FOURTH QUARTERLY REPORT

21 May 1965 - 20 August 1965

GASEOUS ELECTROLYTES FOR BATTERIES AND FUEL CELLS

by

S. Naiditch, Principal Investigator

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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1.0 ABSTRACT

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During the period of this report, cells 52 through 58 and 60 were prepared for measurements. Techniques for the preparation of these cells were varied in order to determine the causes of disturbing effects and to test the performance of cells with different electrolytes.

With the exception of cell 53, the electrolytic salt was introduced into a cell only after it was baked out under vacuum. Sodium iodide dissolved in liquid ammonia was used as the electrolytic solution. An attempt was made to pour the salt in air into cell 53 as a dry powder. When this attempt failed, the salt was dissolved in water. The aqueous solution was then transferred into the cell. Subsequently the water was removed by baking under vacuum. Because of the danger of introducing additional contaminants into the cell with this method, and because it did not provide improved performance, its use was discontinued.

Leads in cells 56, 57 and 58 were platinized in order to test whether some of the disturbing effects which have been encountered in the past can be eliminated by platinizing the surface of the leads in contact with the sodium amalgam. Cell 58 was prepared without adding a salt to the liquid ammonia. Sodium amide, formed by the reaction of sodium with the ammonia, was used as the electrolyte.

With cells 58 and 60 an attempt was made to pump off the hydrogen evolved during the decomposition of part of the sodium ammonia solution in the early stage of preparing the cell. This was partially achieved by pumping off the ammonia and hydrogen and refilling the cell with new ammonia.

Cell 60 is a quartz cell. This cell was built in order to determine the application of quartz as a cell material.

Cells 52, 53 and 54 were tested. Cell 55 ruptured prior to testing. Cells 56, 57, 58 and 60 are in storage at 0°C.

The emf of cell 52 was measured from -20.5° to 151°C. In the course of the the measurements this cell was recycled from below room temperature to above 100°C four times, twice reaching 150°C, which is well above the critical temperature (about 133°C) of the electrolytic solution. Chronopotentiometric measurements were performed at -17 and -26°C. The data seem to indicate that the reduction,

$$Na^{+}(NH_3) + e^{-}(Hg) = Na(Hg),$$

is diffusion controlled while the oxidation,

$$Na(Hg) = Na^{+}(NH_3) + e^{-}(hg)$$

is not diffusion controlled under our experimental conditions.

In cell 53, the conductivity of the electrolytic solution was measured from 19.0 to 154.0°C, i.e., about 20° above the critical point of the solution. Chronopotentiograms were recorded at room temperature.

With cell 54, stable emf data were obtained from 25.2 to 66.7°C. The conductivity of the electrolyte was measured from 25.2 to 63.2°C.

Author

2.0 EXPERIMENTAL

2.1 Cell Preparation

The cells for the studies of gaseous electrolytic solutions consist of four half cells which are connected by three cylindrical conductivity tubes. Above the four half cells is an expansion region followed by a short length of capillary tubing for sealing off the cells. Near one end of the capillary is a freezing cup to ease the seal-off operation. Fig. 1 shows a diagram of the cell. Unless otherwise specified, the filling procedure for each cell (Nos. 52-58 and 60) is as follows.

Prior to sealing the cells to the vacuum system, approximately equal amounts of mercury are poured into each half cell. In addition, a measured amount of NaI powder and a sodium capsule are placed in the vacuum system as shown in Fig. 5 of our third quarterly progress report. After bakeout under vacuum, the breakseal of the sodium capsule is opened and the sodium is distilled on the wall of the glass tubing above the cells. Pre-purified ammonia is condensed on the walls above the cell. This liquid dissolves the sodium and sodium iodide, then drips through the capillary into the cell. During the filling process, the upper mercury electrodes are exposed to more sodium than the lower ones, and, therefore, they dissolve more sodium.

The electrodes of the cells made by this process are sodium amalgams with different concentrations of sodium, hence these cells are concentration cells. The amalgams are formed by the diffusion of metallic sodium from the sodium ammonia solution into the mercury pool at each electrode. The diffusion process proceeds until no metallic sodium is left in the solution. At this stage, the electrolytes in solution are the sodium iodide we added and

the sodium amide formed by the decomposition of the sodium ammonia solution. It is to be noted that the decomposition and amalgamation processes compete for the metallic sodium placed in the cell.

During the period of this report cells 52 through 58 and 60 were built and prepared for the measurements of emf, conductivity and chronopotentiograms. Cells with specific features are described below in greater detail.

In order to control more precisely the amount of electrolyte in a cell, NaI salt was introduced differently into cell 53 than in the other cells. Two methods were tried. At first, an attempt was made to tap a measured quantity of NaI powder into the cell. When this attempt failed, the salt was dissolved in water and the solution was poured into the cell. Subsequently, the water was removed by baking the cell under vacuum. After the bakeout, sodium-ammonia solution was introduced into the cell as before.

This method has some serious disadvantages. In spite of the fact that the system was baked out under vacuum, there is a possibility that some water might remain in the cell. Any remaining water would react with metallic sodium dissolved in the ammonia, thus producing sodium hydroxide and hydrogen. Hence, this method of preparing the cells may introduce more contaminants than the original method. Because of the serious effects due to the presence of contaminants, this technique was not used for the preparation of any other cell.

Cell 55 was prepared with a relatively large amount of sodium dissolved in liquid ammonia, in order to produce high sodium concentrations in the amalgams.

All the four leads in cells 56 and 57 and two of the four leads in cell 58 were platinized. These cells have been prep -ed in order to test whether some of the disturbing effects which have been encountered in the past can be eliminated by platinizing the surfaces of the tungsten leads in contact with the sodium amalgam because there is a possibility that a side reaction might take place at the tungsten surface. It is to be noted that cell 58 permits testing of the performance of platinized and unplatinized leads within the same cell.

As mentioned in the last quarterly report, one possibility for mechanical failure of some of the recent cells is rupture due to excess hydrogen pressure. A foreign material such as mercury may act as a catalyst for the reaction,

$$Na(NH_3) + NH_3 = NaNH_2(NH_3) + 1/2\ H_2 \uparrow$$

which generates hydrogen. In order to reduce the probability of cell rupture through this possible cause, an attempt was made to pump off the hydrogen from cell 58 after the extraction of sodium from the ammonia. The procedure used is as follows.

The cell was filled and subsequently held at about -45°C for a period of two hours. The extraction of sodium was aided by concentrating the ammonia solution through evaporation. However, the mercury was frozen and sodium did not transfer into the frozen mercury. In order to speed up the process, the temperature of the system was raised to 30°C. The ammonia evaporated, and some of the sodium was amalgamated. A portion of the sodium was not in contact with the mercury, and, therefore, the amalgamation was not complete. When the cell was refilled with ammonia, the liquid

turned into the characteristic blue color of a metal-ammonia solution. However, the color was lighter than that of the original solution. One can assume then that an appreciable part of the sodium was amalgamated during the warming period.

It should be mentioned that the hydrogen evolution in cells of low sodium concentration has been sufficiently small so that they do not represent any problem with regard to cell rupture. Generally, difficulties have been encountered only with cells whose initial sodium concentration in ammonia was high. These cells ruptured during storage at $0^{o}C$, presumably due to the higher pressure of hydrogen evolved during the extraction time (about 24 hours).

The other special features of cell 58 are that it was prepared without adding salt to the ammonia (sodium amide produced by the reaction of sodium with ammonia is used as the electrolyte), and that the two leads in contact with electrodes B and C are platinized. However, the leads for the electrodes A and D are not platinized. Cell 58 is now aging in storage at $0^{o}C$.

Cell 60 is a quartz cell. This cell has been built for the purpose of investigating whether any unusual problems arise in the fabrication and handling of quartz cells. If promising results are obtained, it is planned to build and evaluate quartz cells with side arms for introducing controlled amounts of electrolyte into each half cell. The use of quartz should avoid the earlier problem of introducing strains into the side arms of the cell during the sealing operation. This is an important advantage because these strains cannot be sufficiently annealed once the cell is partially filled.

Besides the usual problems of working with quartz, difficulties with the leads for the electrodes were encountered. An attempt was made to use the standard G.E. GSC-3 glass for sealing the tungsten leads to quartz. Tungsten electrodes with diameters larger than 0.040 inch could not be sealed satisfactorily and even seals with 0.040 inch tungsten leads were fragile and prone to leaks and cracks. It was necessary to reduce the diameter of the tungsten leads from 0.080 to 0.040 inch although the greater mechanical strength of the 0.080 inch leads eliminated the previous problem of lead breakage. During the fabrication of cell 60 each lead broke at least once.

Additional difficulties with the quartz cell arose from the cleaning procedure. The standard cleaning procedure developed in this laboratory was a cleaner prepared of 5% HF, 33% HNO_3, 60% water and 2% alconox. This cleaner could not be used as hydrofluoric acid, even at low concentration, was found to rapidly attack the GSC-3 glass seal, thus causing leaks in the cell. It is unfortunate that the above mentioned cleaner could not be used since we have found it to be the most effective cleaner for the removal of these surface contaminants which lead to the decomposition of sodium ammonia solutions.

Cell 60 was filled with a sodium and sodium iodide ammoniacal solution. Hydrogen produced by decomposition was removed prior to sealoff using the method applied to cell 58. During this procedure, ammonia was removed once to pump out the hydrogen. After some time the cell was filled again with ammonia. In this period the metallic sodium was amalgamated.

