

EIGHTH QUARTERLY REPORT
Period Ending 31 July 1966
GASEOUS ELECTROLYTES FOR BATTERIES AND FUEL CELLS

by

S. Naiditch, Principal Investigator

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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UNIFIED SCIENCE ASSOCIATES, INC.

826 south arroyo parkway
pasadena, california 91105
phone 213-681-3486

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1.0 ABSTRACT

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From measurements made this quarter on cell 63, we have established that the cell emfs of sodium amalgam concentration cells are independent of whether the electrolyte is liquid or gaseous. Cell 63 was run to 145°C, about 10° above the critical temperature. Though lost at 55°C upon cooling, amalgam samples from three electrodes were recovered and analyzed, showing sodium concentrations of 15, 4.11 and 0.56 mole percent.

The conclusion that the cell emf of sodium amalgam concentration cells is independent of electrolyte state is based on measurements of cells 58 and 63 and has been predicted from theoretical considerations. These measurements verify the results of the analysis in the fifth quarterly report.

Cell 69, a metal-amalgam insoluble-salt, was run to 100°C and cooled to room temperature. Its zinc and thallium electrodes were well enough behaved to allow observation of individual disturbances and to isolate their causes. In this cell, the two Tl(Hg)/TlCl₂ electrodes were both more unstable and less reversible than the two Zn(Hg)/ZnCl₂ electrodes.

Two additional metal-amalgam insoluble-salt cells were run, producing little useful data. A new cell filling system has been designed and built, permitting the filling of from one to four cells simply, thus making the cell supply more responsive to the needs of the program.

AUTHOR

2.0 EXPERIMENTAL

2.1 CELL FILLING SYSTEM

A new system has been designed and built to reduce the cell loss rate, and increase the versatility and speed of filling. In the new system we condense ammonia into the cell from the gas phase rather than dripping it in as a liquid from a condenser. This, plus the use of valves in all the lines, simplifies the control and isolates each cell.

The new system is set up for filling four cells at one time. It is now practical to fill as few as one or two cells to meet a specific need. A group of four cells has been prepared and filled on this system without loss. The electrode compositions for these cells are given in Table 1.

TABLE 1
COMPOSITION OF THE METAL-AMALGAM ELECTRODES
DETERMINED BY WEIGHT

CELL	ELECTRODE COMPOSITION MOLE % METAL			
	A	B	C	D
61	1.77 Pb	2.48 Tl	1.94 Tl	2.13 Pb
62	1.44 Pb	3.37 Cd	2.60 Cd	2.83 Pb
69	2.35 Tl	7.14 Zn	4.90 Zn	3.84 Tl
71	1.97 Pb	6.65 Zn	9.53 Zn	2.33 Pb

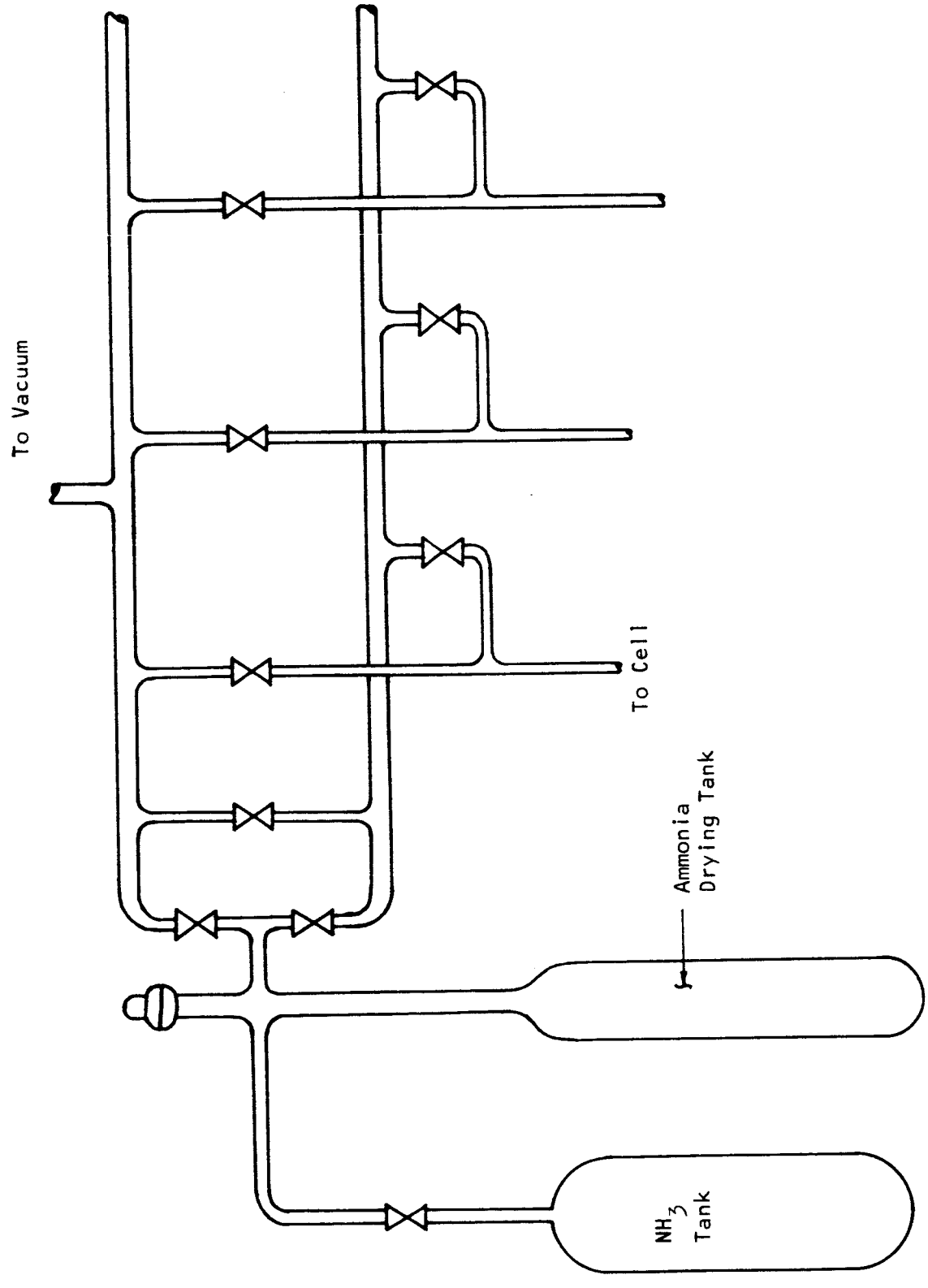


Figure 1. Cell Filling System

2.2 CELLS 61 and 62

Cell 61 failed at 37°C because of a glass flaw. No useful information was gained because of the narrow temperature range (24° - 37°C) covered. The emfs of this cell, which used Pb and Tl amalgam insoluble-salt electrodes, were exceptionally small (< 0.05 volts). Because of the similarity of this and other failures, we are currently analyzing the cell design. We expect to make several minor changes to improve the strength around the electrodes.

Cell 62 (Table II) was unstable at room temperature. It was heated rapidly to 150°C to see if its stability would be altered if the electrolyte were in a gaseous state. No change was noted, so the temperature was dropped rapidly, and the cell failed at 90°C. The general behavior of the cell was poor, the emfs being unstable much of the time.

It was surmised that if the instabilities at room temperature were due to bubble formation, then this effect would be altered at high temperatures. First, the electrolyte would be in a gaseous state so that there would be no surface tension to constrain gaseous material to remain next to electrode surfaces as bubbles. Second, if bubble formation were due to inhomogeneity in the amalgam, the rate of equilibration might be rapid enough at 150°C so that the amalgams would become more uniform and the parasitic currents would therefore diminish. Since no improvement in stability was noted either at 150°C or when the temperature had been dropped substantially below this, the cell was abandoned.

