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Progress Report on
Research Program

ACTIVITIES IN LIQUID AND SOLID BINARY METAL SYSTEMS

Conducted Under
A.E.C. Contract No. AT(30-1) - 1888.
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ABSTRACT

The progress made in the selection of materials and in designing of equipment for making e.m.f. measurements of 600 to 1000°C on liquid and solid binary alloy systems under the subject contract is reported. General status of the program is reviewed briefly.

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I. INTRODUCTION

As a result of the general interest in the thermodynamic properties of liquid and solid binary alloy systems, a research program on the subject was initiated in the Metallurgy Department at M.I.T. in February 1955. The program is supported by the Atomic Energy Commission under Contract No. AT(30-1) - 1888. The general purpose of the program is to experimentally determine the thermodynamic properties of alloy systems principally by the e.m.f. method and the distribution of a solute between two phases. The metal systems under study contain lead, bismuth or silver as one of the components.

In the initial work on the program, effort has been directed to the following problems in order to pave the way for obtaining the best results in the long term:

1. Modify existing experimental techniques or develop new ones so as to increase volume of results obtained by a researcher and also decrease the complexity of the techniques so that results can be obtained by a semi-skilled technician.
2. Evaluate the magnitude of the error inherent in the results from the exchange reaction between the two metals and their ions in the electrolyte.
3. Develop suitable and practical experimental equipment and procedures for obtaining reliable results with the more highly reactive metals such as aluminum.

A major increase in the output of data from e.m.f. measurements is achieved by using multiple legged cells as did Taylor¹, and Elliott and Chipman², instead of the simple "H" type cell having but two legs^{3,4}. However, this complicates the problems of assembling the cell, especially where operating temperatures are above 600°C or where highly reactive metals are studied. The primary reason is that assembled refractory shapes must be used instead of easily fabricated pyrex or vycor bodies. It may be of interest to note that in 1955 a simple seven-legged cell with replaceable electrode holders was designed and used at temperatures from 350 to 600°C in an undergraduate laboratory in the Metallurgy Department at M.I.T. This design has provided ideas for further developments.

The problem of the error due to the exchange reaction has been treated in an unpublished paper by C. Wagner⁵. In it he has shown that the error in the potential obtained with an alloy which is very dilute in the less noble metal (i.e. Cd in the Cd-Bi system) by the reaction

is governed primarily by the difference in the standard free energies of formation per equivalent of the two metal species in the electrolyte and the valences of the metal ions. Thus by comparing measurements on the Pb-Ag system using an oxide electrolyte to those obtained with the same binary system and a chloride electrolyte, one should obtain data on the inherent error and thereby evaluate Wagner's treatment. It is to be noted that the differences in standard free energies of formation per equivalent for silver oxide and lead oxide is approximately 35 kcal while it is but approximately 5 kcal for the corresponding chlorides.

The problem of cell materials is particularly troublesome with the more reactive metals. They react with carbides, all but the more stable oxides, and dissolve virtually all metals which can be used for contacting leads. J. Egan at the Brookhaven National Laboratory has used niobium and tantalum successfully to contain liquid cerium in e.m.f. studies. However, because these metals are attacked by aluminum alloys and because of their expense, the use of other materials is being studied.

II. EXPERIMENTAL WORK

The experimental effort on this program has only recently been built up to the scale planned in the original proposal for 1956. (See "Manpower and Budget") Three graduate students now on the program on a part-time basis are building equipment and the plans for their research will be covered under the topic "Proposed Plans."

The efforts in the laboratory of the principal investigator (JFE) have been directed towards getting some experimental equipment built, developing satisfactory cell designs, finding suitable cell materials, and working out techniques for obtaining steady and reproducible potentials. The general results obtained thus far are summarized below:

A. Cell Design

A cell design consisting of a number of small crucibles nested within a large crucible is generally satisfactory (Figure 1).

The alloys and the pure reference metal electrodes are held in the small crucibles which usually number from four to six. Sufficient electrolyte is added so that its level is above the tops of the small crucibles. If a crucible material is used which has an appreciable electrical conductivity, the individual electrode holders must be suspended from above to avoid short-circuiting the electrodes. (See Figure 2.)