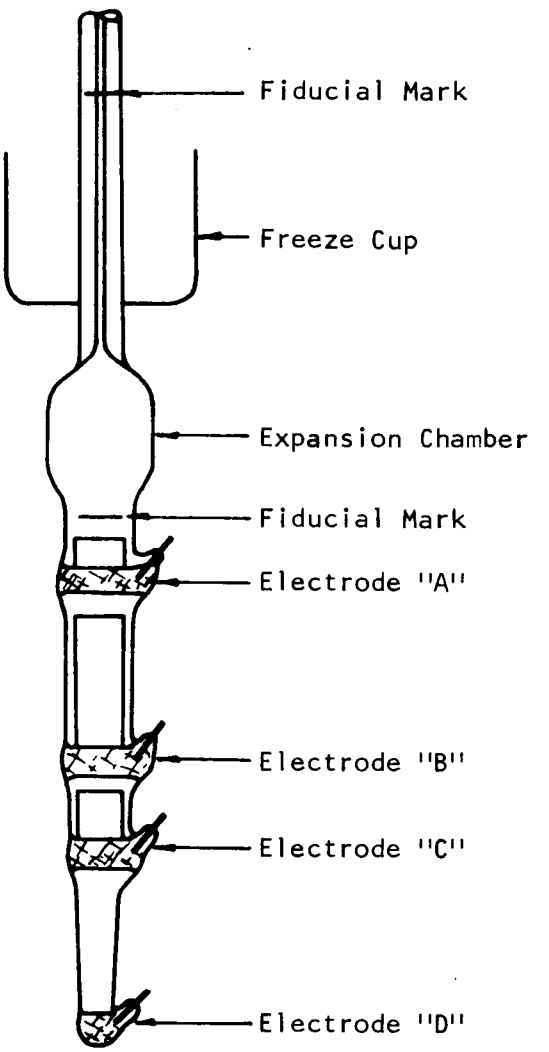


Figure 1. Amalgam Concentration Cell with Electrode Amalgams in Place.

2.2 Instrumentation

Fig. 2 shows a schematic drawing of the circuit used for the measurements of emf and conductivity of the cells. For emf measurements the switch S in Fig. 2 is open. Usually, the electrodes E and C of the cell are used for emf measurements as a function of temperature. Electrical loading of the electrodes is carefully avoided by using only instruments with high input impedance for the measurements. If the emf values are sufficiently stable, the Calibration Standards potentiometric voltmeter (model 110B) is used. When the input voltage is accurately balanced by the potentiometer, the input impedance of this instrument is approximately 10^9 ohms. The accuracy of this instrument is 0.02%, and it is provided with a five digit readout. If for reason of fluctuation the emf of the cells cannot be balanced with sufficient accuracy, a Hewlett Packard millivoltmeter (Model 412A) is used to measure this emf. Although this meter has a lower input impedance (2×10^8 ohms), its input impedance is fixed and is not affected by fluctuations of the emf.

In the recording of chronopotentiograms, the electrodes A and D are used as working electrodes and one of the electrodes E or C as the reference electrode. A block diagram of the circuit is shown in Fig. 3.

When the switch S is closed, a constant current passes through the cell. The variation of the potential difference is measured by the Hewlett Packard vacuum tube voltmeter 412A. A Bausch and Lomb recorder (V.O.M.-5) records the output voltage of the meter. The use of the vacuum tube voltmeter in front of the recorder has the advantage of increasing the input impedance of the measuring system.

Difficulties were encountered when an attempt was made to measure the conductivity and chronopotentiograms simultaneously. It was observed that the voltage between electrodes B and C was altered when the recorder (B and L V.O.M.-5) was connected to electrodes D and C. This apparent instrument interaction is found to be caused by a change in resistance between electrodes D and C, which in turn is due to the fact that the input impedance of the recorder represents a shunt resistor for the cell. The same effect could be produced by replacing the recorder by a resistor of the same size as the input impedance of the recorder. Although it is desirable to measure the conductivity and chronopotentiograms simultaneously, the measurements are now performed separately in order to avoid this effect and to avoid passing current through the reference electrode.

The two circuits shown in Figs. 2 and 3 were combined in one single circuit by means of a ten-pole, ten-position switch in order to facilitate the different measurements. The switch (Daven Type 527-DE) has solid silver contacts and double wipers, giving contact resistance less than 4 milliohm. Fig. 4 shows a block diagram of the circuit.

Six positions (first through fifth and seventh) of the switch are used to measure the six pairs of emf's of the four half-cells. Two positions (sixth and eighth) are prepared for either conductivity or chronopotentiometric measurements. At position six the direction of applied current between electrodes A and D is opposite to that at position 8. In the ninth position, a voltage is applied between one working electrode and the wall of the pressure chamber to check the leakage resistance of the leads going into the chamber. Position ten is used for a fast test of the instrumentation. In this position

the instruments are connected to a network of batteries and resistors which simulate the cell. The functions of the whole circuit are summarized in Table 1.

The cell temperature is determined by measuring the gas temperature in the pressure chamber with a thermocouple. A Leeds and Northrup potentiometer (Model K-3) is used to measure the thermocouple voltage.

