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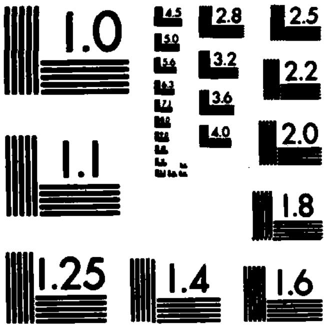

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NOVEMBER 1983

Specific Energies of Concentration Cells Using Room Temperature Chloroaluminate Ionic Liquids

C. J. DYMEK, JR.

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PROJECT 230

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

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FJSRL-TR-83-0013

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This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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Acid-base concentration cells using room temperature ionic liquids have been constructed, discharged, and analyzed in previous work in the Frank J. Seiler Research Laboratory. The ionic liquid electrolytes in these cells are formed by mixing 1-methyl-3-ethylimidazolium chloride (MCl) with $AlCl_3$ at various mole fractions, N, of $AlCl_3$. The proposed electrode processes in the cell are oxidation of the aluminum anode in basic melts, $N < 0.5$, and reduction of $Al_2Cl_7^-$ in acidic melts, $N > 0.5$, to Al at the cathode. The theoretical specific energies of such cells depends on the values of N for the acidic and basic melts and the transport numbers of the M^+, $AlCl_4^-$, and $Al_2Cl_7^-$ ions. This report shows how the specific energy depends on these parameters and how theoretical specific energies were calculated. Theoretical results are also shown to agree with previously obtained experimental results.

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Directorate of Chemical Sciences
The Frank J. Seiler Research Laboratory
Air Force Systems Command
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SUMMARY

Acid-base concentration cells using room temperature ionic liquids have been constructed, discharged, and analyzed in previous work in the Frank J. Seiler Research Laboratory. The ionic liquid electrolytes in these cells are formed by mixing 1-methyl-3-ethylimidazolium chloride (MCl) with $AlCl_3$ at various mole fractions, N, of $AlCl_3$. The proposed electrode processes in the cell are oxidation of the aluminum anode in basic melts, $N < 0.5$, and reduction of $Al_2Cl_7^-$ in acidic melts, $N > 0.5$, to Al at the cathode. The theoretical specific energies of such cells depends on the values of N for the acidic and basic melts and the transport numbers of the M^+, $AlCl_4^-$, and $Al_2Cl_7^-$ ions. This report shows how the specific energy depends on these parameters and how theoretical specific energies were calculated. Theoretical results are also shown to agree with previously obtained experimental results.

PREFACE

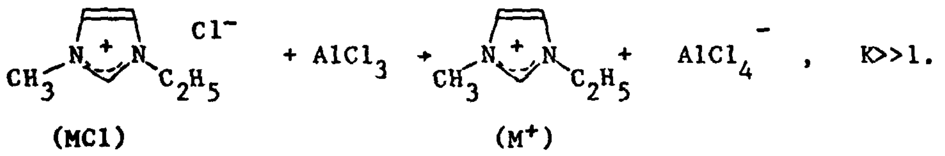
This is a report on work done in Work Unit 2303-F2-11, Room Temperature Molten Salt Battery Research. The report is intended to show how calculations of specific energy made in conjunction with experimental work done in this work unit were actually carried out. Results of the experimental work are being reported in the open literature, unburdened by the relatively laborious step-by-step presentation of the calculation. I wish to thank Capt Auborn, USNR, and Bell Research Labs; Lt Col Fannin, Maj Williams, Dr Wilkes, and Dr Donahue of the Frank J. Seiler Research Lab; and Dr Lowell A. King for many helpful discussions regarding the validity and usefulness of these calculations. I also appreciate the invaluable assistance of Lt Col Fannin in the programming of the calculations. I especially thank Judy Cross for her cheerful, persevering, and expert secretarial assistance in the preparation of this report.

LIST OF FIGURES

LIST OF TABLES

I. Introduction:

Researchers in this Laboratory have discovered a chloroaluminate salt which is liquid at or well below room temperature (1). This salt is formed by mixing 1-methyl-3-ethylimidazolium chloride (MCl) with $AlCl_3$, both solids at room temperature, as shown below:



(1)

When $AlCl_3$ is added in less than stoichiometric amount, i.e., the mole fraction of $AlCl_3$ in the melt, N, is less than 0.5, the anions in the melt are $AlCl_4^-$ and Cl^-. Such mixtures are basic since Cl^- is a Lewis base. When $N > 0.5$, the process,

$$AlCl_3 + AlCl_4^- \longrightarrow Al_2Cl_7^-, \qquad K>>1, \tag{2}$$

occurs, and the anions are $AlCl_4^-$ and $Al_2Cl_7^-$. Such melts are acidic since $Al_2Cl_7^-$ is a strong Lewis acid. The anion mole fraction of each ion as a function of N is shown in Fig 1. At mole fractions greater than 0.50, the reaction,

$$Al_2Cl_7^- + AlCl_3 \longrightarrow Al_3Cl_{10}^-, \tag{3}$$

may also be occurring; but we shall ignore it in the present discussion.

The acid-base properties of these melts are best understood in terms of the equilibrium,

$$Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4^-, \qquad K>>1. \tag{4}$$

Since K for this acid-base neutralization reaction is large, acidic and basic melts can be combined in concentration cells, as has been demonstrated (2). In these cells, a schematic diagram of which is shown in Fig 2, measured specific energies were shown to approach calculated specific energies. The purpose of this report is to show how the specific energy of such a concentration cell can be calculated, given N's of the acidic and basic melts and transport numbers, $t_\pm$ for the M^+ and $Al_2Cl_7^-$ ions. It can be shown that the transport number for $AlCl_4^-$ will not affect the specific energy for a given $t_-(Al_2Cl_7^-)$. This can be seen intuitively from Fig 2 which shows that of the three transporting ions, only $Al_2Cl_7^-$ is involved in the electrochemical reaction. Therefore, in this approach, $t_+(M^+)$ is treated as effectively the sum of $t_+(M^+)$ and $t_-(AlCl_4^-)$, so it is not the same as the true transport number for M^+ obtained experimentally. Since Cl^- flow out of the anolyte would oppose the current and therefore should not occur, $t_-(Cl^-)$ is set at zero.

