

**THE ACTIVITY OF TIN IN TIN AMALGAMS AND THE
STANDARD ELECTRODE POTENTIAL OF TIN**

BY

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of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy.**

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INTRODUCTION

A preliminary investigation of the activities of tin in tin amalgams has shown that a more complete study would be worth while. This work has pointed out methods by which most of the experimental difficulties could be overcome.

In addition, the present problem is to include the determination of the potential of pure tin against the saturated tin amalgam and the electrode potential of pure tin.

The electrode potential of tin has been calculated by means of an equilibrium measurement, but has never been successfully determined by a direct measurement.

In this problem it has been accomplished by using the saturated amalgam and a hydrogen electrode. The E^0 obtained in this manner is then corrected for the potential found for pure tin against the saturated amalgam.

While these three goals are very closely inter-related, it seems best to sub-divide each part of this paper into three parts; namely, (A) the activities of tin in tin amalgams, (B) the potential between pure tin and its saturated amalgam, and (C) the electrode potential of tin.

REVIEW OF THE LITERATURE

A. Electromotive Force of Tin Amalgams

The electromotive force of tin amalgams have been determined on several occasions but in only one case have they been successful. Richards and Wilson (1), in a series of investigations of the electromotive force of liquid amalgams, made a limited study of tin amalgams. This work while highly precise included only a very few measurements. Their object in these studies was to determine the deviations of the observed potential from that calculated by the Nernst equation for the electromotive force of concentration cells. They found in the case of tin that the observed potentials were always lower than those calculated from the Nernst equation.

Lewis and Randall (2) have devised a method by which the activities of a metal in its amalgams may be calculated from the electromotive force of such amalgams. If activities are used instead of mol fractions in the Nernst equation the observed values agree very closely with those calculated. Lewis and Randall (2) first used this method for calculating the activities of thallium in thallium amalgams by employing the data obtained by Richards and Daniels (3).

B. Potential Between Pure Tin and its Saturated Amalgams

The only value reported in the literature for the potential of pure tin against its saturated amalgam has been by VanHeteren (4). He determined the potential using stannous chloride as the electrolyte and electrolytic tin as the tin electrode, and found it to be .90 millivolts as an average of about five measurements, which had an average deviation from the mean of about .70 of a millivolt. This at least shows that the solid phase is not pure tin and that the potential between the saturated amalgam and pure tin is in the neighborhood of a millivolt. It also shows the difficulty in obtaining a reproducible value for the tin electrode.

C. Electrode Potential of Tin

The accepted value for the electrode potential of tin at the present time is based upon the electrode potential of lead and an equilibrium study made by Noyes and Toabe (5). They studied the equilibrium between lead, tin, lead perchlorate and tin perchlorate and found that the electrode potential of tin should be 0.0140 volts more negative than the electrode potential of lead. At present the accepted value for lead is given as -0.122 volts, which has been calculated by Lewis and Randall (6) from data obtained from several different sources. In this calculation several assumptions were made which limits the accuracy of the value. Carmondy (7) has obtained 0.126 volts for the value, while others have obtained values all the way from 0.120 to 0.129. At the present time a research is being conducted in this laboratory by Hatfield (8) on the electrode potential of lead. The method which he is using was developed by Linhart (9) in his determination of the electrode potential of mercury. In this method the indefinite liquid junction potential has been avoided.

While several attempts have been made to determine the electrode potential of tin directly, none have been

successful. Most of these have involved indefinite liquid junction potentials.

Linhart's (9) method for determining the electrode potential of a metal without an appreciable liquid junction potential seems applicable to our problem. Details of this method will be given later.

THEORETICAL DISCUSSION

A. Activities of Tin in Tin Amalgams

It has been shown that when concentrations are used in the Nernst equation for the electromotive force of concentration cells the calculated values do not agree with the observed values except when the concentrations are very dilute. The deviation becomes larger as the concentration increases and may be either positive or negative since it depends upon the metal in question.

This difficulty is not limited to the Nernst equation alone, but is the case in practically all of the physical chemistry equations which depend upon concentration. Many attempts have been made to develop equations which will hold for concentration other than at infinite dilution. The majority of these have only been correction factors for specific cases.

G. N. Lewis (10) has developed a concept which he calls the activity. It can, in a most general way, be defined as "that quantity which when substituted for the concentration of a given substance in the mass action expression will give a constant value for the expression over the entire range of concentration". In

other words, the activity of a substance is its "effective concentration" in a given solution.

Thus, if the activities of a metal in its amalgams are available the potential between any two amalgams may be calculated and should agree very closely with the observed potential.

Lewis and Randall (2) have developed a method whereby such activities may be calculated from the electromotive force of their amalgams.

In order to make such a determination we must first study the type of cell which is to be used. If two electrodes of the same metal and identical in states are immersed in an electrolyte containing their ions, no potential difference can be observed, furthermore, if an infinitesimal amount of current is allowed to pass through the cell a transfer of metal will occur from one electrode to the other. Here also no potential difference can be detected for no change in free energy ΔF has taken place, for the concentration of the metal has not been changed at either electrode. Since $\Delta F = -NEF$, the reversible electromotive force of the cell would also be zero. If a finite amount of current had been allowed to pass there would have been a potential difference established by concentration polarization. Such a process would be

irreversible. F being the Faraday equivalent, N the number of such equivalents passing through the cell and E the electromotive force of the cell. Thus, if the concentration of the two electrodes are the same the activities of the metal will also be the same at both electrodes.

However, if the two electrodes differ from each other in some way, such as different states of strain, or if one electrode is the pure metal and the other is the same metal but containing some impurities there will be a difference in the activities of the metal in the two electrodes. As a result of this inequality of activities there will be a tendency for the metal whose activity is the highest to be transferred to the electrode at which the metal is at a lower activity. The transfer cannot take place unless a current is allowed to flow, but the potential which would cause such a flow can be measured by means of a sensitive galvanometer and potentiometer. If this potential is measured during the passing of an infinitesimal amount of current, it may be considered as the reversible electromotive force of the cell.

It is evident then, that if the potentials of such cells are measured under reversible conditions, that we will have a direct measure of the ratio of the activities of the metals in the two electrodes. This type of cell is well

illustrated by one which has amalgams of different concentrations as its electrodes. This type of electrode is free from strains and is very reproducible.

The electromotive force of cells composed of amalgam electrodes with the corresponding metallic ions as electrolytes are dependent only upon the concentrations of the metals in the amalgams. The change in free energy ΔF in the transfer of metal from one electrode to the other is a function only of the mol fraction N_2 of the metal in the amalgam. This is expressed in the following equation:

$$\Delta F = RT \ln \frac{N_2}{N'_2} \quad (1)$$

Where R is the gas constant, T the absolute temperature and \ln the natural logarithm. Since the mol fraction can only be used in very dilute amalgams we shall employ the activity which holds over the entire range of concentration.

When the activity is substituted for the mol fraction

equation (1) becomes $\Delta F = RT \ln \frac{a_2}{a'_2}$ (2) when a_2 is the activity of the metal in the more concentrated amalgam.
 equation (1) becomes $\Delta F = RT \ln \frac{a_2}{a'_2}$ (2) when a_2 is the activity of the metal in the more concentrated amalgam.

and a'_2 the activity of the metal in the more dilute amalgam.

The two equations become identical when $\frac{a_2}{N_2} = 1$.

Since this is only the case in very dilute amalgams we shall turn our attention to equation (2).

Equation (2) becomes, on the substitution of

$$F = -NEF, \quad E = \frac{RT}{-NF} \ln \frac{a_2}{a_2} \quad (3)$$

Introducing the numerical values of R and F and using common logarithms, equation (3) becomes for tin at 25°C:

$$E = - .02958 \log \frac{a_2}{a_2} \quad (4)$$

R = 1.9885 calories per degree, F = 23874 calories per volt equivalent and N for tin is 2.

From this equation it is readily seen that the electromotive force of a cell composed of two tin amalgams depends solely on the activity of tin in the amalgams, and is independent of the concentration of the electrolyte so long as stannous ions are present.

The equation as it stands permits only the calculation of the ratio of the activities of tin in the amalgams from the electromotive force of such a cell. The activities of the metal in each amalgam can be calculated for the electromotive force between such amalgams by a method developed by Lewis and Randall (2). This method follows:

Equation (4), on rearrangement becomes:

$$\log a_2 = - \frac{E}{0.02958} - \log a_2 \quad (5)$$

If now we let N_2 and a_2 be the mol fraction and activity of tin in any amalgam and N_2^1 and a_2^1 the corresponding values in some particular amalgam chosen as a reference, E will be the electromotive force of a concentration cell in which

one electrode is the amalgam of fixed mol fraction N_2^1 and an amalgam of any other mol fraction N_2 .

If the log of N_2 is subtracted from both sides of equation (5) we get:

$$\log \frac{a_2}{N_2} = \left(\frac{-E}{.02958} - \log N_2 \right) + \log a_2^1$$

When the quantity in the parenthesis is plotted against N_2 , as shown in Figure IV, we see that when $N_2 = 0$, we have by definition that $\frac{a_2}{N_2} = 1$, and the $\log \frac{a_2}{N_2} = 0$. The value of the ordinate when the curve cuts the vertical axis is therefore equal to $-\log a_2^1$. This gives at once the activity of the reference amalgam whose mol fraction is N_2^1 . The value of this limiting ordinate subtracted from the ordinate at any other value of N_2 gives the value of $\log \frac{a_2}{N_2}$, from which a_2 is readily calculated.

This is the method by which we shall calculate the activities of tin in tin amalgam from the electromotive force between such amalgams.

B. Saturated Tin Amalgams

Saturated amalgams are nearly always used in place of the pure metal in establishing the electrode potential of that metal against some reference electrode. In such a measurement it is essential that an electrode be used which quickly reaches equilibrium and that this equilibrium value be reproducible. This is seldom found to be the case when solid metal electrodes are used. The electrodes themselves may be of the purest metal but when their potentials are measured against some reference electrode, reproducible values are difficult to obtain. This variation in potential can be ascribed only to variation in the physical state of the metal, such as being under different stages of strain. This variation is less pronounced in soft metals and may be minimized by using the metal in a very finely divided state or by electrolytic deposition of the metal on a suitable surface.

