

"In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institution shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

— / ————— "

THE TWO-PHASE REGION OF THE GALLIUM-
MERCURY-INDIUM SYSTEM

512
10

A THESIS

Presented to
the Faculty of the Graduate Division
Georgia Institute of Technology

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemistry

By
Perry Alanson Foster, Jr.

June 1955

THE TWO-PHASE REGION OF THE GALLIUM-
MERCURY-INDIUM SYSTEM

Approved:

J. R.
(1)

Date Approved by Chairman: June 3, 1955

ACKNOWLEDGEMENT

I wish to extend my sincere thanks and appreciation to Dr. W. M. Spicer for suggesting the problem as well as offering valuable advice when needed.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
LIST OF TABLES.	iv
LIST OF FIGURES	v
CHAPTER I. INTRODUCTION.	1
CHAPTER II. EXPERIMENTAL	4
Materials.	5
Apparatus.	6
Procedure.	7
Mercury Determination.	9
Indium Determination	11
CHAPTER III. DISCUSSION OF RESULTS	17
CHAPTER IV. SAMPLE CALCULATIONS AND DATA	23
CHAPTER V. SUMMARY	29
BIBLIOGRAPHY.	32
APPENDIX I. Interference and Standard Curves	34
APPENDIX II. A Proposed Mechanism for the Suppression and Recovery of Indium Emission Intensity in the Presence of Gallium	37

LIST OF TABLES

Table	Page
1. The Influence of Gallium on Indium Emission Intensity	14
2. Data for Standard Curve	15
3. Mercury Determinations of Run No. 20.	25
4. Indium Determination Using the Flame Photometer	25
5. Indium Content in Grams for Each Segment Determined by Flame Photometry Over a Period of Time.	26
6. Indium Content in Per Cent for Each Segment Calculated from Data Listed in Table 7	27
7. Average Mercury and Indium Composition at 35° C.	27
8. Average Mercury and Indium Composition at 50° C.	28
9. Environment Control in Interference Studies	40
10. Emission Intensities of Environment Controlled Solutions. . .	41

LIST OF FIGURES

Figure	Page
1. The Influence of Gallium on Indium Emission Intensity . . .	35
2. Indium Standardization Curve.	36
3. Gallium-Mercury-Indium Isothermal Constitution Diagram (35° C.).	19
4. Gallium-Mercury-Indium Isothermal Constitution Diagram (50° C.).	20

CHAPTER I

INTRODUCTION

THE TWO-PHASE REGION OF THE GALLIUM-MERCURY-INDIUM SYSTEM

CHAPTER I

INTRODUCTION

The purpose of this research is to determine to what extent can the known low miscibility of gallium and mercury persist in the presence of an increasing concentration of indium. Another goal is to determine, in a limited way, the effect of temperature on this system. For this reason the two temperatures of 35° C. and 50° C. were chosen. The initial working temperature of 35° C. was selected primarily because the melting point of gallium (29.780° C.)¹ is above normal room temperature and also to minimize the effect of its tendency to supercool² on low temperature runs.

Bartholomay³ in his work observed that gallium and mercury were miscible to a limited extent at temperatures of 35°, 50° and 100° C. Banick⁴ and Denny⁵ have determined constitution diagrams for mercury-indium and gallium-indium respectively. Their work indicated that indium could be expected to be very soluble in either mercury or gallium. This

¹W. F. Roeser and J. I. Hoffman, J. Research Nat. Bur. Standards 13, 673-6 (1934).

²Ibid.

³H. W. Bartholomay, Solubilities in the System Gallium-Mercury, M. S. Thesis, Georgia Institute of Technology, 1950.

⁴C. J. Banick, The System Indium-Mercury, M. S. Thesis, Georgia Institute of Technology, 1952.

⁵J. P. Denny, Journal of Metals 4, 39 (January 1952).

particular property of indium in the presence of mercury and gallium is quite fortunate, since, it is easier to obtain equilibrium in an all liquid system than would otherwise have been possible if this were not true.

It is customary to represent ternary systems such as this one on triangular coordinate graph paper. The three sides of the triangle represent each binary with temperature assuming a third dimension. In order to facilitate determining what effect each of the three components may have on one another within the triangular base block, isothermal conditions are maintained through the use of constant temperature bath and quantitative analysis is then performed on the system.

The method of analysis proposed by Bartholomay⁶ for the determination of mercury was found to be satisfactory in this work also. The mercury determination consisted of simply reacting the sample containing mercury, gallium and indium with concentrated hydrochloric acid in the presence of a small piece of platinum wire. The oxidation potentials of the three components are such that mercury can be separated very nicely from the gallium and indium. The gallium and indium formed soluble chlorides while the mercury remains unaffected. The unreacted mercury can thus be determined quite readily by gravimetric methods.

The determination of the soluble indium and/or gallium chlorides presented a unique problem in itself. Recourse was finally made to flame spectrophotometry with gratifying results.

⁶Bartholomay, op cit.

CHAPTER II
EXPERIMENTAL.

CHAPTER II

EXPERIMENTAL

Materials.---The mercury employed in this study was purified by atomizing it through a fine capillary and into a glass column which was nearly filled with a mixture of 3N HNO_3 and 0.01N $\text{Hg}_2(\text{NO}_3)_2$. The dimensions of the glass column were one and one-half cm. in diameter and approximately 100 cm. long. Following the treatment with HNO_3 the mercury was again atomized through the column, now containing distilled water. The washed mercury was run over filter paper until dry. The mercury thus treated had a bright metallic luster and was stored under argon in a closed container.

The indium used in this study was obtained from the Indium Corporation of America in the form of shot. This indium was reported by the manufacturer to be 99.97 per cent pure with traces of cadmium and zinc. No special purification was followed except for the removal of the oxide film. This can be done either by pickling with 6N HNO_3 solution for approximately ten minutes or, as was found to be more convenient, scrapping off the oxide with a platinum spatula.

The gallium was acquired from the Aluminum Company of America in five gram capsules. The suppliers claim a 99.95 per cent purity with a trace of iron. To facilitate removing the gallium from the capsule, the manufacturer recommended freezing the material in a beaker containing dry-ice and acetone. The brittle plastic capsule can then be broken very easily by a sharp blow. The solid gallium is then transferred to another beaker containing concentrated hydrochloric acid in order to remove its oxide coating. When it appears that the oxide has been dissolved, the

acid is removed and the gallium is rinsed with distilled water. Following this treatment the gallium is transferred to a small Erlenmeyer-type flask having a ground glass top and cover and containing a previously prepared slightly acid GaCl_3 solution. This solution is necessary to prevent the rapid contamination of the gallium from atmospheric oxygen and also to prevent the gallium from wetting the glass; it has a tendency to do this very readily. The slightly acid character of the solution prevents hydrolysis.

Apparatus.--The experimental temperatures of 35°C . and 50°C . were maintained through the use of a constant temperature bath equipped with a Sargent circulating heater, mercurial thermoregulator and relay capable of maintaining temperatures within 0.01°C . Cooling coils are also provided for use during summer months when room temperature often times was higher than bath temperature. This was only true when the working temperature was 35°C .