II. Theory:

Approach. The anode and cathode reactions shown in Fig 2 do not take into account the mechanism for ion transport. Assuming, based on the discussion above, that only M^+ and $Al_2Cl_7^-$ transport charge, the unbalanced anode and cathode reactions are:

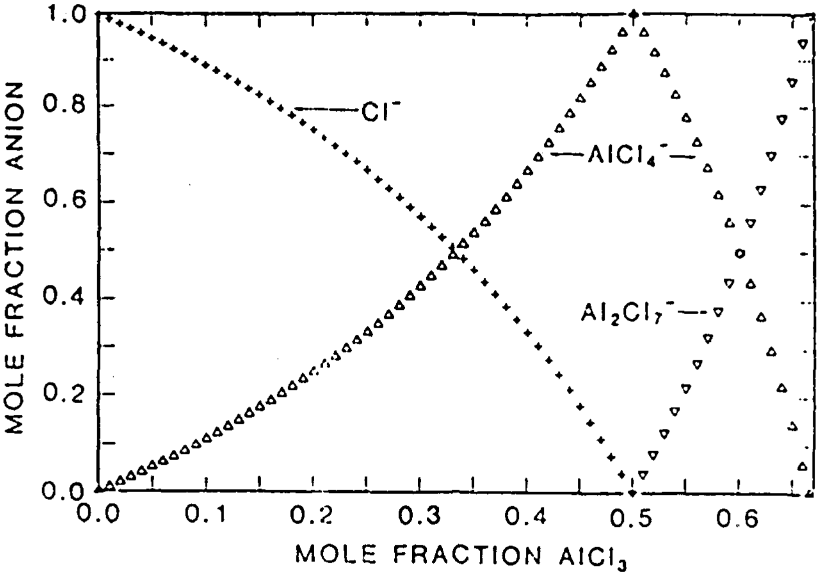


Fig 1 Anion mole fractions in chloroaluminate melts of various $AlCl_3$ mole fraction.

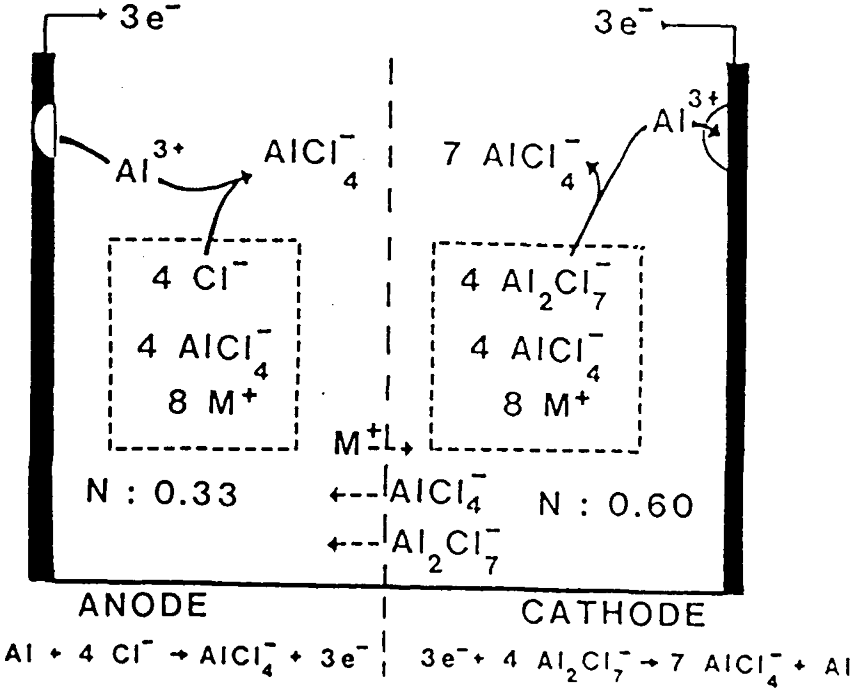


Fig 2. Schematic diagram of concentration cell.

$$\text{ANODE:}\quad (MCl + AlCl_3) + Al + Al_2Cl_7^- \longrightarrow MAlCl_4 + M^+ + e^- \tag{5}$$

$$\text{CATHODE:}\quad (MCl + AlCl_3) + M^+ + e^- \longrightarrow Al + MAlCl_4 + Al_2Cl_7^- \tag{6}$$

These reactions differ from those in Fig 2 in that 1) M^+ and $Al_2Cl_7^-$ are included so that transport of charge by these species can be accounted for and 2) the actual reacting species in the starting electrolytes ($MCl + AlCl_3$) are not specified, thus allowing the mass balance to be carried out for various to-be-specified mole fractions of $AlCl_3$. In each equation, the ($MCl + AlCl_3$) represents the starting melt components with mole fractions to be specified. $MAlCl_4$, or N = 0.5 melt, is on the product side since in theory the cell can be discharged until both acid and basic melts are neutral if stoichiometric amounts of these melts are used as the catholyte and anolyte. The approach then is to specify the starting mole fractions of anolyte (NA) and catholyte (NC) and the transport numbers for M^+ and $Al_2Cl_7^-$ (subsequently designated t_+ and t_{-7}) and then balance the equations for a given amount of charge passed. From the coefficients of the MCl and $AlCl_3$ in the acid and basic melts and the Al reacted, we get the masses of anolyte (MALY) and catholyte (MCLY) and Al transferred (MAL) required to pass the given amount of charge. Then specific energy is calculated from equation (7)

$$\text{SP EN (Whr/kg)} = \frac{(V)\ (Q/96{,}487)\text{eq}\quad (26.8\ \text{Ahr/eq})}{(\text{MALY} + \text{MCLY} + \text{MAL})\ \text{kg}} \tag{7}$$

where V is the load voltage, Q is the charge passed, and 26.8 Ahr/eq is a conversion factor. All the terms in eqn (7) can be measured experimentally (2). Thus the specific energies so calculated can be compared to experimental values to test the model represented by Fig 2 and equations (5) and (6).

