivation effects. They observed hydrogen and nitrogen evolved at the anode and metallic indium suspended in the anolyte which they explain by the following reactions:

1 $In^{+} + 2NH_4^{+} \longrightarrow In^{+++} + 2NH_3 + H_2 \uparrow$

Reaction 1 produces the observed hydrogen.

2 $3NH_2^- \rightarrow \frac{1}{2}N_2 + 2NH_3 + 3e^-$

Reaction 2 produces the observed nitrogen;

3 $3In^+ \rightarrow In^{+++} + 2In^0$

Reaction 3 produces the observed suspended metallic indium.

Davidson and Jirik (11) also studied indium but in acetic acid solutions. They found initial valencies of ions going into solution in 18.6 mole % NH_4Ac at .006 to .011 amp/om^2 in the range of 2.38 to 2.10. They explain this by In^+ ions going into solution and immediately disproportionating into In^{+++} and In^0. This also would explain observed indium particles in the anolyte and the failure to detect In^+ ions in the solution.

Further, McElroy, Kleinberg, and Davidson (10) also studied the dissolution of thallium in liquid ammonia solutions. At current densities of approximately 0.012 amp/cm^2 they obtained initial valencies of 2.01 to 1.19 in NH_4Br, 0.92 to 0.98 in nitrates, 1.34 in NH_4Cl, and 2.33 in saturated KNH_2. Thallium dissolving anodically in acetic acid solution was studied by Davidson and Jirik (11). They dissolved thallium anodes in 3 mole % NaAc at current densities up to 1 amp/cm^2 and obtained dissolution amounts 60% to 100% higher than would be expected for Tl^+ but could find no thallium ions of greater charge than +1 in the solution.

They hypothesized that the excess was due to non-electrolytic oxidation.

Raush, McEinen, and Kleinberg (12) proposed similar mechanisms for the aluminum group in pyridine solution of LiCl. Shug and Sadowski (18) also discuss the dissolution of gallium in terms of Ga^{+} ions as an intermediate step in the dissolution along with the normal Ga^{+++}.

For beryllium (19), gallium (20), magnesium (8), and other anodes it was shown that simultaneously with anodic dissolution, disintegration of the anode into very small metallic particles occurs. This may account for the greater dissolution at the anode than required by Faraday's law. Laughlin, Kleinberg, and Davidson (13) had observed colloidal beryllium particles in the anolyte but assumed them to be the product of disproportionation, as in the case of indium, of a unipositive ion. Detailed examination of these particles (19) at high magnification, however, disclosed deformation twins in the black product which could only have come directly from the anode itself.

In the case of gallium (20), streams of dark material were observed streaming down the face of the anode. High power microscopic examination in both reflected and transmitted light indicated these particles were metallic. It should be pointed out that in all cases where unipositive ions were proposed the presence of these ions in solution could not be detected. From an oxidation potential standpoint (21) In^+ (Equation 3) would disproportionate if it was formed by dissolution; Be^+, however, would not be subject to disproportionation. Also, disproportionation would certainly not be expected to produce metallic particles containing deformation twins.

Equations 1 and 2 proposed by McElroy, Kleinberg, and Davidson are given with little explanation. Equation 1 would result in the buildup of NH_2^-; this is evidently the justification for equation 2. They evidently assume that the electrons are absorbed by the anode. This reaction could account for the observed nitrogen. The validity of equation 2, however, has no bearing on whether or not equation 1 occurs. Alternative equations which would also give the same observed results would be equations 4, 5, and 6;

4 $In^o + 3NH_4^+ \rightarrow In^{+++} + 3NH_3 + \frac{3}{2} H_2$

5 $3NH_2^- \rightarrow \frac{1}{2}N_2 + 2NH_3 + 3e^-$

6 $NH_3 \rightleftarrows \frac{1}{2}NH_4^+ + \frac{1}{2}NH_2^-$

The metallic indium in equation 4 is provided by partial disintegration of the anode into small particles. The electrons produced by equation 5 are taken up by the anode and the amide ion is provided by equation 6 in the solvent.

When Davidson and Jirik (11) dissolved thallium anodically in concentrated acetic acid solutions, they obtained dissolution 60% to 100% higher than would be expected for thallous ions. This would give an initial apparent valence in the neighborhood of 0.5. This was explained as being due to non-electrolytic oxidation. Although thallium is only slightly more active than the other metals studied, it was the only one for which non-electrolytic oxidation was given as a factor. Any other explanation would have to involve some kind of anodic disintegration and would in turn put in doubt the disproportionation of monovalent indium.

III EXPERIMENTAL

A. Equipment and Procedure

The experimental plan was divided into several parts; valency determination by the hydrogen evolution method; valency determination by the use of an amalgamated electrode; disintegration observation experiments; and the study of the particles by oil immersion optical microscopy, electron microscopy, and x-ray diffraction; and quantitative disintegration measurements.

1. Valency Determination by the Hydrogen Evolution Method.

To determine the stable valences of pure indium and thallium in aqueous acid solutions a constant temperature bath and a gas burette were used (See Fig. 1). Approximately 80 ml. of acid were placed in the reaction flask and a weighed sample was put into a platinum basket suspended from a small magnet by a platinum wire. The entire system was flushed with hydrogen and closed before each run. The sample basket was then lowered into the acid by means of an outside magnet.

Initial and final readings were recorded as well as the burette temperature and atmospheric pressure at the time of the final reading. End points were usually fairly abrupt but for certainty an evolution versus time plot was maintained during each run.

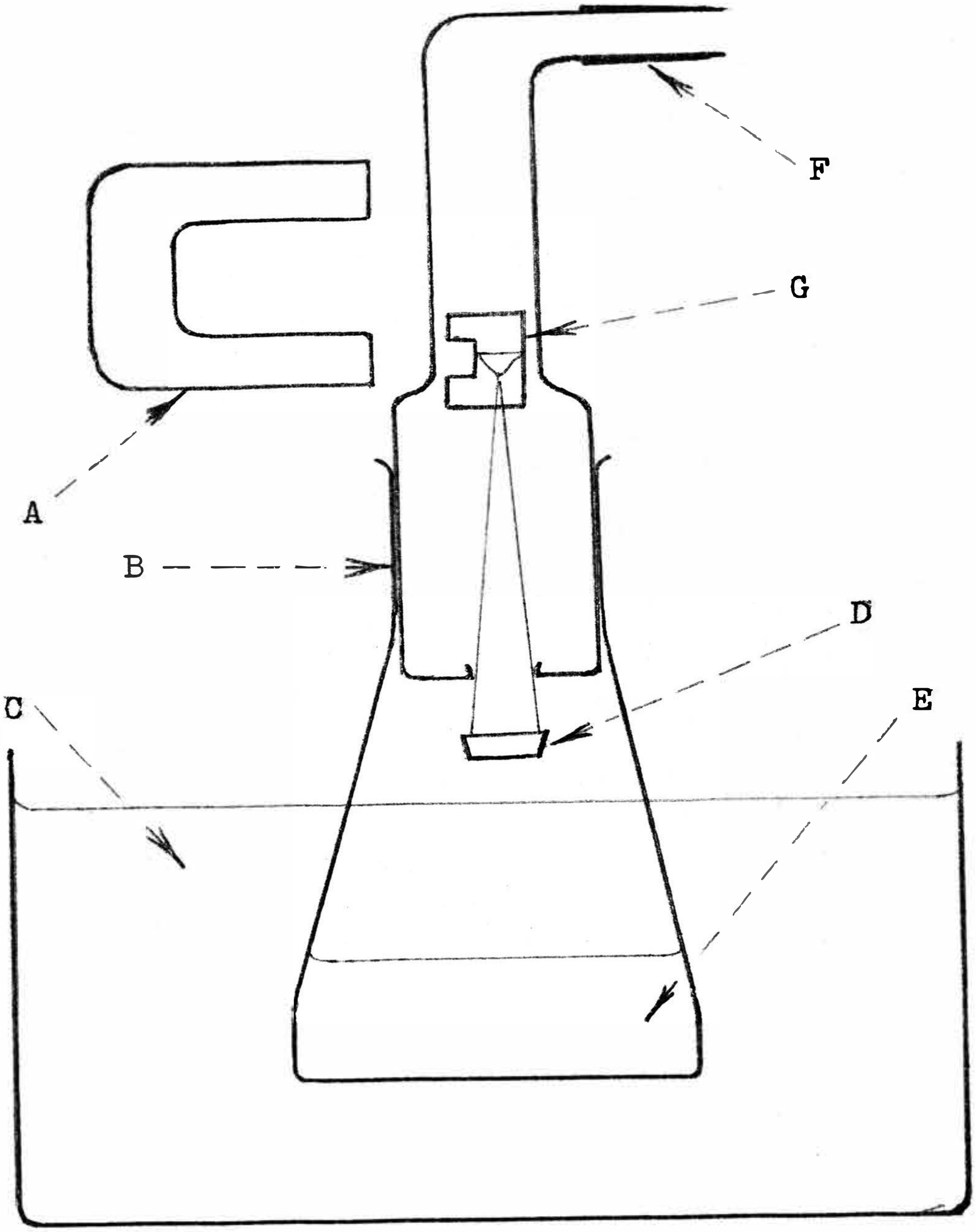


Figure 1

Experimental Setup for Hydrogen Evolution Valence Measurements

A. exterior magnet

B. joint sealed with vacuum grease

C. constant temperature water bath

D. platinum sample basket

E. reaction flask containing acid

F. outlet to gas burette

G. small, plastic covered magnet

The volume of hydrogen was corrected to standard conditions (e.g. dryness, 0^oC, and 760 mm.) and the valency of the ions going into solution calculated as follows:

$$\text{Theoretical } H_2 \text{ Volume} = \frac{\text{weight sample}}{\text{atomic weights}} \quad \text{(assumed valence).}$$

If indium produces In^{+++} ions the theoretical volume of H_2 will be:

$$Vi = \text{sample wt.} \ \frac{(3)(11,200)}{114.76} = (\text{Sample wt.})(293\text{ml}).$$

If thallium produces Tl^{+} ions the theoretical volume of H_2 will be:

$$Vi = \frac{(\text{sample wt.})(1)(11,200)}{114.76} = (\text{Sample wt.})(54.7 \text{ ml.})$$

The valency is then calculated by:

$$\text{Valence} = \frac{\text{connected actual } H_2 \text{ vol.}}{\text{theoretical } H_2 \text{ vol.}} \times \text{assumed valence}$$