Even with such precautions equilibrium is very slow in being attained and not as reproducible as is desired. For this reason the saturated amalgams are used wherever possible for they are not only easily prepared but reach an equilibrium value that is very reproducible, and in a very short time. Furthermore, this type of amalgam

electrode requires no analysis.

If such an amalgam is to be used in determining the electrode potential of the metal against some reference electrode, the potential of the saturated amalgam against the pure metal must be determined. This potential should be zero unless the metal forms a solid solution with mercury. This is very difficult to show by analysis but is relatively easy by electromotive force measurements. In such a cell as this it is not essential that equilibrium be attained at once as in the case of the other cells. Therefore, it would not be as difficult to obtain reproducible values as in the case where the potential is measured against some reference electrode.

C. The Standard Electrode Potential of Tin

The standard electrode potential of a metal is defined as the potential of the metal in its standard state against its ions in a solution in which they are at unit activity. This potential is symbolized by E^0 and represents the tendency of a metal to detach electrons and go into solution as metallic ions.

This potential of a single electrode is determined by reference to the normal hydrogen electrode. The potential of the hydrogen electrode at atmospheric pressure against an aqueous solution containing hydrogen ion at unit activity is considered as zero at all temperatures. In an expression for a cell reaction the hydrogen electrode is placed arbitrarily at the left and combined with the other electrode in question at the right. Since the voltage of the hydrogen electrode is considered to be zero, the voltage of such a cell is a direct measure of the single electrode potential of the metal in question.

The sign of such a single electrode potential is determined by the direction in which negative electricity moves within the cell. The voltage is positive if negative electricity moves from right to left within the cell as written. Thus if the cell is written as follows:



it indicated that the potential of the junction Me^+ / Me is positive and therefore the voltage of the entire cell as written is positive. But if negative electricity within the cell moves from left to right as written the single electrode potential is negative as is the sign of the complete cell.

Getman and Daniels (17) have established a convention to show the relationship between the way a cell is written and the chemical reaction which takes place in the cell. It is "the chemical reaction of a cell is written as that reaction which would cause negative electricity to flow from right to left within the cell". The voltage of a cell so reacting is arbitrarily taken to be positive. Since a positive voltage means that the work, NEF, is likewise positive and therefore the cell does work on its surrounding, and uses up the free energy, or in other words, ΔF is negative and the reaction is spontaneous.

The potential of the junction between a metal and its ions is positive or negative depending upon whether the metal has a greater tendency to lose electrons and become ions or whether the ions have a greater tendency to gain electrons and become the metal again. The former would have a positive potential for the junction $\text{Me}^0 / \text{Me}^+$ while the

latter would have a positive potential for the junction Me^+/Me^0 .

The relationship between the standard electrode potential E^0 and the potential of the electrode E in a solution in which its ions are other than at unit activity is best shown by the following equations. For any reaction, $aA + bB = cC + dD$, the change in free energy ΔF is represented by the following equation

$$-\Delta F = RT \ln K - RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (1)$$

where K is the equilibrium constant, and a the activity of each substance. If both the reactants and the products are at unit activity or if activity quotient is unity $-\Delta F$ becomes $-\Delta F^0$ and the last term becomes equal to zero. We have as a result the equation

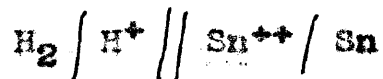
$$-\Delta F^0 = RT \ln K \quad (2)$$

and since $\Delta F = -nEF$ and $\Delta F^0 = -nE^0F$ we can obtain the equation $E^0 = \frac{RT}{nF} \ln K$ and by subtraction in equation (1) we get the more general equation in which all the substances are not at unit activity.

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (3)$$

If now we apply this equation to the particular case in which tin is used as an electrode in a solution of Sn^{++} ions of activity $a_{\text{Sn}^{++}}$ and measured against a hydrogen

electrode in a solution of H^+ of activity a_{H^+} we get the following equation for the electromotive of the cell



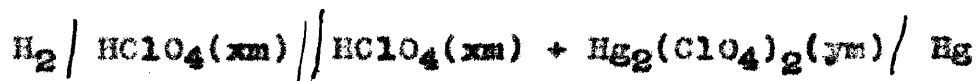
and whose chemical reaction is



$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{H^+}^2 a_{Sn^0}}{a_{Sn^{++}} a_{H_2}} \quad (4)$$

If we measure the potential of such a cell we can calculate the E^0 value for tin provided the activities of the hydrogen ions and stannous ions are available.

Linhart (9) has used a method in his determination of the electrode potential of mercury by which the usual indefinite liquid junction potential has been avoided. His cell is represented by the following expression

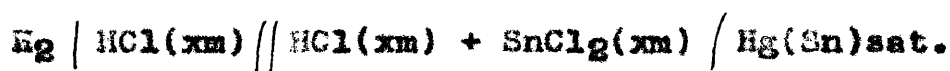


If y is made small in comparison with x the solution becomes almost identical throughout and hence any liquid junction potential would be very small. The E^0 calculated for such a cell would be practically free of any error caused by a liquid junction potential.

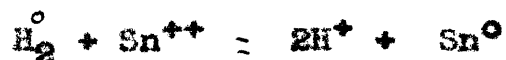
It should be possible to use this type of cell to determine the electrode potential of various metals above mercury in the E.M.F. series by the use of these saturated

amalgams. We shall use it for determining the potential of the saturated tin amalgam from which the standard electrode potential of tin can be calculated by correcting for the potential between pure tin and the saturated amalgam.

This cell would be composed of the hydrogen electrode in x molal hydrochloric acid and the saturated tin amalgam in x molal hydrochloric acid and y molal stannous chloride. It may be expressed as follows:



The reaction taking place in the cell would be



and the electromotive force of such a cell would be given by the equation (4) above.

Before an E^0 value can be calculated the activity of the individual ions must be available. The activities of the ions are calculated by multiplying the molality of the ions by their activity coefficients corresponding to the ionic strength of the solution in which they are used. The activity coefficient is defined as the thermodynamic degree of dissociation. These values are constant in solutions of the same ionic strength, provided the concentrations are not too great. Ionic strength is defined as one-half the sum of the stoichiometrical molality of each ion multiplied by the square of its valence. Thus the activity

of an ion is given by the equation

$$a_+ = \gamma_+ m_+ \text{ or } a_- = \gamma_- m_-$$

Equation (4) becomes, upon substitution of the numerical values for the constants and changing to ordinary logarithms,

$$E = E^{\circ} - .02958 \log \frac{a_{H^+}^2}{a_{H_2}^{\circ}} \frac{a_{Sn^{\circ}}}{a_{Sn^{++}}}$$

The E° value calculated by this equation would be that of tin in the saturated amalgam. Since both the tin and the hydrogen gas are in their standard states a_{Sn} and a_{H_2} become equal to unity. Replacing a by γM we get the following equation for E° of tin in the saturated amalgam.

$$E = E^{\circ} - .02958 \log \frac{(\gamma_{H^+} M_{H^+})^2}{\gamma_{Sn^{++}} M_{Sn^{++}}}$$

To obtain E° for pure tin in its standard state it is only necessary to add the potential between pure tin and its saturated amalgam to the E° value calculated by the above equation.

EXPERIMENTAL DETAILS

A. Apparatus

As tin in its amalgam is very susceptible to oxygen such amalgams must be prepared and kept in a complete absence of air. This has been accomplished by the system shown in the diagrammatic sketch, shown in Figure I. It was constructed entirely of Pyrex glass fused together into one unit. By proper control of stopcocks the entire system could be evacuated to a pressure of less than a millimeter of mercury by means of a Cenco Hyvac pump, after which it could be filled with hydrogen at atmospheric pressure. This cycle was repeated at least five times in order to insure complete absence of oxygen.

Previously distilled mercury was placed in a distilling flask not shown in the figure and after the flask was sealed off the mercury was distilled under a reduced pressure and in the presence of hydrogen into the air condenser A from which it ran directly into the storage flask B. The distilling flask was heated by means of a Cenco Hotcone heater, the current through which was controlled by means of a water cooled resistance in order to regulate the amount of heating.