TABLE 11
 MEASURED EMFS FOR METAL AMALGAM CELL 62
 Electrode A was not Covered with NH₃ at Room Temperature

Electrode A - Pb
 B - Cd
 C - Cd
 D - Pb

TIME HOURS	TEMP. °C	ELECTRODE EMF							
		DA	DC	DB	AB	AC	BC		
0	21	--	+0.1316	0.246	--	--	--	-0.0112	
4.5	20	--	+0.1258	0.235	--	--	--	-0.023	
24.5	47	-0.50	+0.223	0.139	--	--	--	+0.1	
25.3	61	-0.44	-0.3	--	--	--	--	--	
25.8	87	-0.28	--	0.22	0.398	0.500	--	--	
26.2	109	-0.264	+0.294	0.206	0.403	0.524	+0.130	--	
26.9	133	-0.304	+0.297	0.296	0.534	0.545	-0.0971	--	
27.4	136	-0.335	+0.302	0.290	0.350	0.552	-0.0791	--	
28.2	148	-0.57	+0.328	0.274	0.491	0.50	+0.051	--	
28.3	146	-0.83	+0.318	0.282	0.33	0.40	-0.082	--	
29.0	136	--	+0.334	0.160	0.20	0.39	--	--	
29.4	113	--	+0.333	0.060	0.060	0.30	--	--	
30.0	90	--	+0.200	0.040	0.040	0.11	--	--	

2.3 CELL 63

A sodium-amalgam concentration cell, number 63, was run from 20° to 146°C and down to 55°C. During the night, a leak developed in the pressure vessel head seals, the pressure dropped, and the cell ruptured. Samples of three of the four electrodes were recovered and analyzed. The emfs for the six electrode pairs were stable to 0.1%, both in the liquid and dense gaseous states, and generally consistent throughout the entire range. On heating this cell, temperatures were changed every one to two hours during the day to speed the run so that equilibration was not as thorough as in some of the earlier runs. The heating data taken at this rate were generally compatible with the cooling data.

Using the data from this cell and cell 58, along with the analysis presented in the Fifth Quarterly Report, one can conclude that equilibrium emfs of sodium-amalgam concentration cells are independent of electrolyte state. Measurements of both cells 58 and 63 show that there is no change in the cell emf in the region of the transition from the liquid state to the dense gaseous state; i.e., around 133°C. The derived equation for the emfs, E, of such sodium amalgam concentration cells is:

$$E = \frac{RT}{F} \ln a_1/a_2 \quad (1)$$

where T is the temperature in °K, a_1 and a_2 are the sodium activities in the two amalgams in mole percent, and R and F are the gas and Faraday constants. There are no electrolyte terms in this expression.

2.3.1 ELECTRODE AMALGAM ANALYSES

Samples of three electrode amalgams were analyzed by Truesdail Laboratories in Los Angeles. The analyses were done as follows.

The exterior surfaces of the sample containers were carefully cleaned and dried, and the containers with their samples intact were weighed. The samples were then transferred to standard taper flasks, and any residues remaining in the containers were washed into the respective flasks. The sample containers were carefully recleaned and dried and the sample weights determined by difference.

An exact amount of standard hydrochloric acid, the amount and normality of which was governed by the sample weights, was added to each flask. The flasks were agitated for 16 hours by means of a mechanical wrist-action shaker. Blank samples were prepared and handled in exactly the same manner.

At the conclusion of the 16 hours, the samples and the blanks were back titrated with standardized NaOH, using methyl red indicator. The amount of HCl neutralized was determined by comparison with the corresponding blank.

Since there was the possibility of sample contamination with NaNH_2 which would give erroneously high results, Nessler ammonia determinations were performed on the neutralized solutions and applicable corrections made. Only sample D was found to contain ammonia in the solution.

The results of the analyses are

<u>Sample</u>	<u>Sodium Hydroxide, Mole Percent</u>
B	15.0*
C	4.11
D	0.56

*The accuracy of this determination is questionable, since the total sample weight was only 10.3 milligrams and the titration was 0.09 milliliters of 0.01 normal hydrochloric acid.

2.3.2 The Sodium-Mercury Phase Diagram

Before reviewing the experimental emf data, we shall examine the states of the various sodium amalgam electrodes. The compositions for electrodes B, C and D are indicated on the phase diagram in Fig. 2. Although the composition of electrode B is uncertain, it is in the correct direction. As pointed out in earlier reports, the concentration of sodium in the various electrodes generally increases progressively in going from D to C to B to A. Both electrodes C and D should be in the single phase liquid region throughout the range of the experimental measurements. If there are any discrepancies in the phase diagram or in the determined compositions, electrode C would cross from a two phase to a one phase liquid region at relatively low temperatures. Other than this possibility, both of these electrodes should then be single phase liquids throughout the range of measurements. Therefore, deviations in the emfs of the electrode pair DC from Eq. (1) may be due to shifts in equilibria between complex sodium species in the amalgams.

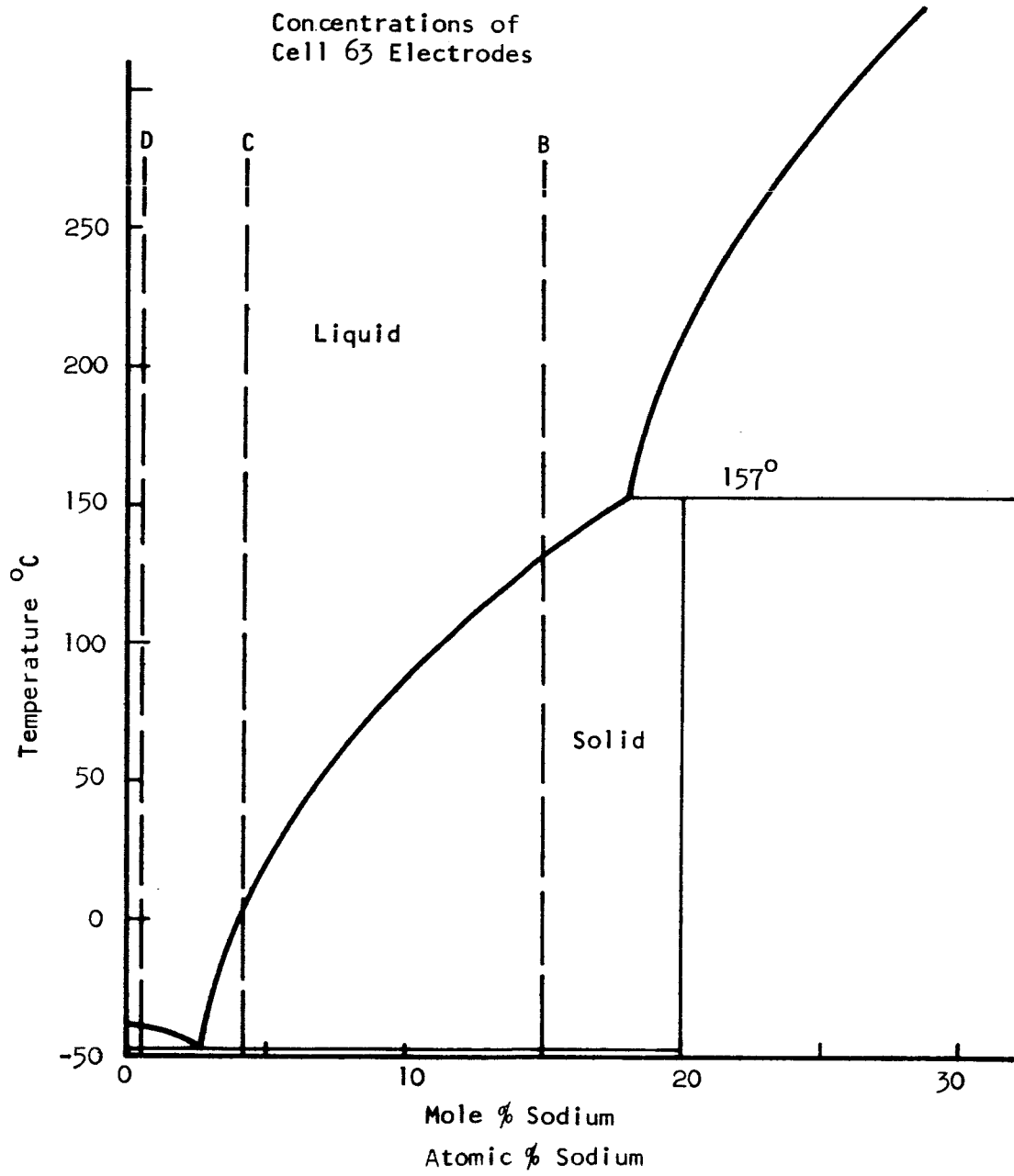


Figure 2. Sodium Mercury Amalgam Phase Diagram

Although the composition of electrode B is uncertain, its general location on the phase diagram is a reasonable one. Since amalgam B is a two phase system for at least much of the temperature range, it may require more equilibration time than do electrodes C and D.