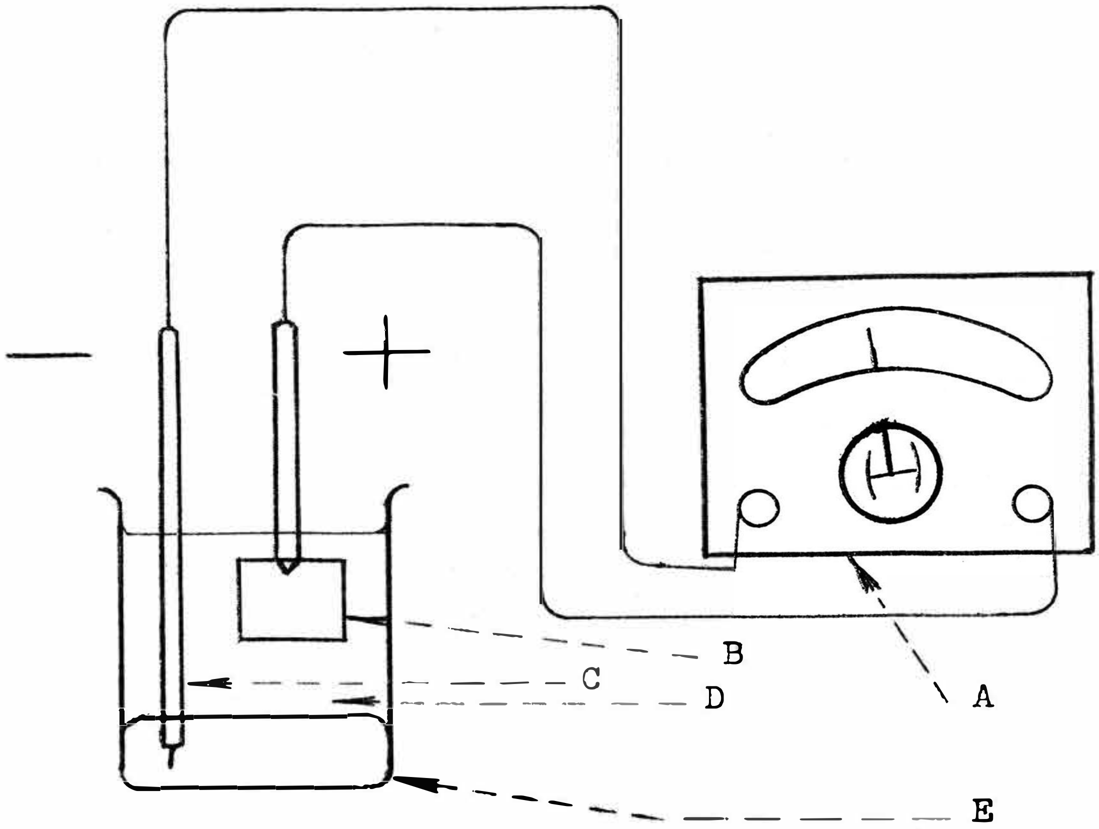
The results of these determinations are given in Tables I and II.

2. Valency Determination by Use of Amalgam Electrodes.

To determine the valency of indium and thallium ions going initially into solution, metal samples were dissolved in triply distilled mercury and allowed to enter into solutions anodically as shown in Fig. 2. The amount of mercury used was about 1 ml. A platinum wire extending from a sealed glass tube was in contact with the amalgam to serve as the anode terminal while a platinized platinum electrode

Figure 2

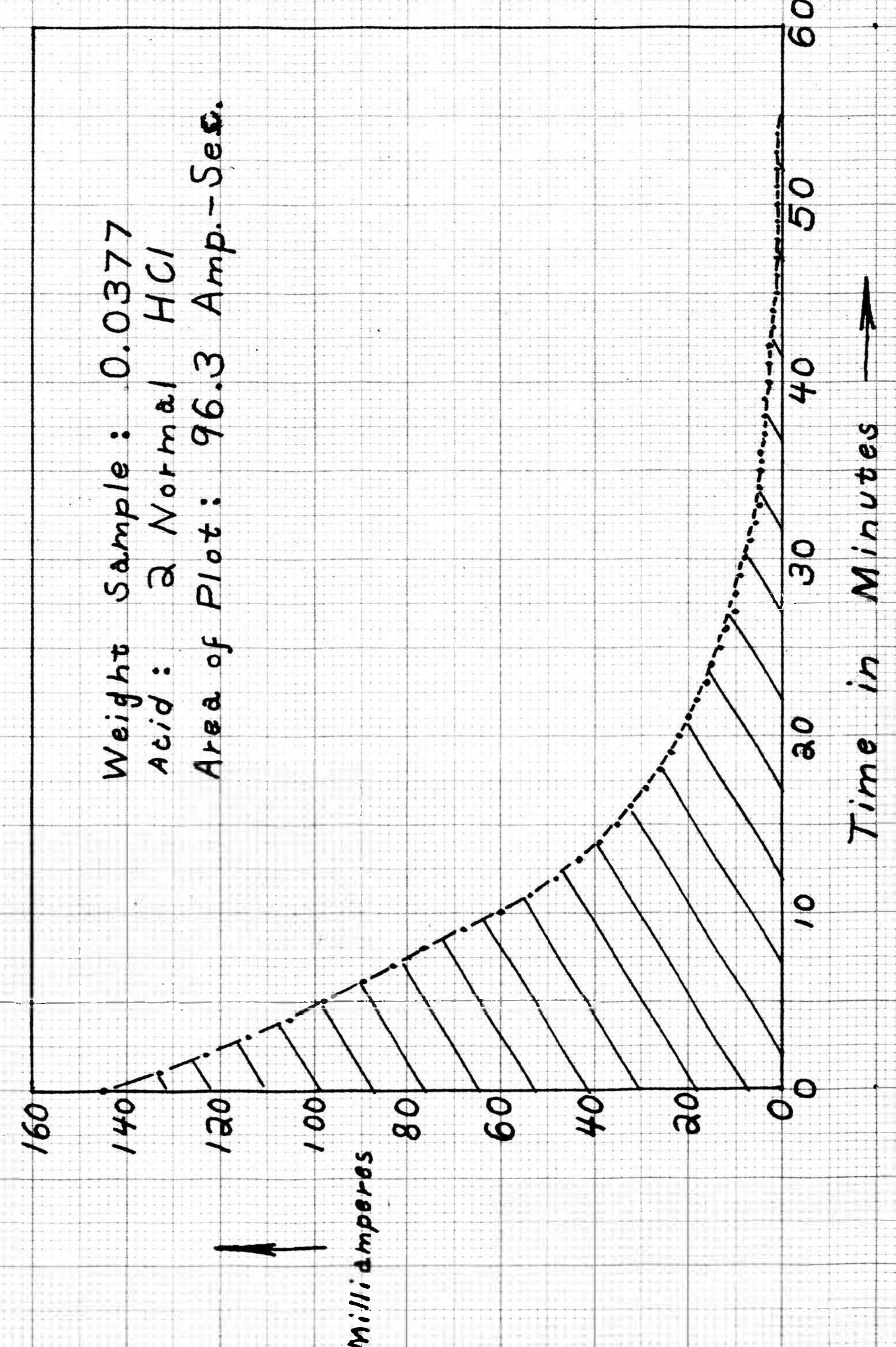
Experimental Setup for Amalgam Electrode Valence Measurements



A.	Weston direct current milliammeter	D.	aqueous acid solution (dissolving medium)
B.	platinum electrode	E.	amalgam containing sample
C.	platinum wire in sealed glass tube		

Figure 2a

Typical Current vs. Time Plot for Dissolution of Indium from Amalgam Electrode



suspended in the acid was used as the cathode. For the proportions used both indium and thallium were completely dissolved in the mercury.

The current produced by each cell was measured by a sensitive milliammeter which was read at 1 minute intervals. These readings were plotted against time and the area under the curves determined with a compensating planimeter. Since the areas were relatively small, four measurements, two clockwise and two counterclockwise, were made and the measurements averaged. A typical plot is shown in figure 2a.

In the runs with perchloric acid the solutions were tested after each complete dissolution with a few drops of silver acetate solution to determine the extent of the reaction:

$$HClO_4 + 8H^+ \rightarrow HCl + 4H_2O$$

by observing the precipitation of AgCl.

The determinations with thallium in HCl and $HClO_4$ required that the amalgam be constantly stirred to break up the films of insoluble TlCl which insulated the amalgam if left intact. The electric stirrer used was slowed by means of a rheostat to avoid excess surface reaction between the amalgam and the acid. The amalgam, on stirring, would tend to form small spheres which would be insulated from the circuit; after zero current was first obtained, the cells were allowed to stand with the circuit open for about five minutes to recoagulate the amalgam. A small additional current could then be obtained whose area was added to the first plot.

Stirring was also used for determination but for a different reason since TlF is soluble. Stirring with HF solutions gave current versus time plots which were less asymptotic to the axes and hence could be more accurately measured. An added precaution in HF dissolution was the protection of the exposed glass with a wax coating.

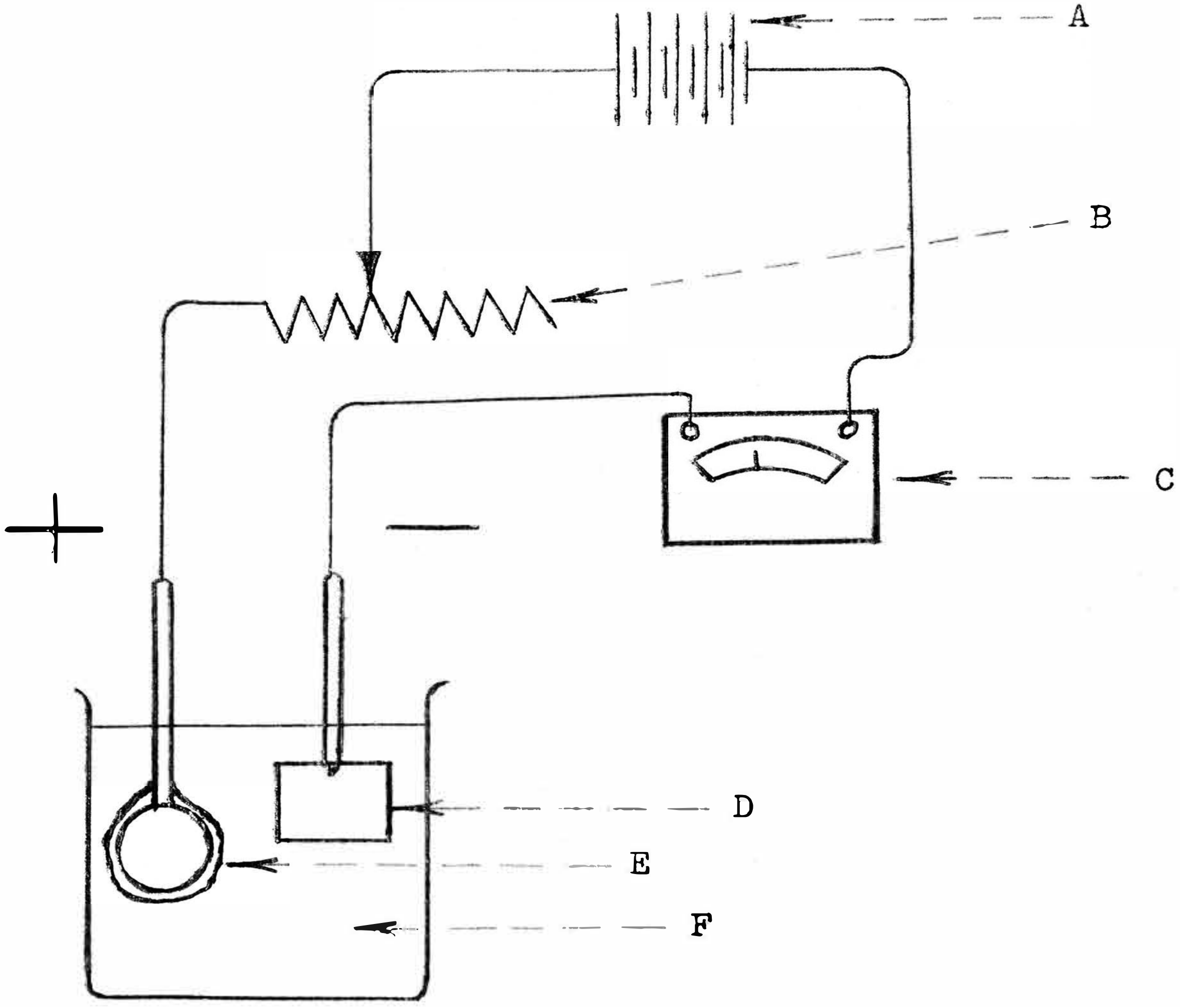
The effect of an oxidizing agent was checked in HF by making several determinations with an addition of a few drops of 3% H_2O_2 was verified periodically by adding a small crystal of $KMnO_4$ and watching for decolorization.