2. Determination of Coefficients in Balanced Cell Reactions.

a) We start by specifying that in the theoretical cell, one equivalent of charge is passed, i.e., the coefficient of e^- is 1.

b) Next we assign a value for t_{-7} which fixes t_+ at $1-t_{-7}$ (recalling that t_+ is effectively the sum of t_+ and t_{-4} and that $1 = t_+ + t_{-4} + t_{-7}$).

c) When the t_{-7} $Al_2Cl_7^-$ is transported across the separator into the basic melt which contains MCl, the following reaction occurs,

$$t_{-7}\, Al_2Cl_7^- + t_{-7}\, MCl \longrightarrow t_{-7}\, MAlCl_4 + t_{-7}\, AlCl_4^- \tag{8}$$

in accordance with equation (4). Since it doesn't matter <u>when</u> in the course of the cell discharge this occurs, we can, for the purpose of simplifying the mass balance, replace the reactant $Al_2Cl_7^-$ in the ANODE reaction by the t_{-7} $AlCl_4^-$ and t_{-7} $MAlCl_4$ formed.

d) All the available evidence (2) demonstrates that 1/3 mole Al is consumed at the anode and deposited on the cathode for each mole e^- passed. Thus the coefficient of Al in both reactions is set at 1/3.

e) At this point, the ANODE reaction can be written.

$$\text{ANODE: } (MCl + AlCl_3) + \underline{1/3\ Al} + \underline{t_{-7}\ AlCl_4^-} + \underline{t_{-7}\ MAlCl_{4\,(r)}} \longrightarrow MAlCl_{4\,(p)} + \underline{t_+\ M^+} + \underline{e^-} \tag{9}$$

where the underlined species have their coefficients specified. The (p) and (r) subscripts distinguish the reactant $MAlCl_4$ formed by equation (8) from the product $MAlCl_4$ of the electrochemical reaction. Now, balance of Al in equation (9) requires that

$$C(AlCl_3) = C(MAlCl_{4(p)}) - 1/3 - 2t_{-7}, \tag{10}$$

and balance of Cl requires that

$$4\ C(MAlCl_{4(p)}) = C(MCl) + 3\ C(AlCl_3) + 8\ t_{-7}, \tag{11}$$

where the C's are the coefficients of the designated species in the ANODE reaction.

f) The MCl in equation (9) is what remains of the MCl initially in the melt, MCl_i, after reaction with the transported $Al_2Cl_7^-$ (equation (8)).

Thus we can write,

$$C(MCl_i) = C(MCl) + t_{-7}. \tag{12}$$

Now $C(MCl_i)$ is related to NA, the initial mole fraction of $AlCl_3$ in the anolyte melt, by

$$C(MCl_i) = \frac{(1 - NA)}{NA}\ C(AlCl_3) \tag{13}$$

Combining equations (12) and (13) gives

$$C(MCl) = \frac{(1 - NA)}{NA}\ C(AlCl_3) - t_{-7} \tag{14}$$

Substitution of equation (14) into (11) gives

$$4\ C(MAlCl_{4(p)}) = \frac{(1 - NA)}{NA} \quad C(AlCl_3) - t_{-7} + 3C(AlCl_3) + 8t_{-7}$$

or simplifying,

$$4C(MAlCl_{4(p)}) = \left[3 + \frac{(1 - NA)}{NA}\right] C(AlCl_3) + 7t_{-7} \tag{15}$$

If we then substitute the expression for $C(AlCl_3)$ in eqn (10) into (15), we get

$$4C(MAlCl_{4(p)}) = \left[3 + \frac{(1 - NA)}{NA}\right]\left[C(MAlCl_{4(p)}) - 1/3 - 2t_{-7}\right] + 7t_{-7},$$

which can be rearranged to give

$$C(MAlCl_{4(p)}) = \frac{-\left[3+\frac{(1 - NA)}{NA}\right](1/3 + 2t_{-7}) + 7t_{-7}}{4 - \left[3 + \frac{(1 - NA)}{NA}\right]} \tag{16}$$

This is the equation used to calculate the coefficient of $MAlCl_{4(p)}$ in the ANODE reaction for specified values of t_{-7} and NA.

g) Now that we have $C(MAlCl_{4(p)})$, we get, from balance of M,

$$C(MCl_i) = C(MAlCl_{4(p)}) + t_+, \tag{17}$$

and with $C(MCl_i)$ determined, we also have $C(MCl)$ from equation (12) and $C(AlCl_3)$ from eqn (13).

At this point, all coefficients in the ANODE reaction, eqn (9), have been calculated, including the initial number of moles of MCl, $C(MCl_i)$, required to produce 1 equivalent of electrons by stoichiometric reaction to the neutral melt.

h) By the same arguments as given in steps (a) through (e), we can write the cathode reaction,

$$\text{CATHODE: } (MCl + AlCl_3) + \underline{t_+}M^+ + \underline{1}e^- \rightarrow \underline{1/3\ Al} + MAlCl_4 + \underline{t_{-7}\ Al_2Cl_7^-} \qquad (18)$$

where the coefficients of the underlined species are known. Thus, we need to determine the CATHODE reaction coefficients, B(MCl), B($AlCl_3$), and B($MAlCl_4$) for a specified mole fraction of the catholyte, NC.

i) We start by noting that the amount of $Al_2Cl_7^-$ which must be present in this melt to produce 1 mole e^- by the CATHODE reaction shown in Fig 2 <u>and</u> transport t_{-7} moles of charge is $(4/3 + t_{-7})$. Then we ask how much $AlCl_3$ and MCl must be present in the melt of mole fraction, NC, to contain this amount of $Al_2Cl_7^-$. Since the reactions,

$$MCl + AlCl_3 \rightarrow MAlCl_4,$$

and (19)

$$MAlCl_4 + AlCl_3 \rightarrow MAl_2Cl_7, \qquad (20)$$

both have K>>1, we can write

$$\text{mol } (Al_2Cl_7^-) = \text{mol } (AlCl_3) - \text{mol } (MCl), \text{ or}$$

$$(4/3 + t_{-7}) = NC\ n - (1 - NC)\ n = (2NC-1)n \qquad (21)$$

where n is the total moles (MCL + $AlCl_3$) of catholyte. Thus, since $B(AlCl_3) = NC\ n$, we can write, using eqn (21),

$$B(AlCl_3) = NC \left[\frac{4/3 + t_{-7}}{2NC - 1}\right] \tag{22}$$

Similarly,

$$B(MCl) = (1 - NC)\left[\frac{4/3 + t_{-7}}{2NC - 1}\right] \tag{23}$$

j) Balance of M in eqn (18) requires that

$$B\ (MAlCl_4) = B(MCl) + t_+ \tag{24}$$

Thus all coefficients in the CATHODE reaction to produce 1 mol e^- and neutral melt are also determined for given values of NC and t_+.