The indium determination was conducted with a Beckman DU flame photometer equipped with a Model 4300 photomultiplier attachment and a Model 4020 hydrogen burner. The instrument must be turned on and allowed to warm for an hour or so before the burner is lit. The instrument can be considered sufficiently warmed when the galvanometer stops migrating to any great extent. An investigation of the flame spectrum of indium indicated the strongest line to be at a wave length of $451.1 \text{ m}\mu$, hence this wave length was used. The photomultiplier's sensitivity was set at full and the selectivity at the midpoint position. The slit width and fuel pressure settings depend upon the concentration range of the

indium. In this investigation a slit width of 0.03 mm. was used initially. Later, a new photomultiplier tube was installed, necessitating a reduction in the slit width to 0.0175 mm. with subsequent enhanced resolution. The oxygen and hydrogen tank pressure were maintained at 40 and 10 pounds per square inch respectively while the panel pressures were 11 and 5 pounds respectively.

Procedure.--Mercury and gallium were pipetted from the previously purified stock solutions in amounts of approximately 0.35 grams of mercury and 0.15-0.20 grams of gallium for each separate run. This amounts to roughly equal volumes. The indium was added in quantities which amounted to increments of 5 per cent of the weight of mercury. This simply means that the first run at a given temperature will contain 5 per cent indium relative to the weight of the mercury used for this particular run; the second run will contain 10 per cent; the next, 15 per cent, etc. As the research progressed it was found advisable to increase the increments to 10 per cent. The relatively small amounts of mercury and gallium employed in each run was dictated by two reasons; one economic and one physical. With gallium selling at five dollars per gram, economy was of considerable import. From a physical point of view, small amounts of mercury and gallium would allow the indium to come to equilibrium more rapidly between and within the two layers than would be possible employing large quantities.

Following careful formulation of the constituents of each run in the manner described above, the mixture was transferred to a small test tube containing an acid solution of gallium chloride and mounted with an automatic stirrer. This assembly was inserted in the 35° C. constant

temperature bath and the mixture was stirred from 15 to 30 minutes. The blended mixture was then transferred to a thin walled pyrex tube having the dimensions 5 mm. by 10 cm. and allowed to stand for a period of approximately 12 hours. Occasional tapping was necessary in order to free the occluded hydrogen which formed as a result of a continuous but slow reaction between the slightly acid protection solution and the gallium and indium.

The use of a steel shot, as proposed by Bartholomay,⁷ for determining the bounding surface between the mercury and gallium had to be discontinued because of the catalytic effect the shot had on the above mentioned reaction. It was feared that the stirring effects of such large quantities of hydrogen rising through the mixture would be detrimental to attaining equilibrium. This was partially verified by preliminary experiments employing the steel shot. These experiments showed the mercury to be distributed in the gallium layer in a nonuniform manner. This fact was not observed by Bartholomay, primarily because of the method employed for determining the composition of the two layers. Bartholomay's determination consisted of allowing the gallium-mercury mixture to stand in the constant temperature bath for a period of time. The steel shot was added and allowed to come to some position which indicated the bounding surface. At this juncture a complete physical separation of the gallium layer was performed right down to the steel shot. The top layer (gallium) was transferred to one container and the bottom layer (mercury) was transferred to another container. Both of these

⁷Bartholomay, op. cit.

containers were then returned to the bath and allowed to come to temperature. Analytical determinations were then performed on each separated layer. It was felt that this procedure does not present an adequate picture of the dynamic conditions as they existed initially with the two materials in contact with one another. Therefore, it was decided to analyze the system in question by extracting segments of sample, through the use of a specially prepared pipette, from the top to the bottom of the columnated mixture without the use of the steel shot and hence without separating the layers before analyzing.

The individual segments were analyzed for per cent mercury and per cent indium. The per cent gallium was obtained by difference. The segment which was obtained from the region of the bounding surface between the gallium and mercury layers will have a composition that is characterized by widely different results than the ones noted for the segments both above and below it. The data obtained as a result of analysis on this "transition zone" segment, of course, was not included in determining the average position of composition points of either the gallium rich layer or the mercury rich layer on triangular coordinate paper.

Mercury Determination.--The determination of the mercury composition of each of the segments mentioned in the previous section consisted of running the pipetted segment down a chute, made by folding a piece of filter paper without creasing, and into a tared weighing bottle containing some protective solution. It is necessary to remove the aqueous protection solution in some way before the segment is allowed to enter the weighing bottle, and the filter paper chute technique proved to be rapid and

efficient. The weighing bottle, cover, protective solution, and segment are now weighed. The difference between this weight and the weight of the weighing bottle, cover and protective solution, of course, gives the weight of the segment.

Concentrated hydrochloric acid was added to dissolve the indium and gallium. Approximately one and one-half ml. was sufficient. The reaction proceeds normally at a very slow rate. If, however, a piece of platinum wire was added and brought into contact with the segment and the temperature was raised to 100° C., the reaction proceeds at a very rapid rate and was usually complete in an hour or so. The reaction temperature need not be precise. Consequently, any type of rheostatically controlled hot-plate will suffice. It is imperative that a condenser be attached to the weighing bottle while it is on the hot-plate in order to prevent splattering and excessive evaporation.

Upon completion of the reaction, as verified by the lack of hydrogen bubble formation, the weighing bottle is detached from the condenser and allowed to cool slightly. The soluble chlorides of indium and gallium are now pipetted into a 100 ml. volumetric flask and brought to volume. The usual procedure of washing with distilled water and incorporating the wash with the concentrated solution was performed. The platinum wire and adhered mercury were removed from the weighing bottle and dried between two pieces of filter paper and transferred to another piece of filter paper for weighing. After this weighing the platinum wire and mercury are dumped into a beaker containing concentrated nitric acid to dissolve the mercury. The platinum is rinsed with distilled water, dried and

weighed. The weight of the platinum wire and filter paper were subtracted from the previously obtained combined weight of filter paper, platinum wire and mercury, yielding the amount of mercury in the segment. The weight of mercury divided by the weight of the segment and multiplied by 100 gives the per cent mercury.

Indium Determination.--The use of flame spectrophotometry as a means of determining indium in the presence of gallium was adopted only after separation by chemical means failed. A discussion of one of the chemical methods employed in this research, namely the one developed and applied supposedly quite successfully by Denny,⁸ is probably opportune.

Denny developed a method for determining indium in the presence of gallium as a result of his work on the gallium-indium system which consisted of dissolving both metals with nitric acid. Advantage was then taken of the relative amphoteric properties of the gallium and indium hydroxides. Both gallium and indium were reported to precipitate upon addition of 20 per cent sodium hydroxide. In a slight excess of this base, however, the gallium hydroxide redissolves while the indium hydroxide does not. The precipitated indium hydroxide was collected on a piece of coarse filter paper and then transferred to a tared porcelain crucible. The indium hydroxide was ignited and determined as the oxide.