Hydrogen bubbles sometimes formed on the amalgam surface but were assumed to be from dissolved hydrogen rather than local circuits. This assumption was based on the observation that bubbles were attached to all parts of the cell (electrode tubes and beaker sides) and none could be seen rising to the surface of the acid. The exceptions to the preceding observation were the determinations made in relatively concentrated acids.

No actual valencies were calculated for these runs. For indium the weight of the sample was compared with the

Figure 3

Experimental Setup for Qualitative Disintegration Studies



A.	wet cell battery	D.	platinum electrode
B.	variable resistance box	E.	wax backed electrode of metal sample
C.	milliammeter	F.	dissolution medium

weight which should have been dissolved by the amount of ampere - seconds under the current versus time plot assuming a valency of 3. In the case of thallium, the theoretical amount of ampere - seconds which should be produced by the dissolution of the sample assuming Tl + 1 was compared with the measured ampere - seconds. For both metals a percent difference between actual and theoretical was computed. The results of the amalgam electrode valence determinations are given in Table III through IX.

3. Disintegration Experiments

Electrodes were constructed of indium and thallium and dissolved electrolytically using current from a direct current source. The exposed area of each electrode was measured approximately, and the electrodes dissolved anodically as shown in Fig. 3. The cathode consisted of a platinized platinum electrode.

Current densities were controlled by using a variable resistance box in the circuit. Various solutions and concentrations were used, the behavior of the anode being observed at increasing current densities. The nature of any film formed or any material streaming down the face of the anode were particularly noted. Care was taken to assume that the anode surface was clean before each run.

If particles fell to the bottom of the beaker, they were agglomerated if possible, and washed thoroughly with distilled water. Agglomeration could often be accomplished by tilting the beaker from side to side; agglomeration facilitated washing and transferring. After the washing to remove salts, the particles were dried and transferred to a microscopic glass slide for examination. Chips of any films which spalled off the anode were also washed and examined.

Unlike the more noble indium particles, the thallium particles were relatively unstable in many media and would rapidly oxidize if not quickly immersed after formation in dry acetone. This was especially ture of the particles in films that were formed on the thallium anode. It was also necessary to examine thallium particles fairly soon after their preparation as they were subject to oxidation by air over a period of time.

To determine the crystalline structure of disintegration particles over a compositional range of indium-cadmium solid solutions, electrodes were made and electrolyzed as described above. The current density and other variables were held as constant as possible from alloy to alloy. The particles thus obtained were examined by x-ray diffraction methods. Powder patterns were made of filings of the parent alloys as well as the disintegration particles.

The results of the above disintegration studies are given in Tables X, XI, and XII.

4. Examination of Disintegration Particles

Particles and films formed by anodic disintegration were examined in three ways: optically by high magnification employing oil immersion, by electron microscopy, and by use of x-ray diffraction powder patterns.

For optical microscopic examination a Reichert research microscope was used. The samples of particles were placed on optical glass slides and examined at progressively higher power until 1430X was reached using an oil immersion objective lens. The material was examined in both reflected and transmitted light. Metallic particles gave lustre in reflected light and appeared completely opaque in transmitted light. Metal particles could be distinguished from any salt particles present since salt particles would appear clear or at least transluscent in transmitted light. Several photographs of the particles were taken through the microscope.

Samples for examination with the electron microscope were transferred from a glass slide into small test tubes. They were then suspended in a few drops of alcohol by ultrasonic vibration. A drop of this suspension was then placed on a small circular 200 mesh wire screen.

The wire screen was then placed on a sample holder which could be inserted in the electron microscope with a minimum loss of vacuum. The samples were then examined at magnifications from 3,500X to 15,000X. The particles appeared as dark areas in the openings of the wire mesh. Particles which were typical of each sample were photographed by means of a camera which could be conveniently swung into the path of the electron beam. Latex marker spheres of a known diameter were added to the samples to aid in determining the size of particles in photographs.

To produce a shadowing behind the particles to give a measure of relative height, some samples were shadowed with sublimed chromium vapor at an angle of approximately 45°. This was done in a vacuum chamber using an electric filament to vaporize the chromium.

For examination of the particles by x-ray diffraction a powder camera was utilized using the asymmetric film loading method. Samples were transferred from a glass slide onto the fiber of a goniometer and subjected to nickel filtered copper radiation for 1 to 1½ hours. When making powder patterns of indium particles it was desirable to use an aluminum screen inside the camera to cut down fluorescence which would give dark backgrounds to the films.

Identification of indium patterns was made by comparing the unknown patterns directly with patterns made under the same conditions using indium filings. This line-for-line direct comparison was also used for metallic thallium particles. For the indium-cadmium particles direct comparison was made with patterns prepared by P.B. Rao(24).

For nonmetallic patterns it was necessary to measure the film lines to determine the "d" values of the material. These "d" values were then compared with those tabulated in the A.S.T.M. files and the material thereby identified.

Photographs and a sample of the x-ray patterns made in the above examinations are given in Fig. 5 through 19.

5. Quantitative Disintegration Studies

To determine the apparent valence or amount of disintegration, a cell was set up as shown in Fig. 4. Anodes were constructed by mounting samples of indium and thallium in lucite in a metallographic mounting press. Electrical contact was made with each electrode by drilling a small hole through the mounting into the metal and inserting the end of a wire. The wires were then enclosed in glass tubes and sealed with wax. The metal, with a known surface area, was next anodically dissolved using a platinum electrode as a cathode.

Before each run the anode was given a surface preparation which consisted of rough polishing on emery paper following by thorough washing with distilled water. During

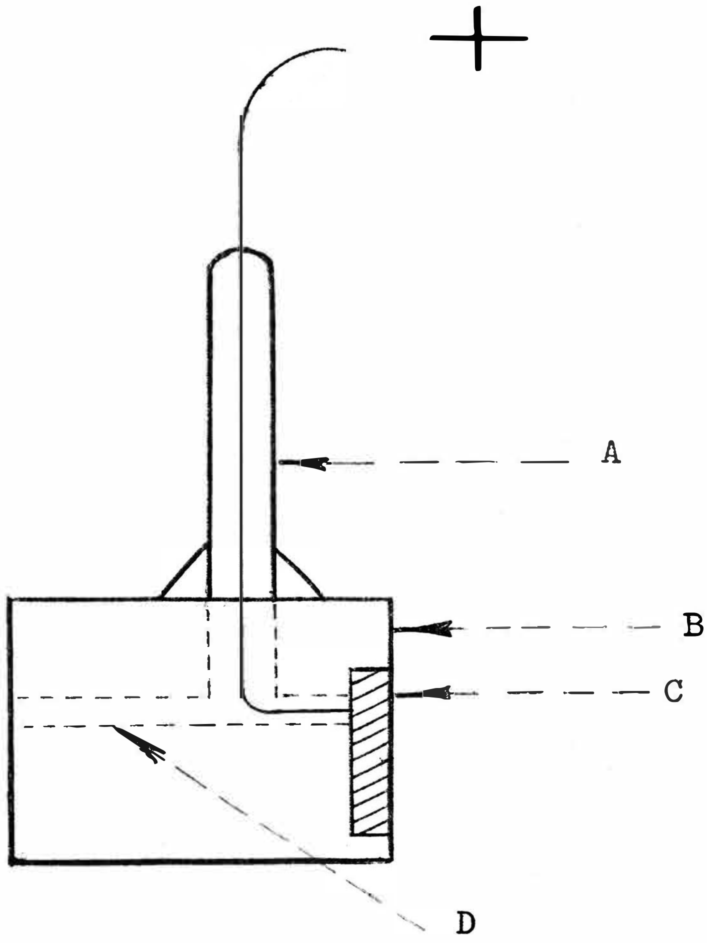


Figure 4

Anode Details for Quantitative Disintegration Studies

A. connecting wire in sealed glass tube

B. lucite mounting

C. metal sample

D. wax-filled holes drilled to connect wire to sample metal

(Same electrical circuit as shown in Figure 3) each run the current was held constant with a variable resistance box. The current was recorded and the time for which it flowed. All factors except the variable being investigated were held as constant as possible from one run to another.

In indium determinations, particles often accumulated on the bottom of the cell. After the decanting of the solution, the particles were dissolved in hot concentrated $HClO_4$ and this $HClO_4$ added to the original solution. All beakers were washed with distilled water after emptying and the washing were added to the solution to be titrated.

The indium solutions were titrated directly with .01 M E.D.T.A. solution which had been standardized against a standard indium chloride solution. Thallium solutions, after transfer to the titrating flask, were oxidized to Tl^{+++} by adding bromine water and boiling off the excess bromine. This was necessary since Tl^{+++} forms a complex with E.D.T.A. while Tl^{+} does not. The thallium solutions were then back titrated with E.D.T.A. and $MgSO_4$ which had been standardized against a standard $Tl_2(SO_4)_3$ solution. The details of the indium and thallium E.D.T.A. titrations are given in the Appendix.

Blank runs were made with each metal at each temperature, acid, and concentration to determine the amount of dissolution due to local curcuits on the anode surface.

The results of these blank runs (when self dissolution did occur) were subtracted from the titrated amount of metal ions in the electrolysis runs. In making these blanks all factors were as near as possible to the closed circuit runs except that no current was passed. Indium had measurable self-dissolution only at fairly high temperatures (80°to 100°C) whereas thallium showed some self-dissolution at room temperature. Trial titrations were also made in each acid to be certain that the various acids caused no problems in the titrations.

The amount of metal titrated was compared to the amount predicted by Faraday's law for the amount of ampere-seconds passed through the cell. From this the percent of disintegration was calculated by:

$$\% \text{ Disintegration} = \frac{\text{(wt. metal titrated)-(wt. metal theoretically by the amp-sec.)}}{\text{wt. metal titrated}}$$

The percent of disintegration was determined as a function of acid, current density, and temperature.