Unfortunately, amalgam A was not recoverable. Amalgam A is undoubtedly more concentrated than the other amalgams because it was solid at room temperature during preparation of the cell. This can also be seen if one examines the emfs. The emfs at room temperature are in consistent agreement with the concentration sequence D-C-B-A. Although we have not yet established the location of electrode A on the phase diagram, it is certainly more concentrated than electrode B.

2.3.3 Experimental Data

The changes in emfs of the three electrode pairs involving the most concentrated amalgam, electrode A (Table III and Fig. 3A, 3B and 3F), are of the order of 200 to 250 mv over the range of 20 to 145°C. These electrodes are well behaved and the emfs vary in a simple manner from 20° (with the electrolytes in the liquid state) to 145°C (in the dense gaseous state). The electrode pairs A-C and A-D are both fairly linear over the range, whereas A-B has a well developed curvature. As we saw in the last section, amalgams C and D are both single phase liquids whereas B is a two phase amalgam over most of the range. The data for these three electrode pairs establish unambiguously that there is no appreciable difference in behavior in the equilibrium emfs of the cells that may be attributed to the differences

TABLE III

MEASURED EMFS FOR SODIUM AMALGAM ELECTRODE CELL 63

Electrode Description: A - Spongy Solid

B and C - Liquid with brown layer 1 mm thick on top

D - Clean liquid

TIME HOURS	°C	ELECTRODE					
		DA	DC	DB	AB	AC	BC
0	22	+0.11781	+0.062991	+0.079585	-0.038145	-0.054733	-0.016602
2	35	+0.1345	+0.06585	+0.08334	-0.05107	-0.06856	-0.01750
20.5	40	+0.15019	+0.06856	+0.08707	-0.06308	-0.08163	-0.01850
23.5	57						-0.01917
24.75	67	+0.1570	+0.07877	+0.099000	-0.09557	-0.11515	-0.02003
43.5	79	+0.2278	+0.08426	+0.1184	-0.1077	-0.1428	-0.03446
44.75	88	+0.2450	+0.08608	+0.1187	-0.1245	-0.1569	-0.03275
46.75	97	+0.2560	+0.08602	+0.1198	-0.1368	-0.1705	-0.03358
47.5	108	+0.2695	+0.0877	+0.11752	-0.15324	-0.18296	-0.02970
48.25	120	+0.2874	+0.0889	+0.1161	-0.1690	-0.1971	-0.02790
49	130	+0.3104	+0.8983	+0.1134	-0.1984	-0.2242	-0.02610
49.5	140	+0.3350	+0.09047	+0.1137	-0.2231	-0.2493	-0.0254
49.75	137.5	+0.3292	+0.09072	+0.1141	-0.2166	-0.2425	-0.02601
50.5	143.0	+0.3312	+0.09212	+0.11549	-0.2168	-0.2425	-0.02584
51.75	144.2	+0.3304	+0.09214	+0.1155	-0.2163	-0.2420	-0.02667
52.5	136	+0.3287	+0.09195	+0.1166	-0.2131	-0.2399	-0.02745
53.5	129.2	+0.3044	+0.09226	+0.1178	-0.1880	-0.2166	-0.02865
55.5	117.2	+0.2948	+0.09157	+0.11905	-0.17603	-0.2035	-0.02739
58.5	102.0	+0.2656	+0.09087	+0.11991	-0.14564	-0.17460	-0.02911
67.5	85.0	+0.23429	+0.08930	+0.12393	-0.11032	-0.14500	-0.03468
73.5	88.8	+0.23615	+0.086932	+0.12067	-0.11533	-0.14914	-0.03378
77.5	78.2	+0.22191	+0.08647	+0.12021	-0.10176	-0.13552	-0.03370
79.5	68.6	+0.20793	+0.08599	+0.11874	-0.08936	-0.12217	-0.03275
85.5	55.2	+0.18894	+0.08561	+0.11503	-0.07383	-0.10328	-0.02975

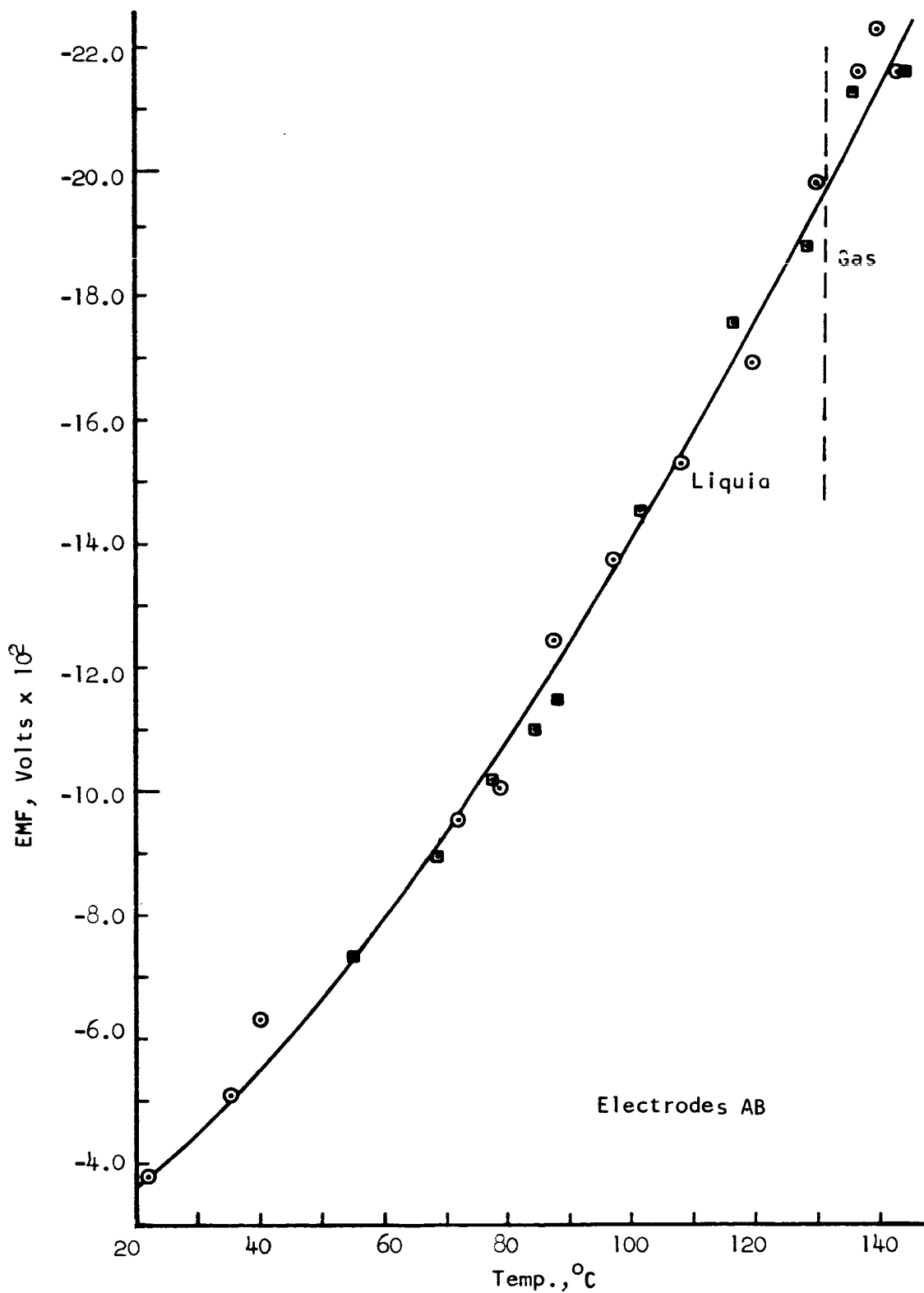


Figure 3A. Emfs for Sodium Amalgam Electrode Cell 63.
 Circled points are heating, squares are cooling