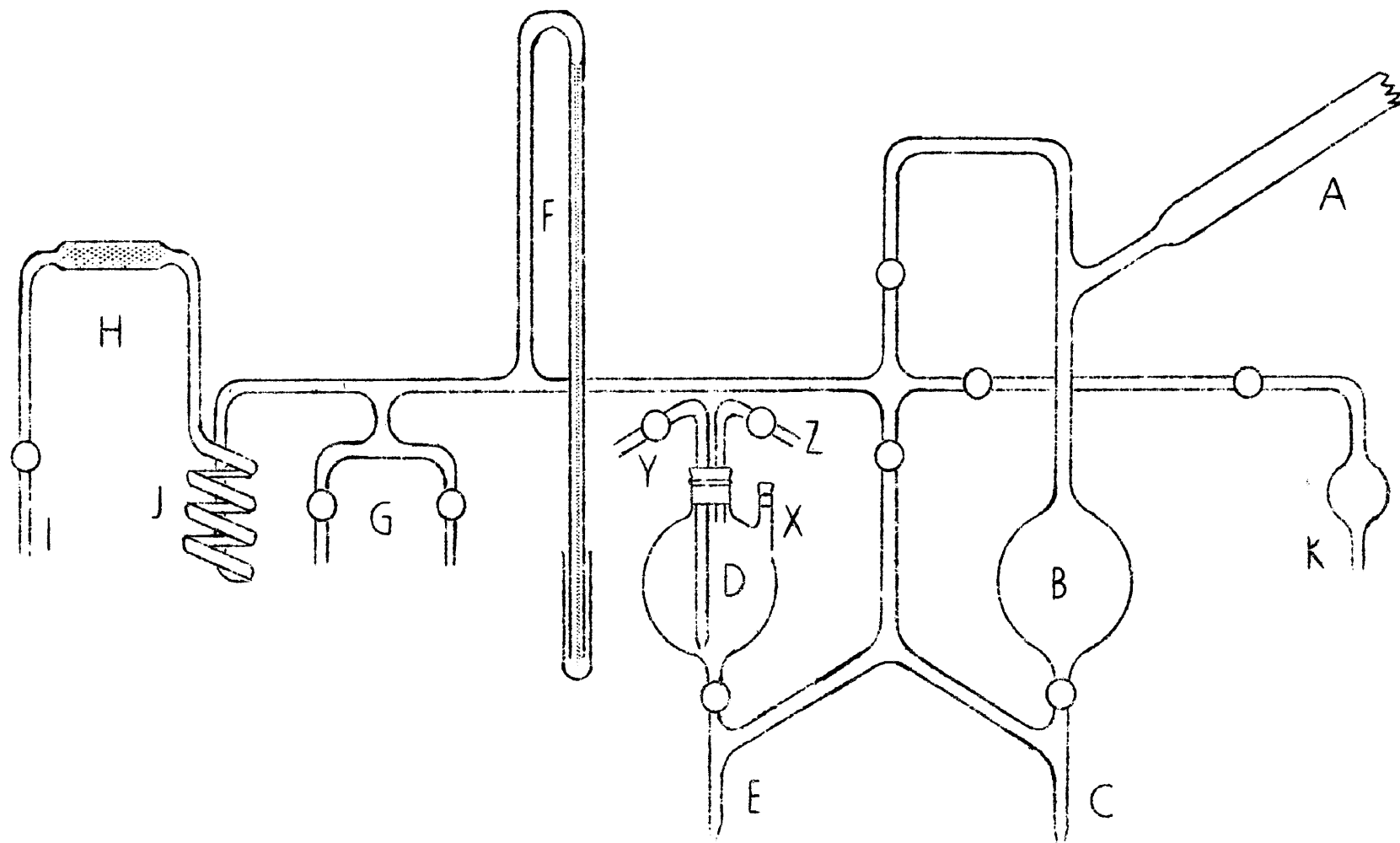
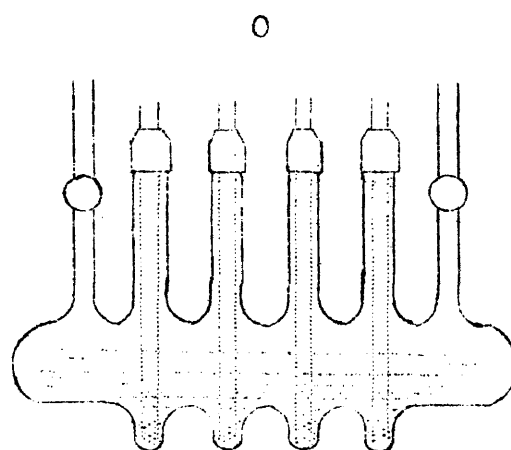
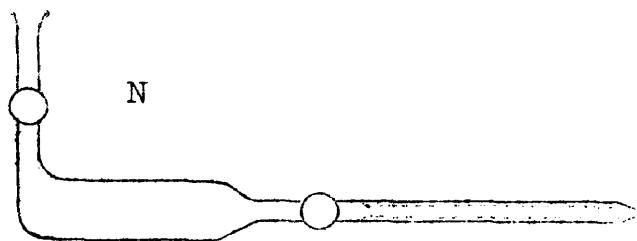
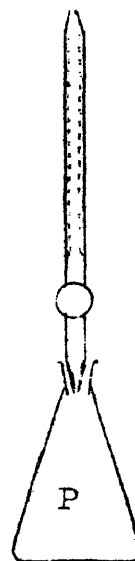
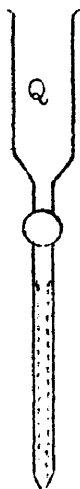
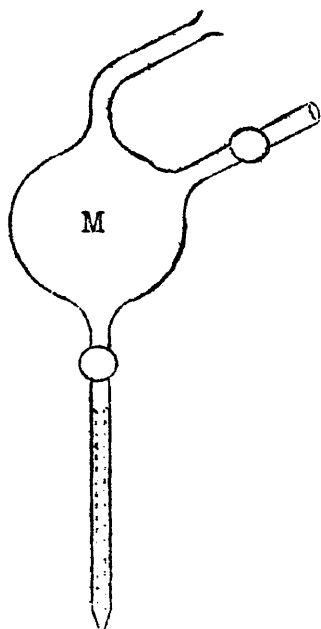


FIGURE I

The mercury in B could be removed in a complete absence of air through the ground glass joint at C by means of suitable pipettes. The ground glass joints at C and E and on the two types of pipettes were of standard taper and could be used interchangeably. The reference amalgam was prepared and stored in flask D which was equipped with a side arm X closed with a well fitting rubber stopper. The rubber stopper at the top of the flask was fitted with two tubes Y and Z, both equipped with stopcocks, one reaching to the bottom of the flask and the other just through the stopper. This stopper was sealed in place with picein cement. The long capillary tube F dipped into a few centimeters of mercury and served both to indicate the pressure in the system and as a safety valve in case of excess pressure. The two stopcocks at G served to connect the system with any other system in which it was necessary to remove all traces of air. The system was connected at I to a hydrogen bomb from which the hydrogen passed through the tube H, which contained copper gauze heated to 450° - 500° by means of an electrically heated furnace. The coil J permitted the hydrogen gas to be cooled before it passed into the rest of the system. The Hyvac pump was connected to the system at K.

The pipette M, shown in Figure II, was used in

FIGURE II



transferring a weighed portion of mercury from B to D in the absence of air for use in preparing the reference amalgam. This same pipette was used in preparing the electrolyte used in filling cell O. It was equipped at the bottom with a capillary outlet tube, closed by a stopcock. At the top was a tube fitted with a ground glass joint, and a side arm fitted with a stopcock.

The pipette N was used in diluting the reference amalgam and in introducing both the reference amalgam and the dilute amalgams into cell O. It was equipped with a capillary outlet tube closed with a stopcock and a ground glass joint as an inlet tube which was also fitted with a stopcock.

The saturated amalgams were prepared in the flask P shown in Figure II. It was connected to a capillary tube and stopcock by means of a ground glass joint.

The funnel Q was used in transferring the saturated amalgam from the flask P to the cells. The capillary outlet was closed by means of a stopcock.

The cell O, shown in Figure II, was used in measuring the potentials between the various amalgams as well as the potentials between the saturated amalgam and the pure tin electrodes. With the cell so constructed, it was possible to measure the potential between three pairs of amalgams in

one filling of the cell. Electrical contact between the amalgams and the external leads were made by use of platinum electrodes. These were made by fusing a short piece of platinum wire in the end of a soft glass tube. These tubes were then filled with mercury in order that contact could be made with the leads to the potentiometer. These electrodes were held in place by rubber slip joints which also served to seal the cell off from the air. The two side arms were used in removing air from the cell and in adding the electrolyte.

The cell in which the potential between the saturated amalgams and the hydrogen electrodes were measured is shown in Figure III. This type of cell made it possible to obtain the potential of two saturated amalgams against two hydrogen electrodes in one filling of the cell. The construction of the half cell in which the amalgams were placed is shown by the diagram. The bulb A was connected to B by means of a ground glass joint which permitted its removal during the introduction of the saturated amalgams. This introduction was accomplished in exactly the same manner used in filling cell O. Rubber slip joints were used in closing the two vertical tubes on B.

The construction of the hydrogen half cell E is clearly shown in the figure. Hydrogen was bubbled through the cell by way of an inner seal at the bottom of the cell.

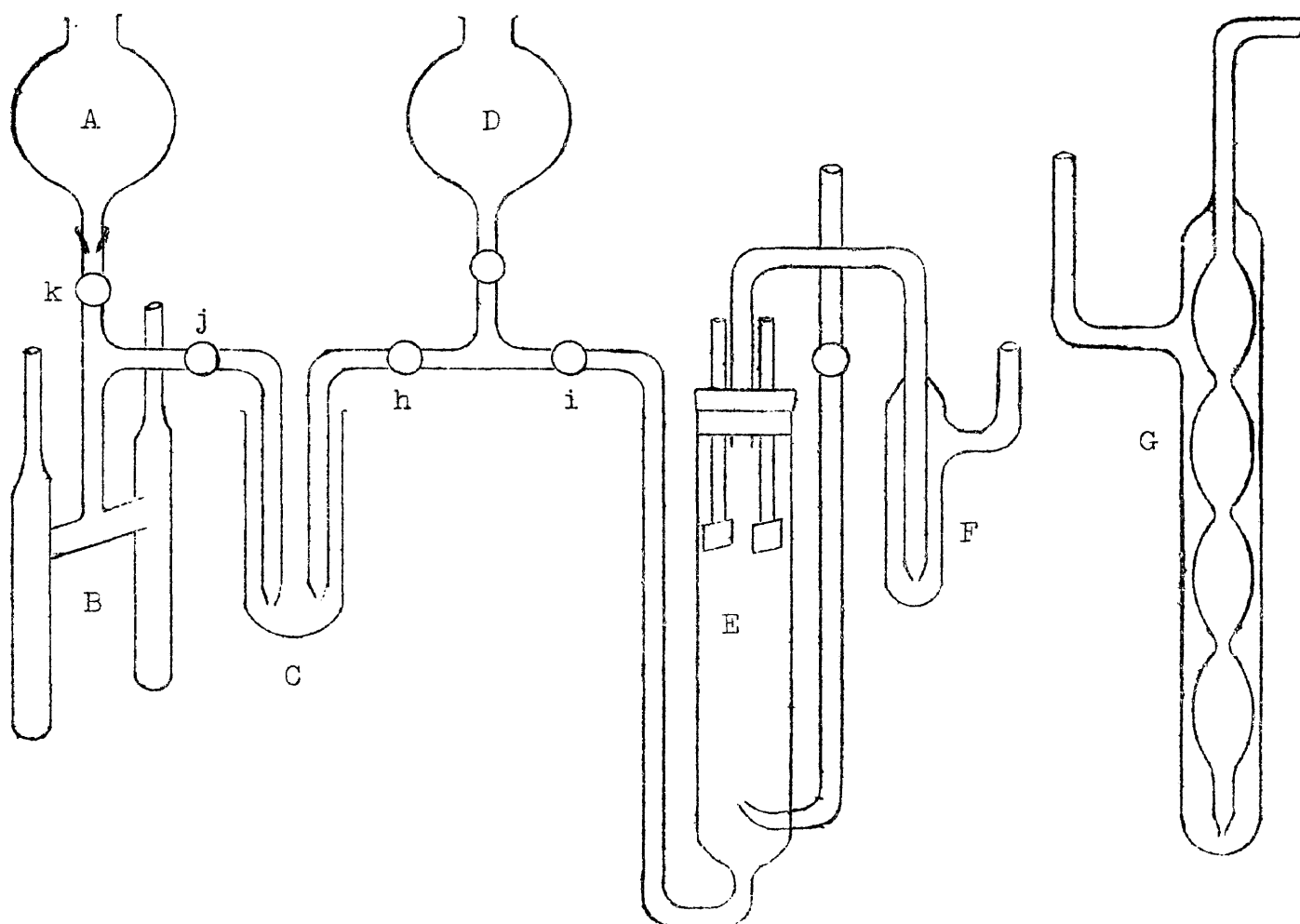


FIGURE III

The two hydrogen electrodes of platinized platinum and the bubbling tube F were fitted in a rubber stopper which closed the top of the cell. The hydrogen was saturated with the electrolyte to be used by passing through the saturator G. The tube C served as a bridge in connecting the two half cells. The stopcocks h and i were unlubricated and then could be kept closed to prevent diffusion of the electrolyte which would be accentuated by the pumping action caused by the bubbling of hydrogen through the cell.