Results of these studies are given in Figures 21 through 25.

B. MATERIALS

The indium and thallium metal used in this investigation were high purity zone refined samples obtained from American Smelting and Refining Company. They were each of 99.999^{+} % purity. The indium-cadmium alloys used were prepared by P.B. Rao(24) from 99.999 + % indium and equally pure cadmium, also obtained from American Smelting and Refining Company.

Acids used were of reagent grade obtained from Fisher and Mallinckrodt chemical companies. Chemicals used in quantitative determinations were all of reagent grade, meeting A.C.S. specifications.

Coulometric measurements were made using a sensitive Weston direct current milliammeter of high quality.

IV EXPERIMENTAL RESULTS

The experimental results are given in the following order:

A. Valency of ions by hydrogen evolution method.
   1. Indium (Table I)
   2. Thallium (Table II)

B. Valency of ions by amalgam electrode method.
   1. Indium (Tables III through V)
   2. Thallium (Tables VI through IX)

C. Anodic disintegration.
   1. Qualitative study
      a. Indium (Figures 5 through 10)
      b. Thallium (Figures 11 through 15)
      c. Indium-cadmium alloys (Figures 16 - 19)
   2. Quantitative study
      a. Indium (Figures 21 through 24)
      b. Thallium (Figure 25)

Table I shows that the stable valence of indium in hydrochloric acid is + 3. These determinations were made using the hydrogen evolution method described in Chapter III.

Table I

Dissolution of Indium in 6N Hydrochloric Acid

Hydrogen Evolution Method

Weight of indium in grams	Difference in burette readings in ml.	Corrected volume of H_2 evolved in ml.	Valence of indium ions
0.0700	23.70	19.8	2.90*
0.0586	20.35	16.7	2.93*
0.1162	38.40	33.60	2.97
0.1109	38.20	32.75	3.02
0.1684	58.00	49.60	3.01

*Some hydrogen was lost in placing the sample in the acid.

All runs were made at 37.5° C.

The following table, Table II, gives the results of the determinations of the stable valence of thallium dissolving anodically in sulfuric acid.

Table II

Valency of Thallium
In 9N H_2SO_4

Hydrogen Evolution Method

Wt. thallium sample in grams	Corrected volume of H_2 evolved in ml.	Theoretical H_2 volume for Tl +1 in ml.	Valency
0.1481	7.95	8.1	0.98
0.2097	15.5	15.5	1.00
0.2025	11.4	11.2	1.02
0.1284	7.4	7.0	1.06
0.3731	20.7	20.4	1.01
0.3082	17.1	16.9	1.01
0.2464	13.7	13.5	1.01
0.2240	12.3	12.3	1.00
		Average	1.01

The above table also gives data obtained by the hydrogen evolution method and shows the valence of thallium to be +1.

Tables III, IV, and V demonstrate that the initial valence of indium entering solution during anodic dissolution is +3 in many types of acids. Details and observations are made for each set of determinations at the bottom of the table. These data were obtained using an amalgam electrode.

Table III

Anodic Dissolution of Indium in 2N Hydrochloric Acid Amalgam Electrode Method

Atmosphere	**Input of** indium in grams	Amp-sec. drawn	Output of indium assuming In^{+3}	Percent diffenence
air	0.0586	148	0.0590	+0.7
"	0.0635	163	0.0646	+1.7
"	0.0793	202	0.0802	+1.1
"	0.0391	98.4	0.0391	0.0
"	0.0377	96.3	0.0382	+1.3
"	0.1106	277	0.1100	-0.5
"	0.1214	313	0.1243	+2.4
hydrogen	0.0471	119	0.0474	+0.6
"	0.0474	118	0.0469	-1.1
"	0.0454	116	0.0458	+0.9

Average difference +0.6 %

All runs made at room temperature.

Table IV

Anodic Dissolution of Indium in Perchloric Acid
Amalgam Electrode Method

Normality of acid	Input of indium in grams	Amp-sec. drawn	Output of indium assuming In^{+3}	Percent difference	Remarks*
4 N	0.0568	142	0.0566	- 0.4	no clouding
"	0.0482	118	0.0470	- 2.5.	"
"	0.0450	112	0.0448	- 0.4	"
"	0.0375	95.2	0.0377	+ 0.5	"
"	0.0436	106.5	0.0423	- 3.0	very slight clouding
"	0.0430	106.5	0.0423	- 1.6	no clouding
"	0.0429	109	0.0432	+ 0.9	"
"	0.0425	107	0.0424	- 0.2	"
"	0.0399	102.5	0.0406	+ 1.7	very slight clouding
"	0.0374	93.8	0.0373	- 0.3	no clouding
"	0.0430	106	0.0421	- 1.6	"
"	0.0518	129	0.0512	- 1.0	"
8 N	0.0298	75.0	0.0296	- 0.7	some clouding

Average Difference - 0.6 %

*Addition of Ag^{+} ions to acid after complete dissolution compared to an addition to a sample of original acid.

All runs made at room temperature, in air atmosphere.

Table V

Anodic Dissolution of Indium in Sulfuric Acid

Amalgam Electrode Method

Strength of Acid	Input of indium in grams	Amp-sec. drawn	Output of indium assuming In^{+3}	Percent difference
4 N	0.0506	125	0.0497	- 1.8
"	0.0439	111.5	0.0442	+ 0.7
"	0.0477	123	0.0488	+ 2.1
"	0.0388	100	0.0396	+ 2.0
"	0.0380	97.7	0.0388	+ 2.0
"	0.0470	115	0.0457	- 2.8
8 N	0.0371	95.5	0.0379	+ 2.1
"	0.0412	104.3	0.0413	+ 0.2
"	0.0295	75.2	0.0298	+ 1.0
"	0.0290	75.4	0.0299	+ 3.1
"	0.0323	79.8	0.0317	- 1.9
"	0.0338	84.0	0.0334	- 1.2
			Average difference	+ 0.5 %

Very slight evolution of hydrogen from the amalgam surface was observed during the runs in 8 N. sulfuric acid.

All runs made in air at room temperature.

Tables VI, VII, VIII, and IX give the valence of thallium ions going initially into solution in various acids to be + 1.

Table VI

Anodic Dissolution of Thallium in Sulfuric Acid

Amalgam Electrode Method

Normality of acid	Input of thallium in grams	Amp-sec. drawn	Output of thallium assuming Tl^{+1}	Percent difference
13 N	0.0296	13.3	0.0282	- 4.7
"	0.0264	12.9	0.0273	+ 3.4
"	0.0405	20.0	0.0424	+ 4.7
"	0.0366	16.9	0.0359	- 1.9
"	0.0474	22.4	0.0475	+ 0.2
"	0.0406	19.5	0.0413	+ 1.7
"	0.0280	13.6	0.0287	+ 2.5
18 N	0.0481	23.8	0.0503	+ 2.2
"	0.0515	24.8	0.0524	+ 1.7
"	0.0517	25.1	0.0531	+ 4.6
"	0.0519	25.4	0.0536	+ 1.3
"	0.1410	64.2	0.1360	- 3.5
"	0.1163	52.9	0.1120	- 3.4
4 N	0.0532	24.1	0.0512	- 3.8
"	0.0997	45.8	0.0971	- 2.6
*9 N	0.1282	59.3	0.1263	- 1.5
* "	0.2486	113.0	0.2407	- 3.2

Average withour stirring + 0.16 %

Average with stirring — 2.3 %

*Last two runs made while stirring amalgam and acid.

Table VII

Anodic Dissolution of Thallium in Hydrochloric Acid

Amalgam Electrode Method

Normality of acid	Input of thallium in grams	Amp-sec. drawn	Theoretical Amp-sec. assuming Tl^{+1}	Percent difference
6 N	0.0739	32.8	34.6	- 5.2
"	0.0750	34.8	35.5	- 1.9
"	0.1267	55.4	59.6	- 8.6
"	0.0810	37.7	38.1	- 1.0
3 N	0.0748	35.9	35.4	+ 1.4
"	0.0742	33.1	34.9	- 5.4
"	0.1491	70.4	70.4	0.0
			Average	- 3.0 %

All runs stirred during dissolution.

Table VIII

Anodic Dissolution of Thallium in Perchloric Acid

Amalgam Electrode Method

Normality of acid	Input of thallium in grams	Amp-sec. drawn	Theoretical amp-sec. assuming Tl^{+1}	Percent difference
4.4 N	0.0814	37.8	38.4	- 1.6
"	0.0749	35.0	35.4	- 1.1
"	0.0987	43.7	46.6	- 6.2
"	0.0969	44.3	45.7	- 3.1
"	0.0370	17.6	17.5	+ 0.6
"	0.0633	28.3	29.9	- 5.3
			Average	- 2.8 %

All runs stirred during dissolution.

Test of final solution with Ag^{+} showed appreciable Cl^{-} to be present in all cases.

Table IX

Anodic Dissolution of Thallium in 4.6N Hydrofluoric Acid

Amalgam Electrode Method

Additive	Input of thallium in grams	Amp.-sec. drawn	Theoretical amp.-sec. assuming Tl^{+1}	Percent difference
None	0.1043	47.2	49.2	- 4.0
"	0.2332	103.9	110.1	- 5.9
"	0.1067	48.9	50.4	- 3.1
"	0.1153	55.1	54.4	+ 1.3
H_2O_2	0.1442	66.6	68.1	- 2.2
"	0.1243	57.2	58.7	- 2.6
"	0.1059	47.5	50.0	- 5.2
"	0.2083	92.0	98.4	- 6.9

All runs stirred during dissolution.

Average without H_2O_2 - 2.8 %
Average with H_2O_2 - 4.2 %

The two following tables, Tables X and XI, show that anodic disintegration of indium and thallium was directly observed in a number of electrolytes.

Table-X

Anodic Disintegration of Pure Indium

Electrolyte		Maximum current density in ma./cm.^{2}	Behavior of anode
18.6 mole % $NH_4C_2H_3O_2$ in conc. acetic acid		100	grey streams flow down electrode surface and fall to bottom of cell, also fine white ppt.
H_2SO_4	0.5 N	450	no particles observed
	4.5 N	500	silvery particles fall to bottom and grey film slides down electrode surface.
HCl	0.3 N	450	no particles observed
	1.0 N	450	no particles observed
	4.0 N	450	no particles observed
	2.0 N	3000	near explosive generation of grey fog, metallic particles settle to bottom of cell.
$HClO_4$	5.0 N	450	grey stream to bottom, rapidly dissolves.
	2.5 N	300	grey stream to bottom, will remain for some time.
HNO_3	4.0 N	450	no particles observed
	2.0 N	350	surface of anode becomes black and flakes off, the flakes are indium sub-oxide containing numerous small metallic particles.

Table X (continued)

Electrolyte		Maximum current density in ma./cm.^{2}	Behavior of anode
KNO_3	3%	500	anode surface becomes dark and flakes off, metallic particles in flakes, also milky white ppt. ($In(OH)_3$).
NaCl	3 %	2500	white ppt.,no particles
	10 %	4000	electrode grey while current is flowing, light grey stream of particles to bottom, also white ppt.