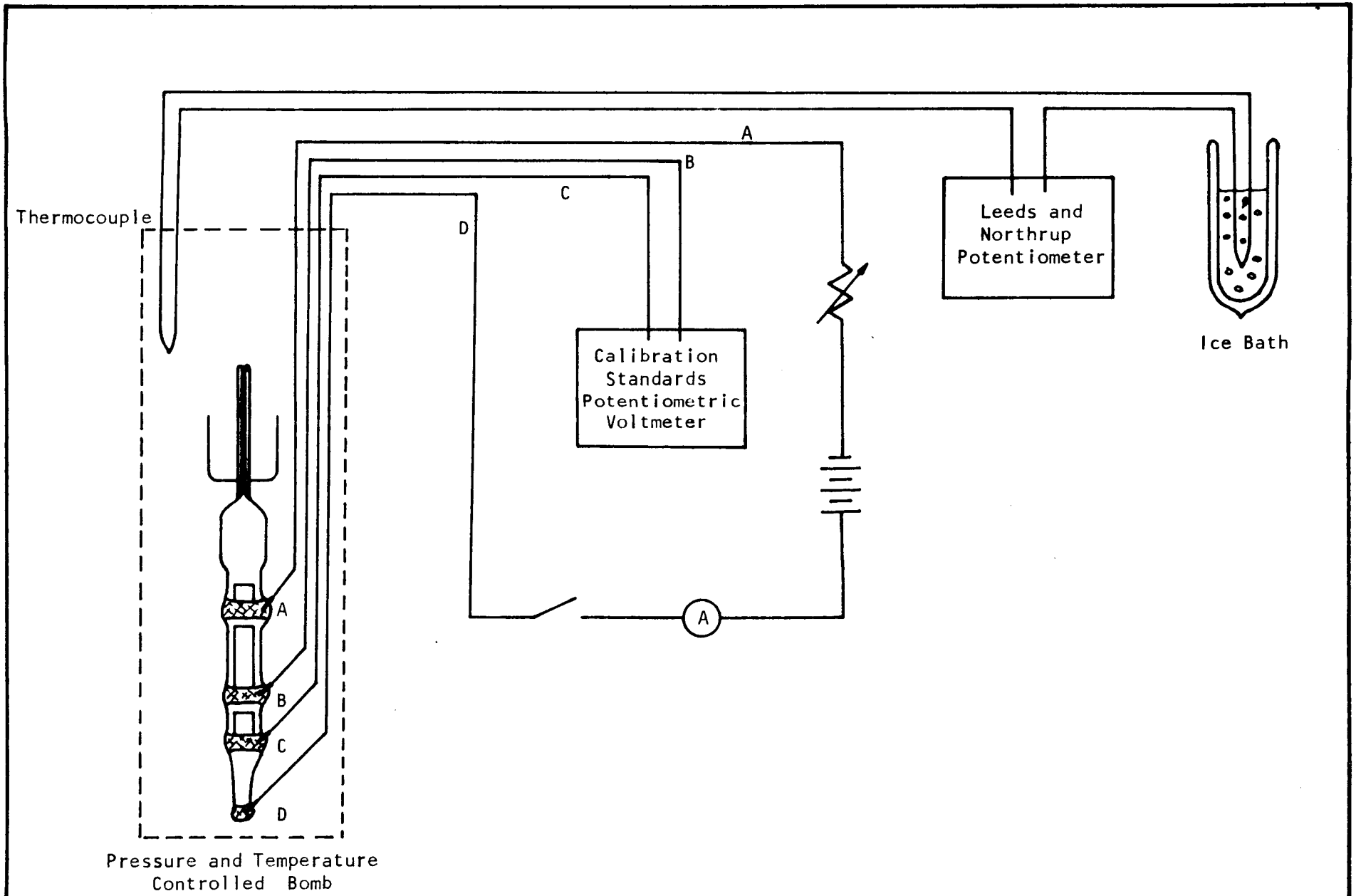


Figure 2. Instrumentation for EMF and Conductivity Measurements

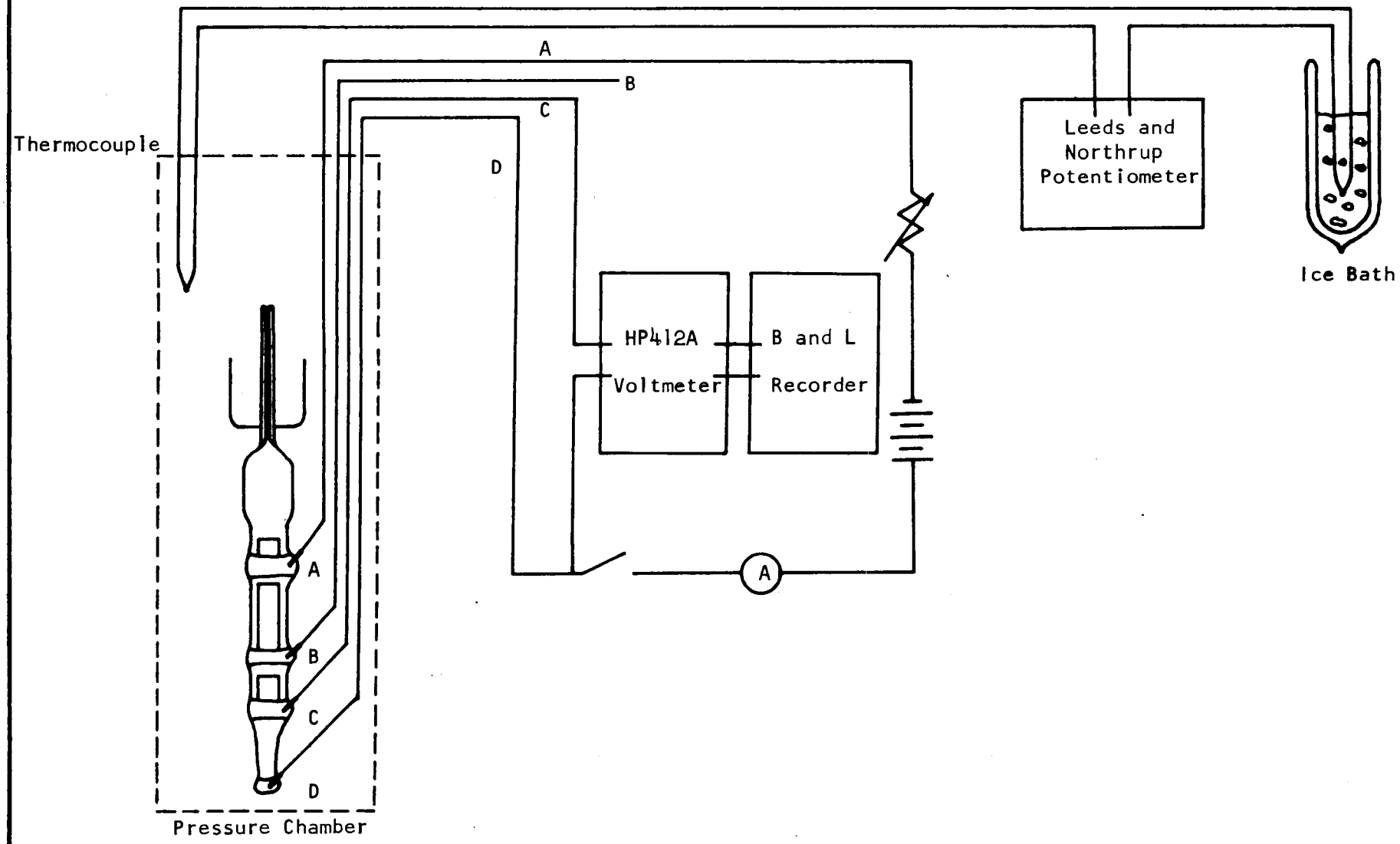


Figure 3. Instrumentation for the Measurements of Potentiograms

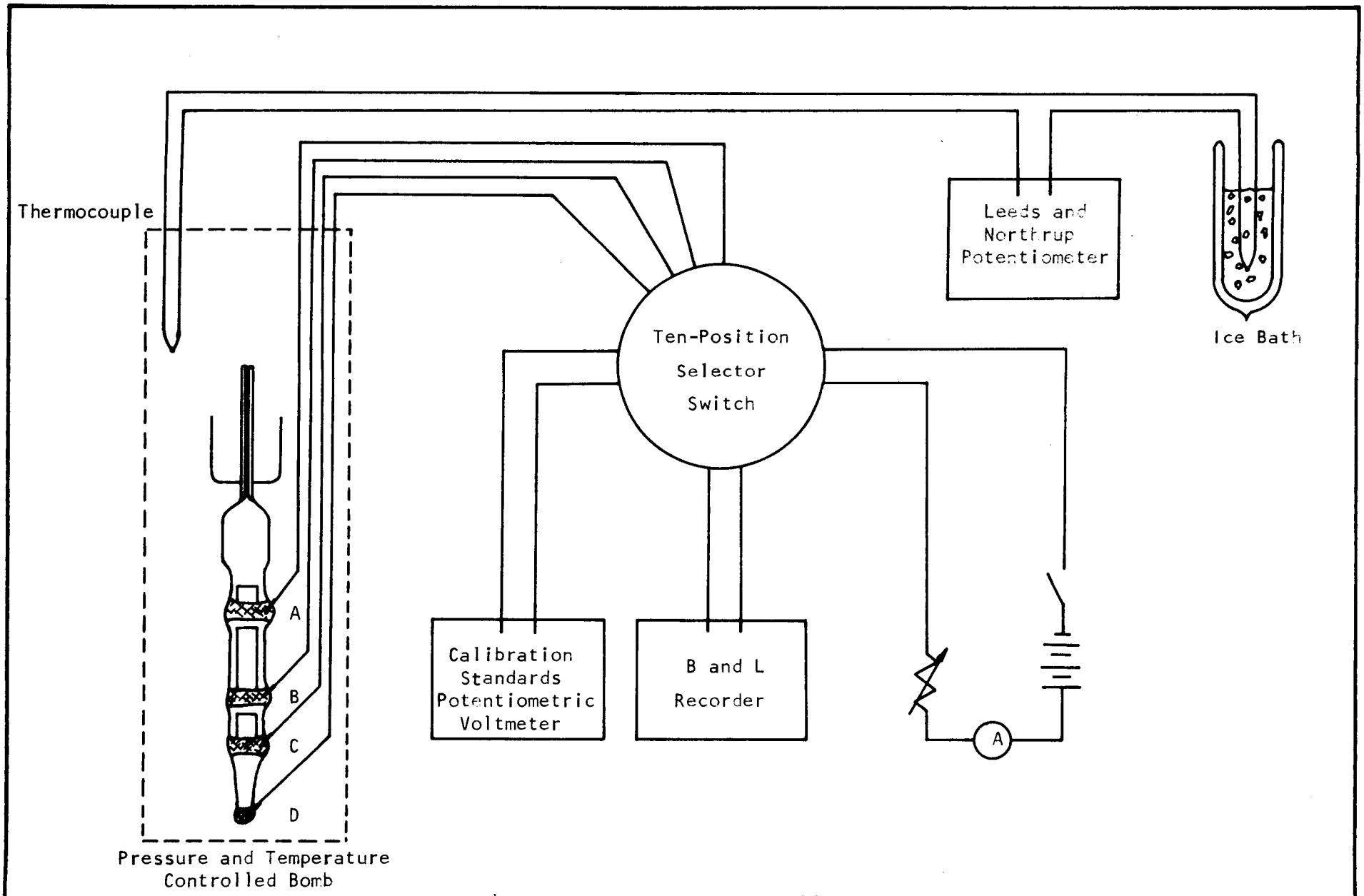


Figure 4. Instrumentation for Combined Measurements of EMF, Conductivity, and Potentiograms

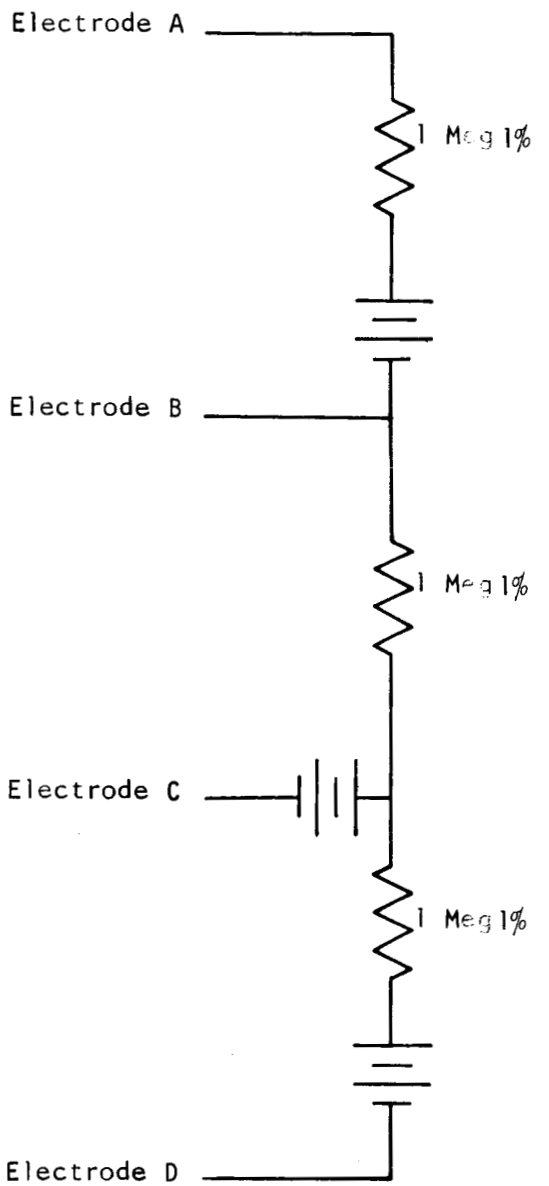


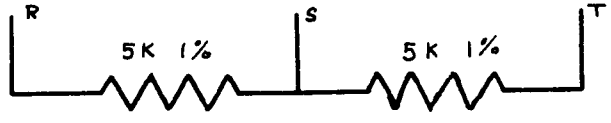
Figure 5. Circuit of Cell Simulator

Table 1. Selector Switch[1] Layout

COMMON POSITION		1	2	3	4	5	6	7	8	9[3]	10[2]
Calibration Standards Potentiometer	+	Cell D	Cell D	Cell D	Cell A	Cell A	Cell B	Cell B	Cell C		Inst.Test R
	-	Cell A	Cell C	Cell B	Cell B	Cell C	Cell C	Cell C	Cell B		Inst.Test S
Micro Amp Power Supply and Meter	+						Cell A		Cell D	Cell A	Inst.Test R
	-						Cell D		Cell A	Bomb Ground	Inst.Test T
B and L VOM 5 Recorder	+						Cell C		Cell D		Inst.Test S
	-						Cell D		Cell C		Inst.Test T

NOTES: 1. The switch is a 10-pole, 10-position switch with low resistance, non-shorting wipers on ceramic wafers.

