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I hereby recommend that the thesis prepared under my supervision by George Frederick Nordblom entitled Surface Tension and Electromotive Force.

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

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SURFACE TENSION AND ELECTROMOTIVE FORCE

A dissertation submitted to the

Graduate School  
of the University of Cincinnati

in partial fulfillment of the  
requirements for the degree of

DOCTOR OF PHILOSOPHY

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## Introduction

Amalgam concentration cells have intrigued investigators for some time mainly because they are among the few best examples of reversible processes known in nature and as such should admit of exact thermodynamic treatment. This reason, of course, did not motivate the early workers who first observed nearly a century ago that amalgamated metals could be used as an electrode\*.

It was Gauguain (3), a French physicist, who investigated the current-producing effects of a voltaic pile whose negative electrode consisted of a dilute amalgam of zinc or cadmium. He noticed that the voltage of this pile increased with the percentage of "oxidizable metal" added; also that further addition of zinc beyond a certain point had no effect upon the electromotive force. From this he concluded that the affinity of the mercury for the amalgamated metal occasioned the voltage variations and that the affinity varied with the concentration.

Several similar papers (4, 5, 6) appeared from time to time until 1877 when the first real progress was made.

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\* A most excellent chronological account of the history of such cells is given by T. W. Richards and G. S. Forbes (1) in the introduction to their historic paper dealing with precision measurements of various amalgam concentration cells. A few minor corrections appear in a second article from the same laboratory (2). The following brief background dealing with the highlights of the early history of this subject is abstracted from their monumental work.

Helmholtz (7) then published a paper on "Galvanic Current Caused by Differences in Concentration". His paper, however, dealt with aqueous cells. He pointed out that the electromotive force obtained varied with the absolute temperature and also presented some experimental work to verify his conclusions.

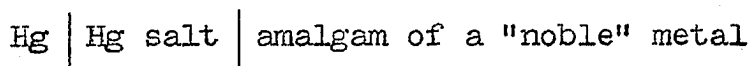
So far amalgam cells had not been regarded in the light of concentration cells. Former investigators considered only amalgamated electrodes and thought of them as being similar to the pure metals. Thus it was that they did not give full weight to the relationship of these electrodes with each other.

Lindeck (8) in 1888 by reason of the scope of his work presented the first data from which the voltages of various zinc amalgam cells, as we know them, could be found. He investigated the electromotive force produced by various concentrations of amalgams of Zn, Cd, Pb, Sn, and Ag against amalgamated zinc in a zinc sulfate solution. In spite of this no advance in theory resulted from this work.

In the following year, Nernst published his fundamental paper (9) "Die Electromotorische Wirksamkeit der Ionen". His paper did not discuss amalgam cells in particular, but its application thereto is manifest.

The first real theoretical treatment of amalgam concentration cells as such came in 1890 when Von Türlin (10) considered them as a possible means of determining the molecular

weights of metals in solution with mercury. For this purpose he divided the amalgam cells into two types. First he considered a cell of the type

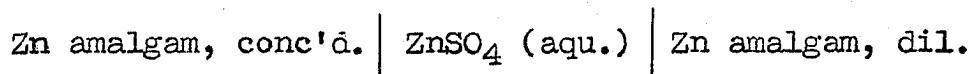


and, applying the osmotic theory developed three years earlier by van't Hoff (11), he concluded that the electromotive force was given by

$$E = 1.728 \times 10^{-4} \frac{n}{v} \frac{T}{273}$$

where T is the absolute temperature and  $\frac{n}{v}$  is the number of kilogram molecules of the metal in a cubic meter of mercury.

The second type



required different mathematical treatment. There existed an analogy between this cell and those aqueous cells investigated by Helmholtz, so he decided that

$$E = 9.5636 \times 10^5 T q K \log \frac{c_2}{c_1}$$

where q is the electrochemical equivalent for the zinc, K the ratio between the molecular weights of mercury and zinc, and  $\frac{c_2}{c_1}$  the concentration ratio of the amalgams. No experimental data were given in support of the formula, but it does establish the priority of Von Túrin in announcing a consistent theory for amalgam cells. However, it is probable that G. Meyer (12) had worked out much of it independently, since one month later, as a postscript to one of his articles, he mentioned the article of Von Túrin and said that for the past two months he had been occupied in determining molecular

weights of zinc and cadmium by a very similar method, and that he would publish the results of this investigation in the near future.

In the meantime, Von Türlin published several articles (13, 14) correcting his earlier work and checking his equation by means of Lindeck's data. However, the credit of checking the theoretical formula goes to G. Meyer (15) who not only developed the equations for zinc amalgam type cells from a consideration of the osmotic work involved in a reversible cycle (a more direct treatment than Von Türlin's), but also presented a host of experimental data on cells of various concentrations of amalgams including those of Zn, Cd, Pb, Sn, Cu, and Na.

Thus it was that the amalgam concentration cell theory, in a form much like we know it today, was developed and checked experimentally. In order that further progress could be made, T. W. Richards and G. S. Forbes (1) and later T. W. Richards with J. H. Wilson and R. N. Garrod-Thomas (2) undertook investigating potentials arising from various amalgam cells with extreme precision. Any deviation occurring between observed results and those calculated from the simple concentration formula\* would then need to be explained and,

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\* The term "concentration formula" will be used in keeping with the work of Richards and Wilson (2) to signify

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2} .$$

They have aptly pointed out that in this form it is not the work of any one man; hence, it would be a gross injustice to attribute to it the name of any previous investigator.

if possible, calculated in advance of experiment. This leads to the subject of the present investigation.

### Purpose

Since the electromotive forces arising from many amalgam cells are known with great accuracy and since no proposed method of calculation will satisfactorily cover all cases within the limit of experimental error, it would seem that some factor not yet considered by other investigators enters into the problem. Such a factor is surface tension and its accompanying surface energy. It is the intent of this thesis to develop thermodynamically an expression relating the differences in level of surface energy of the two electrodes making up the amalgam cell and the electromotive force effected. It is hoped that either this by itself, or in conjunction with some existing "corrective factor", will advance the theory to a plane in keeping with the experimental technique.