A thermostat constructed by the American Instrument Company was used to hold the cells at a constant temperature. This bath was operated at 25°C and was constant to $\pm 0.02^\circ$.

The potentials of the cells were measured with a Leeds and Northrup Type K Potentiometer. An Eppley Standard Cell, with an electromotive force of 1.01388 volts was used as a standard. A Leeds and Northrup Type R Galvanometer, with a sensitivity of 7.5 microvolts per millimeter with an external critical damping resistance of 2000 ohm in series, was used as a null instrument. The deflection of the galvanometer was determined by means of a lamp and scale reading device manufactured by the same company.

Each electrode in a cell had a separate lead to a switch board, from which, by a suitable arrangement of jacks, the potential of any pair of electrodes could be measured by the potentiometer.

The weights used in this work were calibrated and only in the case of the 50 gram weight was it necessary to apply a correction.

B. Materials

The mercury used in the preparation of all amalgams was washed, dried and distilled twice. The first distillation was carried out under reduced pressure with a fine stream of air bubbling through the mercury to oxidize any metals which might have been present. The second distillation was carried out in the system described above in the presence of hydrogen and under a reduced pressure. The mercury was distilled directly into the reservoir B after the distilling flask had been sealed off from the atmosphere.

The tin used in this work was prepared by electrolyzing a hydrochloric acid solution of stannous chloride at a high current density. A platinum wire was used as a cathode and a tin rod as the anode in the electrolysis. The stannous chloride solution was prepared by dissolving C.P. tin in constant boiling hydrochloric acid. The fine needle-like crystals of tin obtained by this method were first washed free of acid with distilled water and then treated with alcohol to remove the excess water,

and dried in a desiccator over concentrated sulfuric acid.

The water used in all cases was twice distilled, the second being carried out using a block tin condenser. The water was freshly prepared just before use.

The hydrogen was obtained from a bomb and was freed of oxygen by passing over copper gauze heated to 450° - 500°C .

The stannous chloride used in this research was Merck's reagent quality.

The hydrochloric acid solutions were all prepared from the constant boiling acid.

C. Method

1. Electromotive Force of Tin Amalgams

In determining the activity of tin in tin amalgams from their electromotive force it is necessary to have the potential difference between each amalgam. As more than one cell of four amalgams were measured it was necessary to have one amalgam of the same concentration in each cell that was assembled. This permits the calculation of the potential between any two amalgams or one in reference to all the others. As a reference amalgam we have chosen one whose concentration is near the concentration of the saturated amalgam, first, because small changes in concentration due to oxidation would have no appreciable effect upon the potential of that amalgam and second, because this amalgam is to be used in preparing all of the other amalgams by diluting with mercury.

This reference amalgam was prepared as follows: the pipette M was used in transferring a weighed amount of mercury from the reservoir B to flask D in a complete absence of air. The air was removed from the system and the pipette by the method of evacuation and filling with hydrogen. The mercury was run out of the pipette into D by way of X, while a stream of hydrogen was escaping. This hydrogen entered the flask D by way of G and Z. The weighed

amount of tin was added in the same way, after which the amalgam was completely mixed by bubbling hydrogen through it by way of the tube Y and G.

It should be mentioned here that the air in the bore of any of the stopcocks could be removed by having the system under a pressure of hydrogen slightly more than atmospheric, and then by momentarily opening the stopcock two or three times the air would be replaced by hydrogen.

Since this reference amalgam was to be used both as a reference potential and in preparing the other amalgam, it was necessary to analyze it at the time each cell was filled. The concentration was found to change very slowly during the interval between the filling of each cell. This change was very small, but the potential of the reference amalgam was corrected for this change. It was no more than .02 millivolts between any two cells.

This reference amalgam was analyzed for tin as follows: a weighed sample of 10 - 30 grams of the amalgam was placed in a sillimanite crucible of 35 - 40 cc capacity and concentrated HNO_3 added a few drops at a time with constant stirring until all of the mercury had dissolved. The crucible and its contents were then heated on a water bath until dry, after which it was carefully heated over a free flame until all of the mercury was distilled off, and then finally ignited to constant weight. The tin was weighed as SnO_2 . All of the above operations were carried

out in a strong draft and under a hood. Duplicate analyses were made on each sample. These always checked within the limits of error in weighing.

Cell O was used to measure the electromotive force between the tin amalgams. The amalgams were placed in the cell by means of the pipette N. This pipette was used both in transferring the reference amalgam to the cell and in diluting the reference amalgam with mercury and its subsequent introduction into the cell.

The pipette was first weighed and then joined to the flask D by means of the ground glass joint at K, then after all of the air in the system and pipette had been replaced by hydrogen the reference amalgam was run into the pipette after which it was weighed and this time joined to B by means of the ground glass joint at C. The air was replaced by hydrogen in the same way as before and the desired amount of mercury run in with the amalgam. After this the pipette was weighed and then introduced into the cell O by way of a slip joint on the vertical tube directly above the cup in which the amalgam was to be placed. During this operation hydrogen was allowed to escape through the tube in which the pipette was being inserted in order to prevent the entrance of any air into the cell. The cell was connected by way of one of its side tubes to the system and could be evacuated and filled with hydrogen just as in

the case of the pipettes. These vertical tubes above the cups before the amalgams are introduced are closed by means of a glass plug in the rubber slip joints. The capillary tube of the pipette was inserted until the tip was just inside the cup at the bottom of the cell. The system was then subjected to the cycle of evacuation and filling with hydrogen in order to replace any air that might have entered and to remove the air which was trapped in the capillary tube of the pipette. The amalgam was then allowed to run into the cell after which the pipette was removed and replaced by the platinum electrode.

This same procedure was repeated for the introduction of the other two diluted amalgams and the reference amalgam. In the latter case it was not necessary to weigh the pipette. The amalgams remained bright indefinitely when allowed to stand in the cell. It usually required the best part of a day to fill a cell, since only one pipette was available.

The electrolyte used in the cell was prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in .06 M HCl from which all oxygen had been removed by boiling under a reduced pressure and subsequent bubbling of hydrogen through it.

The pipette M was used in preparing this solution. The weighed portion of SnCl_2 was placed in the pipette which was then connected to the system and also to the flask containing the air free HCl. After the air had been removed from the

pipette, hydrogen was allowed to pass through it and into the flask containing the HCl , where it was allowed to bubble through the solution for some time. Then the required amount was run into the pipette by reducing the pressure in the system. The pipette was then evacuated until the solution boiled, and then filled with hydrogen to remove the last traces of air. After this the pipette was weighed and connected to one of the side tubes of the cell C. The tip of the capillary on the pipette fitted well inside this tube so that the solution did not come in contact with any of the rubber connections. The air between the stopcocks was replaced by the usual method and then with the cell under a reduced pressure the solution was allowed to run into the cell until it was about two-thirds full. The solution in the cell was boiled at reduced pressure for a few minutes and then filled with H_2 and placed in the thermostat. The potential between each pair of amalgams was then measured at short intervals for several hours and then at larger intervals for several days.

2. The Potential Between Pure Tin and its Saturated Alloys

The saturated alloys used in all cases were prepared and introduced into the cells by the following method: The necessary weight of mercury and tin with a few cc. of .06 N HCl were placed in the flask P. The acid removed any oxide films that might be formed. The flask and its contents were heated in a beaker of boiling water with frequent shaking to insure complete mixing. After the contents had reached the temperature of the water, the capillary tube with stopcock and ground glass joint were fitted to the flask. The one-phase alloy was then run out through the capillary to remove the oxide and excess solid phase, and into a capillary funnel which had previously been inserted in the cell. The stopcock on the funnel was then opened to let the alloy run into the cell. This technique was the same as with the more dilute alloys. These two-phased alloys showed no signs of oxidation and would remain bright as long as they were kept out of contact with air.

The pure tin electrodes were prepared by electrolytically depositing tin on a platinum wire electrode at various current densities and in various electrolytes. These electrodes were prepared just before they were to be put into

the cells. They were carefully washed with the same electrolyte that was to be used in the cell. The tin electrodes were introduced into the cell in the same manner as the platinum electrode used to make contact with the amalgams.

The same electrolytes that was used in the amalgam cells were used in these cells.

3. The Potential Between the Saturated Amalgam and the Hydrogen Electrode

The cells used in determining the potentials between the saturated amalgams and the hydrogen electrodes were assembled in the following manner. The electrolyte that was to be used in the hydrogen electrode half-cell was placed in the bulb D from which it could be run either into the cell E or to the bridge C. After the hydrogen electrodes and the bubble tube were put in their places the electrolyte was allowed to run into the cell until the electrodes were just covered. Hydrogen, after first passing through the saturator G was allowed to bubble through the electrolyte in the cell. This was necessary since the electrolyte and electrodes must be completely saturated with hydrogen before any measurements can be made.

The saturator G and the bubble tube F were both filled with the same electrolyte as used in the hydrogen electrode half-cell.