Table XI

Anodic Disintegration of Pure Thallium

Electrolyte		Maximum current density in ma./cm.^{2}	Products at anode	Remarks
18.6 mole % $NH_4C_2H_3O_2$ in conc. acetic acid		400	metallic particles	particles will oxidize in air after a period of time, X-ray powder pattern of fresh particles shows Tl
H_2SO_4	0.5 N	1300	metallic particles, Tl_2O_3	dark material flakes off anode surface when immersed in acetone
HCl	1.5 N	500	white ppt., TlCl which contains a few metallic particles	current rapidly drops to zero
$HClO_4$	0.13N	1500	flake-like metallic particles, Tl_2O_3, and brown suspension	brown suspension shown by X-ray to be Tl_2O_3
HNO_3	1.0 N	900	white material containing some metallic part.	washed in acetone
HF	4.6 N	1600	no particles	surface darkened
	2.3 N	1100	no particles	surface darkened
	1.0 N	900	no particles	surface darkened
KNO_3	2 %	500	metallic part. and reddish Tl_2O_3	washed in acetone
NaCl	2 %	500	white ppt., no metallic particles	current soon drops to zero

Table XII, which follows, gives the results of the study of the anodic disintegration of a range of indium-cadmium alloys.

Table XII

Anodic Disintegration Particles of Indium-Cadmium Alloys

Weight percent cadmium	Desceiption of disintegration particles
0	entirely tetragonal indium
6.105	tetragonal indium with perhaps a trace of cubic indium
*7.996	tetragonal indium with a trace of cubic indium
10.00	mostly cubic indium with small amount of tetragonal indium
12.152	cubic indium with some cadmium
14.063	cadmium with small amount of cubic indium
16.082	cadmium with only a trace of cadmium

Alloys dissolved anodically in 18.6 mole % $NH_4C_2H_3O_2$ in concentrated acetic acid; the current density was appx. 100 ma./cm.^{2} for all alloys.

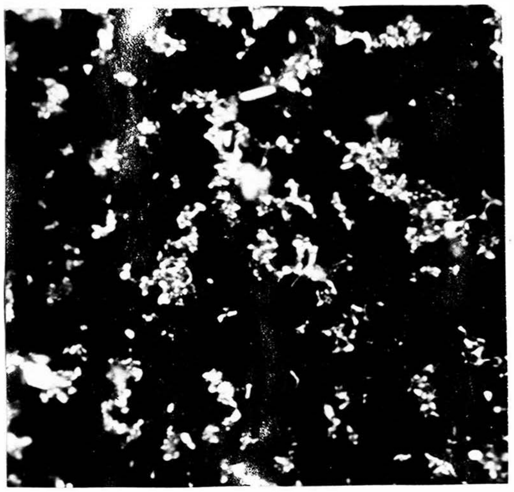
X-rays made using copper radiation, nickel filter, and aluminum screen exposed for 1 hour and 15 minutes.

* X-ray pattern of parent alloy showed it to be entirely cubic.

The following figures give examples of microscopic and X-ray diffraction evidence that the particles observed breaking from the anode during dissolution are truly metallic.

Figures 5 through 9 show agglomerations of small particles obtained under the conditions explained beneath each micrograph. These figures show the particles as they appear in reflected light with the exception of Figure 8 which shows the particles as they appear in transmitted light. The fact that the particles are dark in transmitted light is evidence that they are metallic.

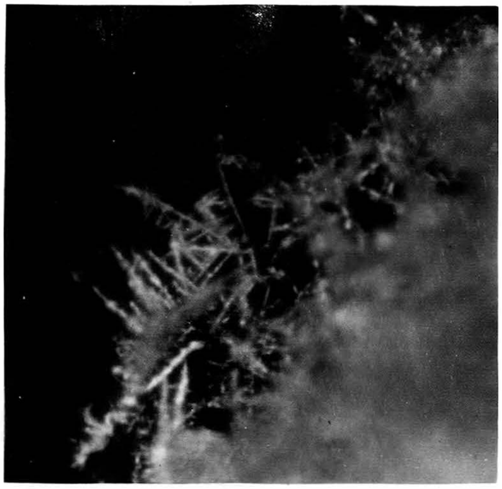
Figure 5



1430 X

Disintegration particles of pure indium anode in 18.6 mole % $NH_4C_2H_3O_2$ in concentrated acetic acid. Current density 70 ma./cm.^{2}, oil immersion objective.

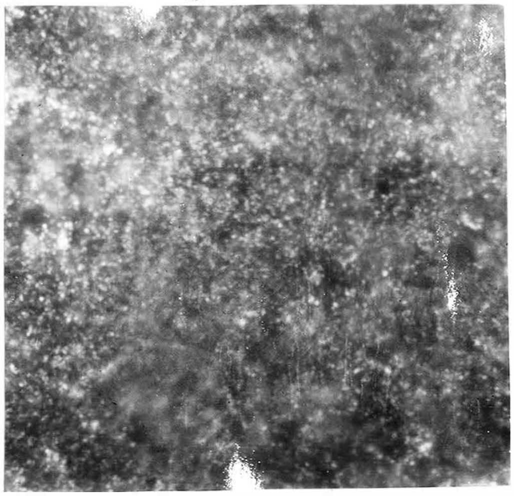
Figure 6



1430 X

Disintegration particles of pure indium anode in 2N HNO_3 , current density 900 ma./cm.^{2}, oil immersion objective.

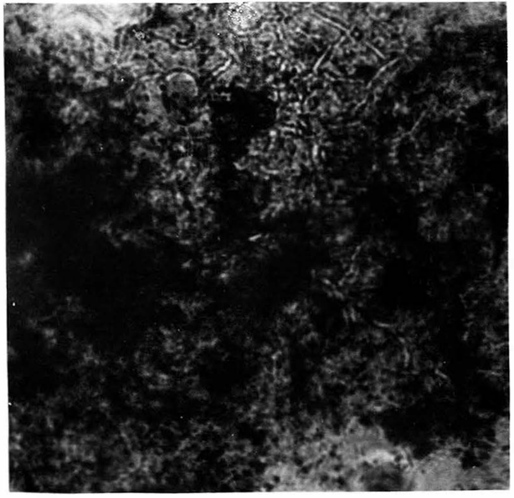
Figure 7



1430 X

Disintegration particles of pure indium anode in 3 % aqueous solution of KNO_3, current density 500 ma./cm.^{2}, oil immersion objective, reflected light.

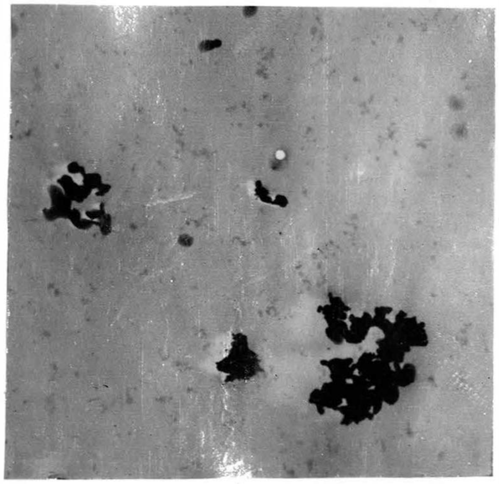
Figure 8



1430 X

Same as Figure 7 in transmitted light.

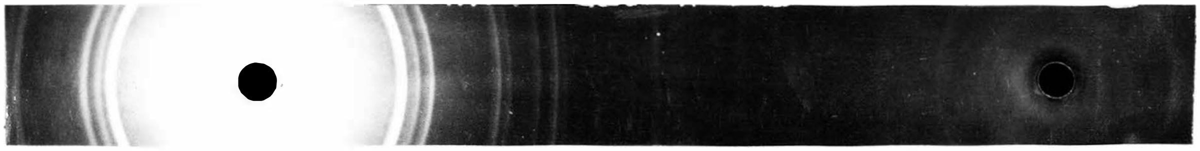
Figure 9



1750 X

Disintegration particles from pure indium anode in 18.6 mole % $NH_4C_2H_3O_2$ in concentrated acetic acid, current density 150 ma./cm.^{2}, electron microscope.

Figure 10



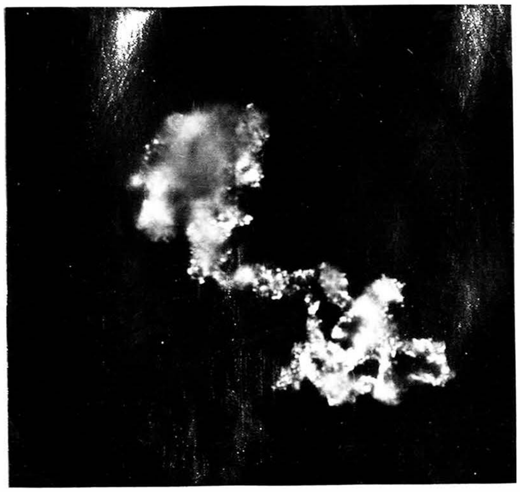
X-ray diffraction powder pattern of particles obtained by anodic disintegration of pure indium, same conditions as in Figure 9, nickel filtered copper radiation using aluminum screen, exposed 1 hour, 15 min.

Figure 10 is definite proof that the particles are metallic indium. The diffraction lines correspond to those of a powder pattern of pure indium filings using the same radiation.

Figures 11 and 12 picture agglomerations of thallium disintegration particles. Figure 13 shows a rather large thallium particle which has a sponge-like appearance. Figures 14 and 15 show individual thallium particles as they appear in an electron microscope. The grey, filmy material is likely an oxide while the dark, regularly shapped particles are metallic thallium.

Figure 16 is a micrograph of agglomerations of nearly pure cadmium particles from anodic disintegration of an indium- cadmium alloy. Individual particles of this material are shown as they appeared through an electron microscope in Figures 17 and 18.

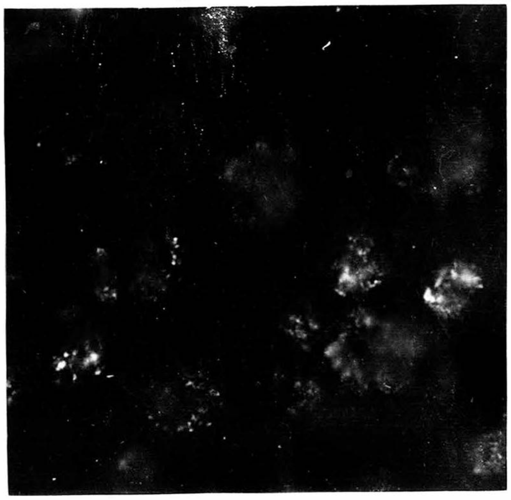
Figure 11



1430 X

Disintegration particles of pure thallium anode in 2N HNO_3, current density 900 ma./cm.^{2}, oil immersion objective.