### Survey of the Literature

A review of the literature since the time of Von Türin and G. Meyer has yielded many diversified explanations and equations correlating to various degrees the measured voltages of amalgam cells with the calculated voltages de-

manded by the concentration formula. An explication of these possibilities as probable supplementary causes of the electromotive force will now be presented.

### The Cady Equation

In 1898, several years after G. Meyer had published his paper on amalgam cells, J. P. Cady (16) presented his extension of the work. For the most part he checked the molecular weights of the amalgamated metals investigated by Meyer. Sodium, nevertheless, was an exception. Using a more concentrated amalgam, he obtained a value of about one half the accepted atomic weight. This agreed very well with a previous determination on sodium amalgam conducted by Ramsey (17), using the vapor pressure method. Thus Cady was led to seek an explanation to the phenomenon. This he found in the heat of dilution of the amalgam involved.

The formula came about in this way. Differentiate the concentration formula,

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2} ,$$

with respect to T, and multiply through by T. Thus

$$T \frac{dE}{dT} = \frac{RT}{nF} \ln \frac{c_1}{c_2} = E_{\text{calc.}}$$

However, the Helmholtz equation, which applies to any voltaic system whatever, states that

$$E = \frac{Q}{nF} + T \frac{dE}{dT}$$

where  $Q$  is the change of total energy involved in the dilution of the amalgam. Substituting  $E_{\text{calc.}}$  for  $T \frac{dE}{dT}$  in this equation gives

$$E = \frac{Q}{nF} + E_{\text{calc.}}$$

and shows that the concentration formula could be true only in case the term  $\frac{Q}{nF}$ , the heat of transfer, were zero. In case it were not zero, then the following obtains:

$$E = \frac{Q}{nF} + \frac{RT}{nF} \ln \frac{c_1}{c_2} .$$

Calculations applied to sodium amalgam using the Cady formula check only fairly well due to the difficulty in obtaining accurate data on the heat of dilution of amalgams. That is to say, all errors are lumped on the smallest term,  $\frac{Q}{nF}$ , causing errors of about the same magnitude as the corrective term.

Richards and Garrod-Thomas (2) examined the Cady equation very carefully and found that it gave results which checked observed temperature coefficients within 5 per cent in all cases and usually within 2 per cent. The discrepancy approached zero as the dilution of the amalgams increased. In no case was this discrepancy greater than the experimental error involved. However, in checking this equation, actual heats of dilution were not used. Rather, it was recognized that the temperature coefficient of the cell,  $\frac{dE}{dT}$ , should be equal to the calculated quantity,  $\frac{R}{nF} \ln \frac{c_1}{c_2}$ , if the equation

was to hold. It was by this means that the equation was checked.

Richards and Forbes

In obtaining extremely accurate values for the voltage of zinc and cadmium amalgam cells, it was observed that these fell naturally into two separate types. Zinc was of the type which gave observed voltages less than those called for by the concentration formula, whereas cadmium gave voltages greater than the calculated values. In explaining the case of zinc, since the voltage was less than expected, polymerization was postulated. For cadmium, two possibilities were presented. First, similar to the case of sodium amalgams elucidated by Haber (18), hydrargyrites could be formed, thereby giving a voltage higher than that calculated. A more probable explanation was found in an abnormal osmotic pressure,  $P$ .

By applying the gas law to Nernst's equation,  $E = \frac{RT}{nF} \ln \frac{P_1}{P_2}$ , it will be noticed that a ratio of volumes may be substituted for the ratio of pressures. Since the resulting equation is considered exact in as far as the gas law holds, this would mean that a portion of the total volume of amalgam containing a mol of cadmium is not effective as a receptacle for the dissolved cadmium.

This volume may be calculated by assuming that the useless space does not vary with the volume and that polymeri-

zation is completely absent.

The ratio of values for useful space in two amalgams may be derived from

$$\ln \frac{V_4}{V_3} = \frac{nEF}{RT} = W \quad (1)$$

where  $V_4$  and  $V_3$  are the ideal or hypothetical values of the useful space.

The actual ratio of the volume is

$$\frac{V_2}{V_1} = \frac{W_2 D_1}{W_1 D_2} \quad (2)$$

found from the weights and densities of the two masses containing the same weight of cadmium. Now, calling the useless space  $b$ , and assuming it to possess a constant value (i.e.,  $V_2 = V_4 + b$  and  $V_1 = V_3 + b$ ), from (1) is obtained

$$\ln \frac{V_2 - b}{V_1 - b} = \frac{nEF}{RT} \quad (3)$$

whence, from (2) and (3),

$$b = \frac{V_1 \left( \frac{W_2 D_1}{W_1 D_2} - \text{anti ln } \frac{nEF}{RT} \right)}{\left( 1 - \text{anti ln } \frac{nEF}{RT} \right)}$$

From an average value of all the cells tested,  $b$  is found to be 14.3 milliliters for cadmium. Richards and Forbes point out that this value is a quantity very near the gram atomic volume of cadmium, 13.0. It may or may not be a mere coincidence. Some of the cells were recalculated on this basis and much better agreement found. Nevertheless, it must be observed that with the cadmium cell there is a constant differ-

ence between calculated potentials by means of the concentration formula and observed potentials for equal increments of concentration.

Richards, Wilson, and Garrod-Thomas

This later work (2) still adhered to the previous hypothesis. Moreover, the work of G. N. Lewis (19, 20, 21), showing that a more accurate method for expressing osmotic effects is found in the generalization that the activity of a substance is proportional to its mol-fraction, was applied to the concentration formula. The formula then becomes

$$E = \frac{RT}{nF} \ln \frac{\frac{n}{n + N_1}}{\frac{n}{n + N_2}}$$

where  $n$  signifies the number of gram molecules of solute, while  $N_1$  and  $N_2$ , those of the mercury in the two amalgams, respectively. Extending this form to the Cady equation, it becomes

$$E = \frac{Q}{nF} + \frac{RT}{nF} \ln \frac{n + N_2}{n + N_1} .$$

It was pointed out, however, that this refinement changes the calculated potentials but slightly. Also the additional accuracy becomes less and less as dilution proceeds.