The saturated amalgams were introduced into the other half cell in the same manner as they were in the preceding cells. The half-cell could be evacuated and filled with hydrogen in the same way as usual by connecting to the system by way of the tube which connected B with the bridge C. The electrolyte of stannous chloride and hydrochloric acid was added to bulb A while a stream of hydrogen was issuing from the stopcock k. After the hydrogen had bubbled through the solution for some time the cell was evacuated and the solution allowed to run in. After the cell was filled the side arm was filled with the solution by opening the stopcock j.

The two half-cells were then placed in position so that they were connected by the tube C. The solution in D was allowed to flow into C until it was about two-thirds full and then a few cc. of the solution in A was allowed to run into the same tube.

The complete cell was then placed in the thermostat at 25°C and the potentials between the saturated amalgams and the hydrogen electrodes measured at frequent intervals during the first few hours, and at longer intervals for the rest of the day. The potential usually reached a constant

value very quickly and remained constant for several hours. The barometer was read each time the potentials were measured. The depth to which the inner tube in F was submersed was determined for each cell.

DATA AND DISCUSSION OF RESULTS

A. The Potentials Between the Various Amalgams and the Reference Amalgam

The potentials between the reference amalgam and twelve different amalgams were determined. The concentrations expressed in mol fraction ranged from $N_2 = 0.0002997$ to $N_2 = 0.00995$.

The electrolytes used in these cells were approximately 0.015 molal in stannous chloride and 0.06 normal in hydrochloric acid. It was found that if the acid was any stronger tin was dissolved from the amalgam, thereby giving a changing potential to the amalgam. If the acid was any weaker excessive hydrolysis took place. Thus the concentration of the acid used was a sort of a mean between the two difficulties. In the solution used only slight hydrolysis took place and since the potentials were constant for at least 24 hours very little tin could have been dissolved by the acid.

In all, five cells were filled and their potentials measured. In each was the reference amalgam and three other amalgams. In some of the cells two of the electrodes were of the same concentration. This showed that the potential

of the amalgams were very reproducible, for their potentials varied no more than .02 of a millivolt.

In each cell six different potentials were measured. This afforded a valuable check on each of the potentials since any three values would give all the values needed.

In Table I are given the measured values for a typical cell. The first column gives the time at which the potentials were measured and in each of the other columns are given the potential of the particular pair of amalgams indicated at the top;

In Table II we have tabulated the potentials of all the amalgams referred to the most dilute amalgam. The first column gives the mol fraction and the second the potential of the amalgams against the most dilute. These potentials have been calculated from the potentials of each of the amalgams against the reference amalgam. This table also gives the potential between the saturated tin amalgam and the most dilute amalgam. This was obtained by measuring the potential between the saturated amalgam and the reference amalgam.

Table I

Time	1 - 2	1 - 3	1 - 4	2 - 3	2 - 4	3 - 4
0:35	.00218	.03759	.00372	.03979	.00152	.04131
0:50	219	3759	370	3979	151	4130
1:40	220	3759	369	3981	148	4128
2:45	221	3759	368	3981	147	4128
3:05	221	37585	368	3981	146	41275
4:00	222	3759	368	3982	145	41275
4:55	223	37585	368	3982	144	4127
5:40	223	37585	368	39825	144	4127
6:50	223	3758	368	39825	144	4127
8:35	224	3758	3685	39825	144	4127
9:30	224	3758	369	39825	144	4127
22:15	224	3755	373	3980	148	4129
23:00	224	3756	373	3981	148	4129
24:00	224	3756	373	3981	148	4130
25:30	224	3756	373	3981	149	4130
27:45	224	3756	374	3981	150	4131
29:00	224	3756	374	3981	150	4131
46:00	223	3756	377	3980	153	4133
49:00	223	37565	3775	3980	153	4133
52:00	223	3756	3775	3979	154	4134

Table II

N ₂	K
0.0002997	0
0.0005459	0.00761
0.0006256	0.00933
0.001234	0.01324
0.002246	0.02504
0.003207	0.02925
0.004209	0.03233
0.005012	0.03433
0.005805	0.03594
0.006760	0.03759
0.008436	0.03931
0.009442	0.04034
0.009950	0.04124
0.01263 (sat.)	0.04345

The concentration of the liquid phase of the saturated amalgam as determined by VanHeteren has been given as 1.21 mol percent. Analysis during this research has shown this value to be low and that it should be 1.263 mol percent, or $N_2 = 0.01263$.

The concentration of tin in the solid phase can be calculated roughly by means of the Harnst equation by using mol fractions instead of activity. Such a calculation gives 92.6 mol percent of tin in the solid phase.

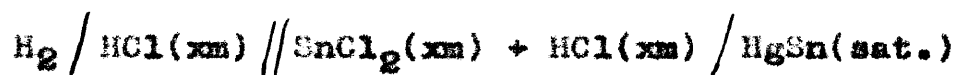
B. The Potential Between Pure Tin and its Saturated
Amalgam

Considerable difficulty was encountered in obtaining reproducible potentials between the saturated amalgams and pure tin. Approximately thirty tin electrodes were prepared by electroplating tin on platinum electrodes from a number of different solutions and at several current densities. Of this number only eleven gave anything like a constant potential. But practically all of the electrodes that gave a constant value were within $\pm .0001$ of a volt of the average value. While the others varied over a large range of potentials, some even being positive against the saturated amalgam. The electrodes that gave a constant value were not prepared from any particular solution or at a definite current density. The following solutions were used in depositing tin on the platinum electrodes: NaOH and SnCl_2 at 80° , 6 N HCl and conc. SnCl_2 , and a dilute HCl and dilute SnCl_2 bath. The latter appeared to give the best results. It is very probable that the best electrodes are prepared at a high current density.

The average of the eleven values which were fairly constant was .0010 volts $\pm .0001$ of a volt.

C. The Potential Between the Saturated Amalgams and
the Hydrogen Electrode

In all, a total of seventeen cells were filled and their potentials measured, which meant that 34 values were obtained for the cell expressed as follows:



A few of these values must be discarded for various reasons.

In cell H both the hydrogen electrodes and the saturated amalgams were rather erratic. It was also noted that some diffusion took place. While a value that was fairly constant for about three hours was obtained, the E° value calculated from it was 10 millivolts higher than any of the other values.

In cells 1, 2, 3 and 4 in which the most dilute acid was used, no constant values were obtained. While the potentials of the two saturated amalgams in the cells were practically the same they slowly increased. In view of the fact that in all the other cells constant values were found almost from the time the cells were placed in the bath, the first few values were averaged and used in calculating E° . Little weight can be given to these values, but most of them were very close to the average value that was calculated from the other cells.

In only two cells did the potentials of the saturated amalgams vary by more than a tenth of a millivolt, these being the amalgams in cell H mentioned above and in cell 3, one of the dilute acid cells. In most cases they varied no more than a few hundredths of a millivolt. These potentials remained constant in most cases for at least 3 hours, varying only with atmospheric pressure.

The data obtained for a particular cell are shown in Table III. The time at which the potentials were taken are given in column one, the potentials between each amalgam and the two hydrogen electrodes in the next four columns and the barometric pressure in the last column.

Table IV gives concentrations of the SnCl_2 and HCl , the average of the potential between each amalgam and the two hydrogen electrodes, the barometric pressure and the depth to which the inner tube in the bubble tube was submersed for each cell.

Table III

Time in Hrs.	Amalgam A		Amalgam B		Submersion 1.3 cm	
	H ₂ elect- rode A	H ₂ elect- rode B	H ₂ elect- rode B	H ₂ elect- rode A	Barometric pressure	
0:10	.18387	.18382	.18395	.18393	777.0	mm.
0:15	.18383	.18385	.18393	.18392	777.0	"
0:25	.18387	.18388	.18393	.18392	777.0	"
0:40	.18387	.18388	.18393	.18392	777.0	"
1:05	.18387	.18388	.18393	.18393	777.0	"
2:00	.18389	.18390	.18396	.18395	776.8	"
2:20	.18389	.18390	.18396	.18395	776.7	"
2:50	.18390	.18391	.18397	.18395	776.5	"
3:45	.18388	.18389	.18395	.18394	776.1	"
5:10	.18388	.18390	.18395	.18394	775.6	"

Table IV

Cell	Molality of SnCl_2	Molality of HCl	<u>E Measured</u>		Barometric Pressure	Submer- sion
			Amalgam A	Amalgam B		
E	.001950	.0959	.18045	.18056	767.2	1.6 cm.
F	.001980	.0959	.18075	.18078	757.8	1.5
G	.000945	.0959	.18980	.19010	762.0	1.4
H	.000900	.0959	.19695	.19751	767.2	1.1
I	.001338	.08785	.18155	.18155	777.6	1.5
1	.0003084	.05536	.18508	.18518	764.2	1.5
2	.000978	.05536	.17040	.17040	762.9	1.5
3	.001012	.05536	.17020	.17065	758.5	1.5
4	.001001	.05536	.17090	.17100	755.3	1.5
5	.001153	.08785	.18410	.18410	764.0	1.5
6	.001703	.08785	.17928	.17938	764.6	1.5
7	.001490	.08785	.18082	.18082	760.3	1.5
8	.0008995	.0933	.18922	.18922	768.4	1.2
9	.000988	.0933	.18758	.18754	769.0	2.0
10	.001369	.0933	.18388	.18393	777.0	1.3
11	.001585	.0933	.18225	.18233	754.6	1.3
12	.001821	.0933	.18045	.18045	758.0	1.3

CALCULATIONS

A. The Activity of Tin in Tin Amalgams

The method which we will use in calculating the activity of tin in tin amalgams from the electromotive force of such amalgams has been developed in the first part of this paper.

The most dilute amalgam was selected as the reference and its activity and mol fraction are represented by A_2^1 and N_2^1 . Then $-E$ in the equation

$$\log \frac{a_2}{N_2} = \left(\frac{-E}{0.02958} - \log N_2 \right) + \log a_2^1$$

will be the electromotive force between the reference amalgam and any other amalgam, whose mol fraction and activity are respectively N_2 and a_2 .