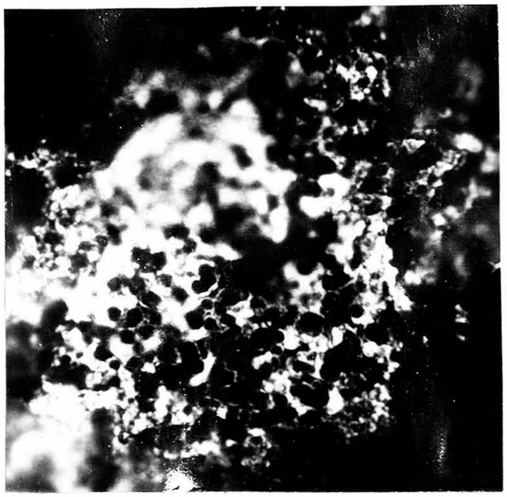
Figure 12



1430 X

Disintegration particles for pure thallium anode in 18.6 mole % $NH_4C_2H_3O_2$ in concentrated acetic acid, current density 350 ma./cm.^{2}, oil immersion objective.

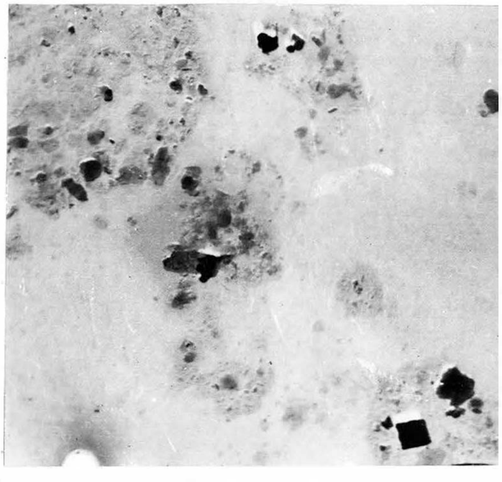
Figure 13



1430 X

Large sponge-like disintegration particle from pure thallium anode in acetic acid solution of $NH_4C_2H_3O_2$, current density 350 ma./cm.^{2}, oil immersion objective.

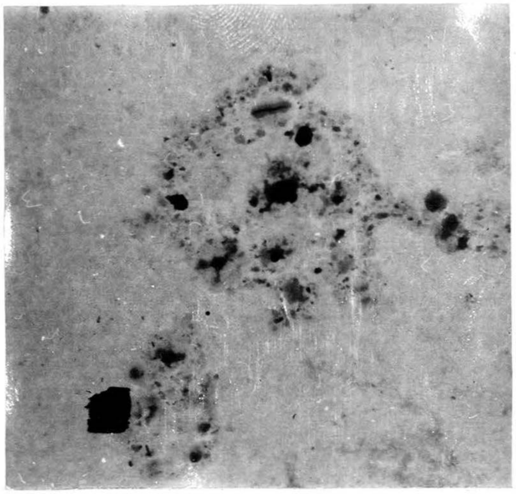
Figure 14



5,000 X

Pure thallium particles, same conditions as Figure 13, electron microscope.

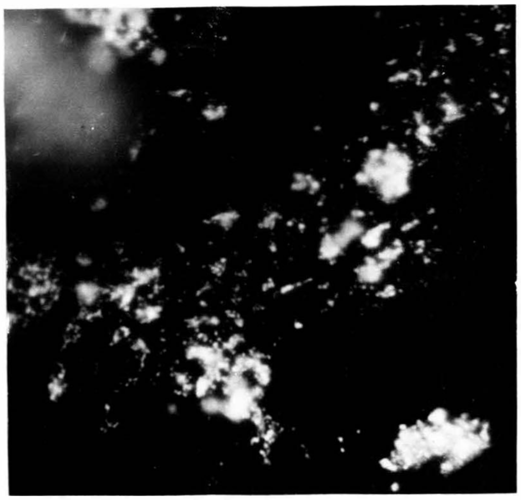
Figure 15



5,000 X

Pure thallium particles, same conditions as Figure 13, electron microscope.

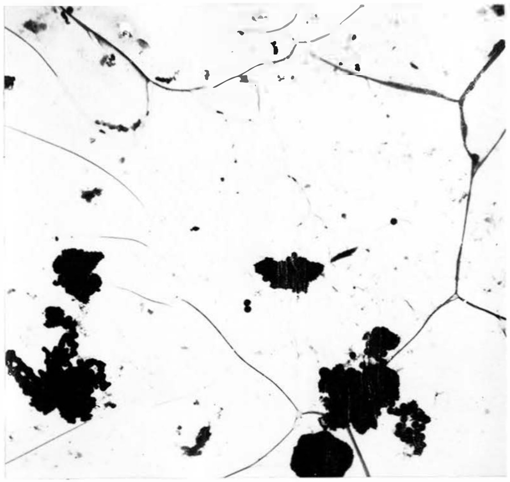
Figure 16



1430 X

Nearly pure cadmium disintegration particles from indium-16.1 % cadmium alloy anode in acetic acid solution of $NH_4C_2H_3O_2$, current density 100 ma./cm.^{2}, oil immersion objective.

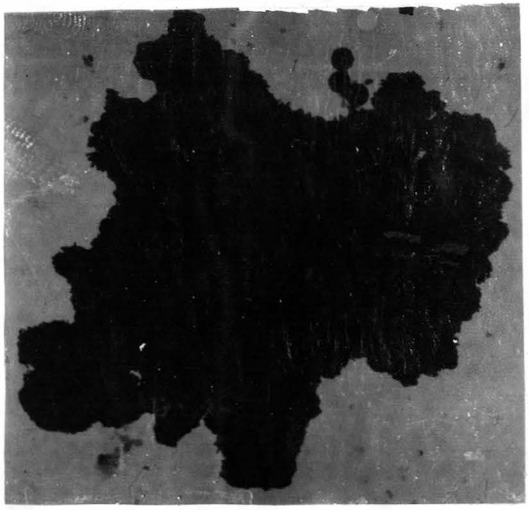
Figure 17



1750 X

Nearly pure cadmium particles from anodic disintegration of indium- 16% cadmium alloy in acetic acid solution of $NH_4C_2H_3O_2$, current density 100 ma./cm.^{2}, electron microscope.

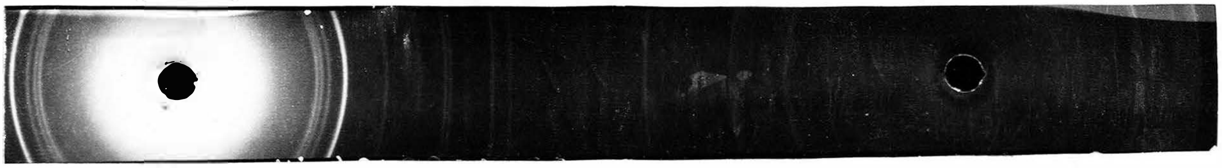
Figure 18



5,000 X

Large disintegration particle, same conditions as Figure 17, electron microscope.

Figure 19



X-ray diffraction powder pattern of disintegration particles from indium-16.1 % cadmium anode showing the particles to be essentially pure cadmium, nickel filtered copper radiation with aluminum screen, 1 hour 15 min.

Figure 19 shows proof that the disintegration particles from the alloy are primarily cadmium. A line by line comparison with a known pattern of cadmium made with copper radiation shows the diffraction lines to be identical.

Figures 21 through 25 give the graphic results of the quantitative disintegration experiments. For both indium and thallium anodes increased current density gives increased disintegration with maxima being reached in Figures 21 and 25. In $HClO_4$ a limiting value seems to be reached.

It can be seen from Figure 24 that no long range relationship exists between temperature and the amount of disintegration.