2. Using the micro amp power supply position 10 provides a check of instrument and power supply accuracy. The outputs of the test circuit below are 50 MV on both the voltmeter and recorder for a 10 μAmp current.



3. A current from A to Ground indicates one of the leads is grounded.

2.3 Results of the Measurements

During the period of this report cells 52, 53 and 54 were tested. The results are discussed below.

2.3.1 Cell 52

During the test of cell 52, it was noted that the working electrode A was solid (or a very stiff liquid). All six combinations of electrodes gave readings with a slight drift towards higher values. In the course of the experiment, this cell was recycled from below room temperature to above 100°C four times, twice reaching 150°C, which is well above the critical temperature (about 133 to 140°C) of the electrolytic solution.

The measured emf values of cell 52 are compiled in Table 2, and the emf values between electrodes F and C are plotted in Fig. 6 as function of temperature. It is seen that over the temperature range of 30° to 100°C, the temperature dependence of the emf values is approximately linear. Above 110°C, the emf values decrease rapidly. This behavior could not be due to the presence of bubbles, since the effect persists above the critical temperature. Because the data drop almost linearly with increasing temperature, an alternative process may be assumed as responsible for causing the drop-off. For example, if the internal resistance of the cell, i.e., resistance of the electrolytic solution, becomes the same order of magnitude as the impedance of the measuring instrument, then the observed emf will start to drop off. Thus, an increase in the resistance of the electrochemical cell (as in Fig. 6) is a possible explanation for the observed behavior at high temperatures.

Plots of emf, measured between one working electrode A (solid amalgam) and a reference electrode C, are shown in Fig. 7. Prior to this measurement, appreciable current had passed through the working electrode D. However, a period of several days had passed before the emf measurements were performed. The three curves of Fig. 7 represent three different sets of measurements taken over a two-day period. Although the values of the emf did not reproduce accurately, it seems that the trend of the measurements was reproducible. Between 40° and $80^{\circ}C$ the emf values of all three curves level off; above this, the emf values rise rapidly. This could be due to a phase separation in the solid amalgam electrode A.

Chronopotentiometric measurements were performed on cell 52 between the electrodes C and D. Electrode D was used as the working electrode, and C was used as the reference electrode. A chronopotentiogram obtained at a cell current of 6 microamperes and a cell temperature of $-17^{\circ}C$ is shown in Fig. 8. Another one obtained at a cell current of 1.4 microamperes and a cell temperature of $-26^{\circ}C$ is shown in Fig. 9. Since the surface area of the working electrode is about 0.8 cm^2, the approximate current densities at its surface were 7.5 and 1.8 microamperes per cm^2, respectively.

The chronopotentiogram in Fig. 8 shows a short plateau. This plateau, which occurs when there is a reduction process taking place at the working electrode, indicates the depletion of some electrode species near the electrode surface. Fig. 9 shows a similar plateau at the reduction phase of the chronopotentiogram. No similar plateau can be seen in the oxidation phase.

The electrode processes corresponding to the reduction and oxidation reactions are

Plots of emf, measured between one working electrode A (solid amalgam) and a reference electrode C, are shown in Fig. 7. Prior to this measurement, appreciable current had passed through the working electrode D. However, a period of several days had passed before the emf measurements were performed. The three curves of Fig. 7 represent three different sets of measurements taken over a two-day period. Although the values of the emf did not reproduce accurately, it seems that the trend of the measurements was reproducible. Between 40° and $80^{\circ}C$ the emf values of all three curves level off; above this, the emf values rise rapidly. This could be due to a phase separation in the solid amalgam electrode A.

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The electrode processes corresponding to the reduction and oxidation reactions are

$$Na^+(NH_3) + e^-(Hg) = Na(Hg)$$

and

$$Na(Hg) = Na^+(NH_3) + e^-(Hg),$$

respectively. Under the experimental conditions described above, the reduction process is diffusion controlled while the oxidation process is not diffusion controlled.

2.3.2 Cell 53

Cell 53 was used for conductivity measurements and for chronopotentiometric studies. The conductivity of the electrolytic solution was measured above its critical temperature. The results of the measurements are summarized in Table 3, and plotted in Fig. 10. The emf data for this cell were not recorded because the emf did not return to their original values after current passed through the cell.

Two chronopotentiograms obtained with cell 53 are shown in Figs. 11 and 12. The measurements were performed at room temperature (27^oC) and at cell currents (between electrode A and D) of 21 and 56 microamperes, respectively. The corresponding current densities at the electrodes amount to 26 microamp/cm^2 and 70 microamp/cm^2. The chronopotentiogram of Fig. 11 corresponds to oxidation at the surface of the working electrode, and the one in Fig. 12 to reduction at this same surface.

2.3.3 Cell 54

The measurements of cell 54 yielded stable emf and conductivity data for the temperature range from 26° to 57^oC. The emf, the ratio of emf to

absolute temperature, E/T, and the conductivities, are summarized in Table 4 and plotted in Figs. 13, 14 and 15 respectively.

Fig. 14 shows that the ratio E/T increases with increasing temperature. This trend is different from that shown by the previously reported measurements of cell 51.

The conductivity data of cell 54 are plotted in Fig. 15 and fitted with the usual parabolic σ - T curve.

2.3.4 Cells 55-58 and 60

Cells 56-58 and 60 are now in storage at $0^{o}C$. Cell 55 ruptured during storage.

A summary of the special features of the cells and the type of data obtained on cells 52-54 are presented in Table 5.

Figure 6. EMF Data for Cell 52 as a Function of Temperature.

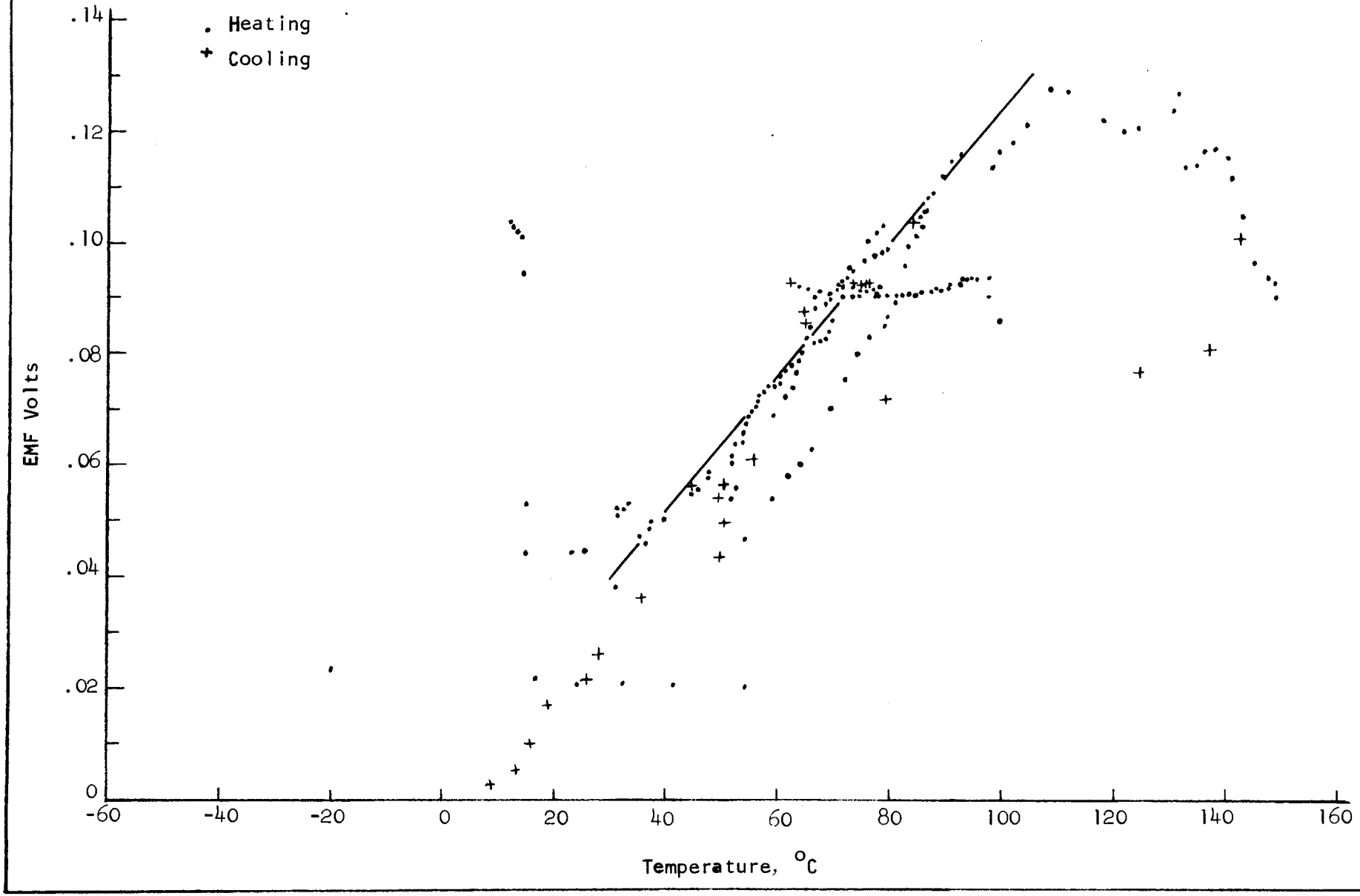


Figure 7. EMF Data for Cell 52 as a Function of Temperature. The EMF between the top working electrode (solid amalgam) and the bottom reference electrode is shown for three runs.