Preliminary investigation by this author indicated that, indeed, the relative amphoteric character of the two constituents might be expected to be a means of separation. Two solutions, one containing gallium ions only, the other indium ions only, were treated with 20 per cent

⁸J. P. Denny, op. cit.

sodium hydroxide. The solution that contained only gallium ions started to precipitate after very little base was added. Precipitation was very heavy up until the solution registered neutral to litmus. At this point the precipitate completely disappeared. The solution containing only indium ions, on the other hand, did not start to precipitate until the neutral point was reached. Several drops in excess, however, and the indium hydroxide started to redissolve. As a consequence of these cursory observations one would surmise that if close control and attention to procedure were followed, this technique might produce the desired results.

Several experiments were conducted on mixed solutions containing known amounts of gallium and indium ions. Sodium hydroxide of the appropriate concentration was added to the mixture in amounts dictated by the previous test on solutions containing only one of the species. Care was taken not to allow too high a basicity and hence redissolve the indium hydroxide and at the same time measures were taken to insure the solution of the gallium hydroxide. Instead of using coarse filter to effect separation as suggested by Denny, it was necessary, because of the fineness of the particle, to employ a tared gooch crucible and asbestos pad. After a thorough rinsing with distilled water, the crucible and indium hydroxide were fired to red heat for several minutes. Upon cooling the characteristic red-orange color of In_2O_3 was observed. The crucible and material were repeatedly fired and weighed until a constant weight was obtained. From the weight of In_2O_3 obtained as a result of the above measurements, the amount of indium can be calculated. This procedure was applied to several known samples. In none of the attempts was it possible to obtain results which were less than 4 per cent error. Obviously, this procedure left much to be desired and therefore it was abandoned.

Flame spectrophotometry, on the other hand, was alledged by the Beckman Instrument Company⁹ to be capable of determining solutions containing indium in concentrations of as little as one part in a million. This, indeed, appeared to be quite attractive. A search of the literature failed to reveal any previous attempts to determine indium in the presence of gallium with this instrument.

As is customary when employing the flame photometer, it is necessary to determine initially the effect of the various constituents of the system on the emission intensity of the element to be determined. Fortunately, this system is comparatively simple since other than the indium, which is to be determined, only gallium and a certain concentration of hydrochloric acid (approximately 0.5 N) is present.

The influence of hydrochloric acid was determined by preparing six solutions containing 100 ppm indium; 6 N hydrochloric acid was added to give concentrations of 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 N. No noticeable effect on emission intensity was observed. Hydrochloric acid was not expected, therefore, to given any difficulties in the concentration range employed in the research. It is also of interest to note that Meloche,¹⁰ while using this instrument to determine indium in aluminum bronze, reported that no effect on indium emission could be observed when hydrochloric acid concentrations as high as 1.0 N were employed.

The influence of gallium on indium emission was determined by preparing four solutions containing 100 ppm indium and 0, 300, 600, and 900

⁹Beckman Instrument Company Incorporated, South Pasadena, California, Data Sheet No. 2, May 1952.

¹⁰V. W. Meloche, Anal. Chem. 26, 1367 (August 1954).

ppm gallium respectively. The results obtained for these samples are given in Table 1 and are plotted in Figure 1 (Appendix I). The depression caused by gallium on the emission of indium is considerable in some cases. However, it is important to note that the intensity gradually increases to a plateau which is indicative of the actual concentration of indium present. This was true in every case.

Interference phenomenon of the type observed in this work has yet to be reported in the literature. Other types of interferences such as enhancing and suppressing effects are quite common. The enhancements and suppressions, however, are not reported to vary with time but remain constant throughout the determinations.

Table 1 The Influence of Gallium on Indium Emission Intensity

Day		1st	2nd	4th	7th	8th
Indium Concentration (ppm)	Gallium Concentration (ppm)	Emission				
100	0	11.9	11.9	11.9	11.9	11.9
100	300	10.8	11.3	11.9	11.9	11.9
100	600	10.7	11.2	11.9	11.9	11.9
100	900	10.6	10.7	11.9	11.9	11.9

A discussion, which apparently explains the observed suppressions, is presented in Appendix II together with experimental evidence which tends to substantiate the mechanism presented.

The evidence presented above certainly indicates that one could proceed with confidence and use the flame photometer to determine indium

in the presence of gallium if sufficient time is allowed to elapse between initial and final readings in order to insure maximum intensity readings.

The indium concentration of an unknown sample can be obtained by comparing the intensity of the unknown against a standard curve and interpolating. Standard solutions were prepared by transferring the required amount of indium stock solution to 100 ml. volumetric flasks and diluting to volume. Standards of 100, 300, and 600 ppm indium were prepared in this manner. The emission of these standards was determined according to the procedure previously described. The data obtained are listed in Table 2 and are plotted in Figure 2 (Appendix I).

Table 2. Data for Standard Curve

Indium Concentration (ppm)	Corrected Intensity
100	11.7
300	33.6
600	67.9

Experience has shown, however, that a curve of this type can lead to erroneous results because of flame instability. The needle adjustment valve on this particular instrument was unable to maintain the same flame intensity over long periods of time. This difficulty can be taken care of by running standards immediately after the individual unknowns. The emission intensity of the unknown determines which standard to use. This procedure yielded excellent results.

Determination of unknown samples were run at various time intervals for periods of a week or more, depending on how long it takes the suppressed readings to come to maximum. The average maximum indium concentrations of those segments coming from the gallium rich layer were calculated. This average result together with the average mercury composition of the layer in question were plotted on triangular coordinate paper as shown on pages 19 and 20. Determination of the points for the mercury rich layer were obtained in the same manner as described for the gallium rich layer.

CHAPTER III

DISCUSSION OF RESULTS

CHAPTER III

DISCUSSION OF RESULTS

The data obtained as a result of averaging the mercury, indium, and gallium content of the various segments for a particular liquid layer (gallium rich or mercury rich) are plotted on triangular coordinate paper for the two operating temperatures of 35° C. and 50° C. These plots are located on the next two pages.

The results obtained at 35° C. indicates that indium is preferentially soluble in the mercury liquid layer up to about 37 per cent indium. From this point on one finds the gallium rich layer rapidly increases in indium content up to the point where solid solution forms. At 35° C. solid solution forms when the indium is present in the mercury layer at a composition of about 62 per cent. It should be noted also that the gallium composition of the mercury layer increases markedly at this juncture. Up to this point the gallium composition remains rather constant.

Attention is now directed to that portion of the curve which represents the gallium rich layer at low indium concentration. A glance at this portion of the curve indicates that without any indium present the mercury composition is about 6 per cent. From this point on, the mercury composition decreases to about 2 per cent with increasing indium composition. After this point the mercury content increases very slowly to 3 per cent with increasing indium composition; then, of course, solid solution forms.