Figure 21

Disintegration vs. Current Density
for
Indium in 2N HCl

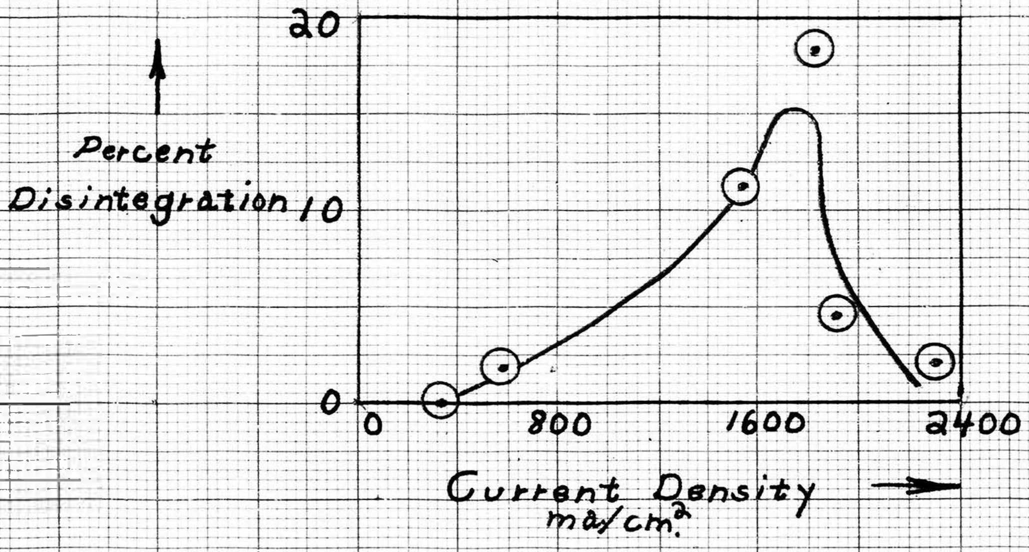


Figure 22

Disintegration vs. Current Density
for
Indium in 3N H_2SO_4

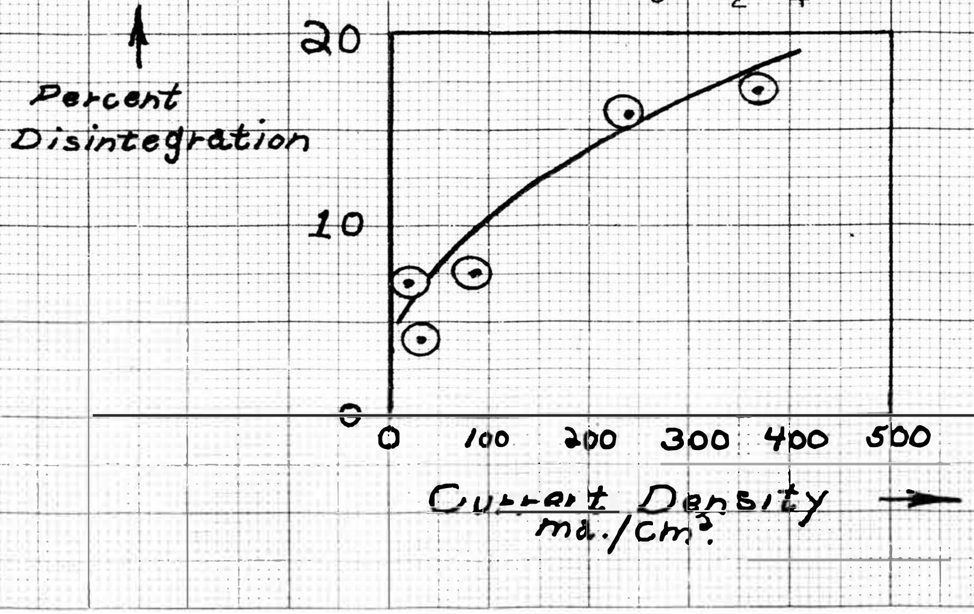


Figure 23

Disintegration vs. Current Density
for
Indium in 5N $HClO_4$

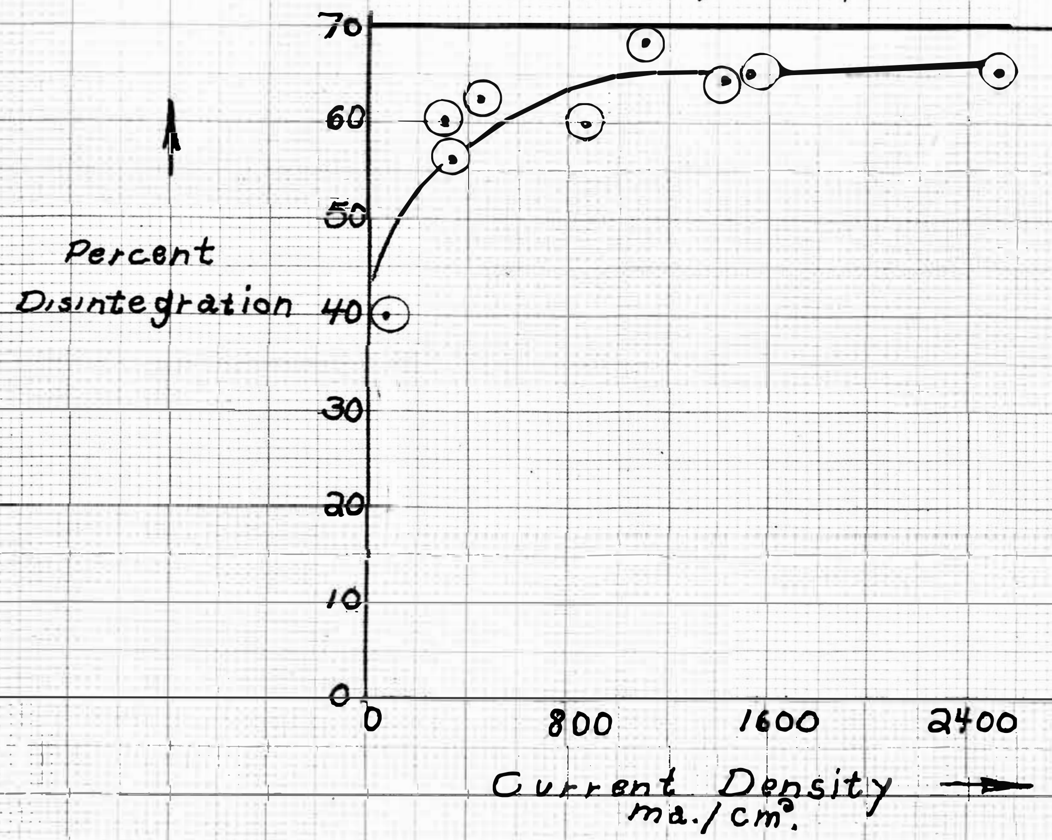


Figure 24

Disintegration vs. Temperature for Indium in H_2SO_4

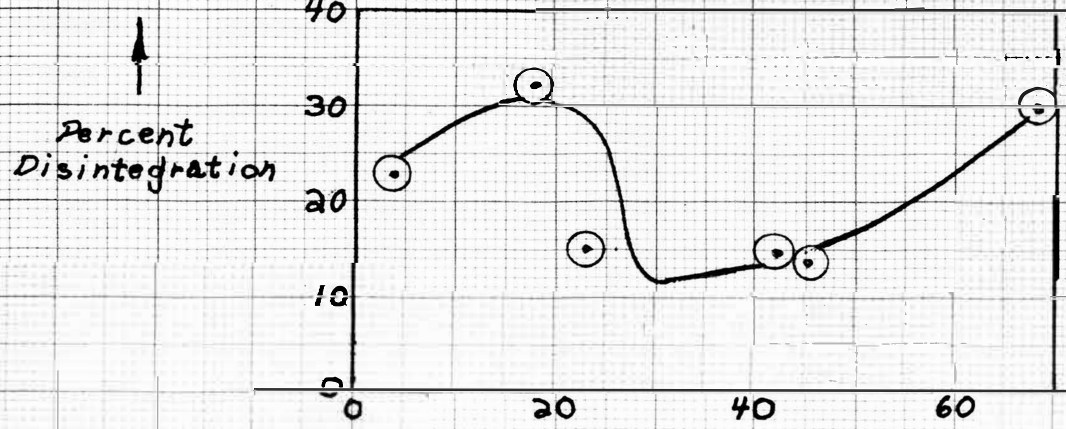
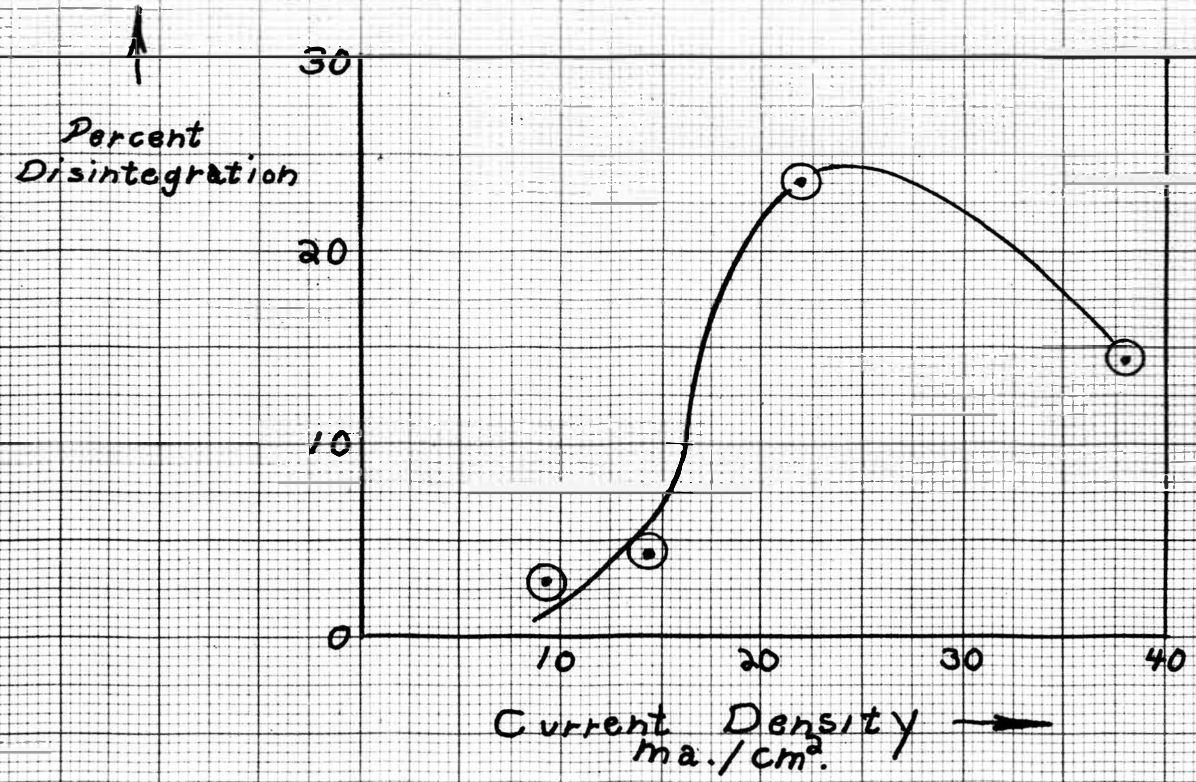


Figure 25

Disintegration vs. Current Density
for
Thallium in 0.5N H_2SO_4



V DISCUSSION

As shown in Tables I and II the valences of indium and thallium during anodic dissolution were 3 and 1 respectively, as measured by the hydrogen evolution method. The valences obtained by this method represent the final or stable valences; they are independent of either disintegration of the anode (the platinum basket served as the cathode) or the formation of short lived monovalent ions. If disintegration of the anode had occurred the metal particles would still displace an equivalent amount of hydrogen from the acidic solution to give the same final valence. If unstable lower valent ions were formed, they would be free to reduce hydrogen ions to hydrogen gas in the acid until a stable oxidation state was reached, again giving the same final valence. For example if one gram equivalent of indium goes into solution anodically producing $+3$ ions only, 33.6 liters of H_2 will be produced as shown in equation 1.

1. $In^{o} + 3H^{+} \rightarrow In^{+++} + 3/2H_2$

If 25% of the anode disintegrates, equation 2A at the anode and 2B in the solution will give a total of 33.6 liters of H_2.

2A. $3/4\ In^{o} + 9/4\ H^{+} \rightarrow 3/4\ In^{+++} + 9/8\ H_2$

2B. $1/4\ In^{o} + 3/4\ H^{+} \rightarrow 1/4\ In^{+++} + 3/8\ H_2$

If the initial ions formed were monovalent, equation 3A at the anode and 3B in the solution would again give 33.6 liters of H_2 at S.T.P.

3A. $In^{o} + H^{+} \rightarrow In^{+} + \frac{1}{2}H_2$

3B. $In^{+} + 2H^{+} \rightarrow In^{+++} + H_2$

Valences measured by the amalgam electrode method also gave valences of 3 and 1 respectively for indium and thallium during anodic dissolution. These valences should be the initial valences of the ions going into solution. Any tendency toward disintegration is eliminated by having the metal dissolved in mercury. However, the oxidation state of the ion formation should be unaffected. With indium, if monovalent ions were formed they would either disproportionate according to equation 4A or be oxidized by H^{+} as shown in equation 5.

4A. $3In^{+} \rightarrow In^{+++} + 2In^{o}$

4B. $In^{o} + 3H^{+} \rightarrow In^{+++} + 3/2H_2$

5 . $In^{+} + 2H^{+} \rightarrow In^{+++} + H_2$

Either of these reactions would take place outside the measurable electric circuit.

Furthermore these reactions would produce hydrogen bubbles in the solution but none were actually observed. Additional evidence from the amalgam experiments that indium goes into solution only as $^{+}3$ ions was the fact that the dissolutions in perchloric acid gave little or no precipitate upon addition of Ag^{+} ions. This meant that **neither** equation 6 or 7 was taking place.

6. $8\,In^{+} + 2ClO_4^{-} + 16H^{+} \rightarrow 8In^{+++} + 2Cl^{-} + 8H_2O$

7. $8\,In + 3ClO_4^{-} + 24H \rightarrow 8In^{+++} + 3Cl^{-} + 12H_2O$

With a thallium anode in the same acid monovalent ions were being formed and a test of the solutions after each dissolution did show Cl^{-} to be present.

