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GASEOUS ELECTROLYTES FOR BATTERIES AND FUEL CELLS

by

S. Naiditch, Principal Investigator

Prepared for

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CONTENTS

Section		Page
	Abstract	1
1.	Introduction	3
2.	Experimental	5
	2.1 Introduction	5
	2.2 Cells	7
	2.2.1 Cell 56	7
	2.2.2 Cell 57	13
	2.2.3 Cell 58	18
	2.2.4 Cell 64	23
	2.3 Equipment Modifications	31
	2.4 Characteristics of the Conductivity Cell	32
	2.5 Effects Due to Contamination of Glass Surfaces	34
3.	Thermodynamic Analysis of Sodium Amalgam Concentration Cells	35
	3.1 Introduction	35
	3.2 Thermodynamic Analysis	36
	3.2.1 Passage of Current Through the System	38
	3.2.2 Transport of Na from One Amalgam to the Other at Constant Temperature and Pressure	39
	3.2.3 The Voltage as a Function of Chemical Potential at Constant T,p	42
	3.2.4 Temperature Coefficient of the Voltage	43
	3.3 Symbols	45
4.	Summary	47
5.	Plans for Next Quarter	49

ABSTRACT

N66-18319

The principal problems studied this quarter were (1) stability of amalgam concentration cells, and (2) their equilibrium emfs relative to the state of the electrolytic solutions, i.e., liquid vs. gaseous. We have obtained stabilities, with respect to short-term fluctuations, of 0.1 microvolts for emfs of the order of 0.1 volt, or 1 ppm, and internal consistencies of the six combinations of the four electrodes of $\pm$ 7 microvolts, or 70 ppm. Also, we have tentatively concluded from our data that the equilibrium emfs of concentration cells are independent of the state of the electrolytic solution.

The emfs of four sodium amalgam concentration cells, using sodium iodide and sodium amide in ammonia electrolytes, with liquid or solid mercury amalgam electrodes, and filled under vacuum, were measured from as low as -20 to as high as 150°C.

We rewired the electrical system and modified the cell preparation procedures. In particular we reduced parasitic currents on the amalgam surfaces by using ultrasonics to increase the uniformity of the amalgam electrodes. The stability now achieved is attributed to the removal of sources of bubbles and spurious emfs. All chemicals used in the cell were of high purity (NaI) or were further purified (Na, Hg, NH_3). The cells were baked out under vacuum to remove traces of volatilizable impurities.

A thermodynamic analysis, including normally neglected terms, has been made. The neglected terms are shown to be many orders of magnitude smaller than

the limits of our measurement. The experimental temperature coefficients of E/T are not compatible with the results of the thermodynamic analysis.

In parallel with the measurements we have been re-evaluating the characteristics of our conductivity cell, which were described earlier, to ensure that the cell is operating properly.

No chemical analyses of the amalgams or electrolytes were carried out this quarter due to cell ruptures; however, the ratios of concentrations of sodium in the amalgams are accurately known from the emfs for the pairs of half cells.

AUTHOR

1. INTRODUCTION

The objective of this program is to study the electrochemistry of dense gaseous solutions. Ammonia has been chosen as the electrolytic solvent because of its conveniently small critical constants. Also, unlike water, it does not attack glass, which is a good structural material for cells.

Since we are interested in operating in the dense gaseous region we cannot use a cell with a gaseous junction. Hence, we have chosen systems in which the electrolytic solution is uniform throughout and is free from junctions between the electrode compartments.

The studies were initiated with zinc, cadmium and thallium amalgam-insoluble halide electrodes, which were extensively studied by Yost and coworkers. We encountered troublesome instabilities when using these electrodes; therefore, we turned to sodium amalgam concentration cells. This was done because these cells can be baked out and filled under vacuum. Our results with both types of cells have clearly demonstrated that bubble formation is a principal source of instability and that impurities have been one of the contributors to bubble formation. The tendency to form bubbles is aggravated in our work because of (1) the relatively high temperatures of the measurements (as the critical point is approached from the liquid side the energy required to form bubbles becomes negligible), and (2) the use of ammonia which has a smaller latent heat of vaporization than water. The amalgam concentration cells are being used as diagnostic tools to enable us to develop the requisite techniques to work in the dense gaseous state. We expect to find no new information regarding the amalgam concentration cells insofar as equilibrium measurements are concerned.

The cells now being studied are sodium amalgam concentration cells with an ammonia electrolytic solvent. They have been measured over most of the liquid range and into the dense gas state (-20 to +150°C) producing emfs of the order of 0.1 V. This corresponds to the ratios of sodium concentrations of 50 between pairs of electrodes. The cells are run in a pressure vessel with the high solvent pressure inside the glass cell being contained by higher environmental pressure. We have, for our most recent cell,obtained short term stabilities of ± 0.1 microvolts for emfs of the order of 0.1 volt and internal consistencies of the six electrode combinations of ± 7 microvolts.

This stability is attributed to the removal of sources of bubbles and spurious emfs. The use of high purity chemicals and of ultrasonic agitation to ensure uniformity in the amalgam electrodes were of particular importance. Also important in removing spurious emfs was the addition of a grounded shield to the high pressure bomb.

[illegible] now being made to interpret our results in detail by thermodynamic analysis. We have examined usually neglected terms, to see if these can account for the large temperature coefficient of E/T. These neglected terms are shown to be many orders of magnitude smaller than the limits of our measurement. Therefore, some of the assumptions in our derivation are invalid. In particular, the state of sodium in the amalgam may vary with temperature, depending on which species are present.

2. EXPERIMENTAL

2.1 Introduction

The following series of measurements were made to develop techniques for producing stable reproducible cells. The cells (Fig. 1) are designed to be inserted into a pressure vessel. Because of the restrictive geometry, d.c. techniques are used to study the electrochemical properties of the cells.

Ammonia was chosen as the electrolytic solvent because of its relatively low critical temperature and pressure. Sodium amalgam electrodes are being used since these can be prepared under vacuum after bake out. More detailed discussions of these aspects have been given in earlier quarterly reports.

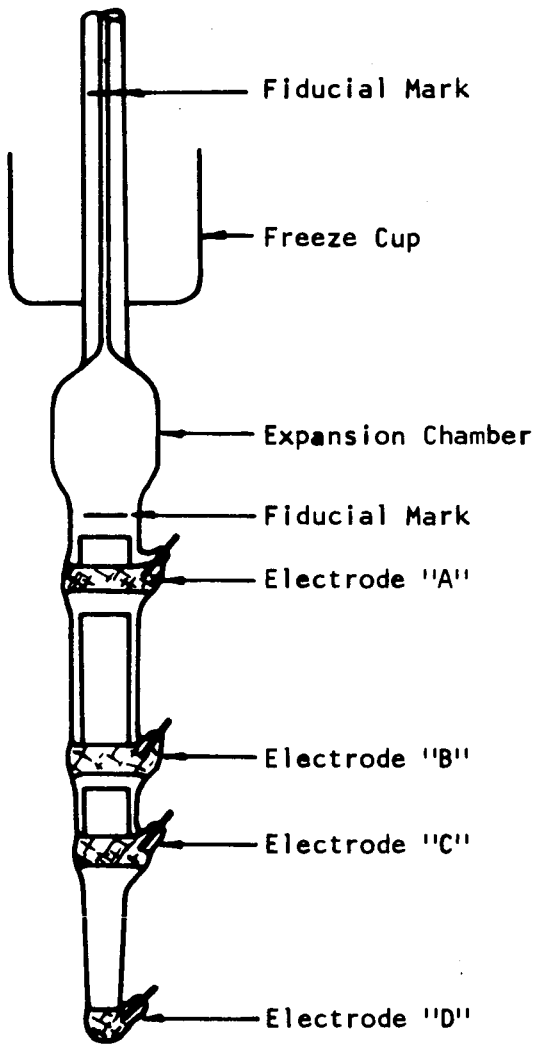


Figure 1. Amalgam Concentration Cell with Electrode Amalgams in Place.

2.2 Cells

2.2.1 Cell 56

Cell 56 was a standard high pressure electrochemical cell (Fig. 1). The lead tips, which contact the sodium amalgams, were platinized. The electrolyte was NaI dissolved in NH_3. In this cell part of lead A was exposed to the electrolyte due to excessive mercury evaporation during bake out prior to filling. We did not find any effects attributable to this exposure. The leads of cell 56 were soldered to the leads passing through the bomb head and covered with fiber glass tubing while the cell was immersed in a dry ice-methanol solution. The mounted cell was then suspended in the bomb by its leads.

The emfs between the pairs of half cells D-A, B-A, C-A, and B-C, were measured as a function of temperature from 21.3 to 71.7°C. The experiment was terminated because the pressure in the pressure chamber dropped suddenly and the cell broke. The data, compiled in Table 1, are plotted in Figs. 2 (E vs T) and 3 (E/T vs T).

In order to examine the accuracy of the measurements we compared the emfs directly measured between one pair of half cells and those calculated from measurements between two other pairs. The directly measured B-C emfs are listed in column 2 of Table 2. The B-C emfs in the third column have been obtained by taking the differences between the B-A and C-A emfs. In the last column, the differences between the two sets of values for the B-C emfs (i.e., those in columns 2 and 3) are given in millivolts. The average

difference between the two sets of values is half a millivolt. This is better than the ± 1% accuracy of the Hewlett-Packard 412A used for this set of measurements.

Cell 56 shows the emfs to be internally consistent within the limits of our measurements. More accurate measurements were not taken because of instability. Figs. 2 and 3 show that the emfs and E/T were linear with temperature from 20 to 70°C, as is true for cell 64.