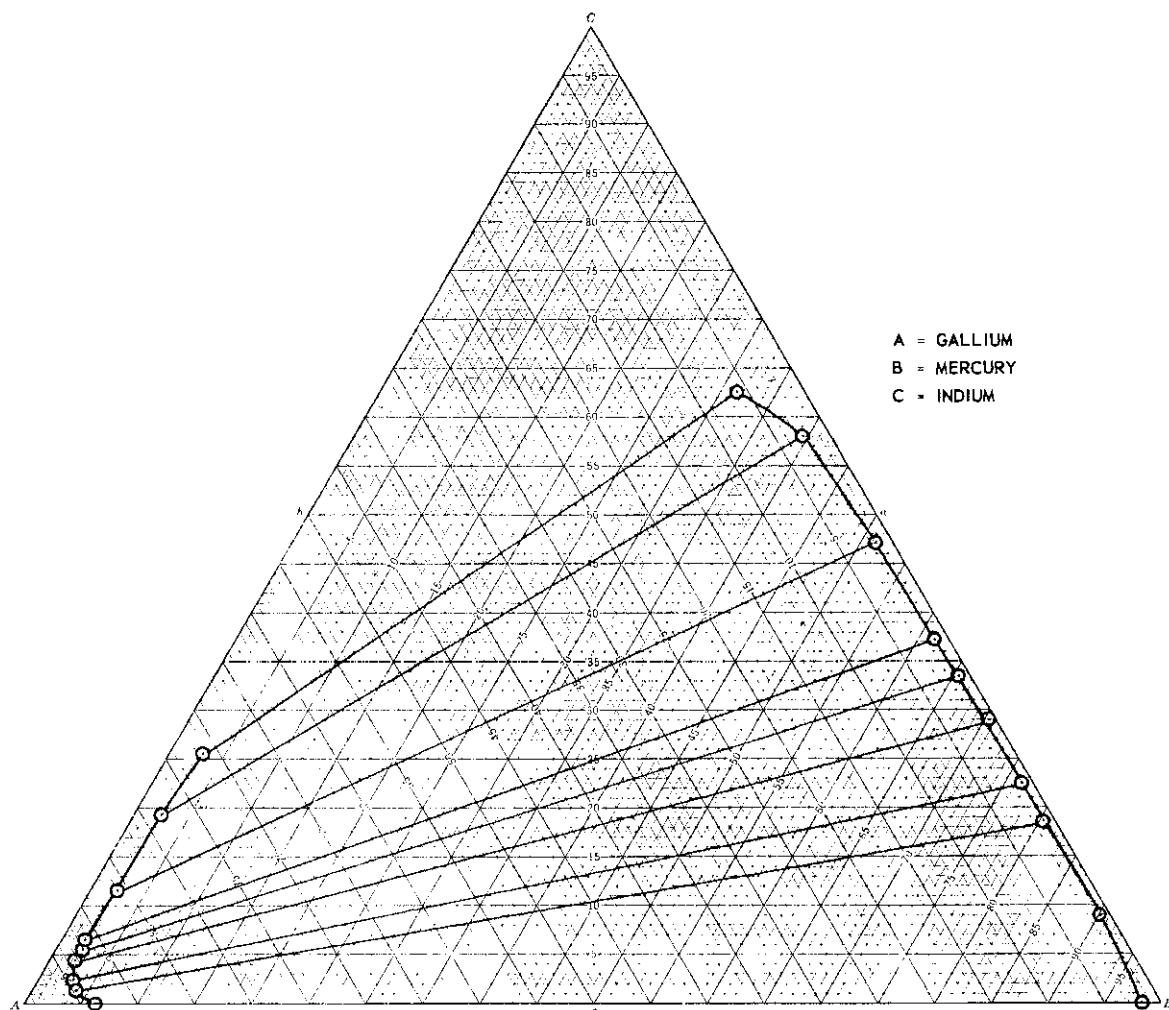


FIGURE 3. GALLIUM-MERCURY-INDIUM ISOTHERMAL CONSTITUTION DIAGRAM (35°C.).

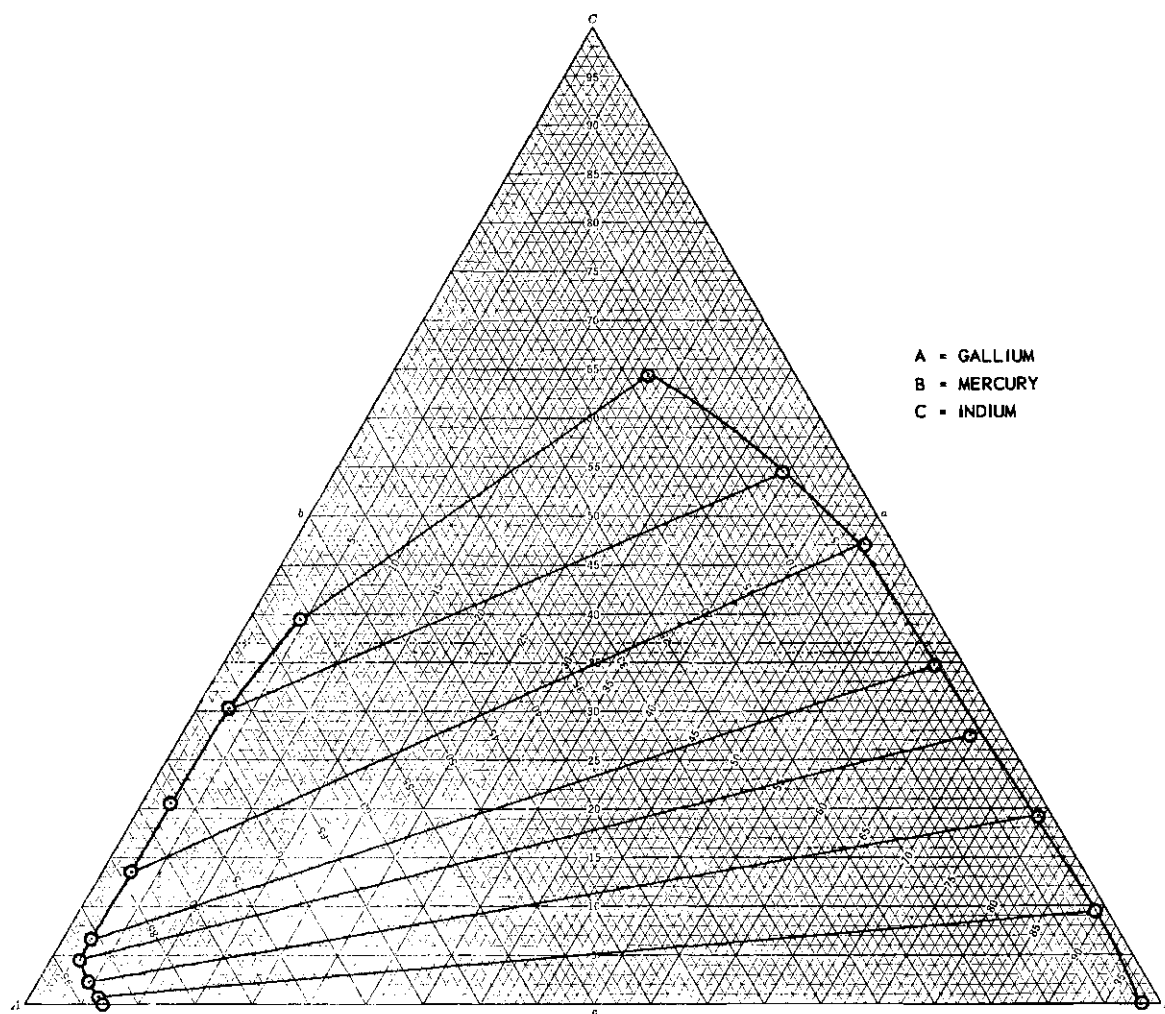


FIGURE 4. GALLIUM-MERCURY-INDIUM ISOTHERMAL CONSTITUTION DIAGRAM (50° C.).