k) If we specify NA, NC, and the load voltage, V, we can now calculate the specific energy for a range of values of t_+ by using eqn (7) in the form,

$$SP\ EN = \left[(26.8) \times (V)\right] / \left[0.14664\ (B(MCl) + C(MCl_i)) + 0.13334(B(AlCl_3) + C(AlCl_3)) + \frac{0.02698}{3}\right] \tag{25}$$

where the coefficients in the denominator are multiplied by the appropriate molecular weights in kg. This equation appears in the program shown in Fig 3 as line 1240. This is a program which uses our Laboratory's Program for Handling Data (PHD) described in Ref (3). It performs the calculation of coefficients as described above.

l) Since it is not practical to construct cells with exactly stoichiometric amounts of anolyte and catholyte, we have chosen to make the anolyte the limiting reagent. To take this into account in theoretical calculations of

```
SPENPHD      20-OCT-1983 14:56

990  INPUT "MOLE FRACTION OF ANOLYTE, NA";NA
991  INPUT " MOLE FRACTION OF CATHOLYTE, NC";NC
992  INPUT "BATTERY LOAD VOLTAGE, V";V
993  INPUT "ELECTROLYTE MASS RATIO, MASS CLY/MASS ALY, ELECRAT";ELECRAT
995  INPUT "FILE NAME";FILE$
996  OPEN FILE$+".DAT" FOR OUTPUT AS FILE #2
998  PRINT #2,"7,";FILE$
999  PRINT #2,"NA,,0"\PRINT #2,"NC,,0"\PRINT #2,"T7,,0"\PRINT #2,"TM,,0"
1000 PRINT #2,"V,VOLTS,0"\PRINT #2,"SPEN,WHR/KG,0"
1001 PRINT #2,"SPENXCLY,WHR/KG,0"
1002 FOR TM=.5 TO 1.00002 STEP .05
1003 T7=1-TM
1010 PRINT " TRANSPORT NUMBER FOR AL2CL7-,T7";T7
1020 PRINT "TRANSPORT NUMBER FOR IMIDAZOLIUM ION, TM";TM
1080 CM=TM\C4=T7\CMACR=T7\CAL=1/3
1090 CMACP=(-(3+(1-NA)/NA)*(CAL+2*T7)+7*T7)/(4-(3+(1-NA)/NA))
1100 CMCLI=CM+CMACP
1110 CMCL=CMCLI-T7
1120 CALCL3=(NA/(1-NA))*CMCLI
1150 BAL=1/3\B7=T7\BM=TM
1160 BALCL3=NC*((T7+4/3)/(2*NC-1))
1170 BMCL=(1-NC)*((T7+4/3)/(2*NC-1))
1180 BMAC=BMCL+BM
1190 ELECRATS=(BALCL3*133.34+BMCL*146.64)/(CMCLI*146.64+CALCL3*133.34)
1195 EXCLYRAT=ELECRAT-ELECRATS
1200 EXCLY=EXCLYRAT*(CMCLI*.14664+CALCL3*.13334)
1220 PRINT\PRINT\PRINT
1230 PRINT "GIVEN THE ABOVE PARAMETERS:"\PRINT
1240 SPEN=26.8*V/(0.14664*(BMCL+CMCLI)+0.13334*(BALCL3+CALCL3)+0.02698*(CAL))
1243 IF EXCLY<0 THEN SPENXCLY=0\ GOTO 1250
1245 SPENXCLY=26.8*V/((26.8*V/SPEN)+EXCLY)
1250 PRINT "BALANCED ANODE REACTION IS"\PRINT
1260 PRINT USING "(##.#### MCL + ##.#### ALCL3) + #.### AL + #.#### ALCL4- + #.##
## MALCL4", CMCL,CALCL3,CAL,C4,CMACR
1265 PRINT\ PRINT USING "---> ##.#### MALCL4 + #.#### M+ + 1.0000 E-",CMACP,CM
1270 PRINT\PRINT\PRINT "BALANCED CATHODE REACTION IS"\PRINT
1280 PRINT USING "(##.#### MCL + ##.#### ALCL3) + #.#### M+ + 1.0000 E-",BMCL,BAL
CL3,BM
1290 PRINT\PRINT USING "---> #.### AL + ##.#### MALCL4 + #.####AL2CL7-",BAL,BMAC,
B7
1292 PRINT\PRINT\PRINT USING "THE STOICHIOMETRIC RATIO OF MCLY/MALY, ELECRATS, IS
 ##.###",ELECRATS
1294 PRINT \PRINT USING "THE SPECIFIC ENERGY IS ###.### WHR/KG",SPEN
1296 IF EXCLY<0 THEN PRINT\PRINT USING "THE STOICHIOMETRIC RATIO EXCEEDS THE SPEC
IFIED MCLY/MALY RATIO, #.##",ELECRAT
1300 IF EXCLY<0 GOTO 1302
1301 PRINT\PRINT USING "SPEC ENERGY INCLUDING EXCESS CATHOLYTE IS ##.## WHR/KG",S
PENXCLY
1302 PRINT #2,"2:,";NA;",";NC;",";T7;",";TM;",";V;",";SPEN;",";SPENXCLY
1305 NEXT TM
1307 CLOSE #2
1310 END

Ready
```

Fig 3 SPENPHD program for calculating concentration cell specific energy for a range of transport numbers.