Hulett, Delury, Crenshaw

While working with the standard cell, its behavior seemed to indicate that mercury reduced the cadmium sulfate

solution, forming a very dilute amalgam with an equivalent amount of mercury passing into solution. Hulett and Delury (22) then conducted a series of precise determinations on cadmium amalgams, extending the research to extreme dilutions in the hope of throwing some light on the value of the equilibrium. That such an equilibrium should exist was shown by Ogg (23) who worked with the system mercury and aqueous silver nitrate solution. Here, the equilibrium concentrations are of sufficient magnitude to be determined analytically.

Using every precaution to exclude oxygen from their apparatus, Hulett and Delury found unmistakable evidence that dilutions greater than one gram of cadmium in  $10^7$  grams of mercury gave erratic potentials which could be accounted for by the assumption of the equilibrium,  $\text{Hg} + \text{CdSO}_4 \rightleftharpoons \text{Cd} + \text{Hg}_2\text{SO}_4$ . To cover this case, a relationship

$$\sqrt{\frac{n_1 P_1}{p_1}} = \sqrt{\frac{n_2 P_2}{p_2}}$$

derived by Nernst (24) was proposed. Here,  $P_1$  and  $P_2$  are the concentrations of cadmium and mercury in the amalgam, while  $p_1$  and  $p_2$  are their respective concentrations in the solution.  $n_1$ , the valence change of cadmium is 2, and  $n_2$ , the valence change of mercury to mercurous ion is 2 because the ion consists of two atoms each.

Since zinc is more strongly electropositive than cadmium, amalgams of greater dilution should be possible before the potential becomes erratic. Crenshaw (25), at the

suggestion of Hulett, undertook this work. As it was expected, concentrations slightly smaller than in the case of the cadmium cells were possible before they became erratic. Concentrations of  $1/10^8$  and  $1/10^9$  seemed to be the order of magnitude of the concentration of mercury ions in solution.

If the proposed reaction,  $Zn + Hg_2^{++} \rightleftharpoons Zn^{++} + 2Hg$  is reversible, it should be possible to start with pure mercury and a two-phase amalgam electrode in a zinc sulfate solution and find evidence of a dilute amalgam forming. Such was the case. The initial high value of 1.09 volts always settled down to about 0.7 volts, indicating a deposition of zinc in the mercury. Thus it is seen, considering the equilibrium relationship, that the actual concentration of zinc in the mercury is dependent on the relative volumes of mercury and solution; at the same time, the reaction must proceed until  $P_1 \times p_2 = K$ .

#### Hildebrand's Equation

Following the suggestion of Richards and his co-workers that the discrepancies which exist between the observed values of potential and the theoretical values may be due either to the formation of hydrargyrites or to polymerization, Hildebrand (26, 27) derived formulae which enabled him to show the effects of each. Assuming the case where hydrargyrites of the general formula  $M Hg_m$  are formed, he deduced the following equation on the basis of the work involved

in isothermal distillation.

$$E = \frac{2.3026 RT}{nF} \left[ m \log \frac{N_2 - m}{N_1 - m} - (m - 1) \log \frac{N_2 - m + 1}{N_1 - m + 1} \right]$$

where  $N$  is the total mols of mercury associated with one mol of solute, and  $m$  refers to the subscript in the general formula,  $M Hg_m$ . Applying this formula to thallium, he found that he had to assume  $m=6$  (i.e.,  $Tl Hg_6$ ) in order for the calculated value to most nearly equal the observed value.

Where the electromotive force is less than that obtained from the concentration formula, polymerization is assumed. This he confirmed (28) for zinc. Using the vapor pressure technique, he found the equilibrium  $2Zn \rightleftharpoons Zn_2$  to exist at 325 C., the temperature of the experiment. Then, setting up an equilibrium equation, assuming the Raoult vapor pressure law to hold and taking an equation for osmotic work, he was able to derive the equation

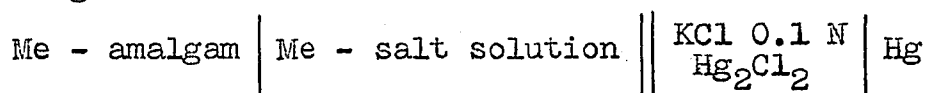
$$E = \frac{RT}{nF} \ln \frac{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}}$$

where  $N$  is the mols of mercury per mol of solute metal, and  $A$  is a constant involving the equilibrium constant. In this instance, the value 11.6 for  $A$  seemed to give the best results. It should be noted that this equation as given is not quite general but applies only to the case of an equilibrium between biatomic and monatomic molecules. Thus, while its use is limited, it may be applied to some other amalgams, such as lead and tin, by merely changing the value of  $A$ .

J. L. Crenshaw (29) has calculated voltages using Hildebrand's equation for zinc amalgam cells covering a wide range of concentrations. He found that the equation could be made to agree with any narrow range of experimental values by choosing the proper number for A. However, having chosen this number for the dilute range, the concentrated range suffers. It may be that an equation allowing for the presence of Zn, Zn<sub>2</sub>, and Zn<sub>4</sub> would fit the observed values perfectly, but without independent evidence of the higher polymers, a more complicated equation would take on the flavor of rank empiricism.

#### Other Work

While not dealing directly with amalgam concentration cells, it is pertinent to note the work of T. Erdey-Grúz and A. Vazsonyi-Zilahy (30) who have investigated electrode potentials of dilute amalgams. Their cell was set up in the following manner:



Investigating amalgams whose metal content varied from 0 to 0.1 gram atoms per liter, they found three distinct regions of concentration where the electromotive force produced might have been caused by different phenomena.