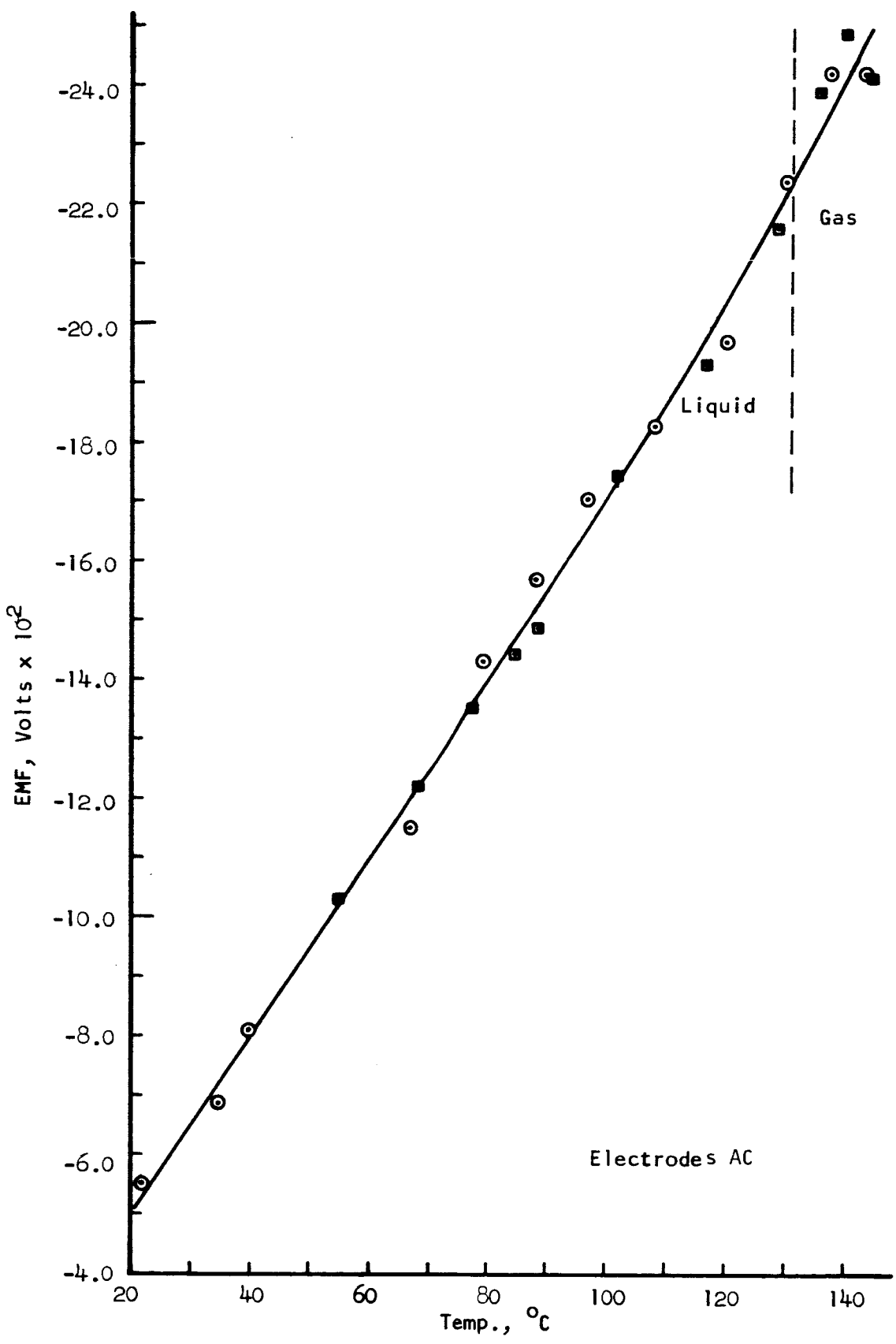


Fig. 3B. Emfs for Sodium Amalgam Electrode Cell 63. Circled points are heating, squares are cooling.

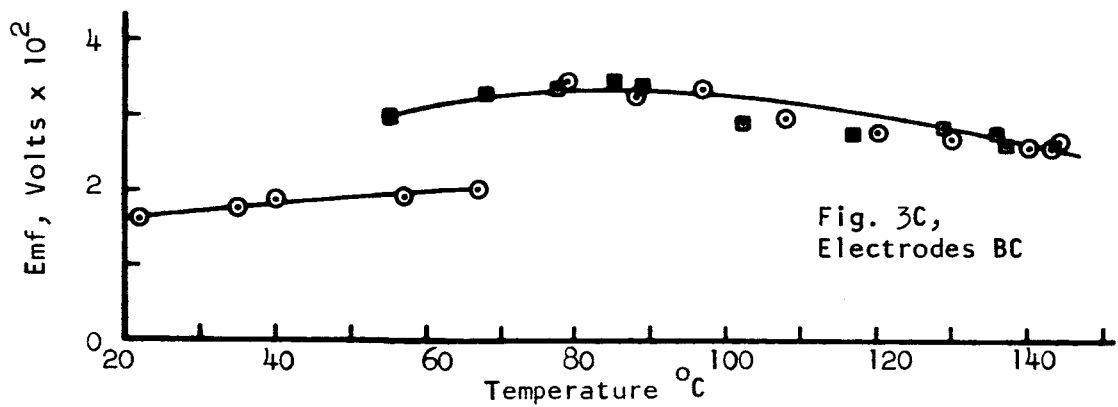
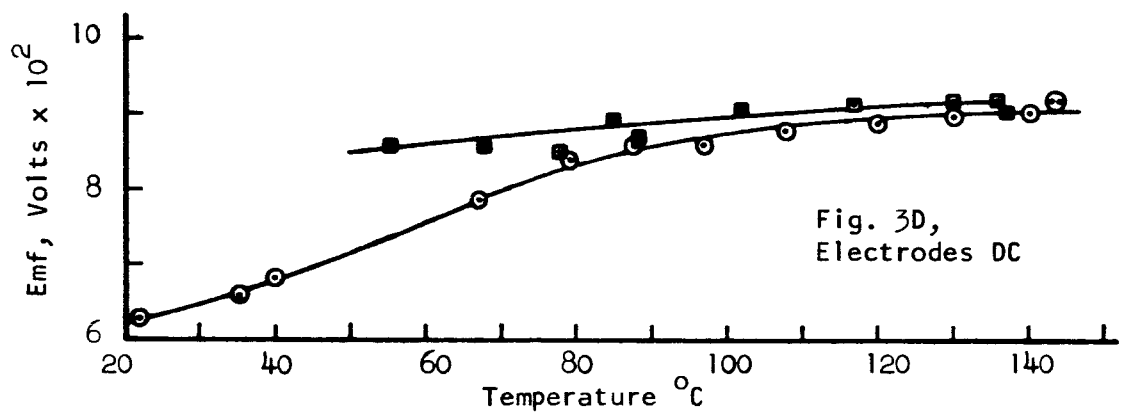
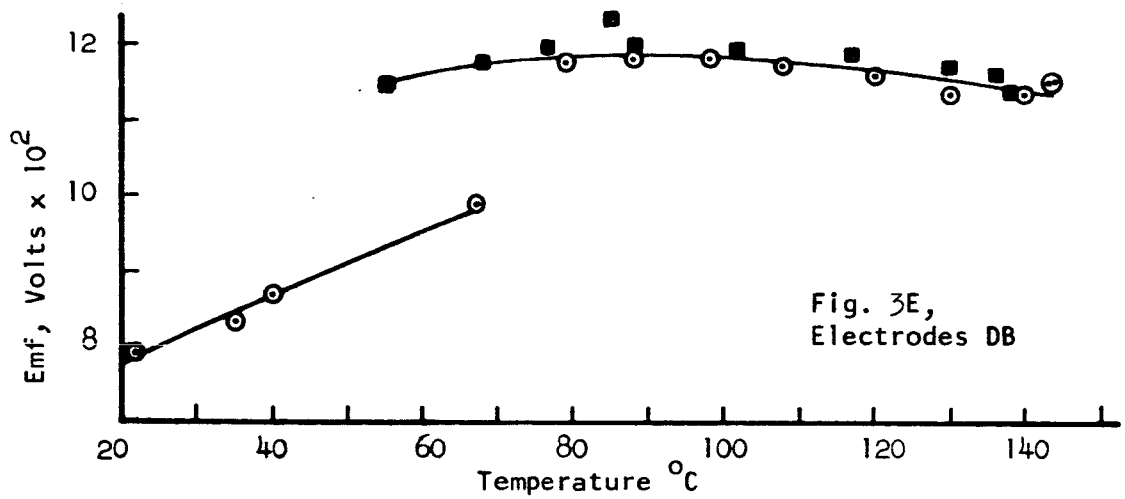