The results obtained at 50° C. are more or less similar to those obtained at 35° C. Except that it is now possible to have more indium in the gallium layer before solid solution commences to precipitate. The gallium content of the mercury layer is rather low at low indium content. The gallium content is seen to increase slightly in the mercury layer as the indium content increases between 27 per cent and 47 per cent following which it increases rather sharply to about 13 per cent gallium at 64 per cent indium. At this point solid solution forms. The same decline in the mercury content at low indium concentrations in the gallium layer is observed at 50° C. as was noted at 35° C. Following this decline the mercury content of the gallium layer remains fairly constant with increasing indium composition until one approaches the vicinity where solid solution forms. Then the mercury content increases to about 6 per cent.

Solid solution was observed when the indium concentrations in the gallium and mercury layers at 35° C. were 26 per cent and 62.5 per cent respectively. At 50° C. solid solution was observed when the indium concentrations in the gallium and mercury layer were 39.5 per cent and 64 per cent respectively. These observations compare rather closely with the results reported by Banick¹¹ for the mercury-indium system and by Denny¹² for the gallium-indium system. Banick reports solid solution formation at 60 per cent indium concentration for 35° C. and at 63 per cent for 50° C. Denny reports solid solution formation in the gallium-indium system at 32 per cent indium for 35° C. and 45 per cent indium for 50° C.

¹¹Banick, op. cit.

¹²Denny, op. cit.

Sample calculations as performed for a particular run are given in Chapter IV together with tables which list the average results of the various points obtained at 35° C. and 50° C.

CHAPTER IV
SAMPLE CALCULATIONS AND DATA

CHAPTER IV

SAMPLE CALCULATIONS AND DATA

The calculations performed on run number 20 were chosen as being rather typical and for this reason they will be considered here in detail. For this run 0.3485 gram of mercury was combined with 0.1462 gram of gallium and 0.1504 gram of indium. This yields 30.15 per cent indium on a basis of $(\text{In}/\text{In} + \text{Hg})100$ and 69.85 per cent mercury on a basis of $(\text{Hg}/\text{In} + \text{Hg})100$. These two percentages should be kept in mind when reviewing the mercury and indium percentages as determined experimentally for the mercury layer of this run (Tables 3 and 6). The gallium concentrations were deliberately omitted in these calculations in order to emphasize the affinity of mercury for indium. The ability of the mercury to attract by far the greater amount of indium relative to gallium in the concentration range of this run is shown quite clearly.

Segment weights together with the amount of mercury found in each segment and the calculated mercury percentage are given in Table 3. The per cent mercury is obtained by simply dividing the weight of mercury by the weight of the segment and multiplying by a hundred.

As was noted earlier in the text, the indium and gallium are separated from the mercury as soluble chloride and are to be analyzed for indium by flame photometry. The results of a typical series of determinations are listed in Table 4. The indium concentration of each segment was calculated directly from the nearest standard. For example the corrected emission intensity of segment 20¹ is 2.0. The nearest standard is standard # 1, with a corrected emission intensity of 11.8 corresponding

Table 3. Mercury Determinations of Run No. 20

Segment No.	1	2	3	4	5	6	7
Segment weight (grams)	0.0431	0.0480	0.0920	0.0841	0.0896	0.1158	0.1388
Hg weight (grams)	0.0012	0.0013	0.0287	0.0591	0.0628	0.0813	0.0983
Per cent Hg	2.78	2.71	31.20	70.27	70.09	70.21	70.82
Average		2.74	*			70.35	

* This segment was obtained from that region in the column which is in the phase demarcation zone.

Table 4. Indium Determination Using the Flame Photometer

Instrument Settings	Selectivity, mid point; λ , 451.1 m μ ; slit, 0.02; Sensitivity, 0.1; photomultiplier, full; load resistor, 2				
	I _{obs.}	I _{blank}	I _{corr.}	ppm	gm '100 ml.
Standard # 1	11.9	0.1	11.8	100	0.010
Standard # 2	37.2	0.1	37.1	300	0.030
Standard # 3	74.6	0.1	74.5	600	0.060
20 ¹	2.1	0.1	2.0	16.95	0.0017
20 ²	2.3	0.1	2.2	18.64	0.0019
20 ³	15.8	0.1	15.7	133.1	0.0133
20 ⁴	30.6	0.1	30.5	246.6	0.0247
20 ⁵	23.2	0.1	23.1	191.0	0.0191
20 ⁶	41.5	0.1	41.4	334.8	0.0335
20 ⁷	50.6	0.1	50.5	408.0	0.0408

to 100 ppm. From the following relationship the indium content of 20¹ was calculated.

$$\text{In content of } 20^1 = \frac{(2.0)(100)}{11.8} = 16.95 \text{ ppm}$$

The data listed in Table 4 represents only one determination on the flame photometer. Because of the possible interferences noted earlier in this paper, it is necessary to make several such determinations in order to insure obtaining maximum intensities. Table 5 lists these results for run No. 20.

Table 5. Indium Content in Grams for Each Segment Determined by Flame Photometry Over a Period of Time

Date	20 ¹	20 ²	20 ^{3*}	20 ⁴	20 ⁵	20 ⁶	20 ⁷
Feb. 12, 1955	0.0014	0.0014	0.0109	0.0210			
Feb. 15, 1955	0.0017	0.0019	0.0133	0.0245	0.0191	0.0334	0.0408
Feb. 19, 1955	0.0018	0.0019	0.0133	0.0243	0.0264	0.0333	0.0411
Feb. 24, 1955					0.0274	0.0347	0.0420
March 1, 1955					0.0242	0.0319	0.0399

* Phase demarcation zone.

By taking the results reported in Table 5 and dividing by the appropriate segment weight and multiplying by a hundred one obtains values of the indium per cent. The result of this type of calculation for run No. 20 is listed in Table 6.

Segment 20¹, 20², 20³, and 20⁴ for the date Feb. 12, 1955, and segment 20⁵ for the date Feb. 15, 1955 show characteristic depressed results and therefore were not used in calculating the averages. For some unexplainable reason the first determination of segments 20⁶ and 20⁷ for the date Feb. 15, 1955, show higher results than those obtained for the final determination of March 1, 1955.