With their more concentrated amalgams, the formula of Nernst seemed to have been obeyed to a greater or less degree. However, as the concentration decreased, there was a

narrow region where the potential fell off very greatly. The concentration where this break occurred varied with the amalgamated metal employed as well as with the solvent used for the metal salt solution. In the case of aqueous salt solutions and amalgams of zinc or cadmium, this point occurs at a concentration of about  $10^{-5}$  gram atoms per liter. This, it will be noted, was about the same concentration at which Hulett and his co-workers found an instability in the potential of their zinc and cadmium amalgams. Furthermore, with less electropositive metals like tin, the break occurs at a slightly greater concentration as would follow from Hulett's reasoning. But, on the other hand, with more strongly electropositive metals as those of the alkali or alkaline earth groups, the break occurs at concentrations as high as  $10^{-3}$  or  $10^{-2}$  gram atoms per liter, which seems contrary to reason. It may be due to a reaction with the solvent because as non-aqueous solutions are employed results are more normal. This band, where potentials drop off greatly with dilution, is rather narrow and varies in width from a ten to a hundredfold change in concentration. At the other end of this band, there is again an abrupt change. This leads to the third region\* which is marked by a rapid leveling off of the potential wherein the electromotive force does not seem to change at all with

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\* Erdey-Grúz and Vazsonyi-Zilahy chose to discuss the phenomenon from the dilute side so that this corresponds to their first region.

increased dilution.

Erdey-Grúz and Vazsonyi-Zilahy do not attempt to derive equations expressing mathematically the behavior of their amalgams in any region. They do, nevertheless, offer an explanation for the third region. It was noticed there that the potentials of the most dilute amalgams do not differ perceptibly from the potential of pure mercury in the same solution. Consequently, the current-producing process must be the same as a mercury electrode in a foreign ion solution. Now Erdey-Grúz and Szarvas (31) previously showed that, under these conditions, the adsorption of ions - chiefly the anion - determines the potential. This then produces a nearly constant electromotive force until the concentration of the metal becomes sufficient to establish control.

A. Frumkin (32) has also found that surface active anions influence electrocapillarity of mercury and the amalgams. He also presents some interesting theory and equations which may be of use in extending this work.

The work of J. E. Trevor (33) should also be mentioned. He has elucidated the Cady equation. It will be remembered that Cady called attention to the fact that his equation held only in the event that the heat of dilution of the amalgam from the one concentration to the other was not a function of the temperature or was negligibly small. Trevor has pointed out that, in general, the heat of dilution is not negligible and shows thermodynamically that "the departure

from proportionality between the electromotive force and temperature is determined wholly by the form of the heat of dilution regarded as a function of the temperature and concentrations of the two solutions of the cell". He finds, in general,

$$E = \Theta \cdot k(h) + \Theta \cdot \phi(\Theta, h)$$

where  $E$  is the electromotive force,  $\Theta$  the thermodynamic temperature, and  $h$  the relative masses of solvent to solute. He goes on to show the form taken by this equation if the heat of dilution is assumed (1) zero, (2) not to vary with the temperature, (3) varies directly with the temperature, or (4) varies inversely with the temperature. The results, like the fruit of most thermodynamic reasoning, are not in a form readily applicable to practical problems. The paper, nevertheless, is a highly interesting theoretical discussion of this heretofore hazy point.

G. N. Lewis and M. Randall (34) have applied the concept of activities to amalgam cells. To do this, activities,  $a_2$  and  $a'_2$ , are used in place of concentrations in the usual concentration formula. After rearranging this to

$$\log a_2 = - \frac{EnF}{RT} + \log a'_2$$

and subtracting  $\log N_2$ , the logarithm of the mol fraction of metal in the dilute amalgam, from both sides, they get

$$\log \frac{a_2}{N_2} = \left( - \frac{EnF}{RT} - \log N_2 \right) + \log a'_2.$$

Now, if the quantity in parenthesis be plotted against  $N_2$ ,

and the curve extrapolated to zero concentration where  $a_2 = N_2$  by definition, then  $\log \frac{a_2}{N_2}$  becomes zero so that  $\log a'_2$ , the logarithm of the activity of the metal in the reference electrode, must be equal to the quantity in parenthesis, the intercept of the curve on the y-axis. From this,  $a'_2$  may easily be found and from the value of E between this electrode and one of any other concentration, the activity of the new concentration may be calculated.

However, as may be readily seen, this method of employing activities is an artificial means of forcing exact results. It tends to hide rather than to elucidate any reason for the deviation between known theory and practice and, therefore, finds a place here only for the sake of completeness.

#### Development of the Equation

In the preceding section many diversified ideas have been promulgated to account for the deviation between the observed value of the electromotive force of an amalgam concentration cell and the value predicted by theory. In none of these theories has the effect of the surface of the electrode been even vaguely alluded to with the possible exception of the work of T. Erdey-Grúz and A. Vazsonyi-Zilahy who mention "capillary active" anions and speak of adsorption of ions on the surface of their most dilute amalgams. Yet,

it is the surface of any electrode which reacts and gives rise to the electromotive force. The nature of these surfaces should therefore be investigated, and the role that they play in the current-producing process ascertained.

### The Surface Phase

Just what is meant by the "surface" of an electrode that it should merit special consideration? Rideal<sup>(35)</sup> has this to say, "It has been found that where one distinct phase adjoins another there exist conditions which distinguish the behavior of a thin layer of matter from that of the general mass in either of the homogeneous phases which bound it". From this it may be seen that the surface, especially in this case of a liquid amalgam and its surrounding electrolyte, is not a mere imagined boundary on one side of which is one phase of uniform properties and on the other side a second phase which is everywhere distinct and homogeneous in itself. Nor is it to be thought that the two separate phases blend rapidly but continuously into one another, so that the boundary is for mathematical convenience rather than of physical significance. Rather, it is a separate and distinct third phase possessing entirely new but measurable properties lying as a lamina between the other two. Like either bulk phase, two of its dimensions may be varied at will, but its third, at right angles to the plane of the lamina, may not. This dimension, it is believed, extends to a depth of only one or two molecules and

resists any attempt at alteration by forming a new superficial phase. It is this surface phase which must give rise to the electromotive force.

### Surface Tension

Surface tension is a measure of the free energy per unit area of the surface phase. But before considering energy relationships, it is well to look at the surface phase from the standpoint of the molecules which it must contain and which must surround it. By doing this, the idea of a "surface film", such as the term "surface tension" might suggest, is easily avoided.