If we plot the quantity in the parenthesis against the mol fraction N_2 as in Figure IV, we can extrapolate the curve to where it cuts the vertical axis at which N_2 is equal to zero. The value of this limiting ordinate must be equal to $-\log a_2^1$, for when N_2 is zero $\frac{a_2}{N_2} = 1$, and the $\log \frac{a_2}{N_2}$ is equal to zero. This gives at once the activity of tin in the most dilute amalgam or the so-called reference amalgam. Furthermore, if the value of this limiting ordinate is subtracted from the ordinate of any

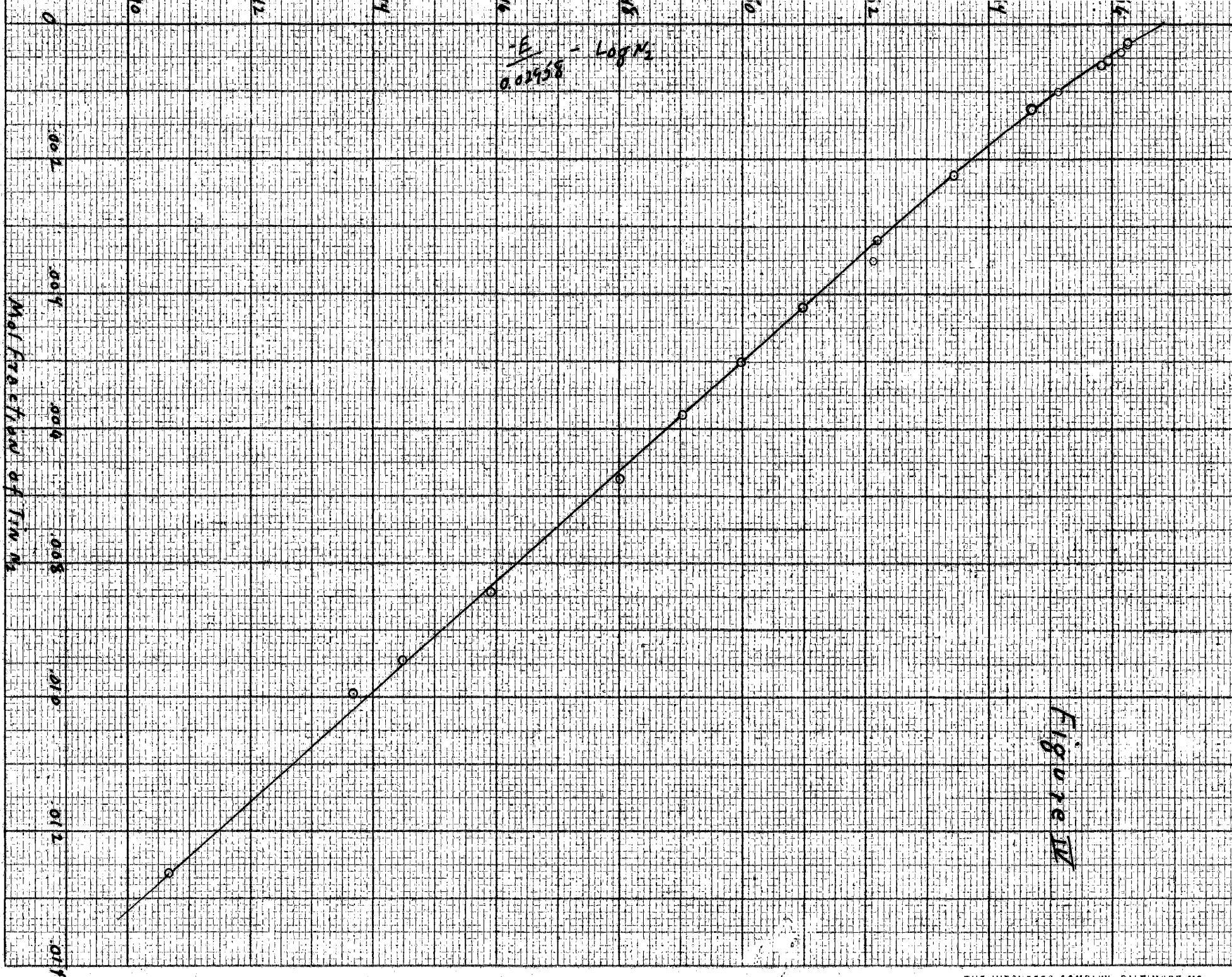


Figure IV

other value of N_2 , it gives at once the corresponding value of the $\log \frac{a_2}{N_2}$, from which the activity is easily calculated.

Since this calculation depends upon an extrapolated value it is essential that both the concentration and electromotive force of the very dilute amalgams be accurately known. A small error in the concentration of these amalgams would cause much larger error in the potentials than would the same error in the more concentrated amalgams. In view of this fact it seemed advisable to incorporate with our values those obtained by Richards and Wilson (1). This would serve both to add weight to the extrapolated value and as a means of comparing the two determinations. While Richards and Wilson only established the potential between four different amalgams these were all in the dilute portion of our curve and therefore are in the region where they would be most useful.

Their measurements were carried out at 30°C. but by use of their temperature coefficients we have calculated the electromotive force of their values at 25°C. These values, referred to the most dilute amalgam are given in Table V.

In relating their values with our own we have used the Nernst equation for the electromotive force of a concentration cell $E = .02958 \log \frac{N_2}{N_2}$ in calculating the potential between their most dilute amalgam and our most dilute amalgam.

Table V

N_2	H
.0002738	0
.0004469	.00628
.001031	.01670
.003524	.03160

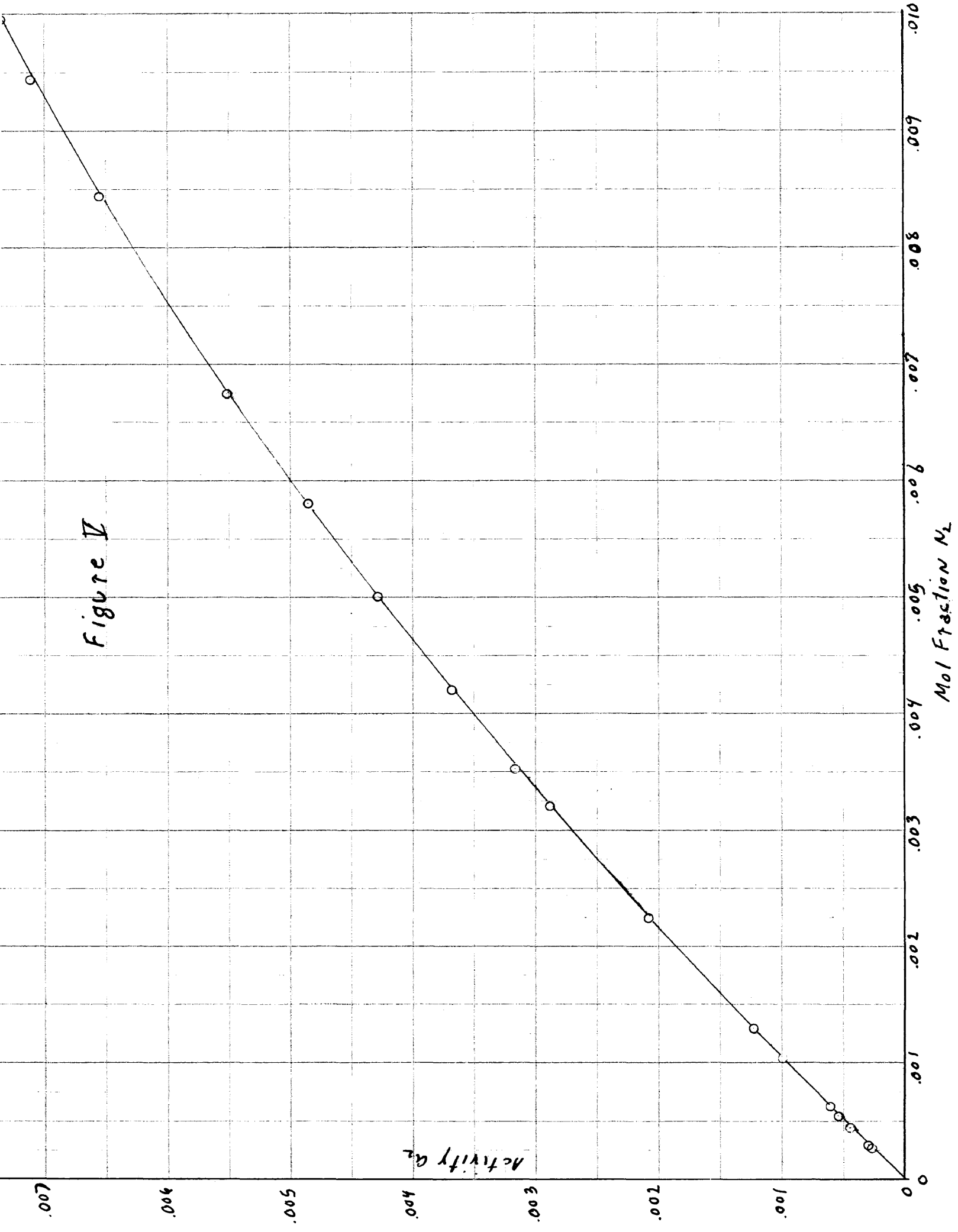
Since these two amalgams are very dilute and their concentrations very close together it is reasonable to assume that the ratio of their mol fractions are not appreciably different from the ratio of their activities. Therefore, we have calculated the potential between the two amalgams by the above equation using their mol fractions. This value is found on the third line in the third column of Table VI.