TABLE 1. EMF DATA FOR CELL 56

TEMPERATURE		EMF, VOLTS							
		B - A		C - A		D - A		B - C	
°C	°K	E, VOLTS	E/T×10^4 VOLTS/°K	E, VOLTS	E/T×10^4 VOLTS/°K	E, VOLTS	E/T×10^4 VOLTS/°K	E, VOLTS	E/T×10^6 VOLTS/°K
21.3	294.5	0.0767	2.604	0.0812	2.757	0.1065	3.616	-0.00485	-16.46
38.0	311.2	0.0901	2.895	0.0940	3.020	0.121	3.888	-0.0043	-13.81
51.0	324.2	0.1075	3.315	0.110	3.392	0.132	4.071	-0.00195	- 6.014
59.0	332.2	0.118	3.552	0.117	3.521	0.137	4.124	+0.0007	+ 2.107
58.0	331.2	0.116	3.502	0.116	3.502	0.137	4.136	-0.0002	- 0.6038
71.7	344.9	0.124	3.595	0.124	3.595	0.146	4.233	-0.00025	- 0.7248
49.0	322.2	0.103	3.196	0.105	3.258	0.128	3.972	-0.0034	-10.55

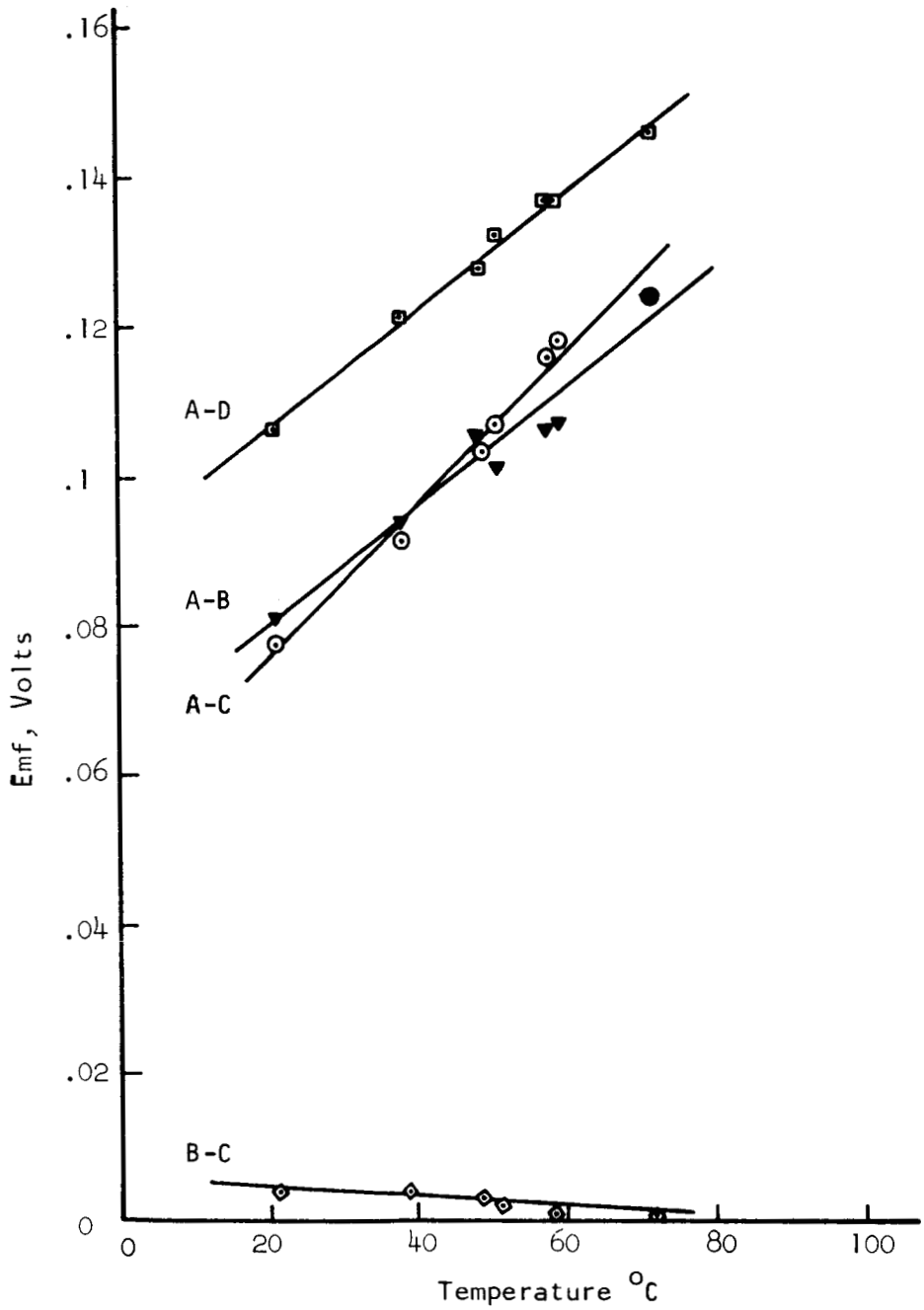


Figure 2. Emfs for Cell 56 as a Function of Temperature

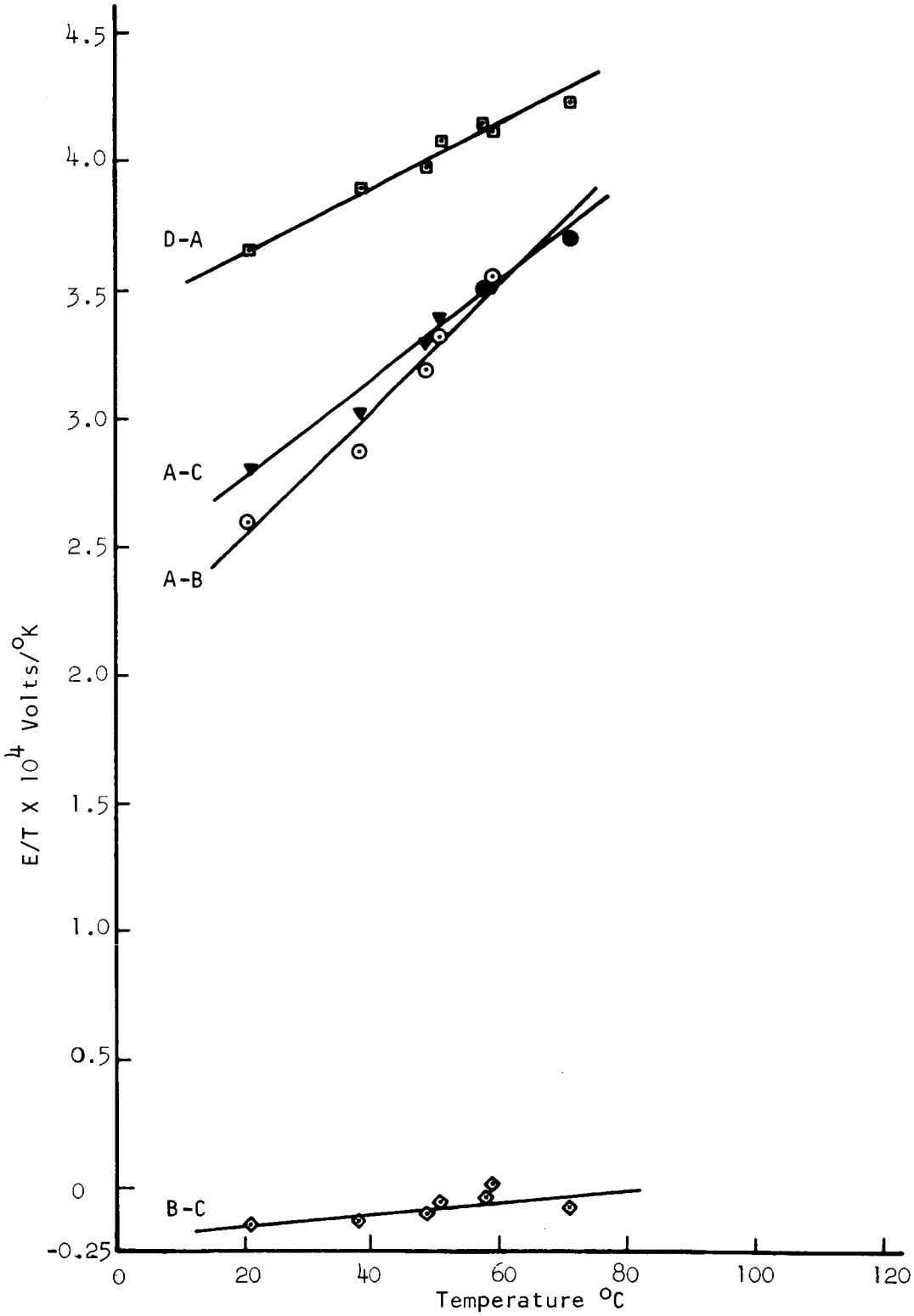


Figure 3. E/T for Cell 56 as a Function of Temperature

TABLE 2. COMPARISON OF THE DIRECTLY MEASURED EMF'S OF B-C WITH THOSE CALCULATED FROM B-A AND C-A FOR CELL 56

TEMPERATURE °C	°K	E(B-C) VOLTS	E(B-A)-E(C-A) VOLTS	DIFFERENCE MV
21.3	294.5	-0.00485	-0.0045	0.3
38.0	311.2	-0.0043	-0.0039	0.4
51.0	324.2	-0.00195	-0.0035	1.6
59.0	332.2	+0.0007	+0.001	0
58.0	331.2	-0.0002	0.000	0
71.7	344.9	-0.00025	0.000	0
49.0	322.2	-0.0034	-0.002	1

2.2.2 Cell 57

Cell 57 was like 56 in its construction except electrodes A and B had exposed leads. Before mounting the cell in the pressure chamber, the glass surface was washed with cold acetone to remove dirt and oil. Then the cell was wrapped with a thin teflon sheet. When the chamber was sealed, it was evacuated until the spurious potentials between the cell leads and the chamber wall dropped to 30 microvolts. During evacuation, the chamber was cooled in order to prevent the cell from rupturing since the internal pressure of the cell is about 8 atm. at 20°C.

Chronopotentiograms were measured at room temperature. The cell current was varied from 0.65 microamp to 7 milliamp., and the working electrode was used either as a cathode (reduction) or as an anode (oxidation). No difference was observed between the chronopotentiograms at oxidation and at reduction or at different current settings. Furthermore, there were no inflection points. The lack of inflections could have been caused by lack of stability in the power supply. This effect was noted on cell 58 and has since been corrected. Because of the inadequate performance of the power supply, no meaningful data were collected.

Cell 57 was recycled twice from room temperature to above 110°C. During the second cycle, the temperature was raised above the critical temperature and the cell broke. Emfs were measured between electrodes A and D (the most stable pair) as a function of temperature. These measurements are given in Table 3 and plotted in Fig. 4.