Fig. 3 EMFS FOR SODIUM AMALGAM ELECTRODE CELL 63
 Circled Points are Heating
 Squares are Cooling

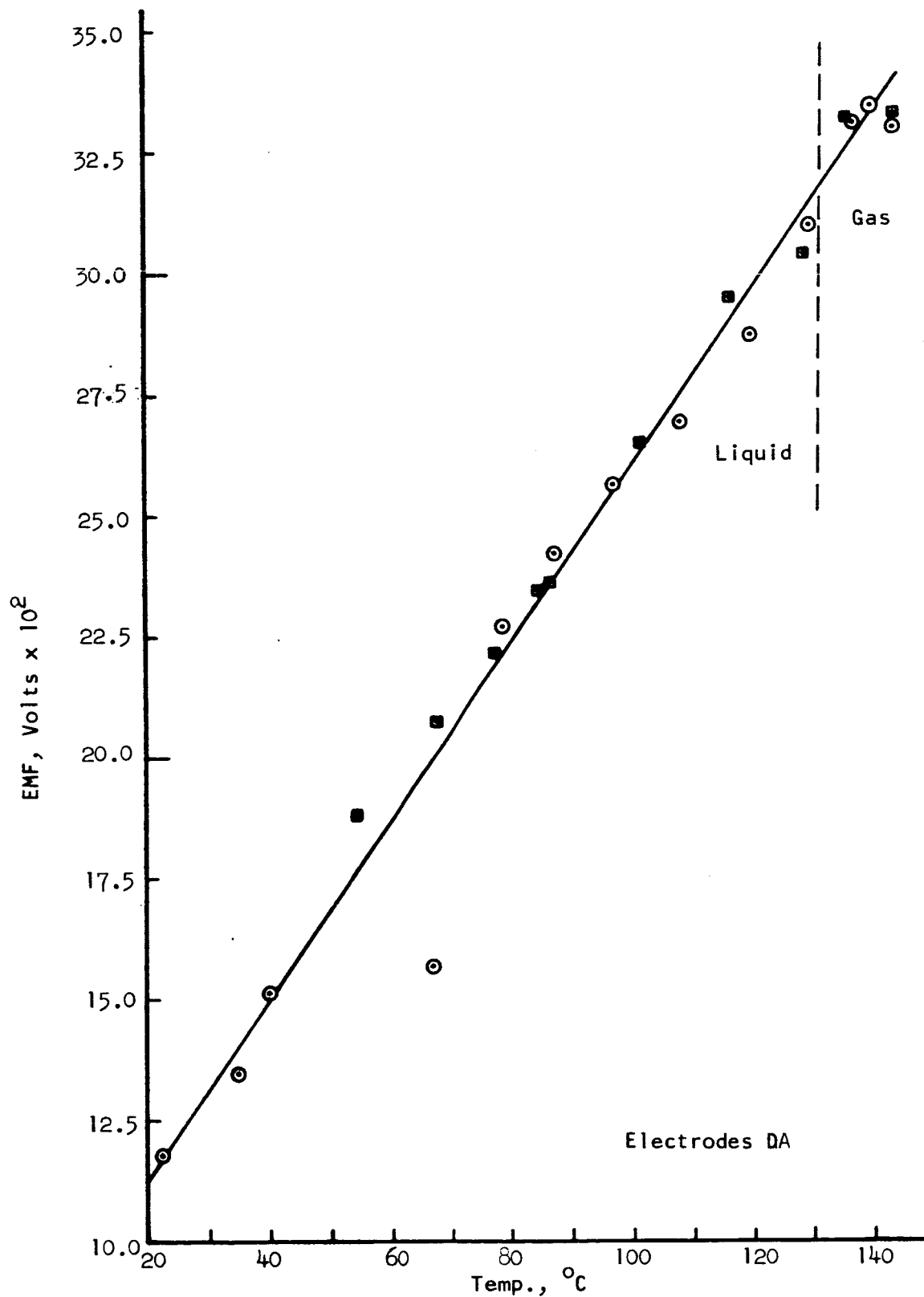


Figure 3F. Emfs for Sodium Amalgam Electrode Cell 63.
 Circled points are heating, squares are cooling.

in liquid-like versus dense gaseous-like properties of the electrolyte, since the emfs increase regularly with increasing temperature throughout the entire range.

In the case of the three electrode pairs involving amalgam A, the change in emfs over the temperature range is large, being of the order of 200 to 250 mv. The initial emfs may be small (40, 55 and 115 mv), but it is the increase in the value at high temperature that is strikingly different from the other pairs.

The emfs of electrode pairs not involving electrode A are a little smaller (15, 60 and 80 mv), and the changes in emfs over the temperature range are much smaller (20 to 40 mv) than for the "A" pairs. The non-A pairs exhibit hystereses or changes of about 10 to 30 mv below 80°C between the data collected at increasing versus decreasing temperatures. A possible explanation of the breaks in the B-C, B-D, C-D curves is lack of equilibration. If one examines the points where a quarter to one day is allocated for equilibration, the behavior of these points seems to be adequate. This would indicate that variations of the order of 10 mv are attributable to lack of thorough equilibration in the system. Variations of 10 mv do not affect the general behavior noted for electrode pairs AB, AC and AD.

All the electrode pairs are well behaved above 80°C. The conclusion drawn earlier that the equilibrium emfs are independent of the state of the electrolyte for amalgam concentration cells is therefore justified for all the electrode pairs for the range of 80 to 145°C.

2.4 CELL 69 (Tl(Hg)/TlCl₂ AND Zn(Hg)/ZnCl₂ ELECTRODES)

Cell 69, a metal-amalgam insoluble-salt cell, has been run to 100°C and back to room temperature. This was done because the glass envelope of this cell was somewhat weaker than usual and the expansion bulb was small. Though of only average stability (± 1 mv), cell 69 was well behaved. The Tl-Zn pairs all have large emfs (Table IV). These are among the highest emfs yet recorded on this program. The temperature coefficients of all the positive emfs of this cell are negative.

There are several features of the emf data which permit conclusions to be drawn about particular electrodes. In the three electrode pairs with Tl amalgam A in common (Fig. 4A, 4B and 4C), those points at 45°, 61° and 74°C are all far from the expected values. This disturbance did not repeat itself on cooling. Fig. 4C, 4E and 4F show an irreversibility in electrode D, the other thallium electrode. Thus, both Tl(Hg)/TlCl₂ electrodes behaved poorly. Both thallium electrodes were one-phase liquids over the entire range, as was electrode C, one of the zinc electrodes. The other zinc electrode, B, was a two-phase amalgam below about 35°C, and a one-phase one above this temperature. The data are too scattered to show effects due to this feature. It is evident from the data that the Zn(Hg)/ZnCl₂ electrodes were considerably better behaved than were the Tl(Hg)/TlCl₂ ones.

At 100°C the electrochemical response rate of this cell was found to be much greater than 1-1/2 hours for a $\pm 10^\circ\text{C}$ temperature change. Thermal equilibrium required about 30 minutes after a 10°C change in temperature.