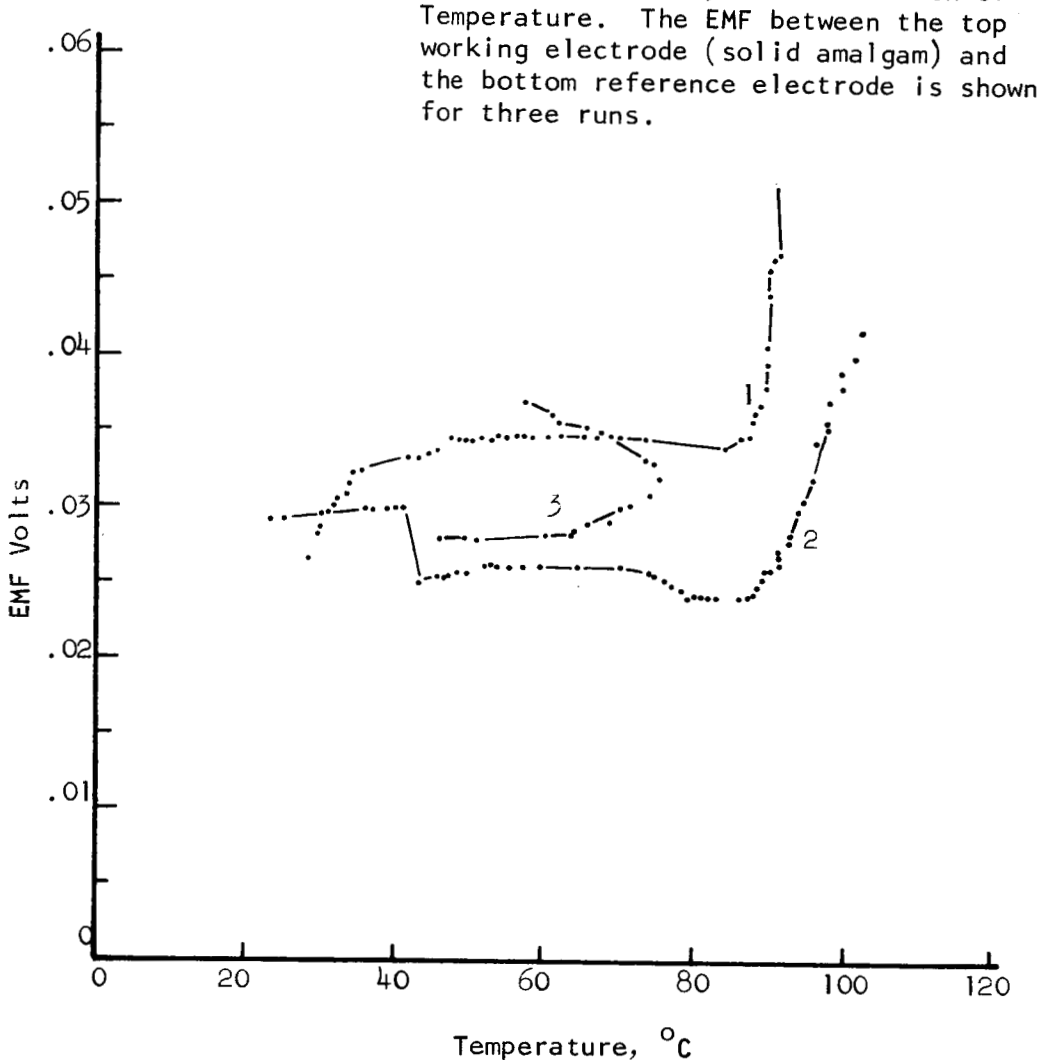


Figure 8. Chronopotentiogram for Cell 52. EMF of the working electrode at which reduction is taking place with respect to a reference electrode is recorded as a function of time.

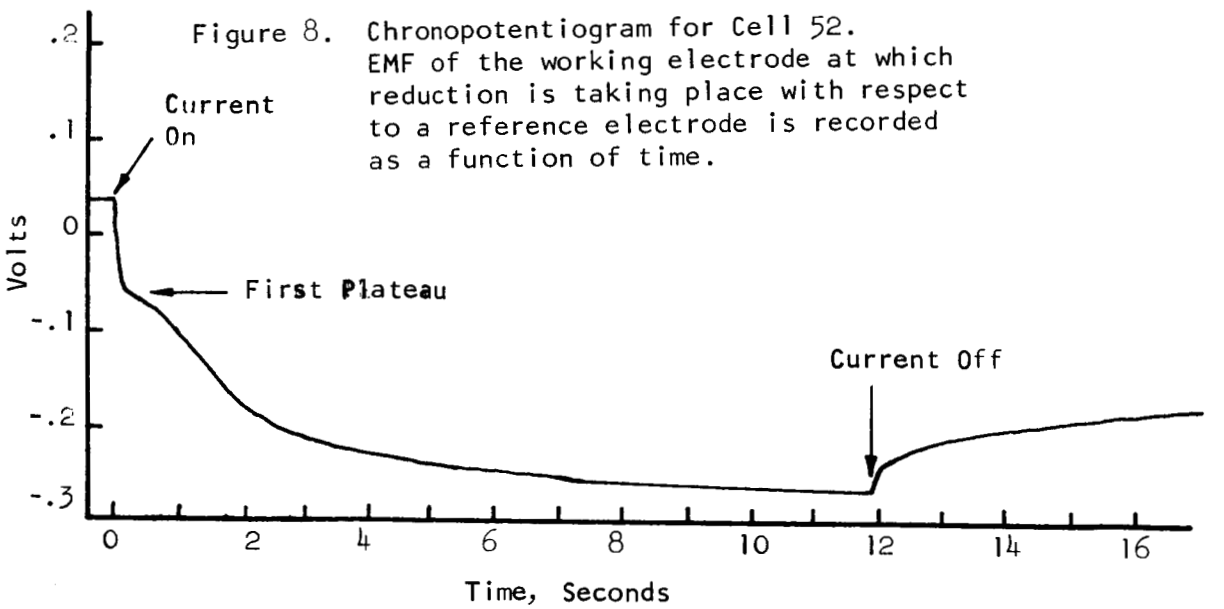
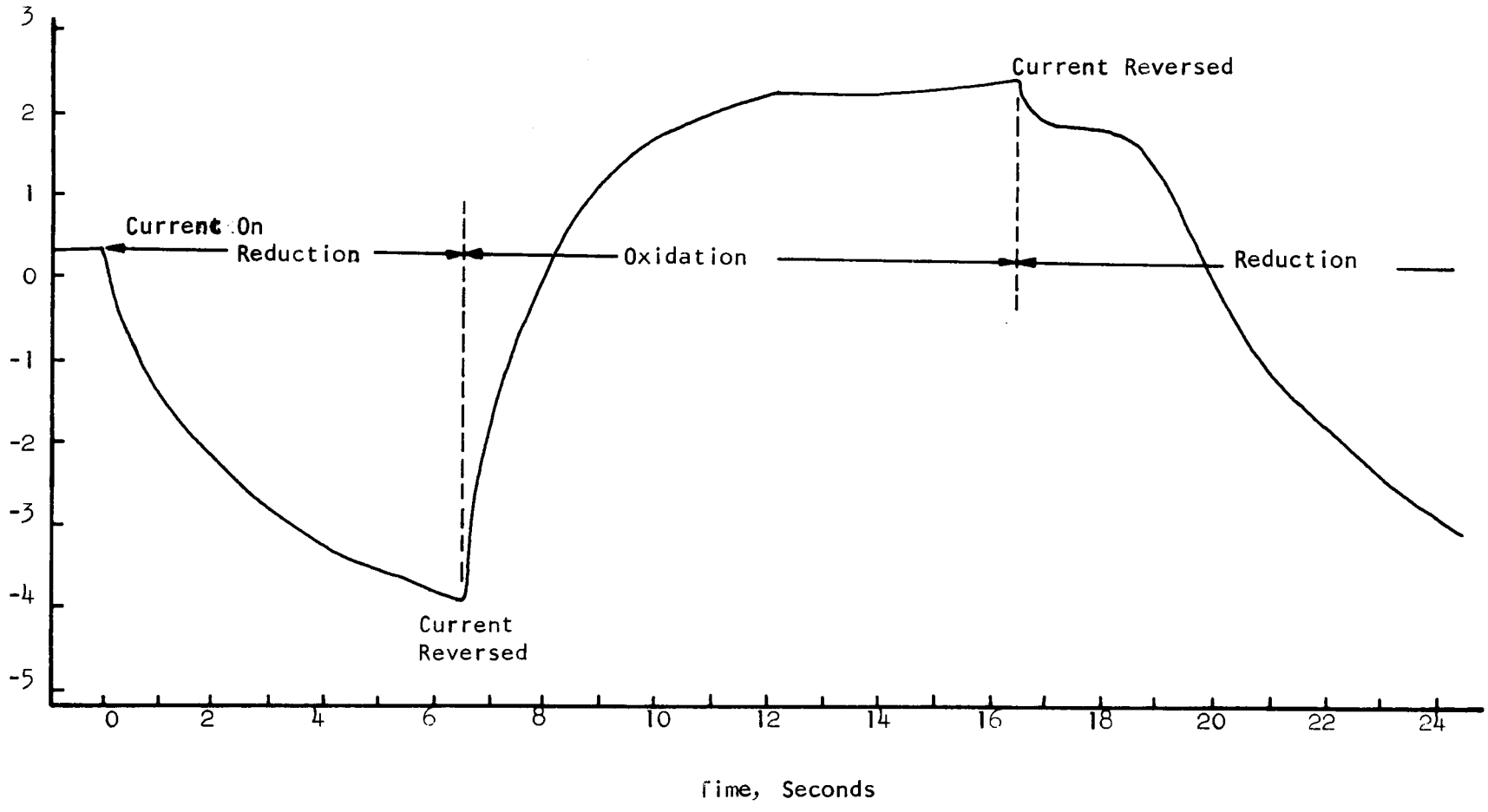


Figure 9. Chronopotentiograms for Cell 52.
The current was reversed twice during this recording.