It is seen that the emfs level off between 80 and 100°C and begin to drop above 110°C. This trend is probably due to rising internal resistance as the temperature was raised. The internal resistance of the cell between electrodes A and D was approximately 7×10^6 ohms at 68°C. This measurement was performed after the first emf versus temperature run using an HP412A VTVM. The two sets of emf data differ at low temperatures by as much as 50%. This may be due to non-uniformity in the amalgams at the beginning of the run. Heating of the amalgams allowed them to come to equilibrium at about 70°C above which the results of the two runs are the same. A third cycle would have verified this conclusion about the low temperature data. Analysis indicated the need for insuring that both the electrolytic and amalgam solutions are uniform. For this reason, on run 64, we introduced the use of ultrasonics which resulted in a very marked increase in stability.

TABLE 3. EMF DATA FOR CELL 57 FROM TWO DIFFERENT RUNS

(EMF was measured between electrodes A and D)

TEMP., °C	EMF, VOLTS	$E/T \times 10^4$, VOLTS/°K	TEMP., °C	EMF, VOLTS	$E/T \times 10^4$, VOLTS/°K	TEMP., °C	EMF VOLTS	$E/T \times 10^4$, VOLTS/°K
First Heating			73.3	0.191	5.512	Second Heating		
25.0	0.035	1.173	74.4	0.194	5.581	20.4	0.076	2.588
30.0	0.044	1.451	74.7	0.194	5.576	25.0	0.079	2.649
33.3	0.048	1.566	75.4	0.196	5.622	30.0	0.080	2.638
36.0	0.050	1.617	76.4	0.197	5.635	34.0	0.083	2.701
41.7	0.056	1.778	76.8	0.198	5.657	40.0	0.089	2.841
44.5	0.060	1.888	78.4	0.199	5.659	45.0	0.096	3.016
45.8	0.065	2.037	78.7	0.200	5.683	55.0	0.121	3.686
49.8	0.072	2.229	79.0	0.2005	5.692	60.0	0.140	4.201
51.2	0.075	2.311	79.5	0.201	5.698	65.0	0.156	4.612
56.9	0.081	2.453	80.6	0.202	5.709	70.0	0.177	5.157
54.2	0.089	2.718	82.4	0.204	5.736	75.0	0.190	5.456
58.2	0.098	2.957	83.8	0.2045	5.728	80.0	0.197	5.577
59.9	0.114	3.422	90.2	0.207	5.696	85.0	0.2005	5.597
62.2	0.125	3.726	93.6	0.210	5.725	90.0	0.201	5.534
63.1	0.132	3.925	96.6	0.210	5.678	95.0	0.2015	5.472
63.3	0.136	4.041	100.9	0.213	5.693	100.0	0.201	5.385
65.8	0.146	4.306	103.3	0.213	5.657	105.0	0.2005	5.301
66.2	0.152	4.478	105.6	0.212	5.596	110	0.200	5.219
67.6	0.160	4.694	106.9	0.211	5.551	115	0.200	5.151
69.0	0.166	4.850	109.6	0.210	5.485	120	0.199	5.061
70.4	0.173	5.034	110.6	0.208	5.419	125	0.195	4.897
71.0	0.181	5.258	113.1	0.208	5.384	130	0.190	4.712
71.6	0.184	5.336	115.4	0.202	5.198	135	0.1845	4.519
72.4	0.186	5.381	116.2	0.197	5.059	140	0.181	4.380
72.4	0.189	5.468						

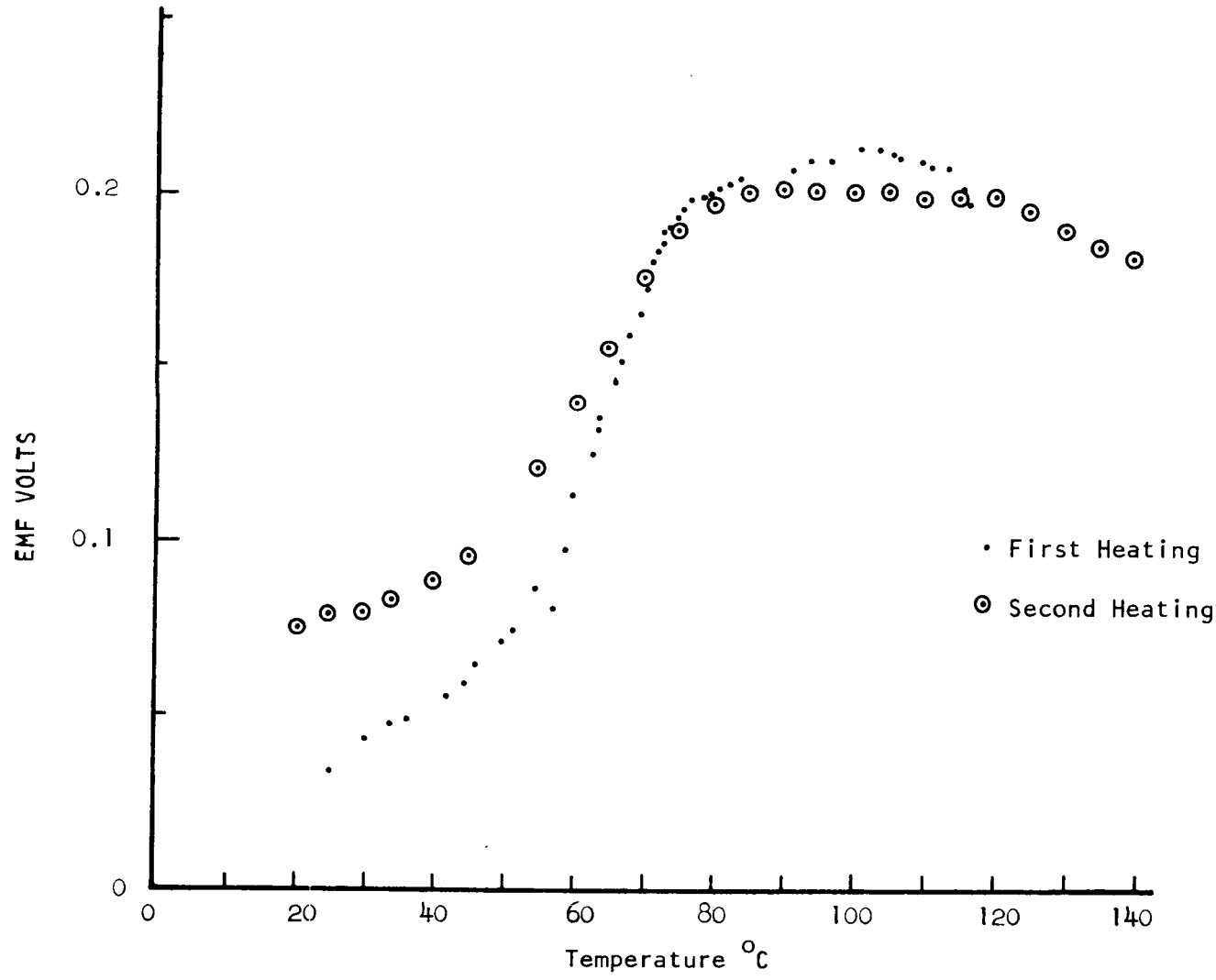


Figure 4. EMF for Electrodes AD of Cell 57

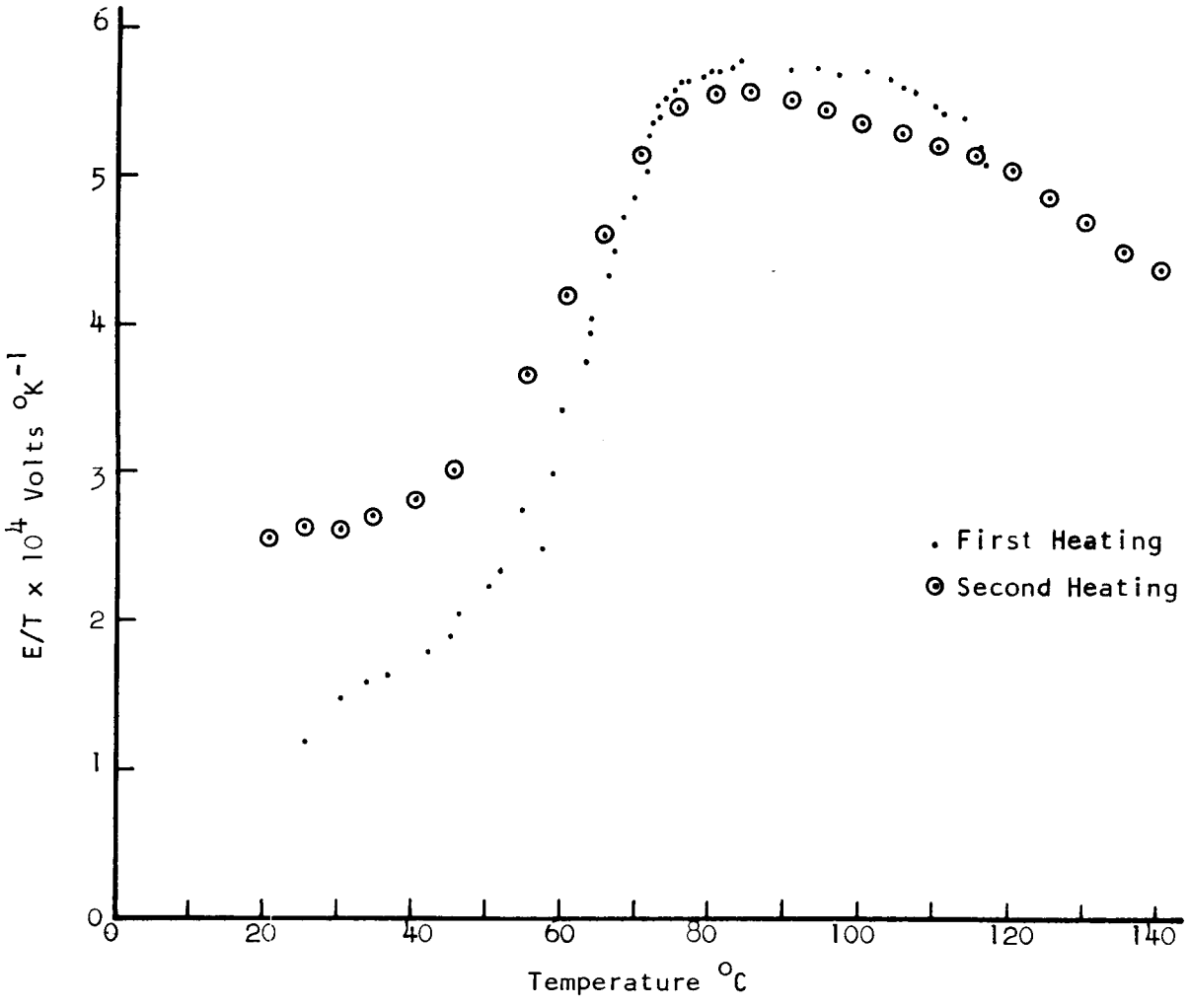


Figure 5. E/T for Electrodes AD of Cell 57

2.2.3 Cell 58

Cell 58 was like 56 and 57 except that only electrodes B and C were platinized and sodium iodide was not added, to see whether sufficient electrolyte is produced by the reaction of sodium with ammonia to operate the cell. The cell was prepared and loaded by the same technique used for cell 57.