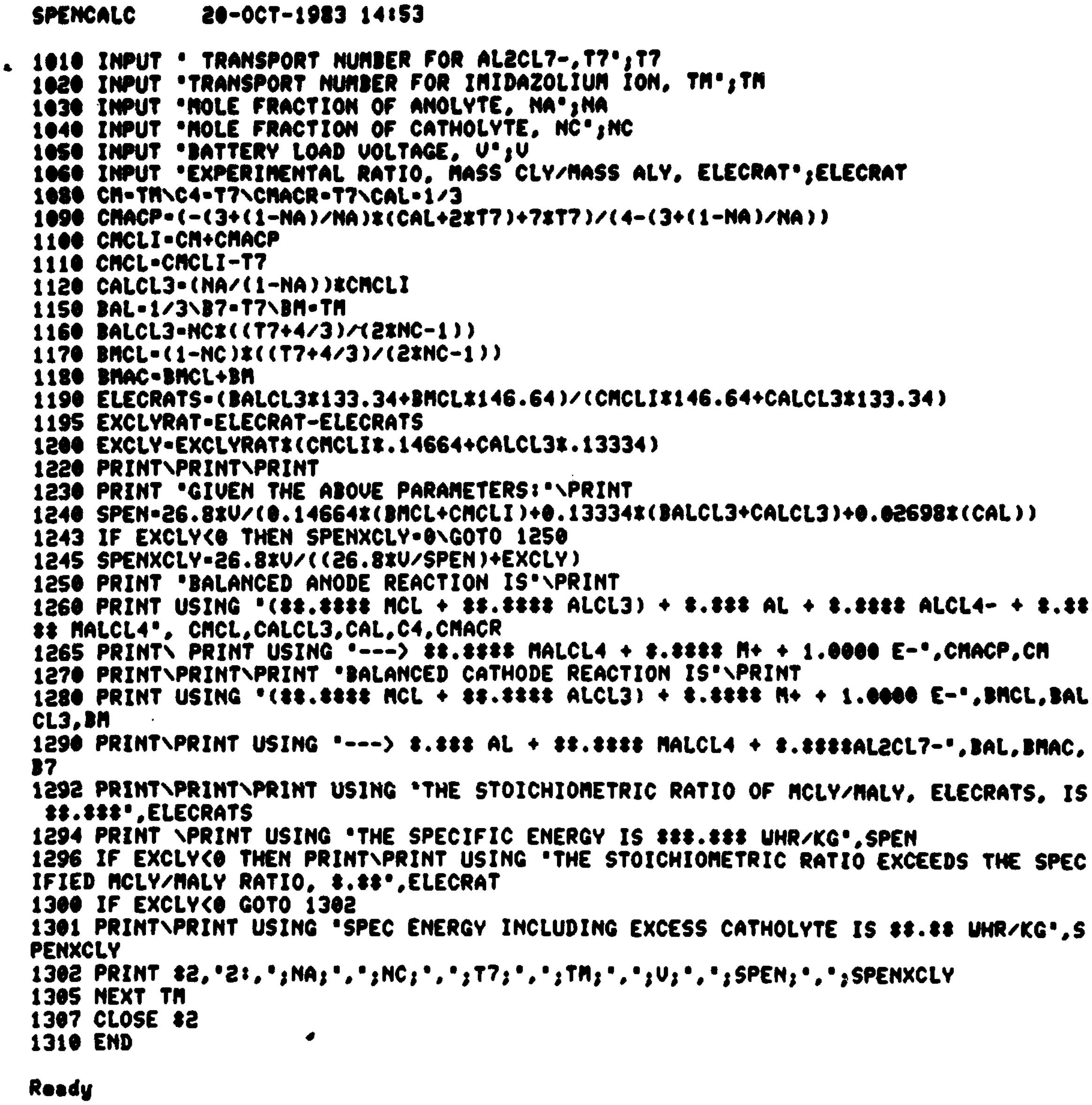
the specific energy, we can specify an actual ratio of mass catholyte to mass anolyte (ELECRAT in the program). The corresponding stoichiometric ratio, ELECRATS, is computed directly from the coefficients of the melt components in the anolyte and catholyte obtained as described above. The mass of catholyte used in the stoichiometric cell is simply ELECRATS x mass(anolyte), and the mass of catholyte used in the cell with excess catholyte is ELECRAT x mass (anolyte). Thus, the difference in these two masses, EXCLY (calculated in line 1200) is simply added to the denominator in eqn (25) to get SPENXCLY, the specific energy for a given mass ratio of catholyte to anolyte, in which there is excess catholyte. If ELECRATS is larger than ELECRAT, so that EXCLY is negative, SPENXCLY is not calculated but set equal to zero.

III. Results:

Results for a cell with t_{-7}, t_{+}, NA, NC, V, and ELECRAT all specified can be obtained using the SPENCALC program shown in Fig 4. This program is virtually identical to SPENPHD except only one set of transport numbers is used and the results are not transferred into a dataset in the PHD files. The results for a given run of SPENPHD which is representative of actual concentration cells discharged in this Laboratory (2), is shown in Fig 5.

Results of runs done with SPENPHD are plotted in Figures 6 and 7. In Fig 6, the catholyte in each run is NC = 0.67, and NA is varied. The specific energies including excess catholyte (SPENXCLY) are shown as dashed lines. Note that there is no curve of SPENXCLY for the NA = 0.03 case because ELECRATS for that case exceeds the specified ELECRAT of 1.5.