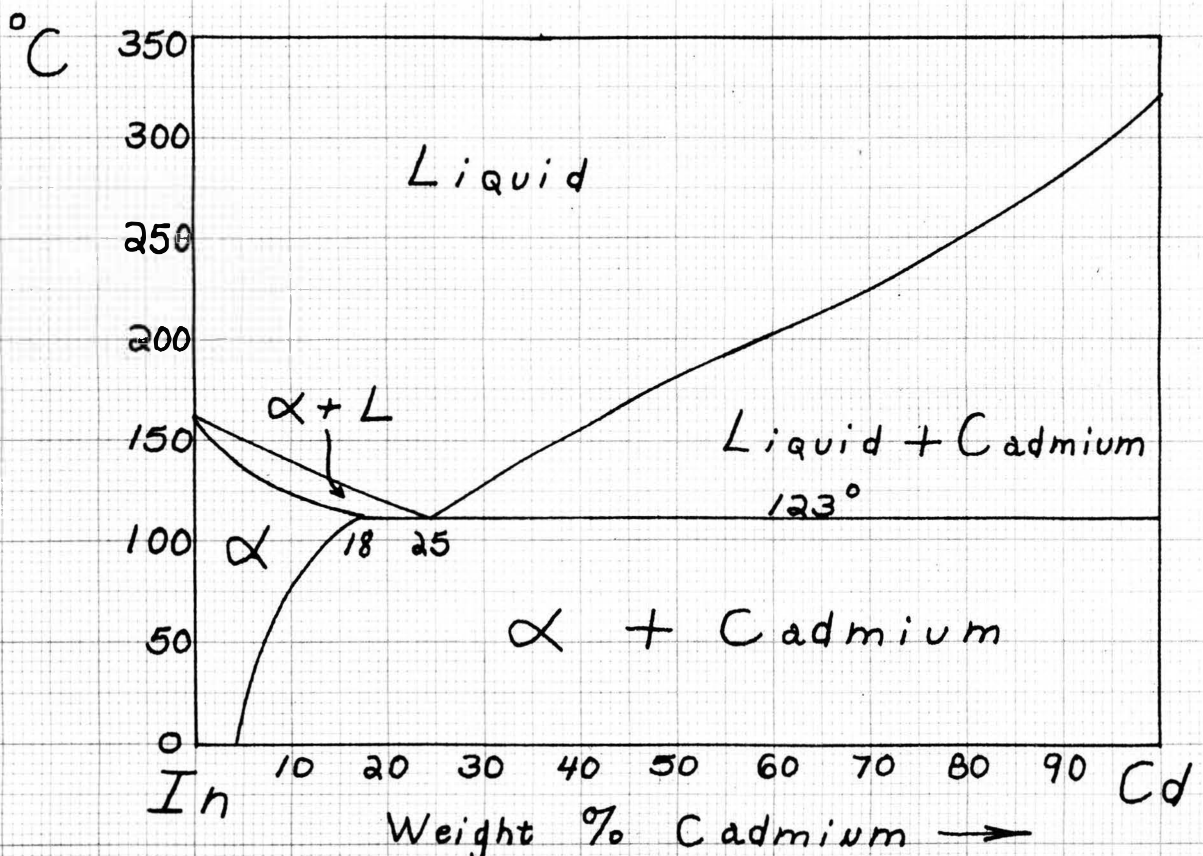
Disintegration of the anodes was observed directly in many acids and salts (Tables X,XI, and XII). Dark material was seen flowing down the face of the anode in many cases. This material dissolved in acids when touched with a platinum wire and gas bubbles were formed on the wire beneath the solution. When a solid indium anode was dissolved in perchloric acid, bubbles could be seen rising from the bottom of the cell beneath the anode. This occurred even at low current densities where no film spalling was visible. High power microscopic examination in transmitted and reflected light and x-ray diffraction data proved definitely that the fine dark material was indium and thallium for the respective anodes.

Although the deviation from Faraday's law during anodic dissolution seems quite likely to be because of disintegration of the anode into small metallic particles, the mechanism of formation of these particles is rather difficult to determine. In some **cases**, especially with nitrates and perchlorates as electrolytes, disintegration seems to depend on the accumulation of a surface film on the anode. As this film forms, some portions of the metal must become insulated from the circuit which prevents dissolution of these portions. As the film builds up it can spall off, carrying atomic aggregates of the anode with it. This agrees with the appearance of metallic particles in films which spalled off the anode surface and were microscopically examined.

In most electrolytes, however, no visible oxide or other films formed on the anode, nevertheless, disintegration took place. Dark streams of material, primarily small metallic particles, flowed down the surface of the anode. A possible mechanism by which this could take place would be the under-mining of some areas of the anode surface which have, for some reason, a lower dissolution rate than most areas of the surface. Thin layers of oxide or other films could be responsible in many cases. Areas having thicker or more tenacious films would be protected from dissolution and would be undermined and break off the surface as other, less protected areas dissolved laterally. Thus, the relationship chemically of the anode and the electrolyte would have a great bearing on the amount of disintegration. This was found to be ture in quantitative disintegration measurements.

The study of anodic disintegration of indium - cadmium alloys throws some light on the mechanism of disintegration (See Table XII). For an 8 weight % cadmium alloy which was shown by x-ray diffraction to be cubic, the disintegration particles were tetragonal. This is likely due to the preferential dissolution of the more active cadmium atoms from the solid solution particles. At higher cadmium contents however, cadmium is insoluble in indium (See Fig. 26) but the disintegration particles were primarily cadmium. Since cadmium is less noble than indium (E^o $Cd,Cd^{++} = .403$; E^o $In,In^{+++} = .342$), it would be expected to dissolve more readily than the solid solution. Evidently the precipitated cadmium particles in the alloy have thicker or more tenacions surface layers and hence are protected from dissolution and undermined by the dissolution of the surrounding solid solution.

Any factors which affect the thickness or tenacity of the thin oxide layers would cause changes in the amount of disintegration. The factors of electrolyte, current density and temperature were investigated (See Figs. 21 through 25).



The Indium — Cadmium System

Figure 26

The Indium-Cadmium Alloy System

Differences in the amounts of disintegration were also noticed for dissolution under the same apparent conditions but these differences were considerably less then the differences for changes in electrolyte, current density, or temperature.

As shown in Fig. 24, no definite trend of disintegration with temperature was found, but rather, an alternating increase and decrease. At certain temperatures the condition of the thin surface layers is evidently such that disintegration is favored. At other temperatures conditions are not as favorable for disintegration.

Disintegration increased in cell electrolytes with an increase in current density (See Figs. 21,22,23, and 26). The higher rate of dissolution at higher current densities evidently causes the undermining of protected areas to be more pronounced. This could be due to the formation of additional thin films at higher current densities and also the fact that the unprotected areas dissolve at a faster rate which should isolate larger chunks of material beneath the protective surface layers.

Some electrolytes showed a maximum in the plot of disintegration against current density (See Figs. 21 and 25). It is possible that after a given current density is reached in a particular electrolyte that the protective surface layers could be torn away by the rapid expulsion of ions from the neighboring areas of the anode surface. This would lower the amount of disintegration. In some electrolytes it was not possible to go to high enough current densities to produce a maximum in the curve because oxygen would start to form at the anode.

Assuming that disintegration occurs by the proposed undermining mechanism, the most important factor for disintegration should be the chemical relationship between the anode and the corrosive medium. Areas which would be relatively inactive in one medium might be more active in another. The experimental results bear this out. Since disintegration of the same anode varied from acid to acid at a given current density, the maximum amount of disintegration also varied with the electrolyte.

The concentration of the acid would also be expected to have some affect on the amount of disintegration. This was investigated with indium in sulfuric acid and it was found that disintegration increases with concentration up to about 3 N and then drops rapidly.

It is possible that factors other than thin surface films could cause areas of the anode to be relatively inactive and be undermined and released as particles. Differences in configuration, the attachment of small gas bubbles, or differences in orientation could also cause certain areas to be reluctant to dissolve.

VI SUMMARY

Indium dissolves anodically in aqueous acid solutions producing In^{+3} ions only. Deviations from Faraday's law and reactions which appear to be the result of monovalent indium ions are due to the disintegration of the anode into small metallic particles.

Thallium dissolves anodically in aqueous acids yielding Tl^{+1} ions only. Oxidation to the +3 state occurs only in the solution in the presence of some oxidizing agent. Thallium is also subject to anodic disintegration.

A possible mechanism for anodic disintegration in the absence of thick or accumulating surface films is the undermining and isolation of areas of the anode surface which have, for some reason, a lower dissolution rate than the rest of the anode. Thin protective films, probably only a few molecules thick, are the most likely cause of little or no dissolution in certain areas. This mechanism is consistent with the experimental results.

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VIII VITA

The author was born at Mason, Illinois on July 18, 1942. He received his elementary education at Watson Grade School in Watson, Illinois and was graduated from Effingham High School in Effingham, Illinois in May 1959.

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IX APPENDIX

A. Procedure for Determination of Indium by Titration With Ethylenediammine Tetraacetic Acid (EDTA).

1. To neutral or slightly acid solution containing indium ions add excess tartaric acid.
2. Add two drops of Eriochrome Black T indicator.
3. Add buffer solution until violet color is obtained. (Buffer is made up by dissolving 13.4 grams of NH_4Cl and 88 ml. of NH_4OH in 1000 ml. of aqueous solution.)
4. Heat to boiling.
5. Titrate to blue-green color with 0.01 molar EDTA solution. (Standardize the EDTA solution by same titration procedure against standard indium solution.)
6. Calculate indium content.

$$\text{gr. In} = \text{molarity EDTA} \times \frac{\text{ml. EDTA}}{1000} \times \text{at. wt. In}$$

$$\text{gr. In} = 0.009814 \times \frac{8.74}{1000} \times 114.76 = 0.00984 \text{ gm.}$$

B. Procedure for Determination of Thallous Ions by Titration with Ethylenediammine Tetraacetic Acid.

1. To acid solution containing Tl^+ ions add excess bromine water.

2. Boil to remove unreacted bromine.
3. Cool and add slight excess standard EDTA solution of about 0.01 molarity.
4. Add two drops of Eriochrome Black T. indicator.
5. Add NH_4OH until a deep blue color is reached.
6. Add standard 0.01 molar $MgSO_4$ solution until color is bright red.
7. Titrate to blue-green color with standard EDTA solution. (Standardize EDTA by direct titration with a standard solution of ions which complex with EDTA; standardize $MgSO_4$ against EDTA and check both solutions by trial titrations with a standard solution of thallium ions.)
8. Calculate thallium content.

$$\text{moles Tl} = \text{moles EDTA} - \text{moles } MgSO_4$$

$$\text{gm. Tl} = \frac{\text{at. wt. Tl}}{1000}(\text{molarity EDTA} \times \text{ml. EDTA} - \text{molarity } MgSO_4 \times \text{ml. } MgSO_4)$$

$$\text{gm. Tl} = \frac{204.39}{1000}(0.009925 \times 10.28 - 0.00910 \times 2.15)$$

$$\text{gm. Tl} = 0.0169$$