TABLE IV

MEASURED EMFS FOR CELL 69 USING KCl ELECTROLYTE IN NH_3

<u>Electrode</u>	<u>Amalgam Metal</u>	<u>Description</u>
A	Tl	Liquid with some powder.
B	Zn	Liquid with thick gray salt layer about 7 mm thick.
C	Zn	" " " " " "
D	Tl	Liquid with exposed metal top and salt around edges.

Cell is too full and expansion bulb is smaller than usual.

TIME HOURS	TEMP. °C	ELECTRODE EMF							
		DA	DC	DB	AB	AC	BC		
0.0	25	+0.032631	0.92870	0.9258	0.8923	0.89593	+0.00367		
1.2	35	+0.04082	0.91457	0.9122	0.8712	0.8746	+0.0025		
4.5	47	+0.01631	0.89290	0.8837	0.86854	0.87782	+0.00947		
21.2	45	+0.0496	0.86	0.8824	0.9319	0.904	-0.025		
26.2	61	-0.01040	0.8256	0.8472	0.9531	0.9321	-0.0210		
29.0	74	-0.0871	0.796	0.824	0.912	0.834	-0.028		
46.0	73	-0.01018	0.776	0.8127	0.8227	0.787	-0.034		
59.7	90	-0.0234	0.714	0.7676	0.7907	0.737	-0.054		
61.7	90	-0.02361	0.711	0.769	0.792	0.734	-0.057		
71.0	89	-0.02338	0.70	0.7648	0.7867	0.726	-0.060		
73.0	98	-0.02808	0.684	0.741	0.77	0.705	-0.067		
75.5	100	-0.02790	0.682	0.739	0.767	0.707	-0.058		
77.5	98	-0.02735	0.687	0.765	0.764	0.709	-0.057		
96.0	90	-0.02424	0.693	0.756	0.780	0.7158	-0.062		
121.0	78	-0.02274	0.777	0.7723	0.7958	0.771	-0.027		
131.7	69	-0.02088	0.793	0.8037	0.8235	0.812	-0.01161		
140.7	59	-0.01929	0.8047	0.8146	0.8329	0.8223	-0.0104		
147.4	50	-0.02156	0.8254	0.8357	0.8565	0.8467	-0.0099		
154.9	39	-0.00898	0.8587	0.865	0.872	0.8657	-0.0057		
166.4	27	-0.0132	0.89314	0.8915	0.8782	0.87974	+0.0036		