In Fig 7, the runs have the same NA, set at 0.33, and NC is varied. Note that all SPENXCLY'S are the same since the denominator in the calculation



```
SPENCALC     20-OCT-1983 14:53

1010 INPUT " TRANSPORT NUMBER FOR AL2CL7-,T7";T7
1020 INPUT "TRANSPORT NUMBER FOR IMIDAZOLIUM ION, TM";TM
1030 INPUT "MOLE FRACTION OF ANOLYTE, NA";NA
1040 INPUT "MOLE FRACTION OF CATHOLYTE, NC";NC
1050 INPUT "BATTERY LOAD VOLTAGE, V";V
1060 INPUT "EXPERIMENTAL RATIO, MASS CLY/MASS ALY, ELECRAT";ELECRAT
1080 CM=TM\C4=T7\CMACR=T7\CAL=1/3
1090 CMACP=(-(3+(1-NA)/NA)*(CAL+2*T7)+7*T7)/(4-(3+(1-NA)/NA))
1100 CMCLI=CM+CMACP
1110 CMCL=CMCLI-T7
1120 CALCL3=(NA/(1-NA))*CMCLI
1150 BAL=1/3\B7=T7\BM=TM
1160 BALCL3=NC*((T7+4/3)/(2*NC-1))
1170 BMCL=(1-NC)*((T7+4/3)/(2*NC-1))
1180 BMAC=BMCL+BM
1190 ELECRATS=(BALCL3*133.34+BMCL*146.64)/(CMCLI*146.64+CALCL3*133.34)
1195 EXCLYRAT=ELECRAT-ELECRATS
1200 EXCLY=EXCLYRAT*(CMCLI*.14664+CALCL3*.13334)
1220 PRINT\PRINT\PRINT
1230 PRINT "GIVEN THE ABOVE PARAMETERS:"\PRINT
1240 SPEN=26.8*V/(0.14664*(BMCL+CMCLI)+0.13334*(BALCL3+CALCL3)+0.02698*(CAL))
1243 IF EXCLY<0 THEN SPENXCLY=0\GOTO 1250
1245 SPENXCLY=26.8*V/((26.8*V/SPEN)+EXCLY)
1250 PRINT "BALANCED ANODE REACTION IS"\PRINT
1260 PRINT USING "(##.#### MCL + ##.#### ALCL3) + #.### AL + #.#### ALCL4- + #.##
## MALCL4", CMCL,CALCL3,CAL,C4,CMACR
1265 PRINT\ PRINT USING "---> ##.#### MALCL4 + #.#### M+ + 1.0000 E-",CMACP,CM
1270 PRINT\PRINT\PRINT "BALANCED CATHODE REACTION IS"\PRINT
1280 PRINT USING "(##.#### MCL + ##.#### ALCL3) + #.#### M+ + 1.0000 E-",BMCL,BAL
CL3,BM
1290 PRINT\PRINT USING "---> #.### AL + ##.#### MALCL4 + #.####AL2CL7-",BAL,BMAC,
B7
1292 PRINT\PRINT\PRINT USING "THE STOICHIOMETRIC RATIO OF MCLY/MALY, ELECRATS, IS
 ##.###",ELECRATS
1294 PRINT \PRINT USING "THE SPECIFIC ENERGY IS ###.### WHR/KG",SPEN
1296 IF EXCLY<0 THEN PRINT\PRINT USING "THE STOICHIOMETRIC RATIO EXCEEDS THE SPEC
IFIED MCLY/MALY RATIO, #.##",ELECRAT
1300 IF EXCLY<0 GOTO 1302
1301 PRINT\PRINT USING "SPEC ENERGY INCLUDING EXCESS CATHOLYTE IS ##.## WHR/KG",S
PENXCLY
1302 PRINT #2,"2:,";NA;",";NC;",";T7;",";TM;",";V;",";SPEN;",";SPENXCLY
1305 NEXT TM
1307 CLOSE #2
1310 END

Ready
```

Fig 4 SPENCALC program for calculating specific energy for a concentration cell with fixed transport numbers.

```
SPENCALC     20-OCT-1983 14:54

 TRANSPORT NUMBER FOR AL2CL7-,T7? .25
TRANSPORT NUMBER FOR IMIDAZOLIUM ION, TM? .75
MOLE FRACTION OF ANOLYTE, NA? .37
MOLE FRACTION OF CATHOLYTE, NC? .60
BATTERY LOAD VOLTAGE, V? 1.1
EXPERIMENTAL RATIO, MASS CLV/MASS ALY, ELECRAT? 1.5


GIVEN THE ABOVE PARAMETERS:

BALANCED ANODE REACTION IS

( 3.5865 MCL +  2.2532 ALCL3) + 0.333 AL + 0.2500 ALCL4- + 0.2500 MALCL4

---> 3.0865 MALCL4 + 0.7500 M+ + 1.0000 E-

BALANCED CATHODE REACTION IS

( 3.1667 MCL +  4.7500 ALCL3) + 0.7500 M+ + 1.0000 E-

---> 0.333 AL +  3.9167 MALCL4 + 0.2500AL2CL7-

THE SPECIFIC ENERGY IS 14.9664 WHR/KG
THE STOICHIOMETRIC  RATIO, MASS CLV/MASS ALY, IS 1.272

SPECIFIC ENERGY INCLUDING EXCESS CATHOLYTE IS 13.6067 WHR/KG
Ready
```

Fig 5 Output from run of SPENCALC

Table 1.

Output of SPENPHD calculation with parameters fixed to match those of experimental cells.

```
FILE: CASE37S60
CASE37S60

   NA        NC          T7          TM         V        SPEN    SPENXCLV
   []        []          []          []    [VOLTS]  [WHR/KG]   [WHR/KG]

  0.37     0.60        0.50        0.50       1.1      12.93      11.76
  0.37     0.60        0.45        0.55       1.1      13.29      12.09
  0.37     0.60        0.40        0.60       1.1      13.68      12.43
  0.37     0.60        0.35        0.65       1.1      14.08      12.80
  0.37     0.60        0.30        0.70       1.1      14.51      13.19
  0.37     0.60        0.25        0.75       1.1      14.97      13.61
  0.37     0.60        0.20        0.80       1.1      15.45      14.05
  0.37     0.60        0.15        0.85       1.1      15.97      14.52
  0.37     0.60        0.10        0.90       1.1      16.52      15.02
  0.37     0.60        0.05        0.95       1.1      17.12      15.56
  0.37     0.60        0.00        1.00       1.1      17.76      16.15
```