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The contacting leads for the metal electrodes are inserted from the top and they need not be insulated from the electrolyte. The greatest difficulty encountered thus far has been obtaining suitable contact between the lead and the liquid metal electrodes, and at the same time provide for a simple method for assembling the cell at the start of the run. It is essential that each lead be centrally located in the electrode crucible. Otherwise surface tension effects cause a thin film of electrolyte to form between the lead and alloy that causes an unsteady potential. This is particularly true if the amount of the alloy is small. The solution of this problem rests with details of the mechanical design which apparently now have been resolved by using spacers of nickel or ceramic sheet and vycor guide tubes.

The problem of solution of the lead wire by the alloy can be minimized by retracting the wire out of the alloy and into the electrolyte while measurements are not being made. Steady, reproducible potentials can be obtained on re-inserting the lead in the alloy if the lead is held in the electrolyte but not drawn out into the protective atmosphere of the cell.

Another source of difficulty has been the presence of gas bubbles at the electrode-electrolyte interface. They form if the liquid electrolyte is poured or pumped into the cold crucible containing the cold metals. The inert gaseous atmosphere is trapped by the electrolyte as it solidifies. This gas and any gas dissolved in the metals can be removed by evacuating the cell as it is brought up to temperature or after the metals and the electrolyte are fluid. However, ebullition of the gas may cause droplets of metal to be carried from one electrode to another, thereby changing the composition of both. Careful evacuation techniques can avoid this difficulty for the most part. A better procedure is to place the solid metals and a block of solid electrolyte in the cell and then seal the system and keep it under high vacuum as the alloys and electrolyte are melted rapidly. The cell is then operated under an inert gas at slightly greater than atmospheric pressure

B. Materials

One of the primary problems faced in obtaining a reversible cell which can operate above 600°C with liquid metals is finding contacting

Figure 1

Cross-Section of Cell of Refractory Crucibles

Figure 2

Cross-Section of Typical Cell Arrangement
With Graphite Electrode Holder

leads and materials for containers which are essentially non-reactive with the alloys or the electrolyte. Further, the materials must not be too difficult to obtain or too expensive because of the extended study planned and because the equipment may be replaced frequently.

Scrutiny of the literature dealing with e.m.f. measurements and the thermodynamic properties of materials led to the trial of the various materials shown in Table 1 for crucible materials and contacting leads. Reactions to the electrolytes and metals which are used in the e.m.f. cells are summarized in the last four columns in the table.

All the materials listed, except perhaps molybdenum, can be used in the cells having chloride electrolyte and alloys of the "less active" metals. If metals or graphite are to be used as electrode containers, the cell design has to be changed (Figure 2) because of the high electrical conductivity of these materials. Porcelain is the most practical material for this type of cell because of its low cost and ready availability in various shapes. In a number of runs, it has been sufficiently inert so that the crucibles can be washed, dried and reused.

The only material found thus far for use in cells having a chloride electrolyte and the "more active" metals like aluminum are alumina and MgO. The solubility of alumina in aluminum apparently is sufficiently low⁶ below 1000°C to be neglected. The high purity alumina refractory ware commercially available has been used successfully in measurements on the Ag-Al system with a chloride electrolyte. Slight discoloration by contact with the chloride has been noted. Niobium contacting leads were satisfactory in these measurements.

Graphite is inert to many chlorides and because of the ease of working it, considerable effort was expended to determine if it could be used as a cell material with the Ag-Al, chloride cell. The hope was that an adherent aluminum chloride layer could be formed between the alloy and the graphite and once formed it would not interfere with obtaining a reversible cell. However, the carbide layer could not be made adherent and it continued to form where the alloy and graphite were in contact, and also at the chloride-graphite interface.

Table I

BEHAVIOR OF MATERIALS IN VARIOUS ENVIRONMENTS AT 600-1000°C

Material	Reaction to Liquid Environments			
	Fused Sodium Borate	Fused Chlorides	"Less Active" Metals (Pb, etc.)	"More Active" Metals (Al, etc.)
Porcelain	$\text{SiO}_2 + \text{Al}_2\text{O}_3$ Soluble, Rapid Solution	No Apparent Attack	No Apparent Attack	Discoloration and Attack
Alumina	Rapid Attack	No Apparent Attack	No Apparent Attack	No Apparent Attack
MgO	Rapid Attack	No Apparent Attack	No Apparent Attack	No Apparent Attack
Boron Nitride	Gassing and Discoloration	No Apparent Attack	No Apparent Attack	Some Reaction
Vycor Glass (Silica)	Slow Attack	No Apparent Attack (became brittle and weak)	No Apparent Attack	Discoloration and Attack
Graphite	Rapid Reaction	No Apparent Attack	No Attack by Non-Carbide Formers	Carbide Formed
Tungsten	Oxidation	No Apparent Attack	No Apparent Attack	Rapid Solution
Molybdenum	Oxidation	No Apparent Attack	Some Solution	Rapid Solution
Niobium	Embrittlement	No Apparent Attack	Some Solution	Slow Solution