It was not possible to measure the conductivity of the solution or to make chronopotentiometric measurements because the power supply was not providing a constant current.

The emfs between electrodes B and C were measured from room temperature to 150°C, i.e., approximately 15 degrees above the critical temperature of the electrolytic solution. These data are given in Table 4 and Fig. 6. At lower temperatures (50, 80 and 100°C, respectively), half an hour was allowed for equilibrium, whereas at higher temperatures only a few minutes were allowed. We planned to come back after reaching higher temperatures and determine equilibration times needed to produce valid readings but cell 58 broke at 150°C. Since we subjected it to an external pressure of 150 atmospheres, the internal pressure in the cell must have been higher than we had anticipated.

On a tentative basis, requiring confirmation, we believe that the equilibrium emfs of our amalgam concentration cells in Fig. 6 are independent of the state of the electrolytic solutions, i.e., whether liquid or gaseous. The process taking place at the sodium-poor electrode is

$$Na^+(NH_3) + e^-(\text{amalgam}) = Na(\text{amalgam})$$

and at the sodium-rich electrode,

$$Na(\text{amalgam}) = Na^+(NH_3) + e^-(\text{amalgam}).$$

If we add these equations, we obtain

$$Na(X_2 \text{ in amalgam B}) = Na(X_2 \text{ in amalgam C}).$$

Thus, the state of the electrolytic solution does not enter into the overall change in state. The emfs should therefore be independent of the amalgam state.

TABLE 4. EMF DATA FOR CELL 58

The emf was measured between electrodes C and B

TEMPERATURE, °C	°K	EMF, VOLTS	$E/T \times 10^3$, VOLTS/°K
23.0	296.2	0.419	1.414
25.0	298.2	0.4185	1.403
30.0	303.2	0.416	1.372
35.0	308.2	0.414	1.343
40.0	313.2	0.412	1.315
45.0	318.2	0.411	1.291
53.4	326.6	0.432	1.322
52.0	325.2	0.426	1.309
81.6	354.8	0.508	1.431
99.1	372.3	0.558	1.498
100.7	373.9	0.569	1.521
105.0	378.2	0.578	1.528
110.0	383.2	0.590	1.539
115.0	388.2	0.597	1.537
120.0	393.2	0.608	1.546
125.0	398.2	0.620	1.557
130.0	403.2	0.635	1.574
135.0	408.2	0.652	1.597
140.0	413.2	0.672	1.626
145.0	418.2	0.690	1.649
150.0	423.2	0.712	1.682

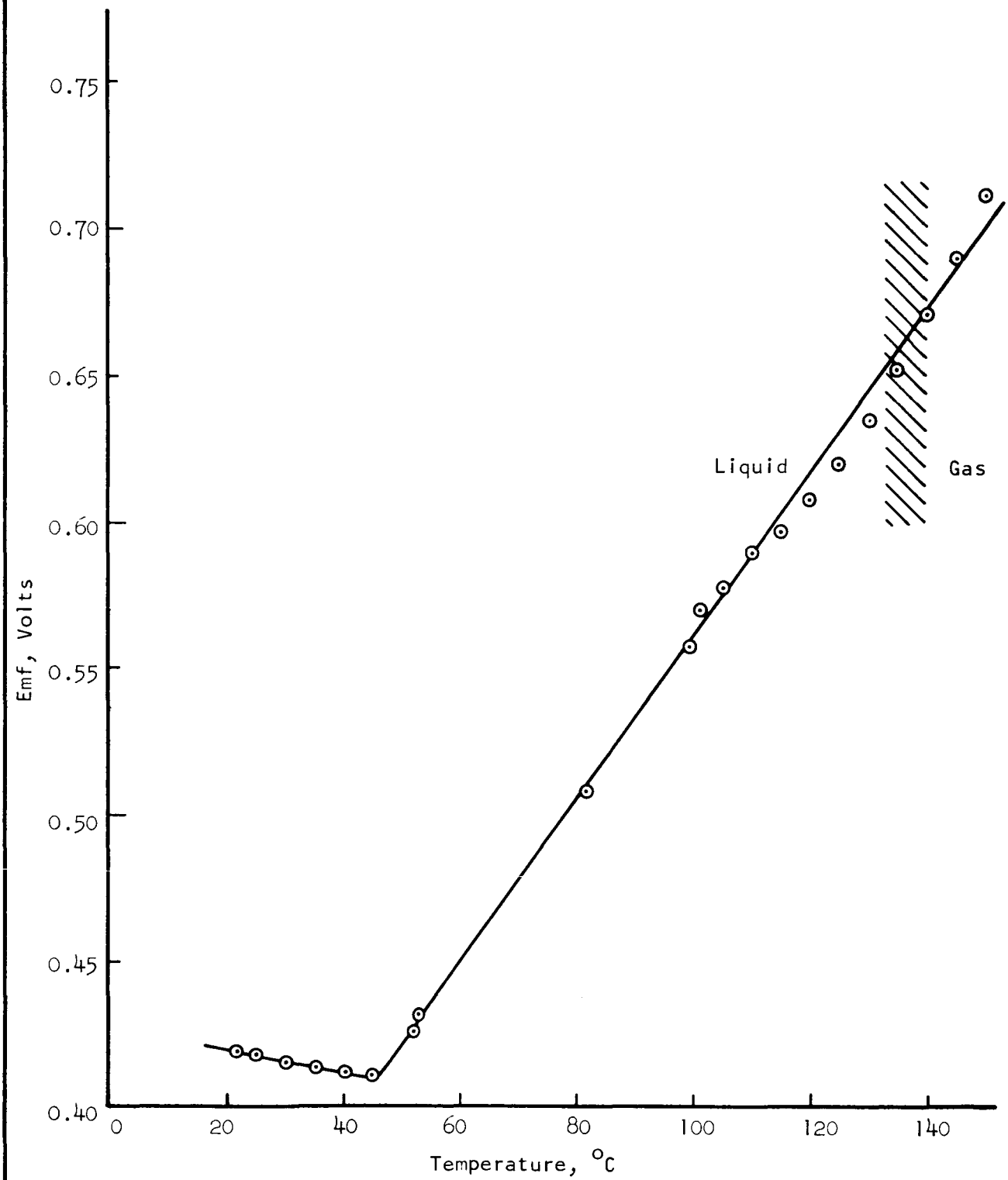


Figure 6. C-B Emfs of Cell 58 as a Function of Temperature

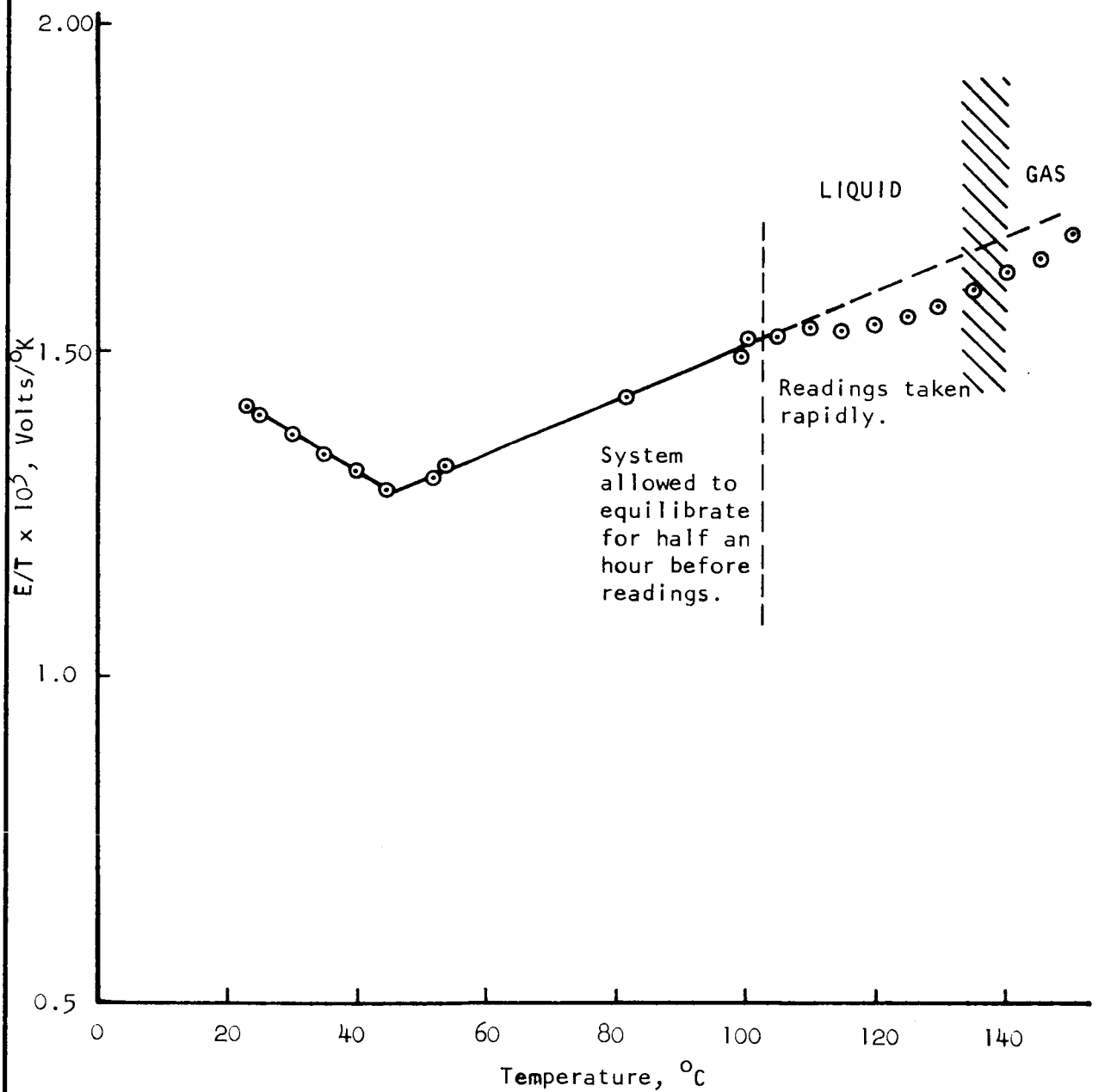


Figure 7. E/T x 10^3 for Cell 58 as a Function of Temperature for Electrode C-B

2.2.4 Cell 64

The cell was prepared with five other cells and stored at $0^{o}C$. At that time electrode A was solid, had a bubble under it, and looked much like dirty zinc sponge. Electrodes B, C and D were liquid and had only a slight scum on the amalgam surface.