Table 6. Indium Content in Per Cent for Each Segment
Calculated from Data Listed in Table 5

Date	20 ¹	20 ²	20 ³	20 ⁴	20 ⁵	20 ⁶	20 ⁷
Feb. 12, 1955	3.25	2.92	11.85	24.97			
Feb. 15, 1955	3.94	3.96	14.46	29.13	21.32	28.84	29.39
Feb. 19, 1955	4.18	3.96	14.46	28.89	29.46	28.76	29.61
Feb. 24, 1955					30.6	29.97	30.26
March 1, 1955					27.01	27.55	28.75
Average		4.0	*			29.1	

*Phase demarcation zone, not used in calculating average.

Tables 7 and 8 list the average mercury, indium, and gallium compositions for the plotted data at 35° C. and 50° C. respectively.

Table 7. Average Mercury and Indium
Composition at 35° C.

Layer	Run No.	Hg Content (Per Cent)	In Content (Per Cent)	Ga Content (Per Cent)
Ga	18	3.8	1.45	95.75
Hg	18	80.1	18.8	1.1
Ga	19	3.5	2.4	94.1
Hg	19	76.2	22.5	1.3
Ga	20	2.7	4.0	93.3
Hg	20	70.4	29.1	0.5
Ga	21	2.3	5.7	92.0
Hg	21	65.3	33.7	1.0
Ga	22	2.0	6.6	91.4
Hg	22	61.3	37.3	1.4
Ga	23	2.4	11.7	85.9
Hg	23	51.1	47.1	1.8
Ga	24	2.3	19.6	78.1
Hg	24	39.7	58.2	2.1
Ga	25	2.9	25.9	71.2
Hg	25	31.4	61.7	6.9

Table 8. Average Mercury and Indium
Composition at 50° C.

Layer	Run No.	Hg Content (Per Cent)	In Content (Per Cent)	Ga Content (Per Cent)
Ga	30	6.5	0.9	92.6
Hg	30	89.7	9.3	1.0
Ga	31	4.6	2.2	93.2
Hg	31	79.6	19.4	1.0
Ga	32	2.8	4.6	92.6
Hg	32	69.8	27.3	2.9
Ga	33	2.6	6.9	90.5
Hg	33	62.5	35.0	2.5
Ga	34	2.5	13.8	83.7
Hg	34	50.2	47.0	2.8
Ga	35	2.8	20.7	76.5
Hg	35	39.7	54.2	6.1
Ga	37	4.9	39.8	55.3
Hg	37	22.2	64.4	13.4

CHAPTER V

SUMMARY

CHAPTER V

SUMMARY

As a result of work by other investigators, gallium and mercury are known to be only slightly soluble in one another, whereas, indium was found to be very soluble in both gallium and mercury when considered individually. In this research the influence of indium on the solubility of gallium and mercury is determined at two temperatures (35° and 50° C.). The data is presented on triangular coordinate paper. The points, with their corresponding tie lines, indicate that indium is preferentially soluble in the mercury layer up to about 37 per cent at 35° C. and 35 per cent at 50° C. As the indium concentration is increased beyond these points more and more indium finds its way into the gallium layer. Finally, when the indium concentration in the mercury layer reaches approximately 62 per cent at 35° C. and 65 per cent at 50° C. a solid solution forms. Further addition of indium simply increases the amount of solid solution that forms but does not change the concentrations in the gallium rich and mercury rich liquid layers.

The change in temperature has the net effect of increasing the indium solubility in the gallium layer to a considerable extent. The increase in temperature slightly increases the concentration of mercury in the gallium layer.

The data was obtained by analyzing a columnated mixture of gallium, indium, and mercury after the mixture was allowed to come to equilibrium at the particular operating temperature. At equilibrium the mercury rich layer separates and is found on the bottom of the column and the gallium

rich layer on top. Segments are extracted from the top to the bottom of the column. Each segment is analyzed for mercury by reacting the segment with concentrated hydrochloric acid in the presence of a small piece of platinum wire. The mercury remains unreacted and can be determined gravimetrically. The indium and the gallium form soluble chlorides. These chlorides are transferred to 100 ml. volumetric flasks and raised to volume.

The indium is determined via flame photometry and the gallium is obtained by difference.

BIBLIOGRAPHY

1. Bish, R. E., "Methods for Locating Two-Liquid Immiscibility." Transactions of the American Institute of Mining and Metallurgical Engineers 194, (1952), 81-82.
2. Bowden, S. T., The Phase Rule and Phase Reactions. London: The Macmillian Company, 1938.
3. Cary, H. H., and Beckman, A. O., "A Quartz Photoelectric Spectrophotometer." Journal of American Optical Society 31 (1941), 682.
4. Dennis, L. M., and Bridgman, J. A., "Gallium." Journal of the American Chemical Society 40, (1918), 1531.
5. Denny, J. P., Hamilton, J. H., and Lewis, J. R., "Constitution of the System of Gallium-Indium." Journal of Metals 4 (January 1952), 39.
6. Giese, A. C., "Mercury Poisoning." Science 91 (1940), 476.
7. Harvey, C. E., Spectrochemical Procedures. Glendale, California: Applied Research Laboratories, 1950, pp. 402.
8. Hume-Rothery, W., Christian, J. W., and Pearson, W. B., Metallurgical Equilibrium Diagrams. London: Institute of Physics, 1952, pp. 311.
9. Jack, J., and Sebba, F., "The Melting of Gallium." Transactions of the Faraday Society 50 (1954), 226-31.
10. Jacobson, C. A., Encyclopedia of Chemical Reactions. New York: Reinhold Publishing Corporation, 1946.
11. Latimer, W. M., and Hildebrand, J. H., Reference Book of Inorganic Chemistry. New York: The Macmillian Company, 1929, pp. 442.
12. Ludwick, M. T., Indium. New York: Indium Corporation of America, 1950, pp. 276.
13. Milner, G. W., "Determination of Gallium." Analyst 80 (1955), 77-8.
14. Milner, G. W., Wood, A. J., and Woodhead, J. L., "The Separation and Determination of Gallium." Analyst 79 (May 1954), 372-9.
15. Nachtrieb, N. H., Principles and Practice of Spectro-Chemical Analysis. New York: McGraw-Hill Book Company, 1950, pp. 324.
16. Powell, P. W., "The Electrical Resistivity of Gallium and Some Other Anisotropic Properties of This Metal." Proceedings of the Royal Society (Series A) (1951), 524-41.