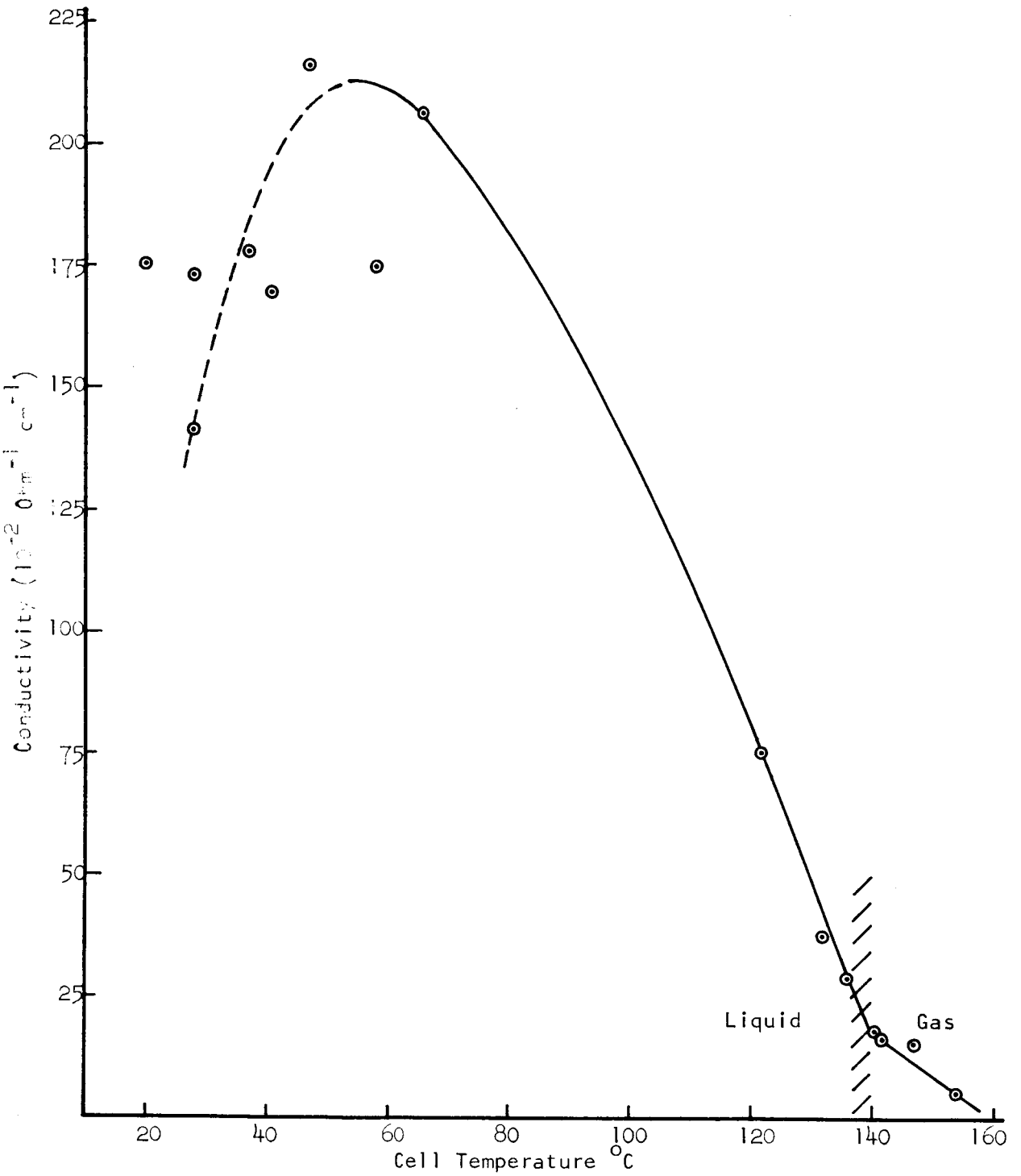


Figure 10. The specific conductivity of the electrolytic solution (NaI in NH_3) as a function of temperature for cell 53.

Figure 11. Chronopotentiogram for Cell 53.
With oxidation at the working electrode.

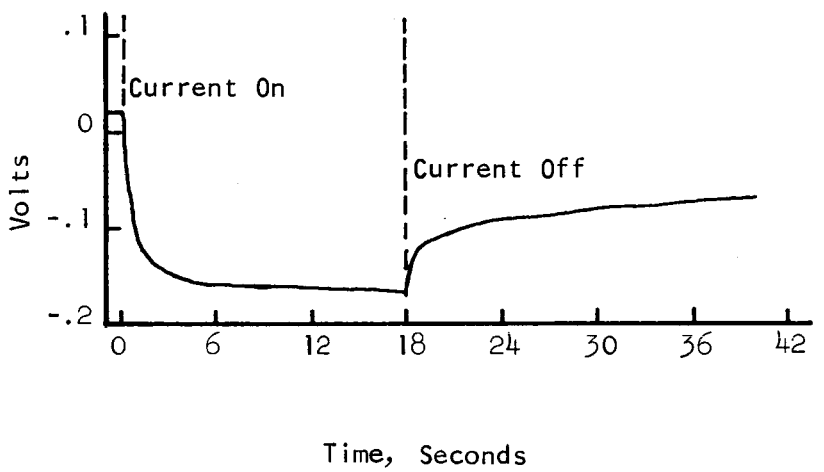


Figure 12. Chronopotentiogram for Cell 53.
With reduction at the working electrode.

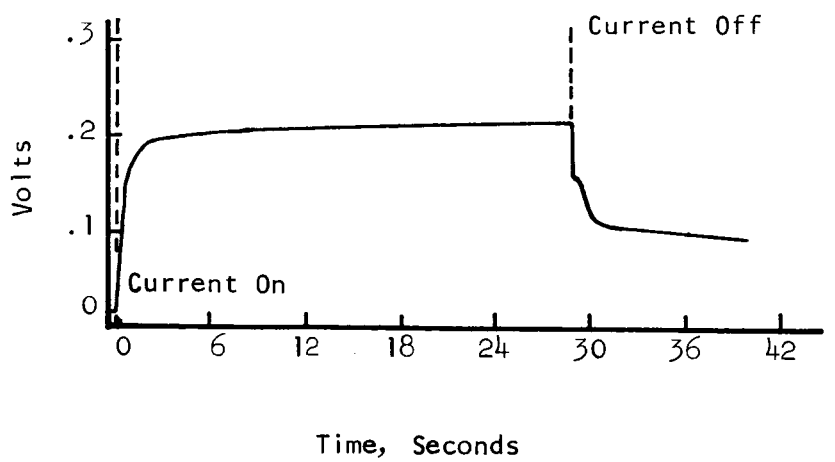


Figure 13. Sodium-Amalgam Concentration Cell 54.
Electrolytic Solution: NaI - NH_3