Molecules in the liquid state are unique in that their vibratory freedom is midway between that of molecules in the solid and gaseous states. That is, they may move relative to one another but are still restrained sufficiently to prevent more than a small proportion of them from escaping into the vapor phase. Now, if a molecule be considered which lies in the bulk of the liquid, it will be found to be attracted uniformly in all directions. In contrast to this, consider a molecule on the surface. It is strongly attracted inwards by the great bulk of molecules in the center and attracted to a lesser extent to the side by its neighboring molecules, but there is no outward attraction to balance the inward pull because of a lower density of similar molecules outside. Hence, there is a great inward attraction perpen-

dicular to the surface for every surface molecule.

This is the attraction which causes surface molecules to move continuously into the body of the liquid faster than those from the body move out to the surface. As a result, the surface contains as few molecules as possible and thus presents a minimum area. In this light, the old idea of a special "contractile skin" or physical tension parallel to the surface of the liquid is without meaning.

Now, bearing this picture in mind, consider surface free energy and so-called surface tension. The spontaneous contraction of a liquid surface demonstrates that there is free energy associated with it. Work must always be done in extending a surface. In the molecular scheme, molecules must be brought from the bulk of the liquid against an inward attractive force and transferred to the surface whenever it is extended. This constitutes work and is of prime importance in any problem dealing with the surface phase.

N. K. Adam <sup>(36)</sup> intimates that the magnitude of this force is fundamental, and that most problems dealing with surface equilibrium may be solved without knowing much else. For this purpose, a mathematical device is used. It consists of substituting for the surface free energy, "a hypothetical tension acting in all directions, parallel to the surface, equal to the surface energy". This is his concept of surface tension. It must have the same dimensions as surface energy  $\left(\frac{\text{mass}}{\text{time}^2}\right)$ , and also must have the same numerical magnitude.

A tension pulling with a force of  $\sigma$  dynes per centimeter will, upon extending the surface one square centimeter, be equivalent to the work of  $\sigma$  ergs per square centimeter. From this, it can be seen that, while surface free energy is the fundamental property of surfaces, surface tension is its mathematical equivalent. It will be so used in this work.

### Properties of a Surface Phase

It is time to consider what properties a surface phase possesses that distinguishes it from the bulk phase which has heretofore been the only phase recognized in accounting for the current-producing process. Other pertinent surface relationships should also be presented here.

### Antonow's Rule

One of the most simple and useful expressions in this field is Antonow's rule. It deals with the relationship between interfacial tension of a usual two-phase (liquid-liquid) system and the individual surface tensions of the two-component phases. It states that the interfacial tension between two phases in equilibrium is equal to the difference of the surface tensions of each phase measured separately against its vapor phase. In symbols, it may be expressed by

$$\sigma_{12} = \sigma_{1'} - \sigma_{2'}$$

where  $\sigma_{12}$  is the interfacial tension between liquid 1 saturated with liquid 2 and liquid 2 saturated with liquid 1. The

primed subscripts refer to the pure liquids saturated with respect to each other. It is obvious that liquid 1 must possess the higher surface tension.

At first sight the usefulness of this equation might be underestimated since it would seem that surface tensions of liquids saturated with respect to one another at various temperatures would not be available. This is true; yet, many cases exist where one of the phases is practically insoluble in the other. Then it is that ordinary surface tension data may be employed with a fair degree of approximation.

The application of Antonow's rule, while rather general, is, nevertheless, fraught with some danger. Not only is its theoretical basis inadequate, but numerous cases have been reported where it does not hold good. The case of mercury and its amalgams are among the exceptions. It might be supposed that since mercury and its amalgams are so insoluble in electrolytes, and vice versa, that this would be an ideal case. This is not true. The deviation from the rule is probably due to electrocapillarity as referred to on page 16. The charges adsorbed on the surface of the mercury repel each other, adding their forces algebraically to the molecular forces already present in the surface. This causes a further lowering of the interfacial tension, giving a value different from that predicted by Antonow's rule.

However, in all known cases, the interfacial tension is always less than the surface tension of the liquid possess-

ing the higher tension. This causes the direction of any introduced error to be known and allowed for. Antonow's rule will be used with full regard as to its uncertainty and then, only for approximations in cases where necessary data is meager or non-existent.

### Influence of Temperature

With only two or three minor exceptions occurring within narrow temperature ranges, surface tension decreases with rising temperature. This is logical when one recalls that at the critical point surface tension becomes zero, and that natural processes usually vary uniformly and continuously. The same general rule and the same line of reasoning applies also to interfacial tensions between two liquid phases. Moreover, in this case, the decrease of interfacial tension may also be ascribed to the increase in mutual solubility of the two liquid phases with temperature.

Here, Eötvös' Law should be mentioned. It is analogous to the gas law,  $PV=RT$ , the product  $PV$  being the free molar volume energy of the gas. Corresponding to the case of the liquid-vapor surface, the molar free energy is proportional to the product of  $\sigma$  and the surface occupied by a gram molecule,  $\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}$ , where  $M$  is the molecular weight, and  $\rho$  the density. The complete law is

$$\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}=K(T_c - T - \epsilon) .$$

$T_c$  is the critical temperature,  $T$  the temperature at which the surface tension is found,  $K$  a universal constant of approximately 2.2, and 6 degrees a corrective factor to compensate for the non-linearity of the  $\sigma$ ,  $T$  curve near the critical point.

### The Gibbs' Equation

The composition of the surface phase of a pure liquid must naturally be the same as that of the bulk phase. However, this is not necessarily true for solutions. In general, the addition of a solute to a solvent will change the surface tension of the latter. Since the free energy of the system strives toward a minimum, the solute will tend to accumulate in the surface phase if the solute lowers the surface tension of the solvent. Should the solute raise the surface tension of the solvent, then the converse will be true. The solute will tend to accumulate in the bulk phase, thereby leaving the surface energy as small as possible. This process of enriching or of impoverishing the surface phase is limited by diffusional processes. It operates between the surface and bulk phases at a rate which is proportional to the difference in osmotic pressures of the solute in the two phases.