17. Prodinger, W., Organic Reagents Used in Quantitative Inorganic Analysis. New York: Elsevir Publishing Company, 1940, pp. 203.
18. Randall, M., and Humphrey, H. B., "New Process for Controlling Mercury Vapor." U. S. Bureau of Mines, Information Circular No. 7206 (1942).
19. Richards, T. W., and Boyer, B., "The Purification of Gallium by Electrolysis, and Compressibility and Density of Gallium." Journal of the Amercian Chemical Society 41 (1919), 133-4.
20. Rollins, O. W., and Deischer, C. K., "Volumetric Determination of Gallium." Analytical Chemistry 26 (April 1954), 769.
21. Sandell, E. B., "Determination of Gallium in Silicate Rocks." Analytical Chemistry 19 (1947), 63-5.
22. Seidell, A., Solubilities of Inorganic and Metal Organic Compounds. New York: Van Nostrand, 1940, pp. 1254. Supplement: Solubility of Compounds. New York: Van Nostrand, 1952.
23. Tyzack, C., and Raynor, G. V., "An X-Ray Examination of the Indium-Rich Alloys of the Systems In + Pb and In + Hg." Transactions of the Faraday Society 50 (1954), 675-84.
24. Wagner, C., Thermodynamics of Alloys. Cambridge, Massachusetts: Addison-Wesley Press, 1952, pp. 161.
25. Walton, H. F., Principles and Methods of Chemical Analysis. New York: Prentice-Hall, 1952, pp. 435.
26. Zittel, H. E., "The Polarographic Determination of Gallium." University of Michigan Microfilms, Publication No. 9214, pp. 63. Dissertation Abstracts 14 (1954), 1303.

APPENDIX I

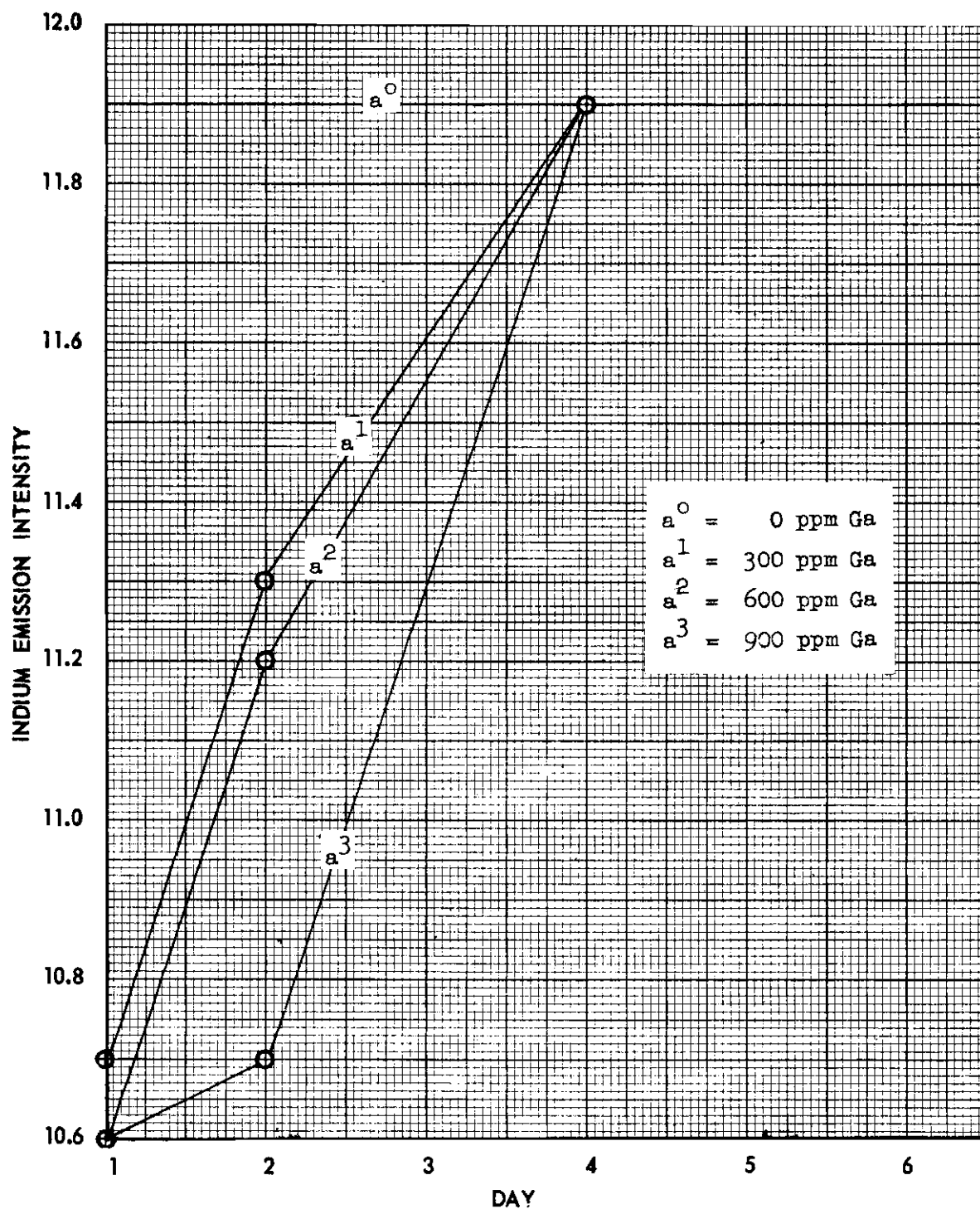


FIGURE 1. THE INFLUENCE OF GALLIUM ON INDIUM EMISSION INTENSITY.