C. Electrolytes

Liquid electrolytes are being used to obtain a good contact between the liquid alloy and electrolyte and to minimize polarization problems which might be present in solid electrolytes due to the slower diffusion rates encountered in solids. The many limitations placed on the electrolyte for a reversible cell severely restricts the selection. Stability in the operating temperature range of the cell, inertness to cell materials, the presence of ionic conductance only, and a host of other requirements means that only fused chlorides or fused borates appear to be practical. The chlorides have the two disadvantages in being rather volatile and in the fact that the free energy of formation per equivalent of many metal chlorides are rather close together. On the other hand, the fluorides generally show higher melting temperatures and are difficult to contain. The bromides and iodides are too unstable and volatile. The chief disadvantage to the borates are their high viscosities and the difficulty of finding inert container materials.

In exploratory work, the eutectic mixture of KCl and NaCl in which a small concentration of the chloride of the less noble metal is dissolved has proved very satisfactory. The eutectic mixture of KCl and LiCl has also been used. The salt mixture is degassed by prolonged heating under vacuum as recommended by Gardener et al⁷. It is then fused under vacuum, filtered under a dry argon atmosphere, and cast into a solid block. The block is transferred to the cell and melted under a vacuum or an inert atmosphere.

If a component with a very low melting point and relatively low stability, such as has AlCl_3 , is to be added to the electrolyte, it is dehydrated and degassed separately by subliming it under vacuum of less than 0.1 mm. of Hg. After the KCl-NaCl mixture is degassed and fused, the purified AlCl_3 is added. The concentration of AlCl_3 in the electrolyte is kept at about 0.2% by weight to avoid losses by volatilization and to minimize the formation of sub-chlorides or the solution of metals. The preparation and use of these chlorides appears to be satisfactory because cells having KCl-NaCl mixtures containing AlCl_3 or PbCl_2 have been operated between 660 and 900°C for several days without any discoloration

or fogging of the electrolyte being noticed.

D. Alloy Electrodes

All electrodes are prepared by weighing out the appropriate quantities of the pure metallic components and alloying them in their containing crucibles as the cell is brought up to temperature. Metals in lump form and 99.90 to 99.999 per cent pure are used. Indications are that the normal time necessary to get the cell temperature equilibrated (one-half to one hour) is sufficient to homogenize the alloys. The only exception occurs when an alloy falls in the two-phase region of the phase diagram at the operating temperature. Then a slow drift in potential is noticed. With Pb-Ag, chloride cells, the potentials of electrodes whose alloys contain both liquid and solid phases drift for a short time but will usually settle down to within 0.1 MV. or less of each other.

E. Miscellaneous

Conventional furnaces, potentiometers, gas tanks and control equipment are used to heat the cells and provide a vacuum or an inert atmosphere as may be needed. The cell is contained in a 65 mm. diameter vycor tube which is closed at one end. No difficulty has been encountered with this material except for some devitrification during cooling after it has been exposed to LiCl vapor at 800 to 900°C for prolonged periods.

III. EXPERIMENTAL RESULTS

In the work of exploring the use of materials and developing designs of cells, a number of results have been obtained. They are, however, preliminary in nature and no alloy system is covered fully. As a consequence, there are no data to be reported in this report. Actually, the points discussed under "Experimental Work" can be considered to be the experimental results obtained thus far as they provide the ground work for the actual study of the alloy systems.

VI. PROPOSED PLANS

In addition to the Principal Investigator, three graduate students are employed as part-time Research Assistants on the program. A laboratory assistant is also employed to carry out work under the direction of the Principal Investigator.