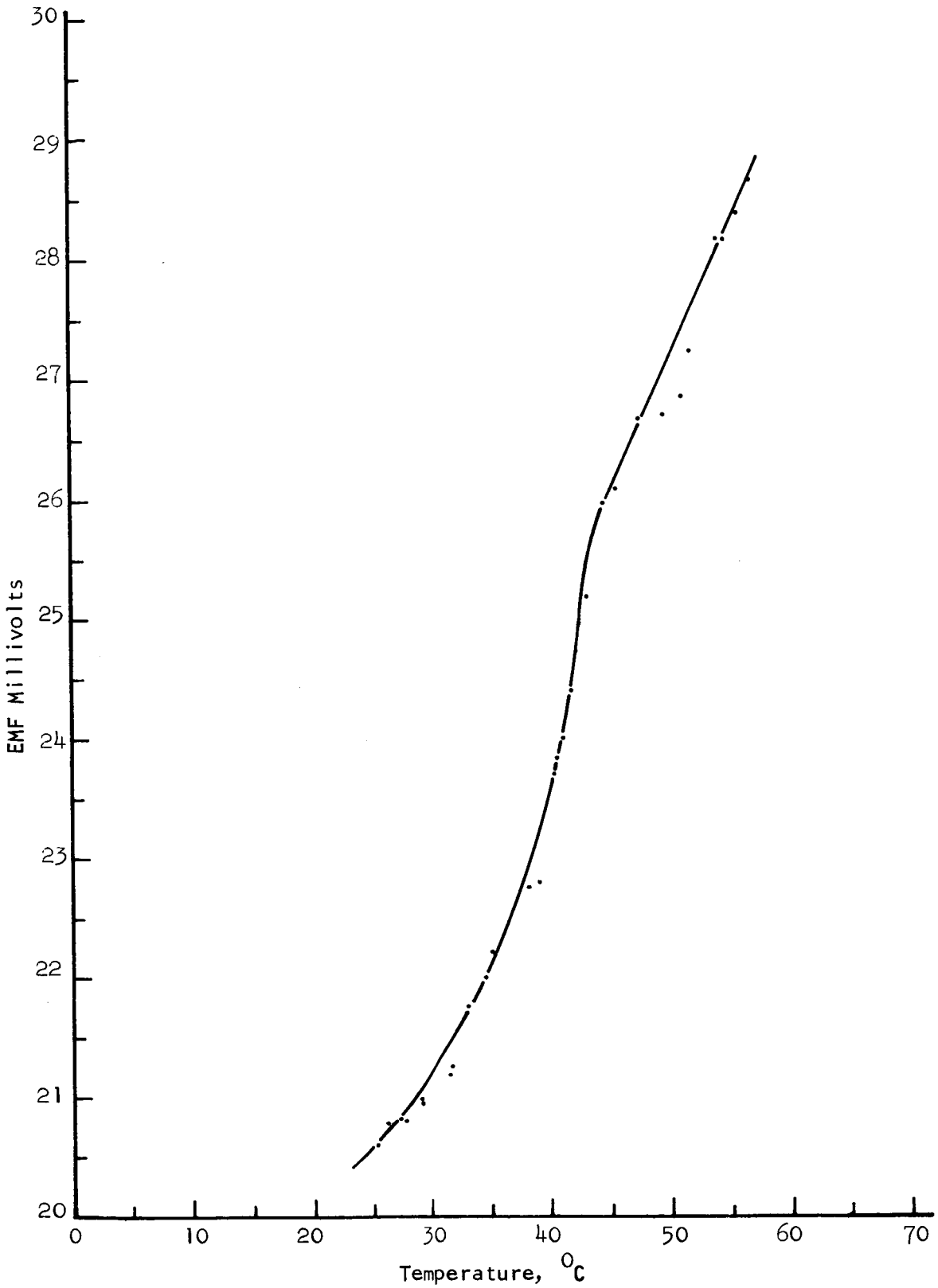


Figure 14. E/T for Cell 54

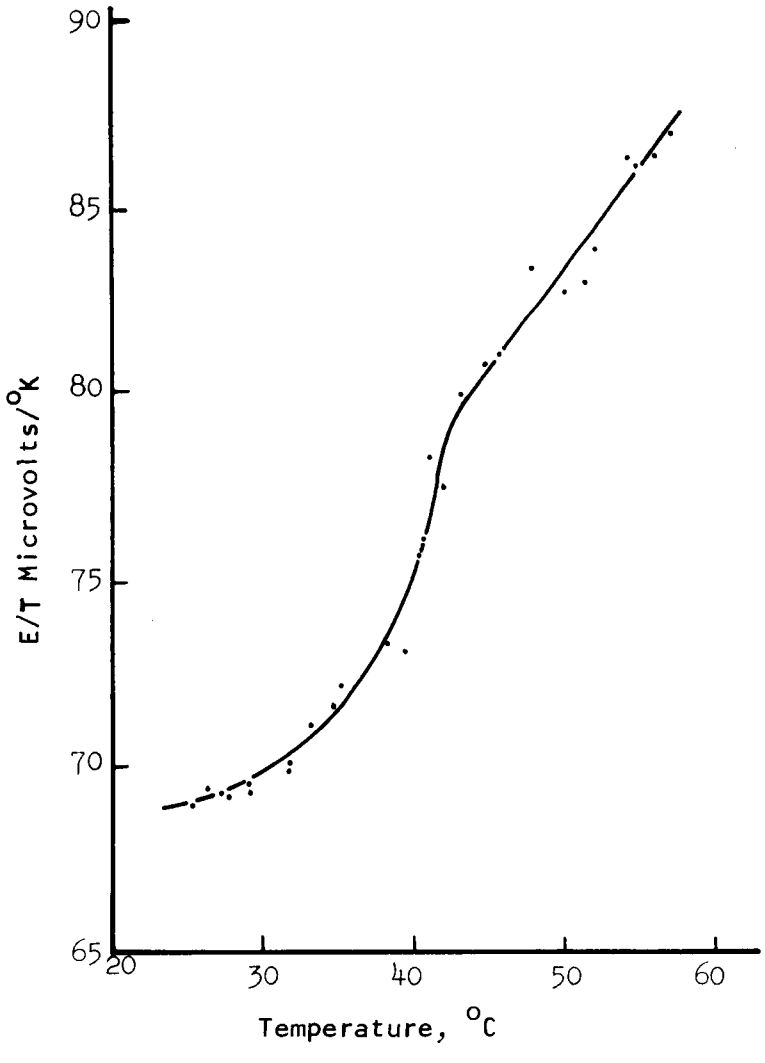


Figure 15. Specific Conductivity of the NaI-NH_3 electrolytic solution used in Cell 54 as a function of temperature.

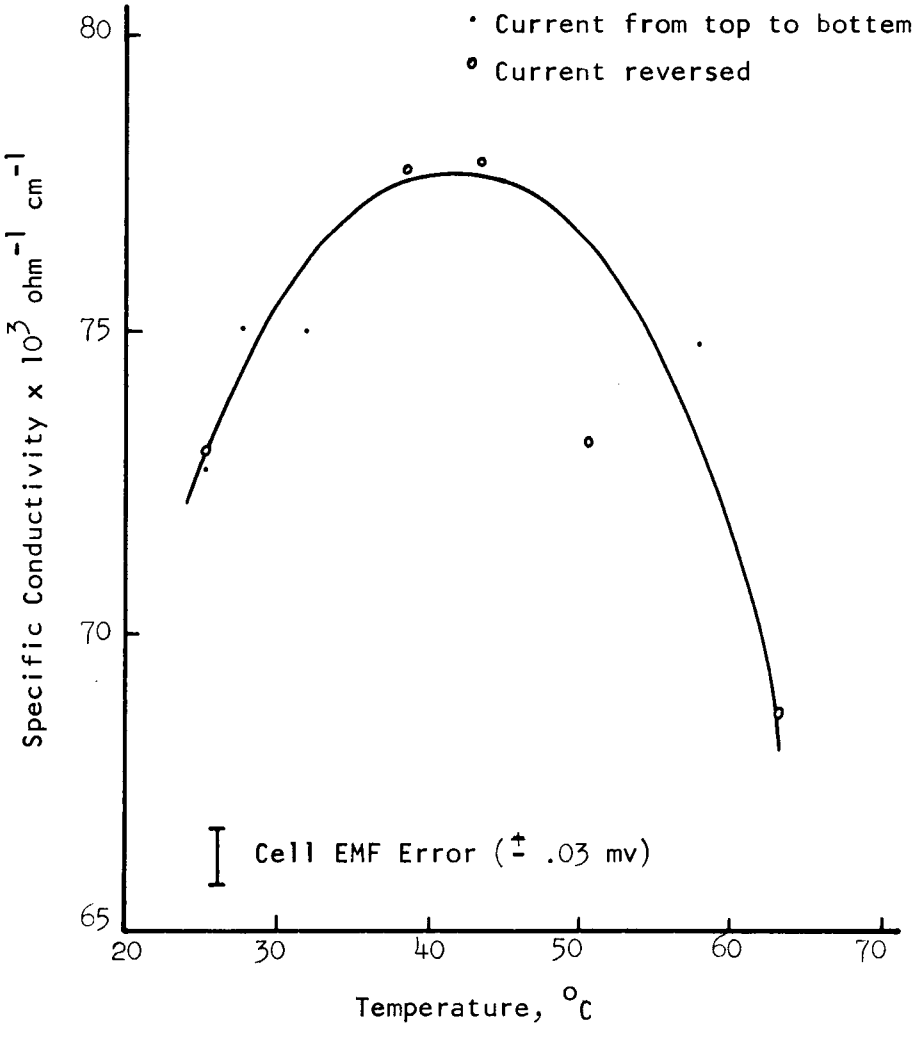


TABLE 2. DATA FOR CELL 52

TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS
First Day		78.2	.1026	87.8	.1090
16.0	.0156	11.2	.1050	88.8	.1116
11.5	.0200	11.2	.1040	90.1	.1146
Second Day		11.6	.1031	92.0	.1154
-20.5	.0233	12.2	.1020	97.5	.1137
23.8	.0205	12.8	.1011	98.5	.1167
31.9	.0206	13.3	.1004	100.6	.1180
41.0	.0203	13.6	.0944	102.8	.1210
53.9	.0203	14.3	.0440	107.8	.1280
49.6	.0496	14.3	.0530	110.6	.1270
51.0	.0538	16.3	.0220	117.4	.1220
51.6	.0569	30.3	.0380	121.1	.1202
49.9	.0580	53.8	.0469	123.4	.1209
48.3	.0540	58.5	.0540	129.8	.1238
52.9	.0639	60.9	.0580	130.2	.1268
54.3	.0660	63.3	.0600	131.8	.1133
58.5	.0690	65.5	.0628	134.0	.1143
60.4	.0722	68.6	.0700	134.8	.1163
61.6	.0737	71.0	.0750	137.3	.1167
62.6	.0765	73.2	.0800	139.2	.1150
64.7	.0826	75.5	.0830	140.0	.1120
64.9	.0843	78.2	.0850	142.0	.1050
64.5	.0873	78.9	.0865	141.5	.1010
66.3	.0900	80.2	.0890	144.0	.0962
70.8	.0918	81.9	.0960	146.7	.0940
72.3	.0947	82.0	.0990	147.5	.0930
75.1	.1000	85.8	.1060	148.0	.0900
76.6	.1020	86.2	.1080	136.0	.0804

TABLE 2. DATA FOR CELL 52

TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS
123.6	.0764	51	.0616	84	.1016
78.8	.0714	52	.0639	85	.1029
54.0	.0604	54	.0678	85	.1048
49.2	.0434	55	.0696	62	.0931
35.0	.0360	56	.0715	63	.0922
27.8	.0260	57	.0734	65	.0914
25.2	.0220	59	.0746	67	.0910
17.8	.0170	60	.0758	69	.0904
15.3	.0100	61	.0770	71	.0904
12.8	.0053	62	.0780	73	.0903
7.8	.0032	63	.0790	74	.0904
Third Day		66	.0820	75	.0905
23	.0448	67	.0827	77	.0909
25	.0478	68	.0838	76	.0920
31	.0510	69	.0860	75	.0927
31	.0524	65	.0877	74	.0928
32	.0524	66	.0880	73	.0923
33	.0533	68	.0890	74	.0914
35	.0477	69	.0900	75	.0912
36	.0490	70	.0920	77	.0910
37	.0500	71	.0939	78	.0906
39	.0507	72	.0960	79	.0904
44	.0550	75	.0970	81	.0904
45	.0557	77	.0980	82	.0904
47	.0580	78	.0986	83	.0905
48	.0585	79	.0990	84	.0905
51	.0597	83	.1000	85	.0907