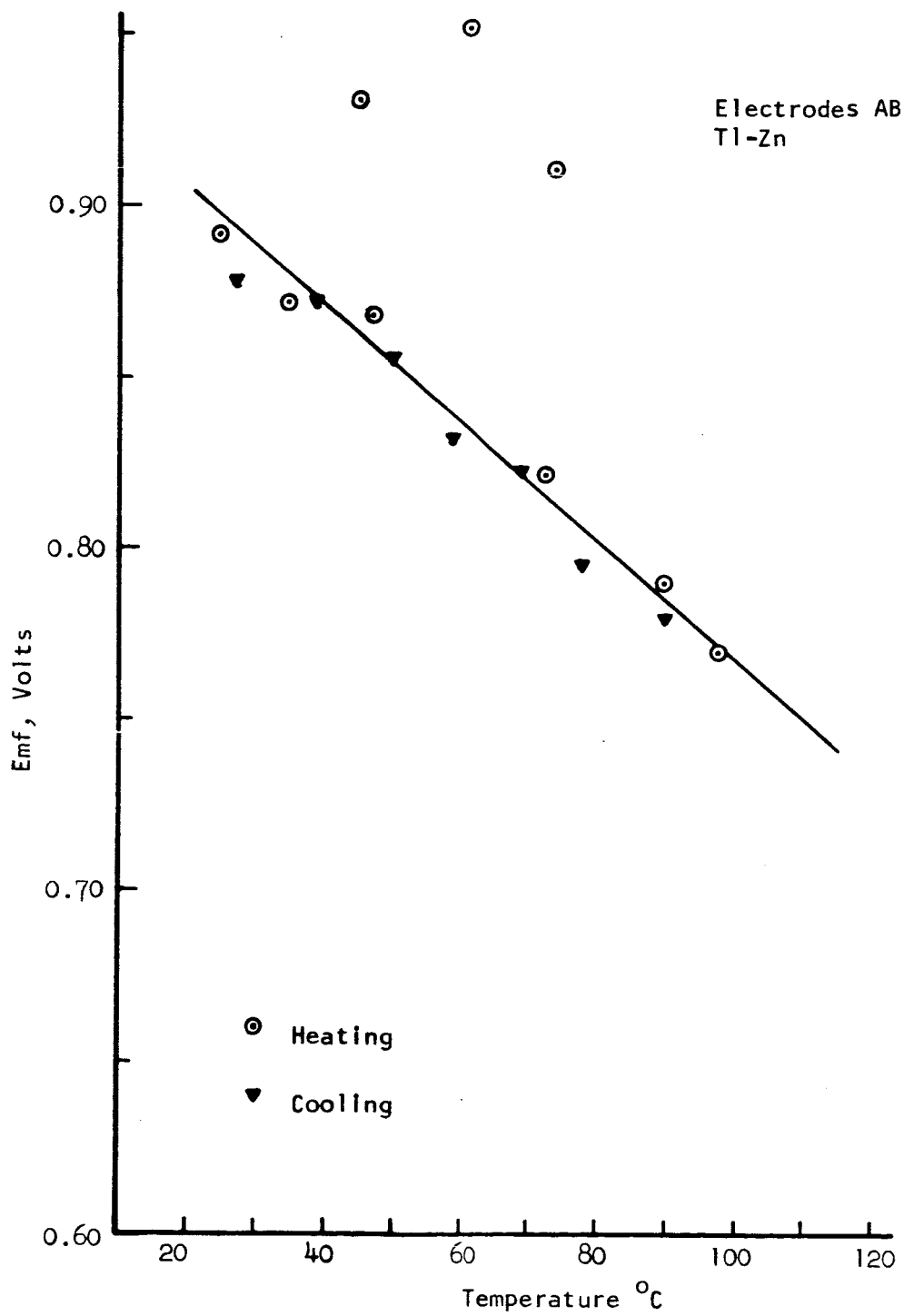


Fig. 4A. EMFS FOR METAL AMALGAM ELECTRODE CELL 69

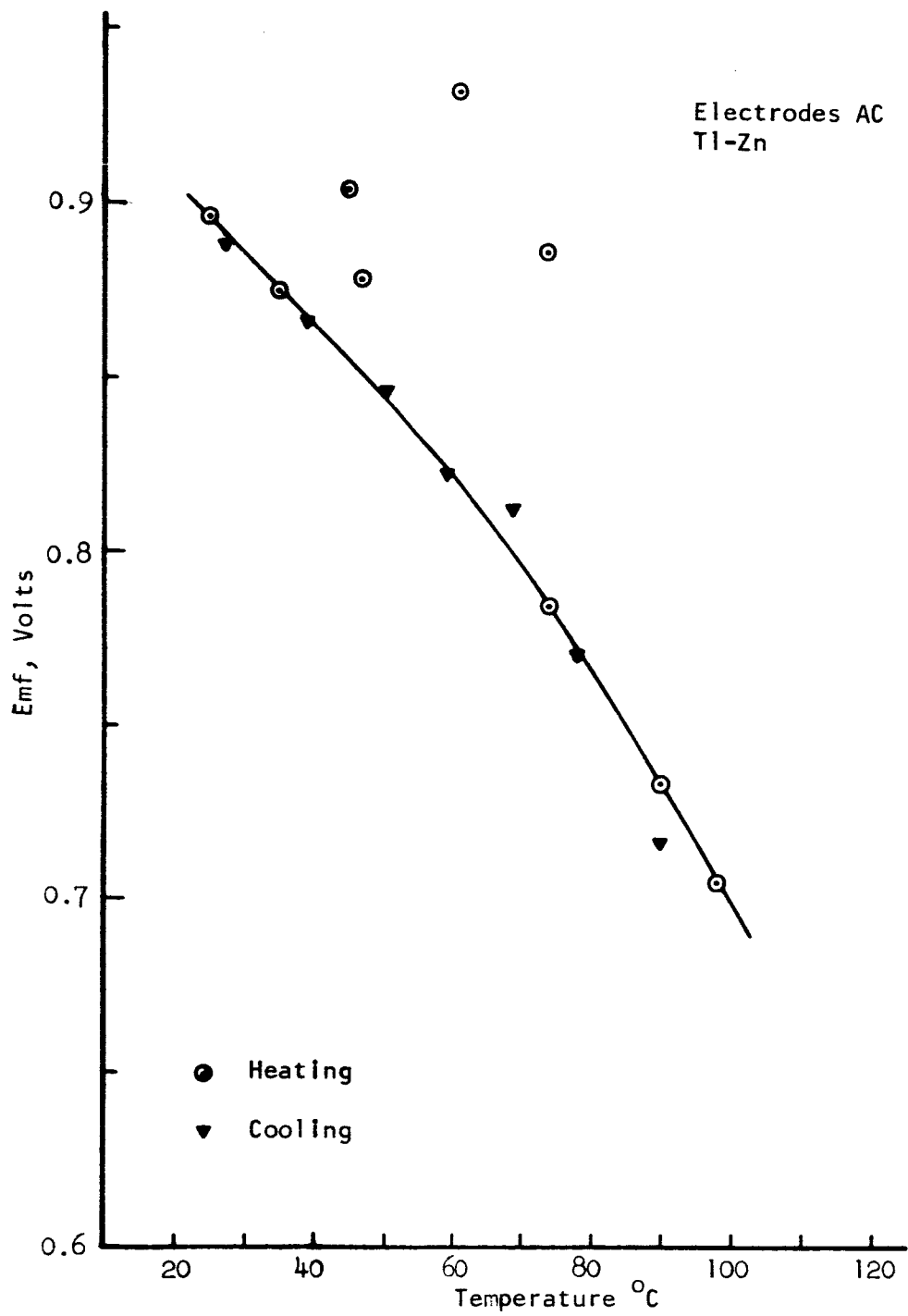


Fig. 4B EMFS FOR METAL AMALGAM ELECTRODE CELL 69

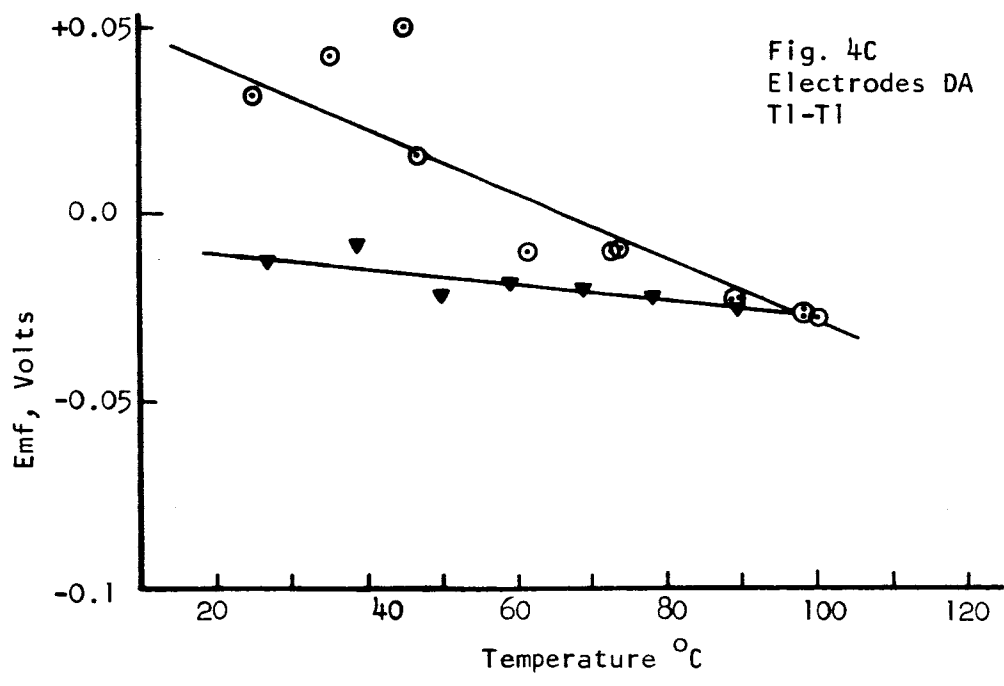
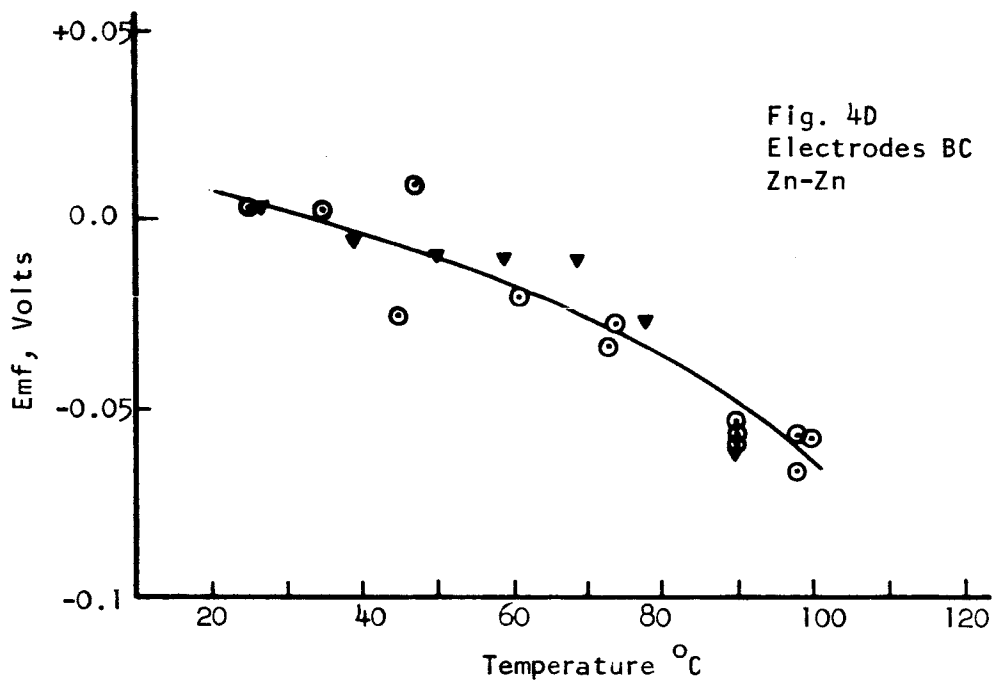


Fig. 4. EMFS FOR METAL AMALGAM ELECTRODE CELL 69
Circles are heating
Triangles are cooling