The mathematical expression of this fact was derived by Gibbs (37) in 1878. His formula is

$$\Gamma = - \frac{c}{RT} \left( \frac{d\sigma}{dc} \right)_a$$

where  $\Gamma$  is the adsorption excess in moles per unit surface,  $c$  the bulk concentration of the solute in the solvent,  $R$  the gas constant,  $T$  the absolute temperature, and  $\left(\frac{d\sigma}{dc}\right)_a$  the change of interfacial tension with respect to concentration, with the area of the interface remaining constant. The negative sign prevails because the value of  $\left(\frac{d\sigma}{dc}\right)_a$  must itself be negative in order for  $\Gamma$  to become a positive quantity.

According to Gibbs' theorem, then, the surface phase, the phase which must give rise to the electromotive force, would not generally have the same concentration as the body phase of an amalgam. In all previous equations relating electromotive force with concentration, it was this body concentration which was used. This does not mean that the concentration formula is incorrect but only that the definition of solute concentration was misconstrued. Since this quantity appears as a ratio, errors due to this source are minimized. Nevertheless, in view of the fact that surface tensions of most amalgams are non-linear functions of concentration in the dilute range under discussion, it is believed that this may account for some of the deviation between theory and practice. Such relationships will presently be derived.

### Equations

Reviewing all available data pertaining to the electromotive force of amalgam concentration cells as the amalgams become more and more dilute, at first sight, the data appear

normal. That is to say, the dilute solution laws seem to hold better and better as the amalgams become more and more dilute. However, as more data on the most dilute amalgams are reviewed, it is noticed that in the most dilute region where the concentration equation should hold best, the deviations from ideal potentials begin to increase. This is noticed in the data of Hulett and Delury (22), Crenshaw (25) and in the amalgam electrode potentials of Erdey-Grúz and Vazsónyi-Zilahy (30). Strangely enough, surface tension data\* as given by V.K. Semenchenko, B.P. Bering, N.L. Pokrovskii and E.E. Shvarva (38) for dilute amalgams change most rapidly in this region, From this background, the first attempt to derive a suitable equation was made.

#### Dilute Solution Consideration

It seemed logical, as the first point of attack, to attempt to correct the concentration term of

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2} \quad (1)$$

in order to conform with the actual surface concentrations as expressed by Gibbs' equation when the area of the amalgam electrode remains constant. Gibbs' equation is

$$\Gamma = - \frac{c}{RT} \left( \frac{d\sigma}{dc} \right) \quad (2)$$

Now, since  $\Gamma$  is the adsorption excess in the surface phase

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\* See Appendix.

over and above that appearing in the bulk phase, it should be added to the concentration term of equation (1) together with an appropriate constant\*, k, designed to make the units of  $\Gamma$ , gram atoms per square centimeter, conform with the units selected for c, gram atoms per liter. This gives

$$E = \frac{RT}{nF} \ln \left[ \frac{c_1 + k\Gamma_1}{c_2 + k\Gamma_2} \right] \quad (3)$$

Using the equivalent of  $\Gamma$  as given in equation (2),

$$E = \frac{RT}{nF} \ln \left[ \frac{c_1 - \frac{c_1 k}{RT} \left( \frac{d\sigma}{dc} \right)_1}{c_2 - \frac{c_2 k}{RT} \left( \frac{d\sigma}{dc} \right)_2} \right] \quad (4)$$

and, after factoring out a c from the bracketed expression,

$$E = \frac{RT}{nF} \ln \left\{ \frac{c_1 \left[ 1 - \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_1 \right]}{c_2 \left[ 1 - \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_2 \right]} \right\} \quad (5)$$

\* k is approximately equal to 6 and depends upon the ratio of the area of the electrode to its volume. It comes about in this way. Let c' be the correct concentration at the surface and c be the usual bulk concentration. Then

$$c' \neq c = \frac{N}{V}$$

where V is the volume containing N gram atoms of solute. Then, if  $\Gamma$ , the surface excess per square centimeter, and a, the area of the electrode, be multiplied, the excess of gram atoms in the surface will result. Thus,

$$c' = \frac{N + \Gamma a}{V} \quad \text{or} \quad c' = c + \Gamma \frac{a}{V}$$

Hence, to obtain the correct surface concentration,  $\Gamma$  must be multiplied by a/V or k, before it is added to the bulk concentration term of equation (1).

To evaluate k, it is observed that liquids are usually handled in parcels whose dimensions are approximately symmetrical. Thus, for either a cube or a sphere of equal linear dimensions, the ratio of a/V may be shown to be 6/d where d is either the length of a side or the diameter depending on the shape assumed. Here, d is taken as one centimeter since that quantity seems a logical amount of material to use.

the right member may be split up into two parts,

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2} + \frac{RT}{nF} \ln \left[ \frac{1 - \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_1}{1 - \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_2} \right] \quad (6)$$

Now, the first term of the right member is the concentration formula, and, therefore, the second term must be a corrective factor giving the change in potential of a cell resulting from an excess (positive or negative) of metal in the interface.

This shall be called  $\Delta E$ , hence,

$$\Delta E = \frac{RT}{nF} \ln \left[ \frac{1 - \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_1}{1 - \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_2} \right]. \quad (7)$$

Now, the quantity  $\frac{k}{RT}$  is so exceedingly small that any natural value  $\left( \frac{d\sigma}{dc} \right)$  might assume still leaves the term  $\frac{k}{RT} \left( \frac{d\sigma}{dc} \right)$  very small. It is a known fact that the natural logarithm of one plus a very small number is approximately equal to that number. Applying this simplifying procedure, equation (7) becomes

$$\Delta E = \frac{RT}{nF} \left[ \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_2 - \frac{k}{RT} \left( \frac{d\sigma}{dc} \right)_1 \right] \quad (8)$$

or

$$\Delta E = \frac{k}{nF} \left[ \left( \frac{d\sigma}{dc} \right)_2 - \left( \frac{d\sigma}{dc} \right)_1 \right] \quad (9)$$

which becomes the final equation. But, through a study of units, it is seen that the right-hand member must be divided by the factor  $10^7$  to change ergs to joules. The question of units for the various symbols will be considered later.