The alloy systems to be studied first and the experimental methods to be used are as follows:

<u>System</u>	<u>Method</u>	<u>Temperature Range</u>
Al-Ag, Chlorides	E.M.F.	660 - 900°C
Ag-Pb, Chlorides	E.M.F.	660 - 900°C
Ag-Pb, Oxides	E.M.F.	750 - 1000°C
Mn-Bi, Chlorides	E.M.F.	660 - 900°C
Ni-Bi, Chlorides	E.M.F.	660 - 900°C
Ni-Pb } Fe-Pb }	Phase	1450 - 1600°C
	Distribution	
Pb-Bi } Ni-Bi }	Phase	600 - 1100°C
	Distribution	

On the completion of work on these systems, the Al-Bi, Al-Pb, Mn-Ag, Mn-Pb, binaries and others will be studied in the next twelve months by the experimental methods deemed most suitable. Determination of the liquidus line for 600 to 1100°C for the binary alloys of many of the higher melting metals and Pb, Bi or Ag by distribution measurements is considered to be an important part of the work.

It is proposed that a longer term aim of this research might be a study of the activities in multi-component systems in which the solvent might be bismuth, lead or other of the lower melting, less active metals. From these results, interaction coefficients among solute atoms could be obtained and some light might be shed on the fundamental behavior of liquid metals. Due to the dearth of information on molar volumes of metals, future work on this subject might be both interesting and valuable in helping to understand the behavior of liquid metals.

V. PERSONAL BUDGET

The following personnel are now engaged on the project:

	<u>Name</u>	<u>Responsibility</u>	<u>Position</u>	<u>Percentage of Time on Project</u>
1.	John F. Elliott	Principal Investigator	Associate Professor	20-25
2.	C. W. Wagner	Advisor	Professor	10
3.	Graduate Student	_____	Research Assistant	33
4.	Graduate Student	_____	Research Assistant	50
5.	Graduate Student	_____	Research Assistant	50
6.	_____	_____	Laboratory Assistant	100

However, the three graduate students have been active on the project only since late in September after the Fall Semester started. Because they were not available earlier on a regular basis, the activity by graduate students on this program at the end of the contract year will be nine man-months (half-time) short of the estimate of 24 made in the original proposal.

TABLE II

ESTIMATED 1956 EXPENSES

<u>Item</u>	<u>Cost</u>
1. Salaries and Wages	\$11,000
2. Overhead	4,250
3. Materials and Services	7,000
4. Travel	450
5. Capital Equipment	1,550
Total	<u>\$24,250</u>
Funds Allocated	29,260
Estimated Balance	<u>\$ 5,010</u>

The anticipated expenditures for the year 1956 on this program are shown in Table II. Charges against Salaries and Wages and Overhead are not as high as estimated originally, primarily because of the late availability of graduate students.

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VI. SUMMARY AND RECOMMENDATIONS

Since the initiation of the present program in February 1, 1956, experiments have been conducted for developing improvements in the cell design for e.m.f. measurements and a number of cell materials have been evaluated. Experimental equipment has been built and electrode potential measurements on alloy systems are now being made. Equipment for phase distribution studies is currently being built. Systems being investigated are Ag-Pb, Al-Ag, Ni-Pb, Fe-Pb, Mn-Bi and Ni-Bi. Others will be undertaken as time permits.

Three Graduate students are now working as part-time Research Assistants on the program so that a reasonably intensive experimental effort is underway.

In view of the progress made in designing, developing and building equipment for e.m.f. measurements, and because actual studies by the e.m.f. technique and by the phase distribution method are getting underway, it is recommended that support at the current level of effort for this work be continued for another year by a renewal of the present contract.

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BIBLIOGRAPHY

1. J. Taylor: J. Am. Chem. Soc. 45, 2865 (1923).
2. J. F. Elliott and J. Chipman: Trans. Faraday Soc. 47, 138 (1951).
3. H. S. Strickler and H. Seltz: J. Am. Chem. Soc. 58, 2085 (1936).
4. H. Seltz and B. J. De Witt: J. Am. Chem. Soc. 61, 2594 (1939).
5. C. Wagner: Unpublished, (1956).
6. L. Brewer and A. W. Searcy: J. Am. Chem. Soc. 73, 5308 (1951).
7. H. J. Gardner, E. C. Brown and G. J. Janz: Technical Report No. 1,
ONR Contract No. Nonr - 591(06).
Rensselaer Polytechnic Institute, (March 1956).