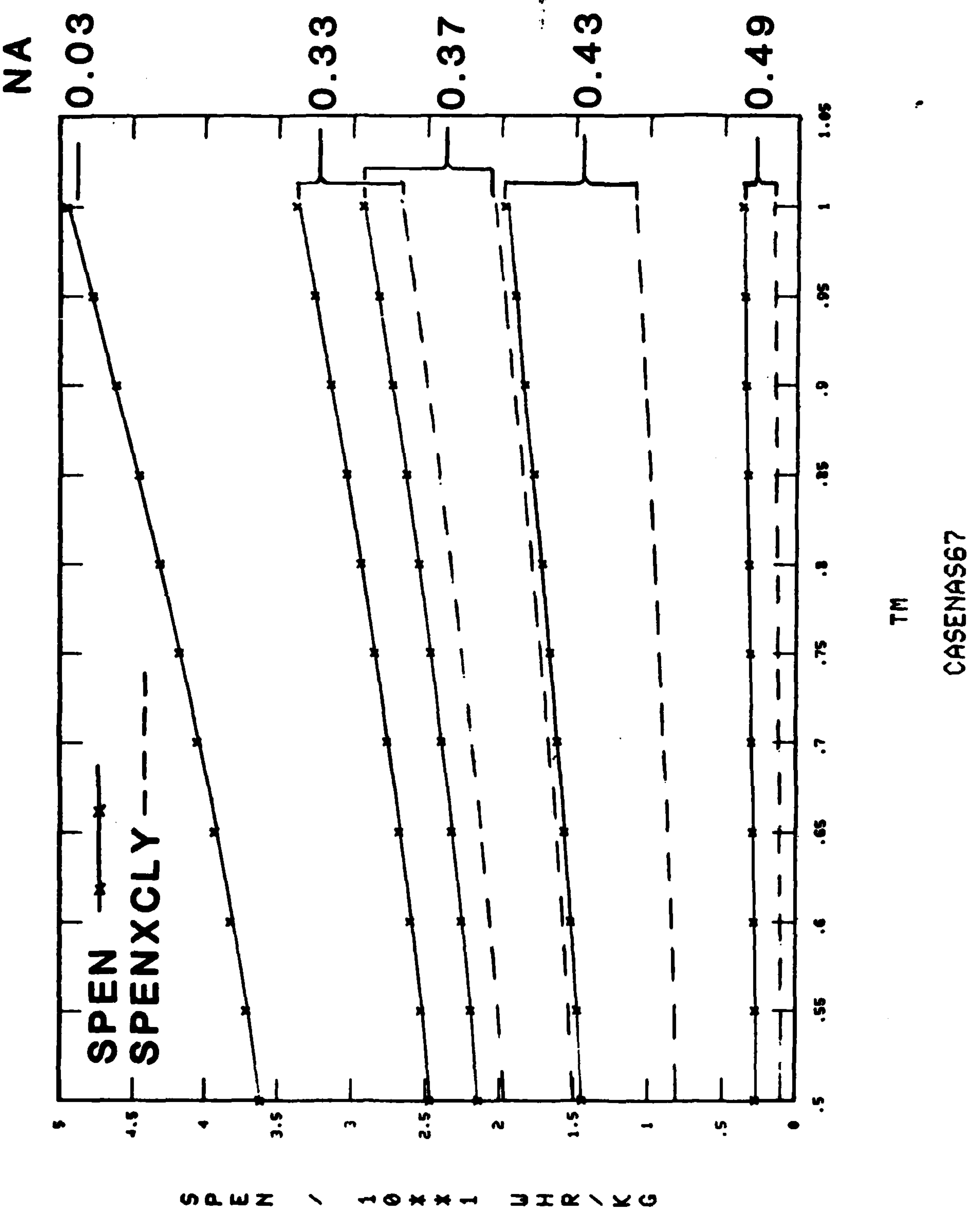


Fig 6 Plotted results of SPENPHD output for cells with anolyte mole fraction varied.

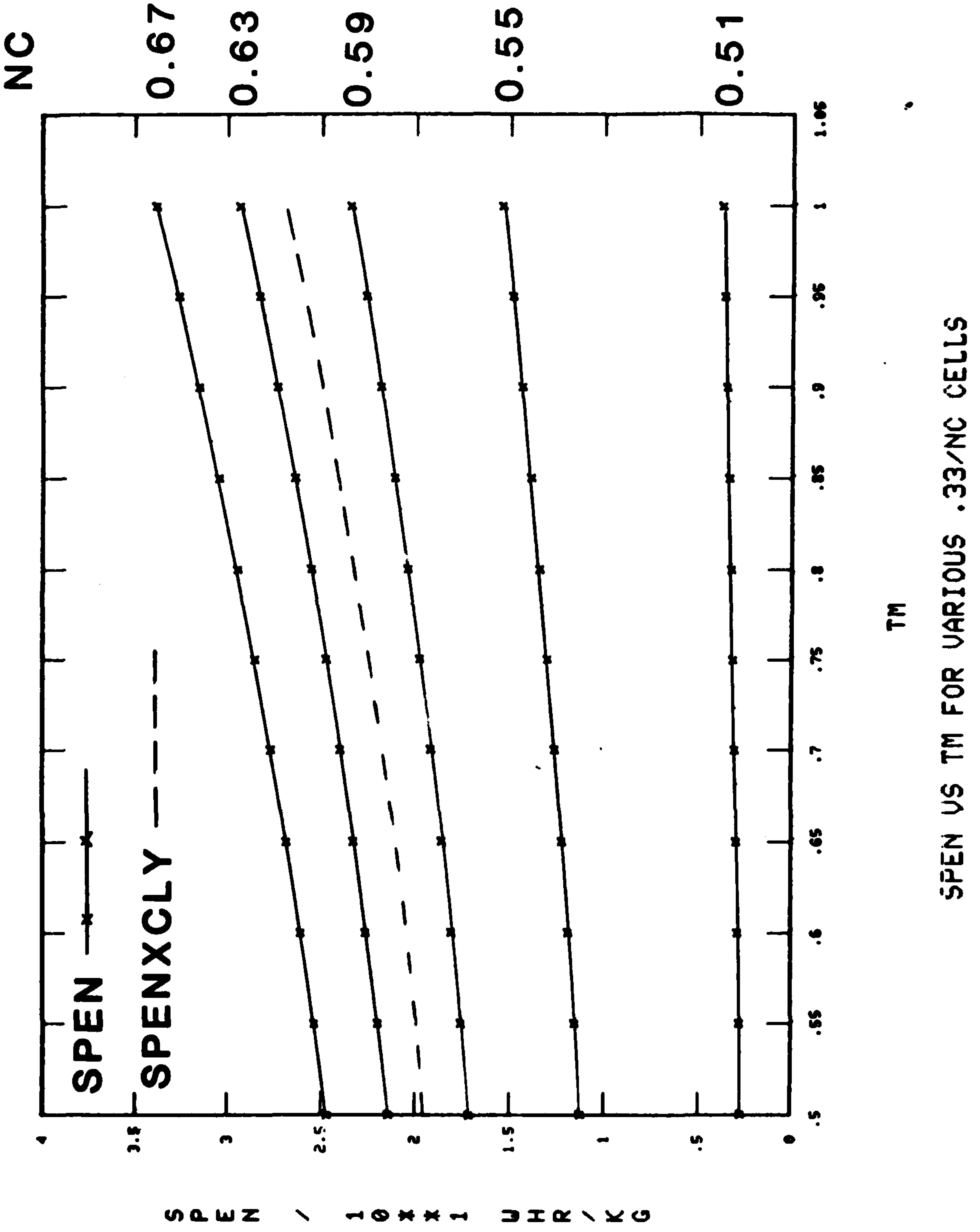


Fig 7 Plotted results of SPENPHD output for cells with catholyte mole fractions varied.

of SPENXCLY is in effect simply 1.5 * MALY, and since MALY is constant for a given NA, SPENXCLY is also constant. (Obviously, MALY would change if the number of equivalents of electrons to be generated were changed from the value of 1.0 used in these calculations.) Note that this value of SPENXCLY does not apply to the cells which have NC of 0.59 or less. These runs have SPENXCLY'S set at zero since the calculated values of ELECRATS for these cases exceed the specified ELECRAT of 1.5.