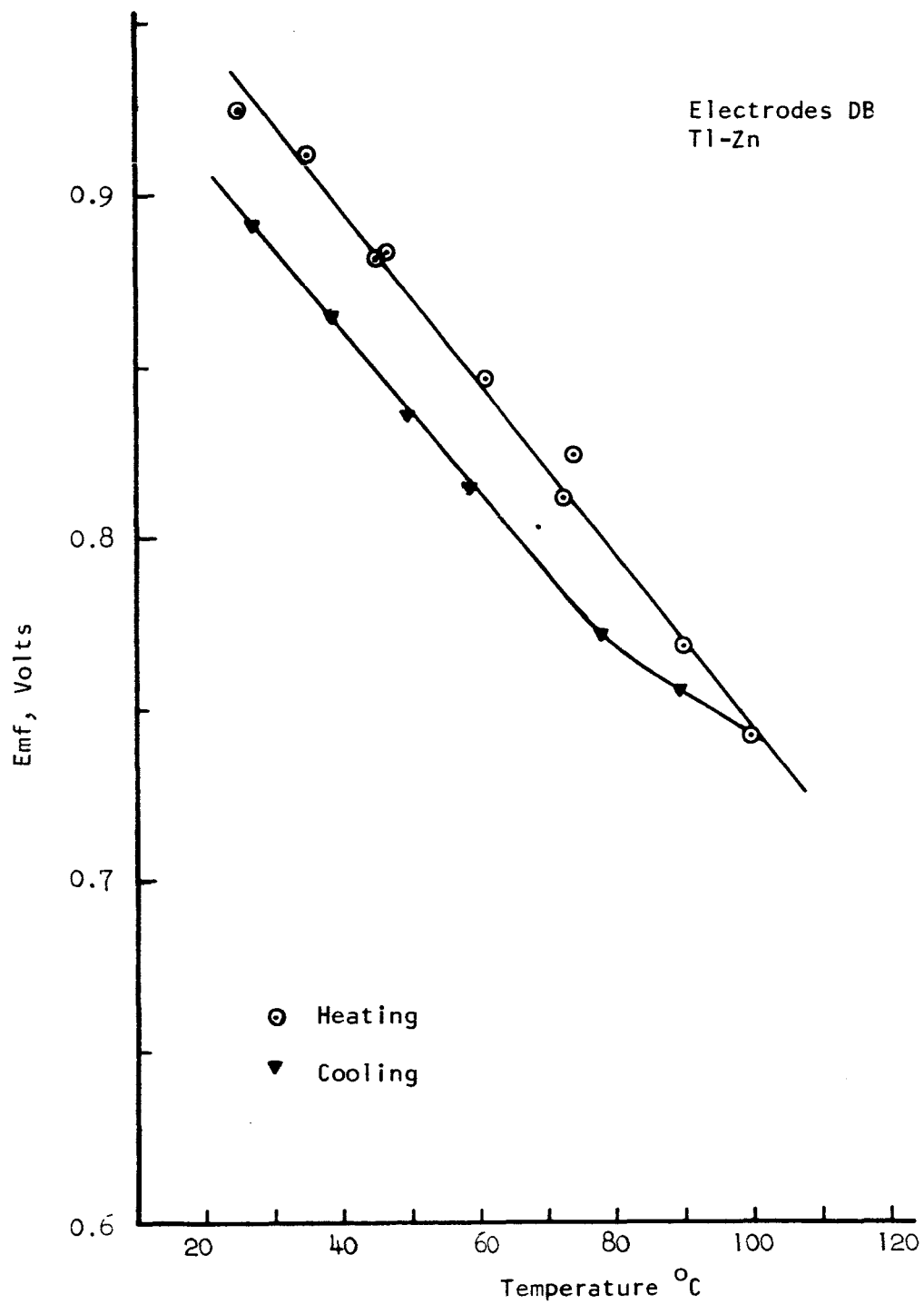


Fig. 4E. EMFS FOR METAL AMALGAM ELECTRODE CELL 69

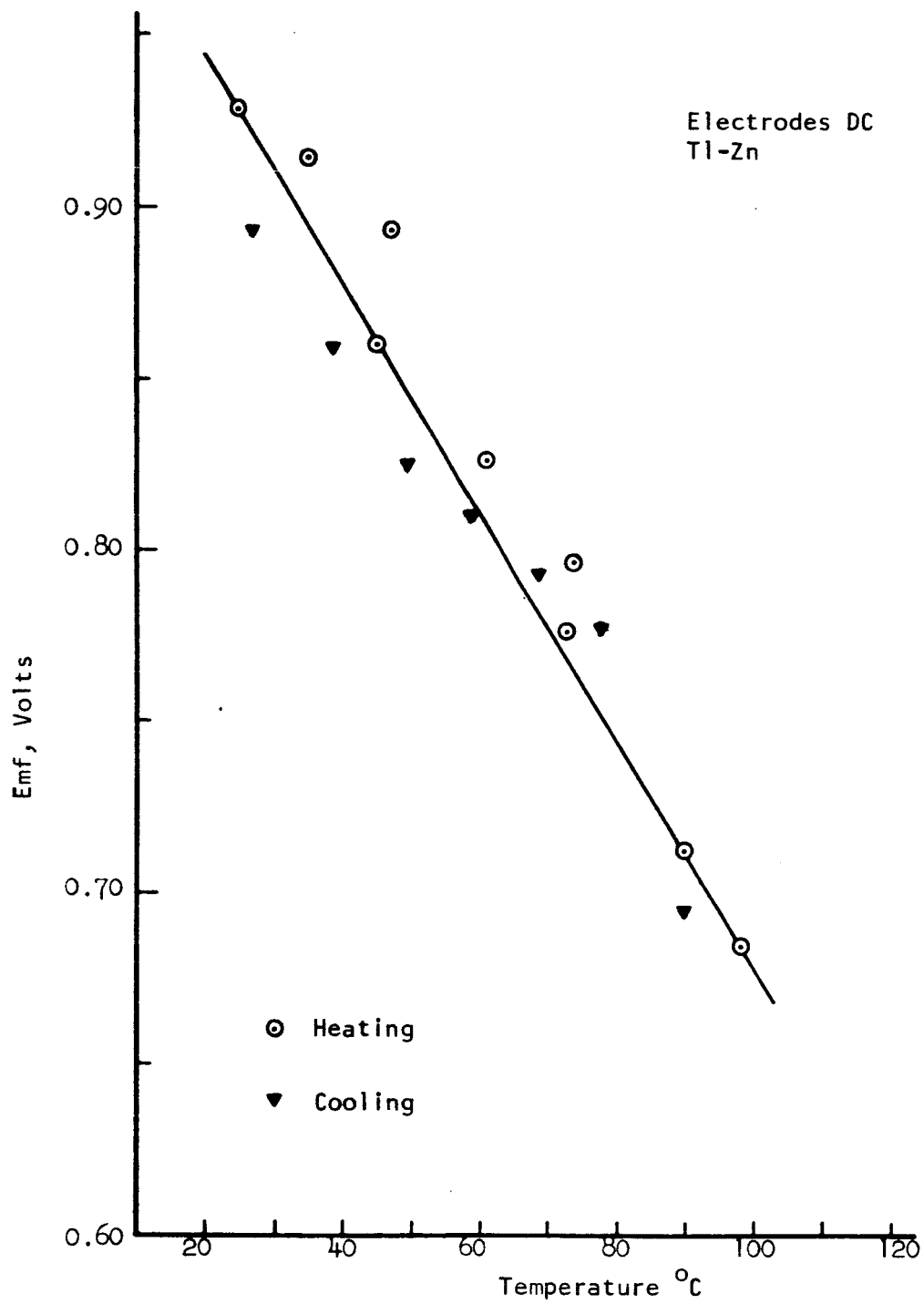


Fig. 4F. EMFS FOR METAL AMALGAM ELECTRODE CELL 69

3.0 SMALL PRESSURE VESSEL MODIFICATIONS

It was planned to modify the top closure of the small pressure vessel during this quarter. The planned modification would have made the closures of the large and small vessels interchangeable, thus expediting the running of cells in both vessels. A study of the existing bomb has shown that, though the modifications are possible, they will be too expensive. We plan to continue to examine this problem as the ability to run two cells at once would accelerate the program.

4.0 SUMMARY

Using cells 58 and 63, we have established that the emfs of sodium amalgam concentration cells are independent of the state of the electrolyte. To complete this phase of the program, we are planning to try to make a reproducible reference electrode, and then to make a final set of measurements.

Using a new cell filling system, we are now able to fill small numbers of cells rapidly. This will enable us to respond to current data more readily.

Previously, we prepared about three months supply of cells at one time.

Now we can prepare a new cell for the next run.

Measurements on cell 69 show that at 100°C the electrochemical equilibration after a temperature change of 10°C requires more than 1-1/2 hours. As a result, we are now allowing 6 or more hours between readings where there is a temperature change.

5.0 NEXT QUARTER

Measurements will continue on the effects of the electrolyte state on the emfs of metal-amalgam insoluble-salt electrodes.

We plan to try to develop a reference electrode for use in ammonia over this temperature range. Our first trial will be a pure metallic-lead insoluble-salt electrode. We will add PbCl_2 to a metallic lead powder, seal off the cell, and evacuate. Then we will subject the cell (under vacuum) to ultrasonics, since this generally leads to evolution of volatile contaminants. After this we will heat the electrode to melt the lead. Then the cell will be filled and sealed off for measurements.

Preparation of a paper on the nature of ammoniacal solutions will be completed and submitted for publication.