Before attaching the cell to the high pressure bomb head, it was subjected to two treatments with ultrasonic agitation. The first, lasting an hour, was carried out with the cell immersed in a dry ice-methanol solution. As a result of the agitation, the emfs changed about 10% as measured with a Hewlett-Packard 412A vacuum tube voltmeter. After four hours storage at $9^{o}C$ the emfs were again measured, this time with the Calibration Standards Electronic Potentiometer, and were found to be stable and 10-25% lower than those measured after the agitation. The cell was then agitated for an hour in a $9^{o}C$ refrigerator. After this agitation, electrode C was solid, the cell was warm to the touch and was bubbling at a high rate due to the high temperature. During this second agitation the emfs only changed 5-10% and little further change was noted after overnight storage at $1^{o}C$.

The bomb leads were then soldered to the cell and covered with teflon sleeving and the entire cell was wrapped with teflon sheet. The preparatory work was done in the refrigerator so as to eliminate the need for placing the cell in dry ice-methanol. During this work, electrode D was broken off about 1/4" from the glass and was spliced using small pieces of copper wire. The splice has given us no trouble.

The cell was then placed in the high pressure bomb, checked for continuity and pressurized to 40 atm. After one hour in the bomb, the emfs were measured using a Calibration Standards Electronic Potentiometer DC110B. They were found to be very stable (± 0.1 microvolts) with respect to short term fluctuations and internally consistent to ± 7 microvolts (± 0.01%).

The temperature cycle shown in Fig. 8 was followed continuously for six days. For the first four days, an A.P.I. optical relay temperature controller was used but the temperature swing associated with this off-on control of ± 1°C caused variations in the cell emf as shown in Fig. 9 (emf vs time with heater cycle shown). As a result of this variation we stopped using the controller and are now controlling the temperature by setting the current and by waiting for equilibrium (about 12 to 24 hours). Though slow, this method has provided us with stable temperatures. Due to leaks, the long time required has caused difficulties in the pressurization system. We plan to rebuild this system.

Cell 64 has now been run from 15° to 56°C and is still in the high pressure bomb. The emf and E/T data is presented in Tables 5 and 6 and Figs. 9 and 10. We anticipate running cell 64 to as high a temperature as the pressurization system will permit, then removing and storing the cell while we rebuild the system.

The internal consistency of cell 64 has been excellent to date. On all runs checked it is within ± 0.1% or better. Later runs with this cell should verify our prediction and tentative conclusion that the cell emf is independent of the electrolyte state.

TABLE 5 - CELL 64

*	TEMP. °C	EMF, VOLTS					
		DA	DC	- DB	- AB	- AC	BC
3	13	0.100838	0.0142858	0.0183090	0.119139	0.0865855	0.0325720
4	14	0.100925	0.0142731	0.0183167	0.119224	0.0866800	0.0325635
6	18.5	0.101659	0.0142490	0.0179611	0.119584	0.0874139	0.0321958
5	25	0.100740	0.014430	0.0156810	0.11883	0.08553	0.033390
2	27	0.099825	0.014389	0.018635	0.11846	0.085480	0.033000
8	40.5	0.101900	0.0155299	0.018700	0.120490	0.0863122	0.0342105
7	41	0.101564	0.015530	0.0187354	0.120345	0.0861249	0.034268
10	56	0.10347	0.01639	0.01876	0.12220	0.08710	0.03512

*Order in which data were taken.

TABLE 6 - CELL 64

*	TEMP. °C	TEMP. °K	E/T, VOLTS °K^{-1}					
			DA	DC	- DB	- AB	- AC	BC
3	13	286	3.52580×10^{-4}	4.99503×10^{-5}	6.40175×10^{-5}	4.16570×10^{-4}	3.02747×10^{-4}	1.13881×10^{-4}
4	14	287	3.51655	4.97321	6.38213	4.15415	3.02021	1.13462
6	18.5	291.5	3.48744	4.8882	6.16161	4.10237	2.99876	1.10449
5	25	298	3.38054	4.8423	5.26208	3.9876	2.8701	1.12051
2	27	300	3.3275	4.7963	6.2116	3.9486	2.8493	1.1000
8	40.5	313.5	3.25040	4.95371	5.9649	3.84338	2.75318	1.09124
7	41	314	3.234522	4.9459	5.96669	3.83264	2.74283	1.0913
10	56	329	3.1450	4.982	5.702	3.7143	2.647	1.067