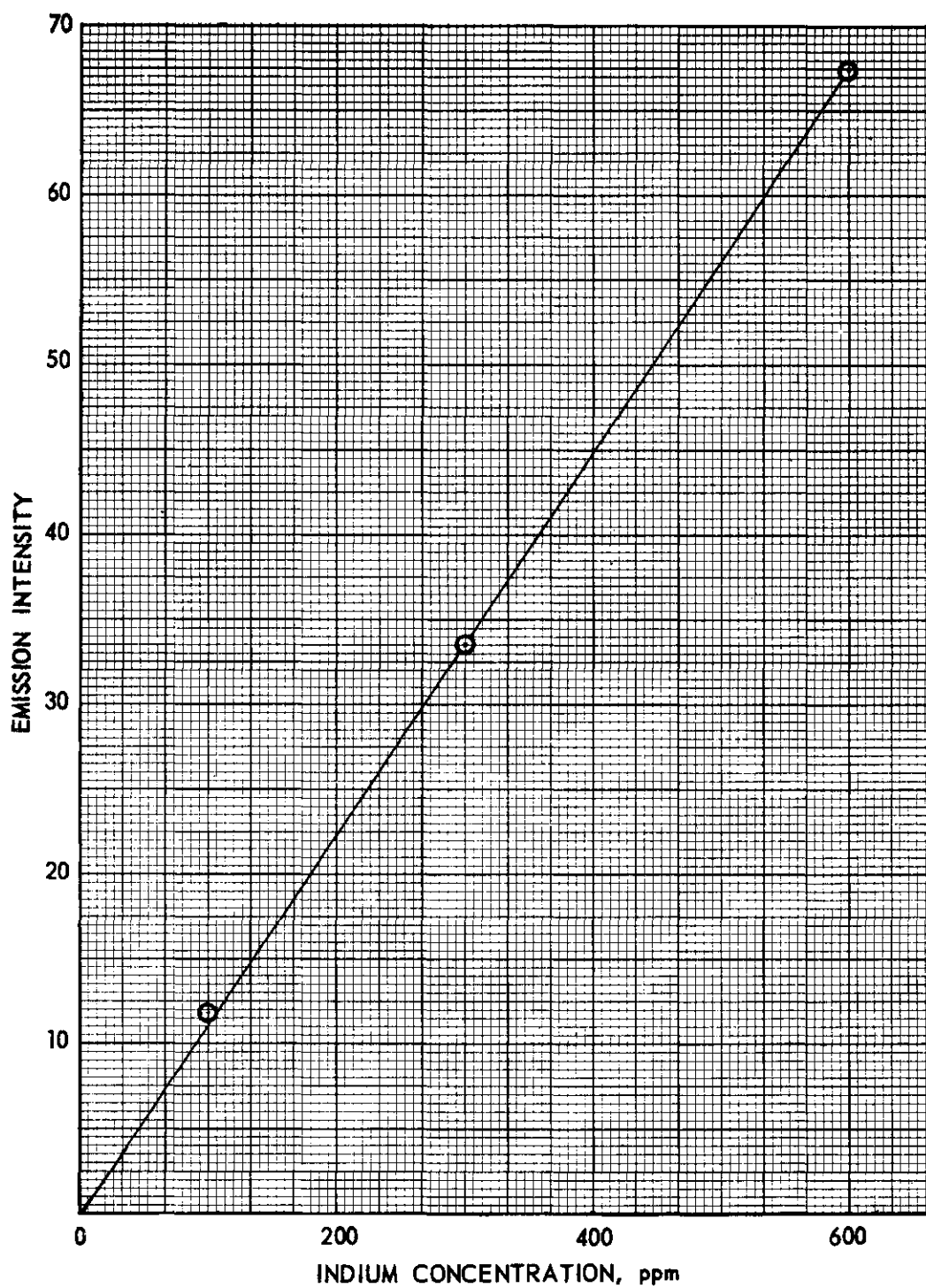


FIGURE 2. INDIUM STANDARDIZATION CURVE.

APPENDIX II

APPENDIX II

A PROPOSED MECHANISM FOR THE SUPPRESSION AND RECOVERY OF
INDIUM EMISSION INTENSITY IN THE PRESENCE OF GALLIUM

The discussion which follows formed the substance of a paper presented by D. Schleuter and P. Foster before the Georgia Academy of Sciences on April 29, 1955, and is to be published at a later date in the Academy's bulletin.

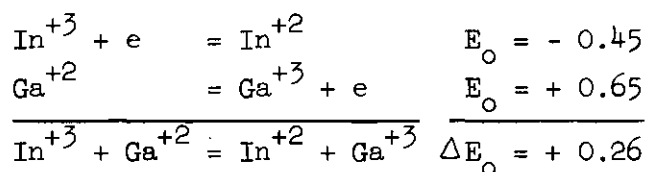
The initial suppression followed by recovery of emission intensity of the indium in the presence of gallium as a function of time indicated strongly that the phenomenon could be explained in terms of some form of oxidation-reduction mechanism.

Latimer¹² states that only the In^{+3} specie has been known to exist in an acid solution, whereas it is quite possible to have both Ga^{+3} and Ga^{+2} under similar conditions. This means, of course, that the standards employed in this research could contain only In^{+3} . The use of standardized curves as a means of determining the indium concentration of an unknown sample would indicate the amount of In^{+3} present, only. If other cations are present in solution, such as Ga^{+2} , which have the ability to reduce the effective In^{+3} concentration, then it would appear reasonable to expect the type of results reported.

Indeed, a utilization of Latimer's¹³ oxidation potential presents a favorable free energy for the reduction of In^{+3} by Ga^{+2} .

¹²W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. 2nd Edition. New York: Prentice-Hall, 1952.

¹³W. M. Latimer, op. cit.



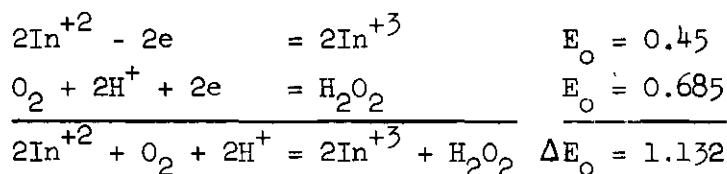
$$\Delta F = -nF\Delta E_o$$

Also, calculation of the equilibrium constant K_e from the above ΔE_o indicates a favorable equilibrium.

$$\Delta E_o = \frac{0.05916}{n} \log K_e$$

$$K_e = 1.75 \times 10^4$$

As mentioned previously, although a depression in the emission of indium was initially observed, the emission gradually increased to values which were indicative of the true concentration. This can also be explained in terms of oxidation potentials, if one considers atmospheric oxygen as the instrument of oxidation.



Substituting this value of ΔE_o in the following expression we again obtain a favorable free energy.

$$\Delta F = -nF\Delta E_o$$

The subsequent calculation of the equilibrium constant from

$$\Delta E_o = \frac{0.05916}{n} \log K_e$$

yields a rather substantial K_e

$$K_e = 2 \times 10^{38}.$$

Clearly, these calculations indicate that the reduction of indium from the +3 to the +2 state by Ga^{+2} is possible. This reaction, followed

by the oxidation of the In^{+2} to In^{+3} due to the action of atmospheric oxygen certainly is very probable.

To substantiate the occurrence of the proposed interfering reactions the indium solutions listed in Table 9 were prepared.

Table 9. Environment Control in Interference Studies

Solution	Indium (ppm)	Gallium (ppm)	Environment
b ¹	100	100	Argon was bubbled through solution for 30 minutes. Solutions were maintained under argon.
b ²	100	300	
b ³	100	600	
c ¹	100	100	Oxygen was bubbled through solutions for 30 minutes after preparation.
c ²	100	300	
c ³	100	600	

The "b" solutions were kept under argon in hope of preventing the atmospheric oxidation reaction from taking place. In other words the emission intensity readings of the solutions should remain suppressed as long as they were maintained under argon. This indeed was the case as the results in Table 10 will verify. The oxidized solutions "c" on the other hand, should give maximum intensities from the very start. This too is verified in Table 10.

Table 10. Emission Intensities of Environment
Controlled Solutions

Day	1st	2nd	4th	6th	7th
Solutions	Emission				
Std.*	11.9	11.9	11.9	11.9	11.9
b ¹	11.9	11.9	11.9	11.9	11.9
b ²	10.8	10.8	10.9	10.9	10.9
b ³	10.5	10.6	10.6	10.7	10.7
c ¹	11.9	11.9	11.9	11.9	11.9
c ²	11.9	11.9	11.9	11.9	11.9
c ³	11.9	11.9	11.9	11.9	11.9

*
Standard solutions, 100 ppm indium only.