Table 1 is a listing of the results of a SPENPHD calculation with NA, NC, V, and ELECRAT values which were used in actual concentration cells. These data are plotted in Fig 8 along with the experimental data reported in (2).

IV. Discussion:

The highest theoretical specific energy that one can associate with the concentration cell discussed here would be that obtained with pure $AlCl_3$ as the catholyte and pure MCl as the anolyte. In such a case, we could write the following cell reactions:

$$\begin{array}{ll}
\text{ANODE:} & \mathrm{Al + 4Cl^- \rightarrow AlCl_4^- + 3e^-} \\
 & \\
 & \mathrm{3e^- + AlCl_3 \rightarrow Al + 3Cl^-} \\
 & \mathrm{3Cl^- + 3AlCl_3 \rightarrow 3\,AlCl_4^-} \\ \cline{2-2}
\text{CATHODE:} & \mathrm{3e^- + 4AlCl_3 \rightarrow 3AlCl_4^- + Al} \\ \hline
\text{CELL:} & \mathrm{4\,Cl^- + 4AlCl_3 \rightarrow 4AlCl_4^-}
\end{array}$$

Even for this cell the specific energy is only 98 Whr/kg assuming a load voltage of 1.4 V as in the cells discussed above. Thus the cell is clearly not being studied as a potential high energy density battery. These calculations and their comparison to experimental results were primarily intended to increase understanding of the electrochemistry of the $MCl/AlCl_3$ melts.

The experimental results in Fig 8 are in reasonable agreement with the calculated results. It should be recalled that the t_+ values of the abscissa are true transport numbers for the experimental results only. For the calculated results the abscissa values are actually $t_+ + t_{-4}$. Thus a strict comparison of the calculated with experimental results would require the calculated curves to be displaced to the left by an amount equal to the value of t_{-4}. However, experimental results show that the value of t_{-4} in these cells is probably small, a value of -0.05 ± 0.18 having been reported (2).

We see lower SPEN values for the experimental data because the discharges of actual batteries can't be carried to neutral melt formation. The average final NA in the experimental cells (2) was 0.48, whereas in calculations done here, the final NA is 0.50 (with NA = 0.37 initially in both cases). Thus there is strong evidence that the model of the concentration cell used in these calculations is fundamentally correct.

V. Conclusions:

We can calculate the specific energy for $MCl/AlCl_3$ concentration cells as a function of electrolyte concentrations and transport numbers. The calculated values are in good agreement with previously obtained experimental data, supporting the model on which the calculations are based.

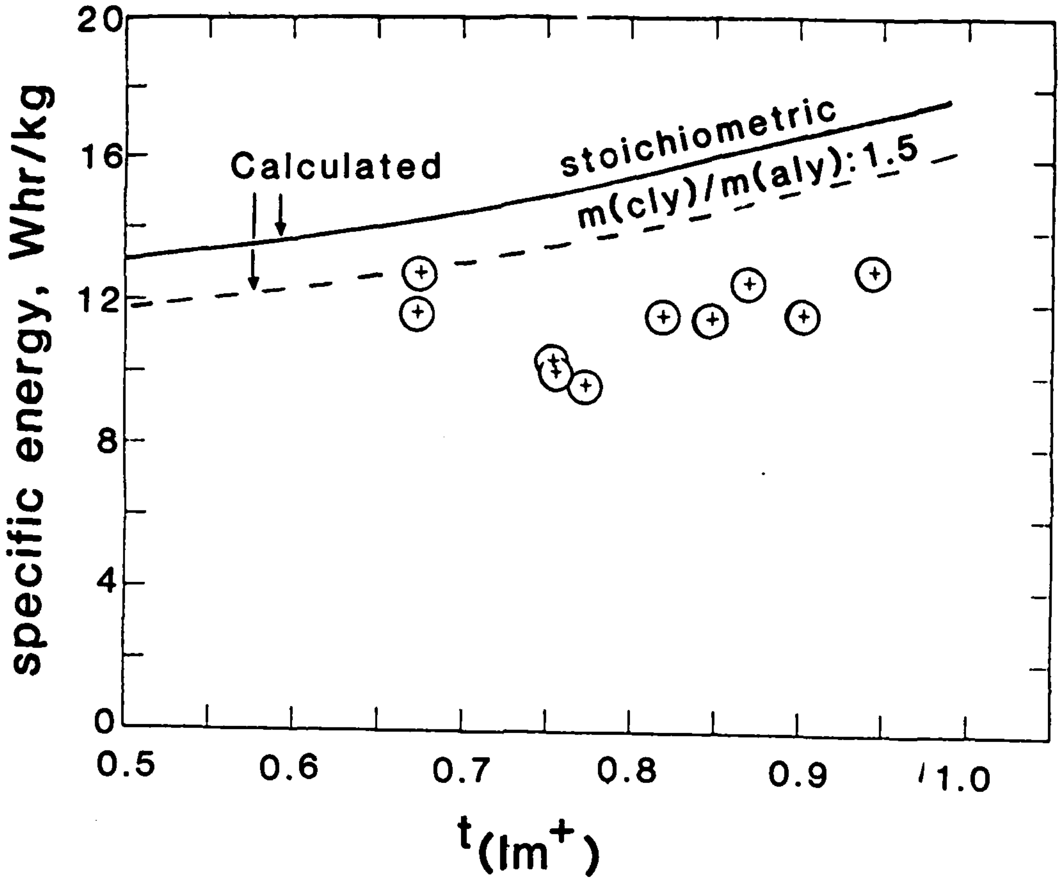


Fig 8 Plotted results of SPENPHD calculation for cell with parameters fixed to match experimental cells compared to experimental results, ⊕.

VI. References:

(1) J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., 21, 1263-4 (1982).

(2) C. Dymek, Jr., J. Williams, D. Groeger, and J. Auborn, "A Concentration Cell Using Room Temperature Chloroaluminate Molten Salts", 164th Electrochemical Society National Meeting, Washington DC, 9-14 Oct 1983.

(3) A. A. Fannin, Jr., "PHD: A Data Handling Program in DEC Basic", FJSRL-TR-83-0002, February, 1983.