*Order in which data were taken

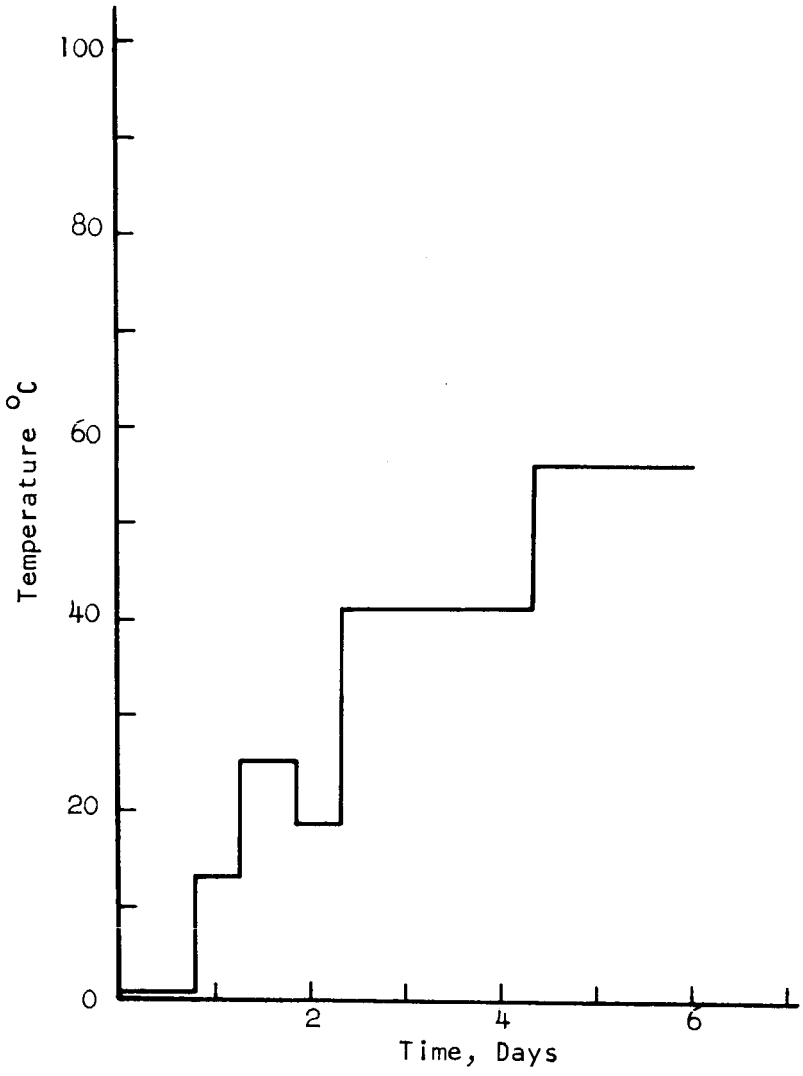


Figure 8. Temperature Cycle for Cell 64

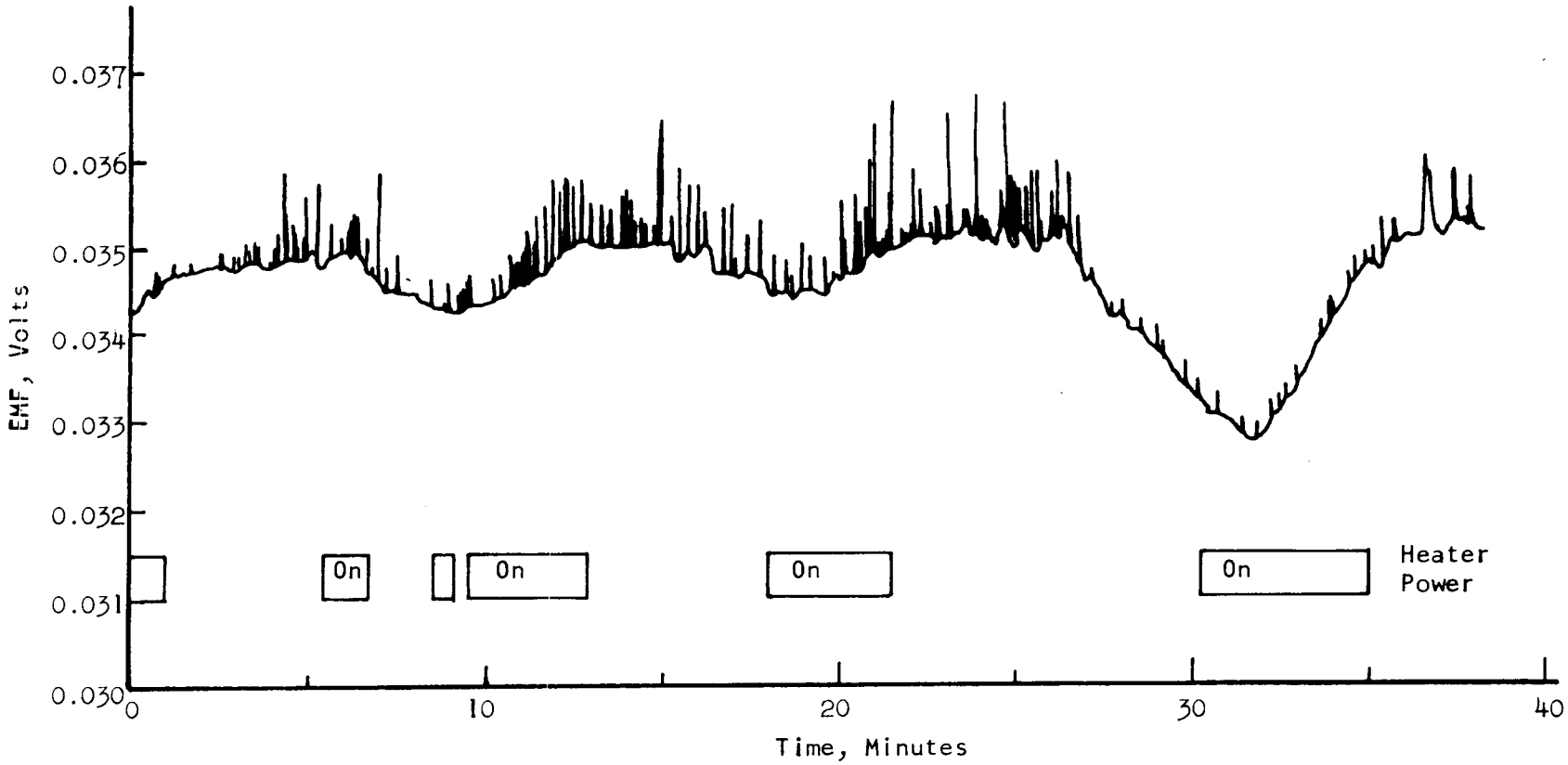


Figure 9. EMF as a Function of Time Showing Heater Cycles for Cell 64, Electrodes B-C

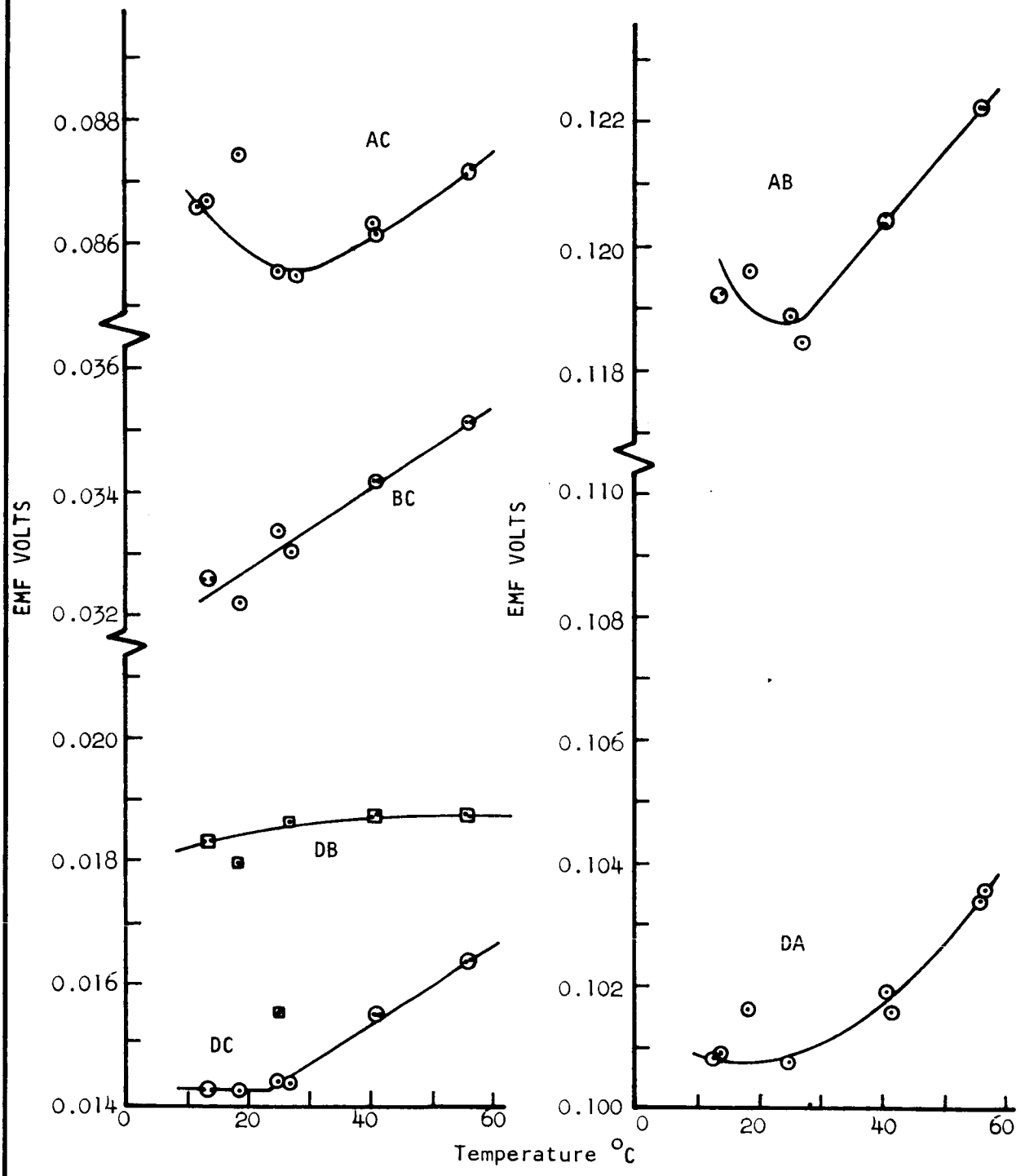


Figure 10. EMF Data for Cell 64

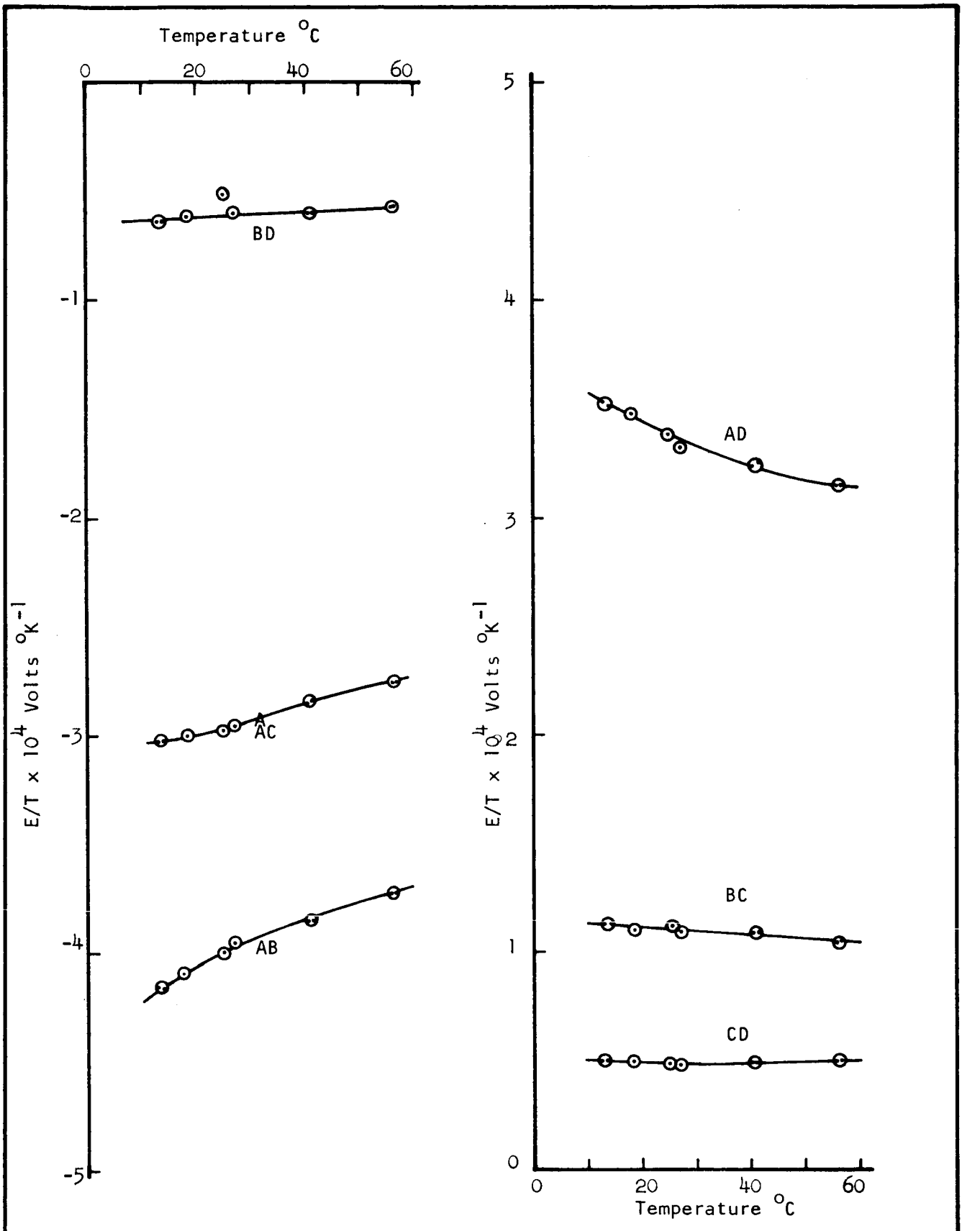


Figure 11. E/T Data for Cell 64

2.3 Equipment Modifications

During this quarter two equipment improvement projects were carried out. First the voltage dividing network of the constant current power supply was replaced. The new 1000 volt battery source has permitted the internal impedance to be increased to above $10^7\ \Omega$ and the range to 1000 μA.

The second improvement consisted of refinements to the bomb shielding. A ground wire was run to a water pipe ground and connected to provide a continuous shield for the leads from the bomb to the selector switch. This ground reduced the spurious emfs to the limit of instrument resolution (1 μV).

2.4 Characteristics of the Conductivity Cell

The three cell parameters (the length L, the effective cross sectional area A and the cell constant K) of cell 62 have been determined by the techniques described in our second quarterly report (21 November 1964--20 February 1965).

Using the measured geometrical dimensions of the conductivity tube, we obtained a cell constant of 23.14 cm^{-1}.

Using the effective area and effective length determined by the dip-rod method with mercury and with a rod diameter of 0.328 cm, we obtained a cell constant of 22.14 cm^{-1}.