### Free Surface Energy Consideration

In order to check the above derivation and also possibly to obtain more complete information on the current-producing process, an attempt was made to evolve the relationship from thermodynamic reasoning. The following derivation is based upon a consideration of the decrease in free surface energy and the equivalent electrical free energy produced.

The symbols used are:

- $\Delta E$  = the potential due to surface effects
- $\sigma$  = interfacial tension
- $S$  = free surface energy
- $N$  = the number of gram atoms of metal transferred
- $c$  = the concentration of metal in the amalgam
- $\rho$  = the density of the metal used
- $\rho'$  = the density of the mercury
- $M$  = the atomic weight of the metal
- $M'$  = the atomic weight of the mercury
- $a$  = the area of the electrode
- $V$  = the volume of the electrode
- $p$  = the "shape factor"
- $n$  = the valence change of the solute metal
- $F$  = the faraday
- sub 1 = concentrated amalgam
- sub 2 = dilute amalgam

Then, at constant temperature and pressure,

$$\sigma = \sigma(c) , \quad (10)$$

and the surface free energy is given by

$$S = \sigma a . \quad (11)$$

Considering the electrodes to be of sufficient size so as not to affect the concentration of the solute metal, the decrease in free energy per  $dN$  gram atoms of solute metal electrolyzed from the concentrated to the dilute amalgam may be represented as  $dS_2 - dS_1$ . The equivalent electrical free energy is

$\Delta E_n F dN$ . Thus

$$dS_2 - dS_1 = \Delta E_n F dN . \quad (12)$$

Now through the differentiation of equation (11), it follows that

$$dS_2 - dS_1 = \sigma_2 da_2 - \sigma_1 da_1 + a_2 d\sigma_2 - a_1 d\sigma_1 . \quad (13)$$

Applying condition (10), then,

$$dS_2 - dS_1 = \sigma_2 da_2 - \sigma_1 da_1 + a_2 \left( \frac{d\sigma}{dc} dc \right)_2 - a_1 \left( \frac{d\sigma}{dc} dc \right)_1 \quad (14)$$

Now, the volume of the amalgam electrode is made up of  $N$  gram atoms of solute plus  $N'$  gram atoms of solvent of atomic weights  $M, M'$  and densities of  $\rho, \rho'$ , respectively. If volumes be assumed additive, and they may at extreme dilution, then

$$V = \frac{MN}{\rho} + \frac{M'N'}{\rho'} \quad (15)$$

whence

$$dV = \frac{M}{\rho} dN \quad (16)$$

But volume and area are interrelated by the following equation wherein  $p$  represents a constant, the "shape factor"

$$V = pa^{\frac{3}{2}} \quad (17)$$

whence

$$dV = \frac{3}{2} pa^{\frac{1}{2}} da \quad (18)$$

or, substituting equation (16) in (18) and rearranging, it is obvious that

$$da = \frac{2M}{3pa^{\frac{1}{2}}\rho} dN . \quad (19)$$

But, if the right-hand member be multiplied and divided by  $a$ ,

equation (17) may be applied to the denominator, reducing the expression to

$$da = \frac{2aM}{3V\rho} dN \quad (20)$$

Now taking the expression for concentration,

$$c = \frac{N}{V}, \quad (21)$$

differentiating with respect to N, and applying equation (16), it follows that

$$\frac{dc}{dN} = \frac{1}{V} - \frac{N}{V^2} \frac{M}{\rho} \quad (22)$$

These expressions are now in a form to be utilized. Referring back to equation (14), substitute equations (20) and (22). This gives

$$dS_2 - dS_1 = \left[ \sigma_2 \frac{2a_2M}{3V_2\rho} - \sigma_1 \frac{2a_2M}{3V_2\rho} \right] dN + \left[ a_2 \left( \frac{d\sigma}{dc} \right)_2 \left( \frac{1}{V_2} - \frac{NM}{V_2^2\rho} \right) - a_1 \left( \frac{d\sigma}{dc} \right)_1 \left( \frac{1}{V_1} - \frac{NM}{V_1^2\rho} \right) \right] dN \quad (23)$$

The above equation may be simplified if the second term of the right-hand member of equation (22) be considered negligible. This is permissible since for dilute solutions N will be very small and  $V^2$  very large. Furthermore, if the area and volumes of both electrodes be made equal and equation (12) applied, then

$$\frac{a}{V} \left\{ \left[ \frac{2M}{3\rho} (\sigma_2 - \sigma_1) \right] + \left[ \left( \frac{d\sigma}{dc} \right)_2 - \left( \frac{d\sigma}{dc} \right)_1 \right] \right\} = \Delta E_{nF} \quad (24)$$

In practice, the difference between the interfacial tensions of the two amalgam electrodes is generally much less

than 50 dynes per centimeter, excluding the alkali metals. This amount introduced into the first term of the quantity appearing in brackets is insignificant as compared to the value of the second term. Thus, the whole first term may, in most cases, be neglected without introducing an error of more than 0.5 per cent. Therefore, equation (24) may be reduced to

$$\Delta E = \frac{a}{VnF \times 10^7} \left[ \left( \frac{d\sigma}{dc} \right)_2 - \left( \frac{d\sigma}{dc} \right)_1 \right] \quad (25)$$

which is the same as equation (9) derived before. From a comparison of the two equations, it is apparent that  $k$  is equivalent to  $\frac{a}{V}$  for the two equations to be similar.

#### Predictions

After studying equation (25), several important conclusions may be drawn. First, it is noticed that  $\Delta E$  becomes zero when  $\left( \frac{d\sigma}{dc} \right)_2 = \left( \frac{d\sigma}{dc} \right)_1$ . For this to occur, the interfacial tension vs. concentration curve must be linear between the two concentrations of amalgam studied. This is actually the case at high concentrations of all amalgams for which there are data. This would mean that the surface concentration is proportional to the bulk concentration, and the concentration formula applies insofar as it holds.