Table VI

N_2	$-\log N_2$	E	$\frac{(-E}{.02958} - \log N_2$	$\frac{a_2}{N_2}$	a_2
0	$-\infty$	0	3.5682	1	0
.0002738	3.5626	0	3.5626	.9872	.0002703
.0002997	3.5233	.00116	3.5625	.9870	.0002958
.0004469	3.3498	.00626	3.5614	.9845	.0004400
.0005459	3.2629	.00877	3.5594	.9818	.0005349
.0006256	3.2037	.01049	3.5583	.9799	.0006115
.001031	2.9867	.01670	3.5512	.9616	.0009915
.001284	2.8914	.01940	3.5472	.9528	.001224
.002246	2.6486	.02620	3.543	.9249	.002077
.003207	2.4940	.03041	3.5221	.8993	.002883
.003524	2.4530	.03180	3.5213	.8976	.003164
.004209	2.3759	.03354	3.5098	.8742	.003679
.006012	2.3000	.03549	3.4998	.8545	.004281
.005805	2.3362	.03710	3.4904	.8360	.004853
.006760	2.1701	.03875	3.4801	.8164	.005518
.008436	2.0739	.04097	3.4590	.7777	.006560
.009442	2.0249	.04200	3.4448	.7527	.007107
.00995	2.0022	.04244	3.4369	.7391	.007354
.01263	1.8986	.04461	3.4067	.6894	.008704

In Table VI are given the mol fractions N_2 of the amalgams, $\log N_2$, the potentials between each amalgam and the most dilute amalgam, the value of $\left(\frac{-E}{.02958} - \log N_2\right)$, the ratio of $\frac{a_2}{N_2}$ and the activity of tin in each amalgam. At the top of column four is given the extrapolated value obtained from the curve in Figure IV. The values indicated by red circles are those obtained from Richards and Wilson's(1) data. These points show the very good agreement of the two determinations, as well as to decrease the uncertainty of the extrapolated value.

Figure V



In Figure V the activities of tin in tin amalgams have been plotted against their mol fractions with the exception of the saturated amalgam. The points enclosed in the red circles are those obtained from the data of Richards and Wilson (1).

B. The Standard Electrode Potential of Tin

The potential of the hydrogen electrode is considered to be zero only when the pressure of the hydrogen gas is at one atmosphere. Thus if the pressure of the hydrogen is at any other pressure the potential of the cell must be corrected for pressure by means of the following equation:

$$E = .02958 \log \frac{760}{P},$$

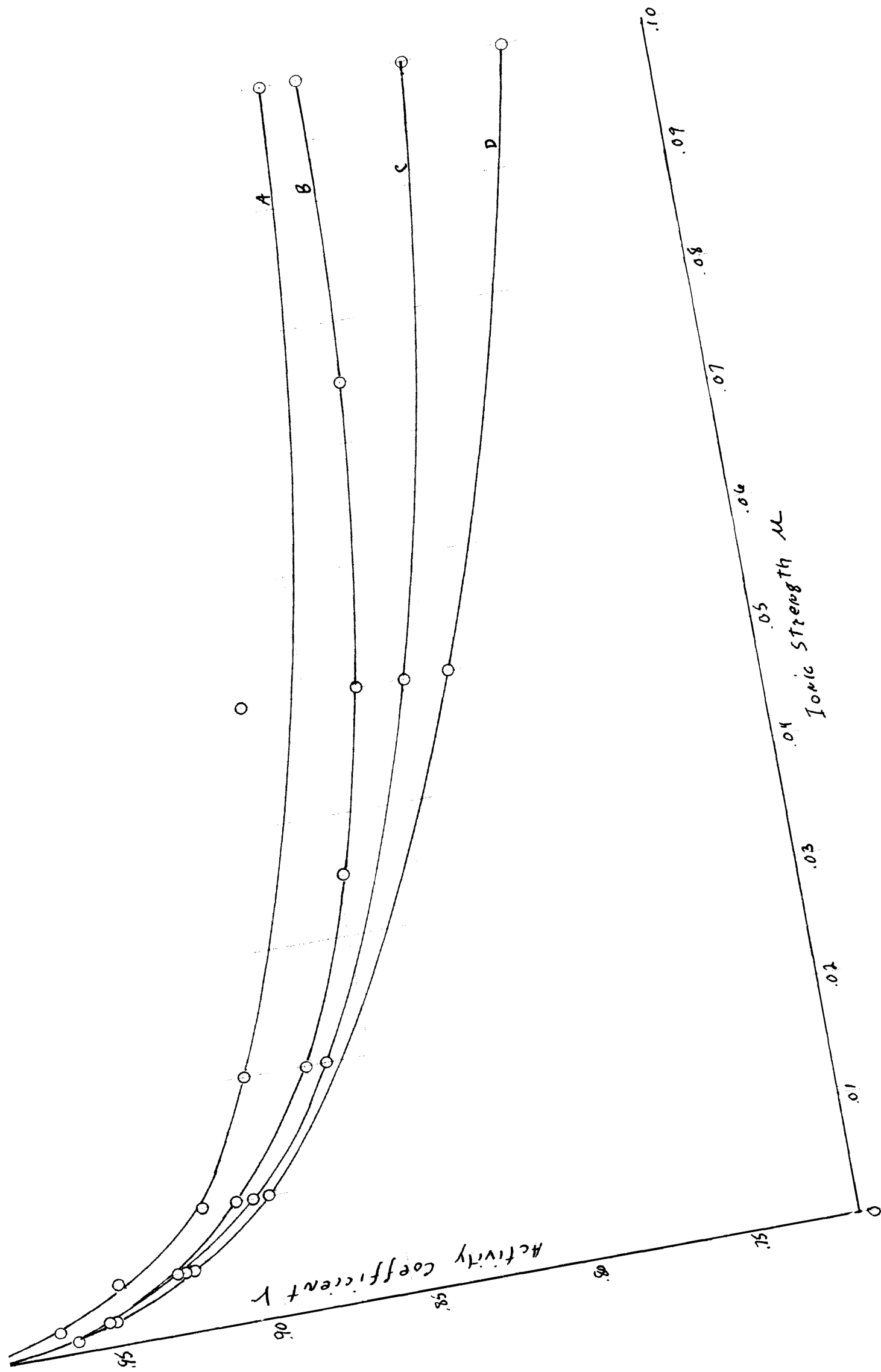
where P is the pressure of hydrogen in any cell. This pressure is obtained in the case of our cells by subtracting the vapor pressure of water at 25°C. from the barometric pressure and adding the pressure caused by the depth of the liquid in the bubble tube. This potential is subtracted from the measured value.

The equation which is to be used in calculation of the E° values was developed in the first part of this paper and is as follows:

$$E = E^{\circ} - .02958 \log \frac{(V_{+H^{+}} m_{H^{+}})^2}{V_{+Sn^{++}} m_{Sn^{++}}}$$

The activity coefficients of the hydrogen ion at various ionic strength as given by Lewis and Randall (11) appear to be inconsistent, for when the activity coefficients γ_+ are plotted against the ionic strength μ as shown by the curve A of Figure VI, several of the points do not fall on the curve. For this reason the activity coefficients of the hydrogen ion have been calculated from the activity coefficients of hydrochloric acid obtained by Randall and Young (12). These values for the activity coefficient of hydrochloric acid at various ionic strengths are shown by the curve C of Figure VI. These values appear to form a very smooth curve with all the points falling on the curve. In order to obtain the γ_+ of the hydrogen ion from the mean activity coefficient γ_{\pm} of hydrochloric acid, it is necessary to have the γ_- for the chloride ion. To obtain γ_- for the chloride ion we must assume that γ_+ for the potassium ion and γ_- for the chloride ion in potassium chloride are equal and therefore equal to γ_{\pm} for potassium chloride. This is very nearly correct since the transference numbers of the potassium ion and the chloride ion are very close together. We have plotted the γ_{\pm} of potassium chloride as determined by Seatchard (13) at various ionic strengths. This curve is shown in Figure VI and indicated by the letter D. The γ_+ for the hydrogen ion was calculated at various

Figure VI



ionic strengths by squaring the γ_{\pm} of hydrochloric acid and dividing by the γ_{\pm} of potassium chloride at corresponding ionic strengths. The results of such a calculation are shown by the curve B in Figure VI. The calculated values of γ_{+} for the hydrogen ion are somewhat lower than those of Lewis and Randall (12). The values from which the four curves were plotted are given in Table VII.

Randall and Murakami (14) have determined the activity coefficient γ_{+} of the stannous ion in stannous chloride in the presence of hydrochloric acid. Using these activity coefficients in calculating E° we get a value that is fairly constant but which is only a few millivolts higher than E° for lead.

Since lead chloride and stannous chloride are both weak salts and both divalent metals their activity coefficients should be very nearly the same. Lewis and Randall (15) have calculated the activity coefficients of lead chloride from data obtained by Bronsted (16).

Table VII

Ionic strength	γ_{\pm} HCl	γ_{\pm} KCl	$\gamma_{H+calc.}$	γ_{H+} Lewis & Randall
.002	.9526	.9508	.9544	.97
.005	.9286	.9260	.9311	.95
.010	.9040	.8990	.9090	.92
.020	.8740	.8674	.8806	.90
.035	.8477	.8372	.8585	-
.050	.8293	.8150	.8441	.88
.075	.8096	.7875	.8320	-
.100	.7955	.7640	.8285	.84

These values at various ionic strengths are as follows:

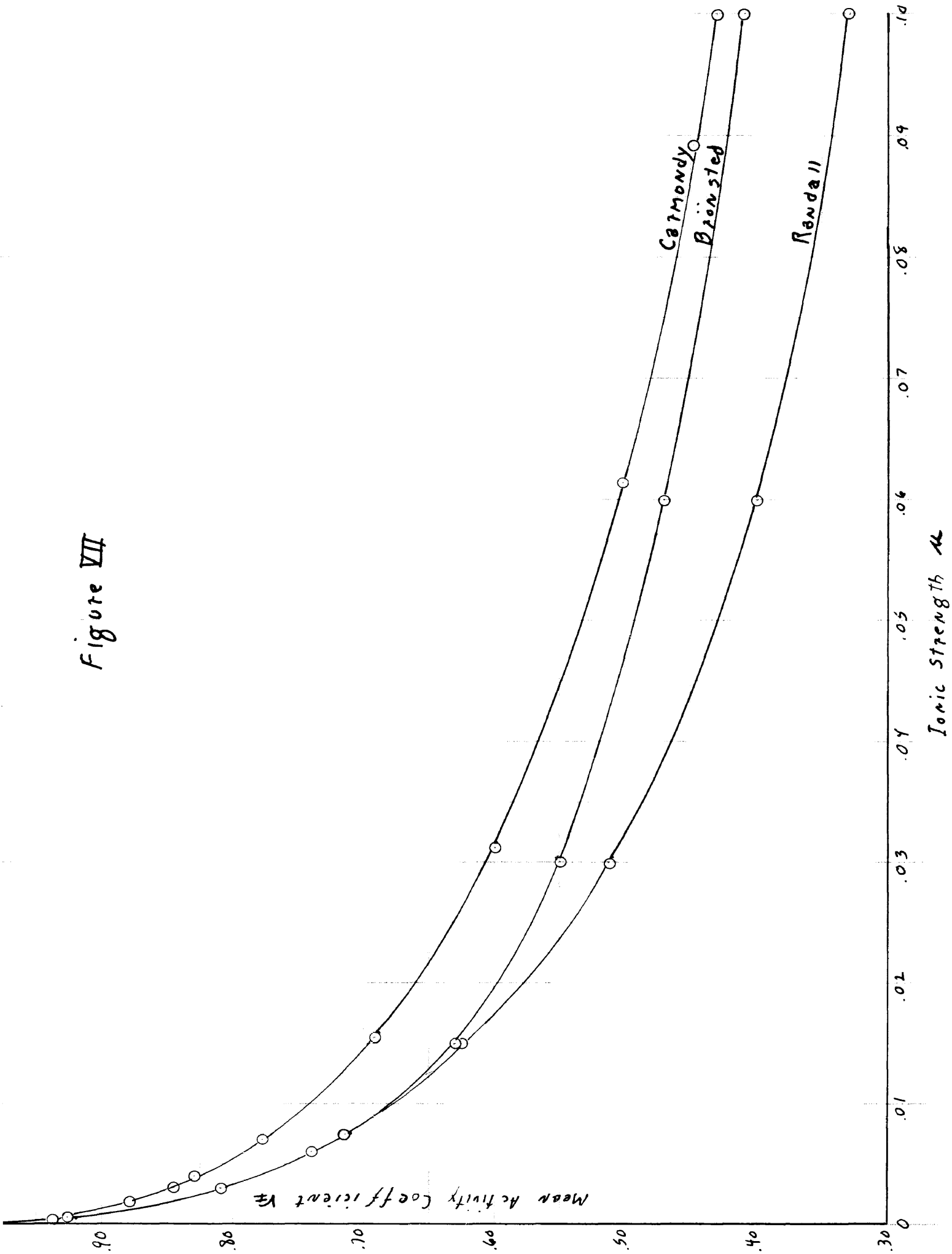
μ	0.003	0.006	0.005	0.03	0.06	0.117
γ_{\pm}	0.81	0.74	0.63	0.55	0.47	0.39

The γ_{\pm} values were plotted against the ionic strength as shown by the curve in Figure VII.

We have calculated the E^0 values of the cells by using activity coefficients γ_{+} of lead ions which were obtained by cubing the γ_{\pm} of $PbCl_2$ and dividing by the square of the γ_{-} of the chloride ion taken from the curves at the ionic strength of the solution used in each cell.

By the same method as above we have calculated E^0 values for each of the cells by employing the activity coefficients of $PbCl_2$ obtained by Carmondy (7). The results of his values were also plotted against the ionic strength in Figure VII. As a means of comparison the γ_{\pm} values of $SnCl_2$ obtained by Randall and Murakami (14) are also plotted

Figure VII



against the ionic strength.

The E° values obtained by these three series of calculations are given in the last three columns of Table VIII. The first column gives the number of the cell and amalgam. Column two is the measured potential corrected for pressure.

Any value that differs from the average value by more than four times the average deviation is not included in the final average. To the average value in each case must be added the potential between the saturated amalgam and pure tin, thus increasing the potential of all three by one millivolt.

The E° value obtained by use of Randall and Murakami's (14) values for the activity coefficient of stannous ions seems unreasonable in view of the value which Noyes and Toabe (5) have obtained for the equilibrium between lead and tin, which indicates that the standard electrode potential of tin should be .0140 volts higher than the standard electrode potential of lead.

The present accepted value for lead calculated by Lewis and Randall (6) from several sources is 0.122, which would make the value for tin 0.136. Hatfield (8) in this laboratory has just completed a determination of the electrode potential of lead by the same method which we have used for tin, using the following cell:



Table VIII

Cell No	Amalgam	E Measured	Randall	E ^o Bronsted	Carmondy
E	A	.18019	.1291	.1375	.1395
	B	.18030	.1292	.1376	.1396
F	A	.18034	.1294	.1379	.1398
	B	.18037	.1295	.1379	.1399
G	A	.18946	.1294	.1377	.1397
	B	.18964	.1296	.1379	.1399
H	A	.19669	.1361	.1443	.1463
	B	.19725	.1366	.1449	.1469
I	A	.18147	.1290	.1371	.1392
	B	.18147	.1290	.1371	.1392
1	A	.18477	.1309	.1378	.1396
	B	.18487	.1310	.1379	.1397
2	A	.17006	.1306	.1366	.1394
	B	.17006	.1306	.1366	.1394
3	A	.16977	.1307	.1368	.1396
	B	.17024	.1312	.1372	.1400
4	A	.17044	.1303	.1373	.1401
	B	.17054	.1304	.1374	.1402
5	A	.18378	.1295	.1374	.1396
	B	.18378	.1295	.1374	.1396
6	A	.17897	.1295	.1375	.1397
	B	.17897	.1295	.1375	.1397
7	A	.18044	.1293	.1373	.1395
	B	.18044	.1293	.1373	.1395
8	A	.18898	.1294	.1376	.1396
	B	.18898	.1294	.1376	.1396
9	A	.18736	.1289	.1372	.1392
	B	.18732	.1289	.1371	.1397
10	A	.18379	.1294	.1376	.1397
	B	.18384	.1294	.1377	.1397
11	A	.18177	.1292	.1375	.1395
	B	.18185	.1293	.1375	.1395
12	A	.18003	.1291	.1374	.1394
	B	.18003	.1291	.1374	.1394
Average			.1293	.1375	.1396
			<u>.0010</u>	<u>.0010</u>	<u>.0010</u>
		E ^o	.1303	.1385	.1406

He obtains .1249 volts for E^0 for lead. If .0140 volts is added to this we get .1389 which is in good agreement with the value that we get using Bronsted's activity coefficients.

Carmondy (7) has determined the electrode potential of lead to be .1264 if to this is added the value of Noyes and Toabe (6) we get .1404 for tin which compares very closely to the value that we get when we use his activity coefficients for lead ion instead of Bronsted's (16).

These results indicate that while the measured potentials are satisfactory the calculation of an exact E^0 value must await the determination of more accurate activity coefficients. They further indicate that the activity coefficients of tin must not be far removed from those of lead and that those found for stannous ion must be in error in some way since they are approximately only half those which have been obtained for lead.

In view of the value of 0.1249 volts that Hatfield (8) has found for the electrode potential of lead, which on adding the equilibrium value of Noyes and Toabe, gives 0.1389 volts for the electrode potential of tin, we shall consider the E^0 value that has been calculated from Bronsted's (16) activity coefficients to be more nearly the true value. The average deviation of his value is $\pm .0004$ volts, thus our value of 0.1385 is within this deviation of the value calculated from his value for lead.

DISCUSSION OF ERRORS

A. The Activity of Tin

The mol fractions of tin in the tin amalgams have a precision of 0.2 of one percent as determined by analyses. Such an error would cause a difference of 0.03 millivolts in the potential of any amalgam. The potentials as determined for nearly all of the amalgams were constant within this value.

The potentials of the amalgams could be measured to ± 0.01 of a millivolt by means of the type K Potentiometer. A change in temperature of a tenth of a degree produces only a change of 0.01 of a millivolt in the potential of the amalgams. Since the temperature of the thermostat was constant to within $\pm .02^{\circ}$, no error would result from this source.

Any error caused by oxidation should be very small since the potentials remained constant for a long period of time.

The error in the activities of tin should therefore be in the same order of magnitude as that in the mol fractions, namely .2 of one percent.

B. The Potential Between Pure Tin and its Saturated Amalgam

The only source of error in the determination of the potential between the saturated amalgam and pure tin that needs to be considered is that due to the difficulty in attaining an equilibrium value. The error from this source far overshadows any other error that might be present.

Since the tin in each electrode is of the same purity the difficulty in obtaining an equilibrium value must be ascribed to a difference in physical states of the metal. In other words the metal must be under different degrees of strain.

That this is true is readily seen from the fact that out of a total of thirty electrodes prepared and measured only eleven gave anything like an equilibrium value. Their potentials varied over a wide range and did not reach an equilibrium value.

The constant values of each of the eleven electrodes were averaged and the average deviation from the mean was about a tenth of a millivolt. Thus the potential between the saturated tin amalgam and pure tin has been determined to ± 0.1 of a millivolt.

C. The Standard Electrode Potential of Tin.

The average deviation from the mean of the calculated values for E° is ± 0.2 of a millivolt. This error is slightly more than can be accounted for considering the various factors which influence the calculation.

The measured potentials themselves can be determined to within ± 0.01 of a millivolt by means of the potentiometer, and need not be considered, as it would have no effect on the final result.

The potentials of the saturated amalgams themselves do not vary more than a 0.1 of a millivolt, as shown by the two amalgams in any one cell.

The molalities of the hydrogen ion are in error by no more than 0.2 of one percent. The same is true for the activity coefficients for the hydrogen ions. Such an error in either case would make a difference of less than 0.1 of a millivolt in the calculated E° value.

The molalities of the stannous ion are precise only to about 0.5 of one percent as are the activity coefficients of the stannous ion, but since neither of these values are squared in the equation for calculating E° such an error in either would cause a difference of less than 0.1 of a millivolt in the E° value.

We can, therefore, readily see that without considering any error due to oxygen being present that the average deviation of the means of 0.2 of a millivolt is as well as could be expected. The values that deviate more than this average can readily be explained by the presence of oxygen.

CONCLUSION

1. The activities of tin in tin amalgams at 25°C. have been calculated from the electromotive force of the amalgams. These values are for the entire range from $N_2 = 0$ to $N_2 = .01263$, the saturated amalgam.
2. The concentration of tin in the liquid phase of the saturated amalgam at 25°C has been found to be 1.263 mol percent instead of 1.21 mol percent as found by VanHeteren.
3. The potential between pure tin and its saturated amalgam at 25°C. has been determined as .0010 volts \pm .0001 volts.
4. The standard electrode potential of tin has been found to be 0.1385 volts \pm .0002 volts.

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