Using the known conductivity of mercury at 20°C and the resistance of the mercury column in the conductivity tube measured with and without a dip rod, we obtained the following values of cell constant:

Rod Diameter, cm	K, cm^{-1}
None	24.00
0.205	24.00
0.328	23.99
0.404	23.99

The resistance of the mercury column was determined from the slope of the voltage-current curves.

Despite knowing the length L of the conductivity tube to 1% by several methods there is a 4% error in cell constant. We are now in the process of finding its cause and of learning to make and calibrate more accurate cells.

Perhaps a part of this error is due to the fact that the conductivity tubes in our cells are made out of ordinary glass tubing, that may be out of round and consequently not uniform in cross-sectional area. This non-uniformity is probably a major cause of the scattering of the K values. In order to eliminate this geometrical effect, we are fabricating a test cell in which the conductivity tube is made out of precision-bore tubing. We plan to measure the cell constant of this cell by the same techniques used previously.

2.5 Effects Due to Contamination of Glass Surfaces

The pressure chamber has usually been evacuated to remove alcohol and water from the cell surface. This need and the related effects have been briefly checked in order to see whether we had missed any pertinent aspects or data.

An empty cell was dipped in a dry ice alcohol mixture, wrapped with a thin teflon sheet, then mounted inside the pressure chamber. There were appreciable emfs between the cell leads and between the leads and the chamber wall. These emfs ranged from 0.077V to 0.430V with source impedances of the order of 5×10^5 ohms. Some of these electromotive forces decreased slowly with time.

In order to remove the water or alcohol from the surface of the cell, the chamber containing the cell was evacuated with a mechanical pump for 15 minutes. This procedure reduced the spurious emfs by a factor of approximately ten thousand. Subsequent heating to 120°C with the chamber under vacuum did not seem to affect the residual electromotive forces.

3. THERMODYNAMIC ANALYSIS OF SODIUM AMALGAM CONCENTRATION CELLS

3.1 Introduction

Our recent voltages are stable to one part in 10^6. In addition, we have been measuring temperature coefficients over most of the liquid range. We therefore have carried out the following analysis both to see how we can use our experimental data for obtaining other thermodynamic quantities as well as for probing into the sources of the relatively large temperature dependence of E/T.

The equation we derived for the simplest model of the amalgam concentration cell compatible with our conditions includes a higher order term. Under our experimental conditions this term is of the order of 4×10^{-14} volts. From this we must conclude that the relatively large observed temperature coefficients of E/T are due to a failure in one of the assumptions listed in the next paragraph.

3.2 Thermodynamic Analysis

In the following treatment of the sodium amalgam concentration cell, we neglect (a) solubilities in the electrolytic solution of the components of the amalgam electrodes (sodium and mercury); (b) transport of the solvent with that of the ions; (c) parasitic reactions of the solvent with the amalgams, (d) solvation of the components of the amalgam, (e) oxidation of iodide at anode, (f) phase separations in the amalgam electrodes, and (g) the existence of more than one species of sodium in the amalgam.

The basic operation of the cell is the transfer of dN equivalents of sodium from amalgam A', with mole fraction of sodium X', to amalgam A'', with composition X''. The whole system is under a single pressure due to the single electrolytic solution which is at a single temperature. The pressure due to the solution, which is the vapor pressure when the solution is in the liquid state and the pressure of the solution itself when it is in the gaseous state, is always many orders of magnitude greater than the vapor pressures of the amalgams under our range of experimental conditions.

In the following we develop the necessary equations by using two different approaches. First, the increase in the Gibbs function for the system is derived for the passage of current through the system. Second, the system is divided into three subsystems, each electrode being separated from the electrolytic solution by walls that are semi-permeable to Na^+. One subsystem contains the amalgam A', the second the other amalgam A'', and the third the electrolytic solution. Each system is under the same

pressure, p, and temperature, T. Then the increase in the Gibbs function is derived for the same change in state of the system as the first case, i.e., when the transformation was associated with the passage of current.

In an amalgam concentration cell, Na (X' in Hg)/NaI (X_2 in NH_3)/Na (X'' in Hg), the two half cell reactions are

$$Na\ (X')_{Hg} = Na^+\ (X_2)_{NH_3} + e^- \qquad \text{anode} \qquad (1)$$

and

$$Na^+\ (X_2)_{NH_3} + e^- = Na\ (X'')_{Hg} \qquad \text{cathode} \qquad (2)$$

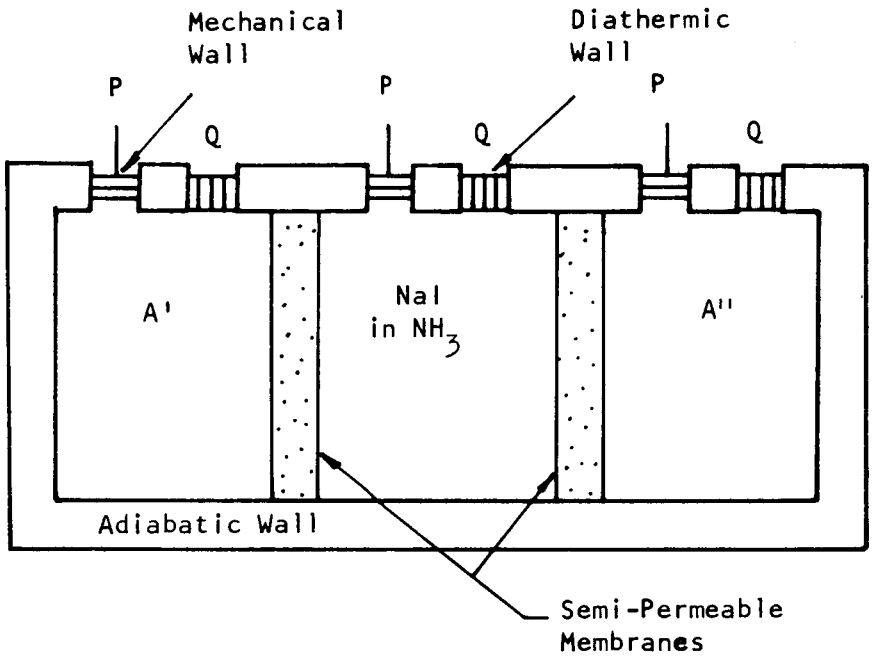
The electrolytic solutions in each half cell are identical (except for the difference in the trace solubilities of the amalgams), hence there is no liquid (or gaseous) junction potential in the cell.

The net process is the sum of the above equations.

$$Na\ (X')_{Hg} = Na\ (X'')_{Hg} \qquad (3)$$

3.2.1 Passage of Current Through the System

Assume that there is a single temperature and a single pressure in the system.



The change in internal energy U of the system is then,

$$dU = Q - W_m - W_e$$

or, if the transformations are carried out reversibly,

$$dU = TdS - pdV - EFdN$$

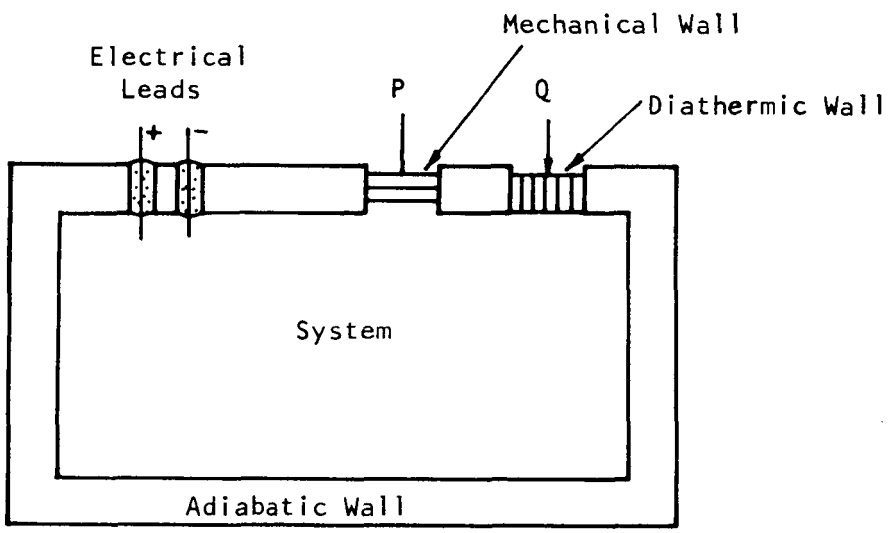
where dN is the number of Faradays of electrons passed across the boundary.

The change in the Gibbs function, $G = U + PV - TS$, is

$$dG = -SdT + Vdp - EFdN \qquad (4)$$

3.2.2 Transport of Na from One Amalgam to the Other at Constant Temperature and Pressure

The same change in state in the system will now be examined by an alternative procedure. Two semi-permeable membranes which are permeable only to Na^+ will be introduced between each amalgam and the electrolytic solution.



By assumptions, and equation (3), the only effect of passage of dN electrons through the system at constant T and p is the transfer of dN moles of sodium from amalgam A' to A'', both amalgams being at T,p. The overall change in state is

$$A_i'(n_1',n_2') + A_i''(n_1'',n_2'') = A_f'(n_1',n_2'-dN) + A_f''(n_1'',n_2''+dN) \quad (5)$$

where n_1' is the number of moles of Hg in A' and n_2' that of Na in A'. The subscripts i and f refer to the initial and final states.

The change in the Gibbs function for the change in state at constant p,T is determined as follows:

(i) Reduce the pressure on amalgam A' at constant T from p to p', and on A'' from p to p'', the p' and p'' being the vapor pressures of sodium in the amalgams.

$$\Delta G = \int_{p}^{p'} V_i' dp = -\int_{p'}^{p} V_i' dp$$

and

$$\Delta G = -\int_{p''}^{p} V_i'' dp$$

(ii) Reversibly transfer dN moles of Na from A' to A''

$$\Delta G = \Delta \mu dN$$

where μ' is the chemical potential of sodium in A'. This equation is simply derivable by vaporization of dN moles of Na from A' at constant p', for which $\Delta G = 0$, expansion of this vapor at constant temperature, for which $\Delta G = \int V dp = dN\ RT \ln(p''/p')$ for a perfect gas, and condensation into A'' at constant p''.