In general, this condition is rare for the usual dilute amalgams studied. Rather,  $\left( \frac{d\sigma}{dc} \right)_2 > \left( \frac{d\sigma}{dc} \right)_1$  obtains. The actual sign of the slope then becomes important. For those metals which raise the surface tension of mercury, such

as zinc or cobalt, the slope is positive. This makes  $\Delta E$  positive and the observed voltage should be greater than that calculated without taking into account the free surface energy. On the other hand, those metals which lower the surface tension of mercury, such as the alkali metals, have negative slopes and, thus, make  $\Delta E$  negative. The observed electromotive force should then be less than that calculated while neglecting the free surface energy.

### Calculations

The units of the various quantities appearing in equation (25) are:

- $\Delta E$ , volts.
- $a/V$ , about six reciprocal centimeters.
- $\sigma$ , dynes per centimeter.
- $c$ , gram atoms per cubic centimeter.
- $n$ , a number representing the valence change.
- $F$ , the faraday, 96,500 coulombs.

Hence, for zinc, using the data taken from the Appendix for a dilute amalgam of a concentration of 0.01320 gram atoms per liter,  $\frac{\Delta\sigma}{\Delta c} = 152,000$  erg centimeters per gram atom. If the more concentrated amalgam be taken as 0.0433 gram atoms per liter, then  $\frac{\Delta\sigma}{\Delta c} = 56,000$  erg centimeters per gram atom.

$$E = \frac{6}{2 \times 96,500 \times 10^7} [152,000 - 56,000] = 3 \times 10^{-7} \text{ volts}$$

If the reference electrode be a two-phase electrode, then  $\left(\frac{\Delta\sigma}{\Delta c}\right)_1$  becomes zero, and  $\Delta E$  becomes  $4.7 \times 10^{-7}$  volts.

For a potassium amalgam between the concentrations of 0.00228 and 0.0089 gram atoms per liter,  $\Delta E$  becomes

$$\Delta E = \frac{6}{2 \times 96,500 \times 10^7} - [19.2 \times 10^6 + 4.4 \times 10^6] = - 4.6 \times 10^{-5} \text{ volts}$$

These values are necessarily mere approximations since actual interfacial tension data are not available. It has, therefore, been assumed that the slopes of curves for either interfacial or surface tension vs. concentration are identical. This would be true if Antonow's rule held exactly. The results, then, are reliable only to the extent of showing the magnitude of the correction factor,  $\Delta E$ .

### Conclusions

It will be remembered that the purpose of this thesis was to determine the effect of the surface condition of the amalgam electrode upon the electromotive force obtained from the cell. This has been done. It is regrettable that the magnitude of this potential due to surface energy turned out to be so small since it had been hoped that the difference of surface conditions between two electrodes would account almost entirely for the discrepancy between the observed and the calculated potential of the cell.

With such small values as  $\Delta E$  represents, an experimental check of equation (25) would be extremely difficult. A collection of suitable data would, however, be of value not only in checking this equation but also in further substantiating Gibbs' equation which has, for so long, been the ob-

ject of experimental verification due to the difficulty in finding a means of measuring the actual surface concentrations. If surface effects of the electrodes could be suitably isolated from other current-producing processes, this voltage method would afford an excellent measure of surface concentrations.

## APPENDIX

TABLE I  
Surface Tension of Some\* Amalgams

Metal	c ( $\frac{\text{g. at.}}{\text{L.}}$ )	$\sigma$ ( $\frac{\text{dynes}}{\text{cm.}}$ )	Metal	c ( $\frac{\text{g. at.}}{\text{L.}}$ )	$\sigma$ ( $\frac{\text{dynes}}{\text{cm.}}$ )	
Hg		410	Zn	0.00992	411	
K	0.00164	392		0.0165	412	
	0.00289	368		0.0701	415	
	0.00540	326		0.1210	417	
	0.0123	296		0.153	419	
	0.0252	289		0.360	420	
	0.0257	286		0.880	420	
	0.0830	282	Cd	0.00744	409	
	0.0918	283		0.0174	408	
	0.1782	284		0.0700	407	
		0.610		406		
Na	0.00305	386		0.822	406	
	0.00537	368	Ba	0.00287	407	
	0.0130	356		0.00548	398	
	0.0167	354		0.00735	392	
	0.0332	348		0.0150	384	
	0.0369	337		0.0422	366	
	0.0523	328		0.1154	356	
	0.09112	337				

\* See footnote, p. 39.

SURFACE TENSION VS. CONCENTRATION OF AMALGAMS\*

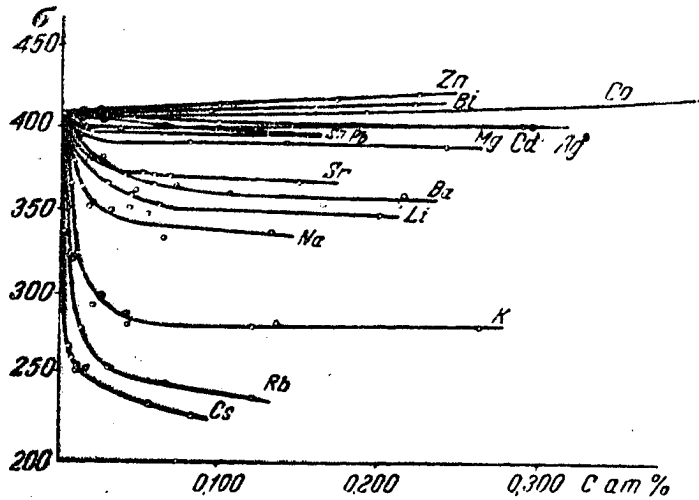


Рис. 1.

FIGURE 1

\* These data are due to V.K. Semenchko, B.P. Bering, N.L. Pokrovskii and E.E. Shvareva (38). A more complete table appears in their article including such additional metals as Cs, Rb, Li, Sr, Mg, Ag, Cu, Pb, Sn, Bi and Co.

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