TABLE 2. DATA FOR CELL 52

TEMP °C	EMF, VOLTS
87	.0914
89	.0917
90	.0920
91	.0927
92	.0933
93	.0934
94	.0935
95	.0936
97	.0900
99	.0860
23	-.0002
After 1 Hr.	
40	.0150
0	.0159
Fourth Day	
Emf's now measured between the top "working" electrode and the lower reference electrode.	
28.1	-.0267
28.9	-.0280
29.4	-.0288
30.4	-.0297
31.0	-.0300
31.8	-.0305
32.8	-.0309
33.5	-.0316
33.9	-.0322
35.0	-.0326
41.5	-.0331
42.7	-.0331
42.8	-.0332
43.0	-.0333
44.6	-.0334
44.8	-.0334
44.7	-.0334
45.0	-.0335
44.8	-.0337
45.4	-.0344
47.0	-.0345
47.8	-.0345
48.3	-.0345
49.2	-.0345
50.0	-.0345
51.1	-.0345
52.4	-.0345
53.3	-.0347
54.2	-.0347
55.5	-.0347
56.2	-.0347
57.2	-.0346
57.5	-.0346
58.0	-.0346
59.2	-.0346

TABLE 2. DATA FOR CELL 52

TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS
60.0	-.0347	101.0	-.0567	143.4	-.0990
61.1	-.0346	103.6	-.0572	144.1	-.0990
62.9	-.0347	105.2	-.0575	146.0	-.1000
64.8	-.0347	106.1	-.0577	146.1	-.1023
66.5	-.0347	107.5	-.0583	148.3	-.1040
68.6	-.0346	110.3	-.0582	149.6	-.1049
69.6	-.0345	111.6	-.0580	151.0	-.1047
73.5	-.0345	113.9	-.0576	151.0	-.1069
83.5	-.0339	116.2	-.0584	141.0	-.1080
86.0	-.0344	116.9	-.0594	137.6	-.1041
86.6	-.0346	117.8	-.0610	130.3	-.1002
87.2	-.0356	120.0	-.0653	126.3	-.1000
87.7	-.0362	120.5	-.0696	120.7	-.0938
87.8	-.0368	121.1	-.0709	114.[illegible]	-.0940
88.3	-.0373	123.2	-.0758	Fifth Day	
89.0	-.0379	123.6	-.0775	23.0	-.0291
89.6	-.0394	125.9	-.0829	25.1	-.0292
89.6	-.0406	127.0	-.0863	30.6	-.0296
89.6	-.0439	128.5	-.0874	36.5	-.0298
89.8	-.0455	130.5	-.0884	36.7	-.0298
90.3	-.0463	131.0	-.0892	39.6	-.0298
90.9	-.0468	133.2	-.0914	39.9	-.0299
90.2	-.0515	134.7	-.0947	41.0	-.0299
91.0	-.0531	136.7	-.0975	43.1	-.0252
96.1	-.0555	138.0	-.0995	46.6	-.0256
97.6	-.0559	140.7	-.1010	45.8	-.0256
99.5	-.0563	142.7	-.1003	47.0	-.0257

TABLE 2. DATA FOR CELL 52

TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS	TEMP °C	EMF, VOLTS
48.6	-.0257	86.6	-.0243	101.4	-.0400
50.2	-.0258	87.0	-.0244	102.0	-.0417
52.0	-.0263	88.0	-.0246	102.0	-.0439
52.8	-.0263	89.1	-.0248	45.9	-.0283
53.9	-.0263	88.2	-.0250	49.2	-.0282
57.2	-.0261	89.0	-.0257	51.5	-.0283
57.5	-.0262	89.5	-.0260	60.0	-.0284
57.7	-.0262	90.0	-.0263	63.7	-.0284
59.3	-.0262	91.2	-.0267	64.1	-.0287
64.5	-.0262	91.2	-.0269	66.1	-.0291
69.3	-.0262	91.4	-.0276	68.8	-.0293
70.3	-.0261	92.2	-.0279	70.5	-.0300
73.9	-.0257	92.7	-.0285	71.2	-.0303
74.1	-.0256	93.6	-.0299	73.0	-.0313
74.5	-.0255	94.5	-.0305	74.9	-.0320
76.0	-.0252	95.8	-.0320	74.4	-.0328
77.5	-.0250	96.3	-.0345	72.8	-.0333
78.6	-.0247	97.4	-.0353	67.6	-.0350
79.3	-.0246	97.9	-.0356	66.1	-.0353
79.8	-.0246	97.9	-.0363	62.3	-.0358
80.9	-.0245	99.5	-.0329	61.0	-.0365
81.8	-.0244	99.5	-.0390	57.3	-.0370
86.3	-.0243				

TABLE 3. DATA FOR CELL 53

TEMP °C	CONDUCTIVITY (OHM CM)$^{-1}$
19	1.75×10^{-2}
28	1.73
28	1.42
37	1.77
41	1.70
47	2.16
58	1.76
66	2.06
122	0.758
132	0.375
136	0.293
141	0.178
142	0.163
147	0.149
154	0.050

Emf's are omitted from this table since conductivity measurement affected emf. The emf's did not return to their original values after conductivity measurement.

TABLE 4. DATA FOR CELL 54

TEMP °C	EMF, VOLTS	E/T MICROVOLTS/°K	CONDUCTIVITY (OHM CM)$^{-1}$
25.2	.02060	69.0	7.36×10^{-3}
25.2			7.30×10^{-3}
26.2	.02079	69.4	
28.9	.02096	69.4	
27.5	.02080	69.2	
27.4			7.50
27.3	.02082	69.3	
28.9	.02095	69.3	
31.6	.02129	69.8	
31.6			7.50
31.7	.02136	70.0	
33.0	.02175	71.0	
34.5	.02200	71.5	
35.0	.02223	72.1	
37.9	.02277	73.2	
38.5			7.80
39.2	.02282	73.0	
40.3	.02371	75.6	
40.5	.02385	76.0	
41.0	.02400	78.3	
41.8	.02439	77.4	
43.0	.02519	79.7	
43.6			7.82
44.5	.02597	81.7	
45.4	.02610	81.9	
47.5	.02668	83.2	
49.8	.02672	82.7	
50.6			7.38
50.9	.02686	82.9	

TABLE 4. DATA FOR CELL 54

TEMP °C	EMF, VOLTS	E/T MICROVOLTS/°K	CONDUCTIVITY (OHM CM)$^{-1}$
51.8	.02723	83.8	
54.0	.02819	86.2	
54.4	.02817	86.0	
55.7	.02838	86.3	
56.7	.02867	86.9	
57.4			7.46
58.5	.02821	85.0	
62.0	.02940	87.7	
61.9	.02857	85.3	
62.6	.02816	83.9	
63.2			6.72
64.0	.02826	83.8	
65.2	.02825	83.5	
66.8	.02806	82.5	
69.1	.02314	82.2	
69.6	.02808	81.9	
69.9	.02782	81.1	
69.8	.02752	80.2	
69.6	.02765	80.7	
69.3	.02794	81.6	
69.1	.02804	81.9	
68.9	.02814	82.3	
68.6	.02828	82.7	
68.1	.02843	83.3	
67.3	.02919	85.7	
67.2	.02963	87.0	
66.9	.03016	88.7	
66.7	.066	194.2	

TABLE 5. SUMMARY OF EXPERIMENTAL RESULTS

CELL NO.	COMMENTS	DATA		
		TABLES	FIGURES	TEMPERATURES, °C
52	Amalgam in electrode A was a solid (or a very stiff liquid).	2 EMF	6,7 EMF vs T	-20.5 to +150.0
			8 Chronopotentiogram	-17.0
			9 "	-26
53	NaI was introduced into cell by using H_2O instead of NH_3	3 Conductivity	10 σ vs T	+19.0 to +154.0
			11,12 Chronopotentiograms	+27
54	- - -	4 EMF, E/T, Conductivity	13 EMF vs T	+25.2 to +66.7
			14 E/T vs T	+25.2 to +66.7
			15 Conductivity	+25.2 to +63.2
55	Relatively large amount of Na was dissolved in liquid NH_3. Cell ruptured during storage.			
56	All electrodes were platinized.			
57	All electrodes were platinized. Cell has an additional quantity of NaI.			
58	Electrodes B and C were platinized. $NaNH_2$ was used instead of NaI as electrolyte.			
60	Cell constructed of quartz instead of pyrex.			

3.0 CONCLUSIONS

The method of preparing cell 53 by introducing the electrolyte in aqueous solution will be discontinued. Although it permitted a better control of the concentration of the dissolved salt than our standard procedure, the possibility that traces of water could remain in the cell after the bakeout is a serious disadvantage of this method.

Chronopotentiometric studies of cell 52 seem to indicate that, under our experimental conditions, the reduction,

$$Na^{+}(NH_3) + e^{-}(Hg) = Na(Hg),$$

is diffusion controlled while the oxidation,

$$Na(Hg) = Na^{+}(NH_3) + e^{-}(Hg)$$

is not. This result was not as apparent in the chronopotentiograms of cell 53.

Cells 52 and 53 have been operated approximately 20° above the critical temperatures of the electrolytic solutions. In particular, cell 52 has been recycled twice from room temperature to 150°C. Emf's were measured with cell 52, and electrolytic solution conductivities with the other cell. The scatter of data in this region has been reduced to an apparently satisfactory level.

4.0 PROGRAM FOR THE NEXT QUARTER

Tests will be continued on cells 56-58 and 60, which have been prepared during this quarter. Additional cells will be prepared. Using a temperature controller to maintain a constant cell temperature, we shall perform experiments to determine whether the time needed for establishing the electrochemical equilibrium at the electrodes is longer than it is presently anticipated.