(iii) Recompress the two amalgams from p' and p'' to p.

$$\Delta G = \int_{p'}^{p} V_f' dp$$

and

$$\Delta G = \int_{p''}^{p} V_f'' dp$$

ΔG for the overall process is:

$$\Delta G = \Delta\mu \cdot dN + \int_{p'}^{p} (V_f' - V_i')dp + \int_{p''}^{p} (V_f'' - V_i'')dp \qquad (6)$$

The magnitudes of the last two terms will now be evaluated using a number of reasonable simplifying assumptions. The compressibility of the amalgams is negligible.

The volumes are treated as additive functions, i.e.,

$$V = n_1V_{10} + n_2V_{20}$$

where molar volumes of the pure liquids V_{10}, V_{20} are substituted for the partial molar volumes. The subscripts 1, 2, refer to the solvent Hg, and solute, Na, respectively, and 0 to the pure liquid. Then

$$\Delta V' = V_f' - V_i' = (n_1'V_{10} + n_2V_{20})_f - (n_1'V_{10} + n_2V_{20})_i$$

$n_{1f}' - n_{1i}'$ is zero since no mercury has been transported. Hence

$$\Delta V' = (n_{2f}' - n_{2i}')V_{20} = \Delta n_2' \cdot V_{20} = -dN \cdot V_{20}$$

Similarly,

$$\Delta V'' = dN \cdot V_{20}$$

$$\Delta G = \Delta\mu \cdot dN - dN \cdot V_{20} \int_{p'}^{p} dp + dN \cdot V_{20} \int_{p''}^{p} dp$$

$$= \Delta\mu \cdot dN + V_{20}(p' - p'')dN$$

Assuming that $p' = P_oX_2'$, where P_o is the vapor pressure of pure sodium,

$$\Delta G = \Delta\mu \cdot dN + V_{20}P_o(X_2' - X_2'')dN \qquad (7)$$

3.2.3 The Voltage as a Function of Chemical Potential at Constant T,p

The voltage is measured at constant T,p. Hence we drop the variations in T,p in equation (4), obtaining

$$dG = -EFdN \qquad (T,p \text{ constant}) \tag{8}$$

Equation (7), which was derived at constant T,p, states that

$$\Delta G = \Delta u \cdot dN + V_{20}P_o(X_2' - X_2'')dN.$$

Since these changes in Gibbs function are for the same change in state, they are equal, and therefore

$$-EF = \Delta u + V_{20}P_o(X_2' - X_2''). \tag{9}$$

This expression differs from the usual expression for the emf in the inclusion of the last term, whose magnitude we shall now estimate. For a value of P_o of Na at 400^oK of 1.3×10^{-6} torr, the last term is of the order of 1×10^{-9} cal/mole or 4×10^{-14} volts. Since P_o is an exponential function of temperature over the liquid range, the magnitude of this term decreases rapidly with decreasing temperatures. Hence, for the assumptions made regarding the cell, equation (9) reduces to

$$-EF = \Delta u, \tag{10}$$

the usual equation for the amalgam concentration cell.

3.2.4 Temperature Coefficient of the Voltage

The relationship of the voltage to chemical potential, equation (10), was derived at constant T,p. We shall deduce the temperature coefficient of the voltage from equation (10) by two equivalent methods. The direct method, that of differentiating equation (10) with respect to T, may appear to be unsatisfactory to some of the readers, since we are differentiating with respect to T, an equation which was derived at constant T. Therefore, we follow it with an alternative differentiation that is conceptually satisfactory although this process is completely equivalent to direct differentiation. Here, we write down the expressions for E at two temperatures, T_a and T_b since equation (10) is valid at any constant temperature. Then we take the limit as $(T_b - T_a) \rightarrow 0$.

We shall now carry out the direct differentiation of equation (10). For convenience we rewrite equation (10) in terms of E/T as follows:

$$\frac{E}{T} = -\frac{R}{F}\ln\frac{a''}{a'} \tag{11}$$

$$= -\frac{R}{F}\ln\frac{X_2''}{X_2'} - \frac{R}{F}\ln\frac{\gamma''(T)}{\gamma'(T)} \tag{12}$$

Differentiating, we obtain

$$\frac{\partial\, E/T}{\partial\, T} = -\frac{R}{F}\,\frac{\gamma'}{\gamma''}\,\frac{\partial(\gamma''/\gamma')}{\partial\, T} \tag{13}$$

Thus, if our assumptions are correct, the temperature dependence of E/T arises only through the temperature dependence of the ratio of the activity coefficients of sodium in the two amalgams. Hence, the temperature coefficient of E/T should be very small - in contrast to our data.

In this connection, we have been reviewing the literature on the state of sodium in amalgams. Sodium forms compounds rather than simple solutions. We plan to discuss these data in a future progress report.

We shall now use the second approach to derive dE/dT.

Let $\Delta T = T_b - T_a$

$$\Delta E = E_b - E_a$$

$$\Delta a' = a'_b - a'_a$$

Then,

$$\Delta E = RT_b \ln \left(\frac{a''}{a'}\right)_b - RT_a \ln \left(\frac{a''}{a'}\right)_a$$

$$= R(T_a + \Delta T) \ln \frac{a''_a + \Delta a''}{a'_a + \Delta a'} - RT_a \ln \frac{a''_a}{a'_a}$$

$$= RT_a \left[\ln \frac{a''_a + \Delta a''}{a''_a} - \ln \frac{a'_a + \Delta a'}{a'_a}\right] + R\Delta T \ln \frac{a''_a + \Delta a''}{a'_a + \Delta a'}$$

Expanding $\ln (1 + \epsilon)$ in a power series,

$$\Delta E = RT_a \left[\frac{\Delta a''}{a''_a} - \frac{\Delta a'}{a'_a} + O(\Delta a''^2)\right] + R\Delta T \ln \frac{a''_a + \Delta a''}{a'_a + \Delta a'}$$

Where $O(\Delta a''^2)$ indicates the order of the remainder of the power series,

$$\lim_{\Delta T \to 0} \frac{\Delta E}{\Delta T} = RT \left[\frac{1}{a''} \frac{da''}{dT} - \frac{1}{a'} \frac{da'}{dT}\right] + R \ln \frac{a''}{a'}$$

or

$$\frac{dE}{dT} = RT \frac{d \ln (a''/a')}{dT} + R \ln (a''/a')$$

This result is identical with that obtained by direct differentiation as used in the first approach, namely,

$$\frac{dE}{dT} = \frac{d}{dT} \left[RT \ln (a''/a')\right]$$

3.3 Symbols

A'	Amalgam A', which contains n_1' moles of Hg, n_2' moles of Na
A''	Amalgam A''
a'	Activity of Na in amalgam A'
E	Voltage of the cell
F	Faraday's constant
G	The Gibbs function, where $G = U + pV - TS$
n_2'	Number of moles of Na in amalgam A'
dN	The number of Faradays of electricity passed through the cell
p	Pressure on the amalgams
P'	Vapor pressure of Na in amalgam A'
T	Temperature
V'	Volume of amalgam A'
V_{10}, V_{20}	Molar volumes of pure liquid Hg, Na respectively
X'	Mole fraction of Na in amalgam A'
γ'	Activity coefficient of Na in amalgam A'
μ'	Chemical potential of Na in amalgam A'

Superscripts

'	Amalgam A'
''	Amalgam A''

Subscripts

1	Hg
2	Na
i	Initial state at a constant temperature
f	Final state at a constant temperature
a	Change in state at temperature a
b	Change in state at temperature b

4. SUMMARY

During this period we have stressed stability and internal consistency of the data.

On cell 56, the internal consistency of four pairs of electrodes was $\pm$ 0.5 millivolts from 21.3 to 71.7°C. This is a little better than the accuracy of the Hewlett-Packard 412A, VTVM, used for this set of measurements. Emfs of four pairs of electrodes were measured as a function of temperature and were linear with respect to T. E/T for three electrode pairs had a large positive temperature coefficient. We have not yet determined unambiguously the cause of this large temperature coefficient. The fourth pair had small values of E/T and a small temperature coefficient.

Cell 57 was the first cell which was stable when the electrolyte was in the gaseous state.

In cell 58, no salt was added. We found that enough sodium amide was produced by reaction of sodium with ammonia to provide electrolyte. The cell was run from 25 to 150°C with the highest temperature approximately 15 degrees above the critical point of the electrolytic solution. We can tentatively conclude from the data that the equilibrium emfs of these amalgam concentration cells are independent of the state of the electrolytic solutions.

With cell 64 we achieved a two order of magnitude stability and uniformity improvement. This was due to improved bomb shielding and the use of ultrasonic agitation which provided more uniform electrodes. No instability was detectable from 13 to 50°C; that is, the short term stability was 0.1 microvolts. Comparison of the six electrode pairs of four electrodes gave an

internal consistency of $\pm$ 7 microvolts (an improvement of two orders of magnitude over our best earlier results) at an average emf of about 100 millivolts. At 56°C the cell is still giving good results and measurements will continue into the next quarter.

Large changes in the cell emf are noted for cells 58 and 64 at 45° and 22°C respectively. These changes reflect state or composition changes in one electrode with respect to the other electrodes. In cell 64 pairs AC, AB, AD show changes. There was a change in state in electrode A at 24°C. This state change may be either physical or chemical.

The characteristics of the conductivity cells are being redetermined. We have reached the limits of accuracy achievable with ordinary glass tubing. Cells are being fabricated using precision bore tubing.

No chemical analyses were run this period. The first cell broke and cell 64 is being retained in situ for further studies. However, very accurate ratios of sodium compositions in the various amalgams are determinable from the emfs.

In this period, we have produced highly stable cells that are internally consistent and have tentatibely shown that the equilibrium emfs are independent of whether the electrolytic solution is in the liquid or gaseous state.

5. PLANS FOR NEXT QUARTER

Measurements of the emfs of cell 64 will be continued. When we reach the limit of the pressurization system the cell will be removed and stored. We will then rebuild the high pressure bomb, replacing several leaking valves and seals as well as the cracked ceramic liner tube. This cleaning and rebuilding of the high pressure bomb will enable us to run overnight without a pump or external gas reservoir.

The determination of the factors affecting the cell constant will continue. In particular we plan to fabricate a special cell using precision bore tubing for use in these studies.

The vacuum system for the preparation of the samples has been in use for a long time. Although the system has been cleaned after each run it is not pumping down satisfactorily. The system will therefore be overhauled.

An adequate number of sodium amalgam concentration cells are on hand. A new series of cells will be prepared with Pb, Cd, Zn and Tl amalgam-insoluble salt electrodes.

The thermodynamic analyses will be extended. They are expected to produce additional information on the amalgam concentration cell.