

## THERMODYNAMIC DETERMINATIONS FOR LITHIUM/THIONYL CHLORIDE AND LITHIUM/ BrCl-THIONYL CHLORIDE CELLS AS A FUNCTION OF TEMPERATURE AND DEPTH OF DISCHARGE

ESTHER SANS TAKEUCHI\*

*Wilson Greatbatch Ltd , 10,000 Wehrle Dr , Clarence, NY 14031 (U S A )*

KENNETH J TAKEUCHI\*, CAROL BESSEL and ERIC EADS

*Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214 (U S A )*

(Received March 14, 1988, in revised form June 23, 1988)

### Summary

The voltage *versus* temperature response of sixty-four lithium/thionyl chloride and lithium/BrCl-thionyl chloride cells at seven depths of discharge was measured from  $-10$  to  $50$  °C. The data were then used to determine internal energy and entropy values for the two systems. The internal energy of the thionyl chloride cells ranged from  $-90.1$  to  $-86.9$  kcal/eq. and the entropy ranged from  $-15.0$  to  $-8.6$  cal/K-eq. The internal energy of the BrCl-thionyl chloride system ranged from  $-88.9$  to  $-86.2$  kcal/eq. and the entropy ranged from  $-5.7$  to  $-23.5$  cal/K-eq. The relative contribution of entropy to the free energy of the cells increased with depth of discharge for the BrCl-thionyl chloride cells.

---

### Introduction

Lithium cells have proven to be useful in implantable medical applications as they have excellent volumetric energy density and can be hermetically sealed [1]. Frequently, medical applications require very long cell lifetimes under low drain rates, which makes predictions of lifetime based on real time data often impractical. A useful tool for the estimation of cell lifetimes is microcalorimetry which allows the measurement of the heat dissipation of cells either under load or on open circuit voltage [2]. The heat dissipation of a cell under load can then be related to the self-discharge rate of the cell, which is a good predictor of cell lifetime.

The heat dissipation of a cell under low drain rate can be interpreted by the following equation

---

\* Authors to whom correspondence should be addressed

$$Q_T = Q_R + Q_P + Q_{SP} + Q_{SD} \quad (1)$$

where  $Q_T$  is the total dissipated heat as measured by the microcalorimeter,  $Q_R$  is the heat dissipated by the resistor on the cell,  $Q_P$  is the heat attributed to polarization,  $Q_{SP}$  is the heat attributed to entropy and  $Q_{SD}$  is the heat attributed to self-discharge.  $Q_T$  is measured by the calorimeter.  $Q_R$  and  $Q_P$  are calculated from the loaded voltage of the cell. Accurate determination of  $Q_{SD}$ , the heat attributed to self-discharge, depends on having accurate values of the entropic heat contribution,  $Q_{SP}$ , at various depths of discharge for the cell systems under study. Therefore, proper interpretation of microcalorimetric data for the estimation of cell lifetimes requires knowledge of the thermodynamic parameters of cells.

Cells for implantable biomedical applications have been designed utilizing both lithium/thionyl chloride and lithium/BrCl in thionyl chloride chemistries [1, 3 - 8]. Calorimetry has been applied in the prediction of cell life under very low rate discharge for these chemical systems [1, 4, 7, 8]. In some cases, however, entropic heat contributions were not considered. This paper describes the determination of the change in voltage with temperature and the calculation of entropy and internal energy from those measurements for lithium/thionyl chloride and lithium/BrCl-thionyl chloride cells. Statistically significant data were accumulated based on the measurement of 64 cells at seven depths of discharge at temperatures from  $-10$  to  $50$  °C.

## Experimental

### *Construction of experimental thionyl chloride and BrCl-thionyl chloride cells*

All cells for this study had identical construction. The cells were rectangular with dimensions of  $8.6 \times 45 \times 23$  mm, and had cases and lids made from 304L stainless steel. The anodes,  $15.32$  cm<sup>2</sup> surface area, were formed by pressing lithium onto a screen that had been welded to the pin of a header equipped with a glass-to-metal seal. The anodes were surrounded by separator prior to insertion into the case. The cases were equipped with one carbon cathode on each flat wall which was fabricated by pressing Teflon-bonded-carbon onto a nickel current collector. The cells were vacuum filled with electrolyte and close welded to provide an hermetic seal. The electrolytes consisted of 1 M lithium tetrachloroaluminate either in thionyl chloride or in a six to one molar ratio of thionyl chloride to bromine chloride. The stoichiometric capacity of the thionyl chloride cells was 2.9 A h and 3.0 A h for the BrCl-thionyl chloride cells.

### *Discharge of thionyl chloride and BrCl-thionyl chloride cells*

Cells were discharged to six depths of discharge at  $37$  °C under  $2$  k $\Omega$  loads where the current density was  $0.1$  mA cm<sup>-2</sup>. This rate of discharge required 2 months for the cells to reach  $2.0$  V under load. Voltage measure-

ments were taken twice a day by a computer-controlled measuring system that was designed and built in-house

#### *Determination of entropy of thionyl chloride and BrCl-thionyl chloride cells*

Open circuit voltages of cells were measured at temperatures of  $-10$ ,  $0$ ,  $10$ ,  $20$ ,  $30$ ,  $40$  and  $50$  °C. Temperatures were controlled by the use of circulating constant temperature baths that were accurate to  $\pm 0.1$  °C. Each cell was allowed to equilibrate a minimum of six hours, although voltage was stable in a shorter time. Six cells of each chemistry were tested in an undischarged state. Six cells of each chemistry that had been discharged to  $2.0$  V under load were tested. In addition, five groups of four cells of each chemistry, were partially discharged before undergoing test. A total of 64 cells was used for the entropy determinations, 32 of each chemistry. Beginning of life cells were tested within two weeks of manufacture. The discharged cells were stored for a minimum of two months after removal of the load.

### Results and discussion

The change in Helmholtz free energy,  $\Delta A$ , of an electrochemical cell at constant volume can be related to open circuit voltage,  $E$ , by eqn. (2).

$$\Delta A = -nFE \quad (2)$$

The free energy is composed of internal energy ( $\Delta U$ ) and entropy ( $\Delta S$ ) as shown in eqn. (3)

$$\Delta A = \Delta U - T\Delta S \quad (3)$$

The internal energy and entropy can be obtained from measurements of the open circuit voltage of a cell at different temperatures as can be seen in eqns. (4) and (5).

$$\Delta S = nF (\partial E / \partial T) \quad (4)$$

$$\Delta U = nF (T(\partial E / \partial T) - E) \quad (5)$$

#### *Thionyl chloride cells*

The voltage of thirty-two thionyl chloride cells was measured at temperatures from  $-10$  to  $+50$  °C. Six cells were tested undischarged, six cells discharged to  $2.0$  V under load ( $2.6$  A h delivered capacity) and groups of four cells each were partially discharged 210, 390, 800, 1200 and 1670 mA h prior to test. A typical discharge curve for one of the thionyl chloride cells is shown in Fig. 1.

Voltage *versus* temperature was plotted for all cells at the same depth of discharge, as shown in Fig. 2. Table 1 summarizes the change in voltage as a function of temperature at seven depths of discharge with 95% confidence limits indicated. The values ranged from  $0.65$  to  $0.37$  mV K<sup>-1</sup>. The mean

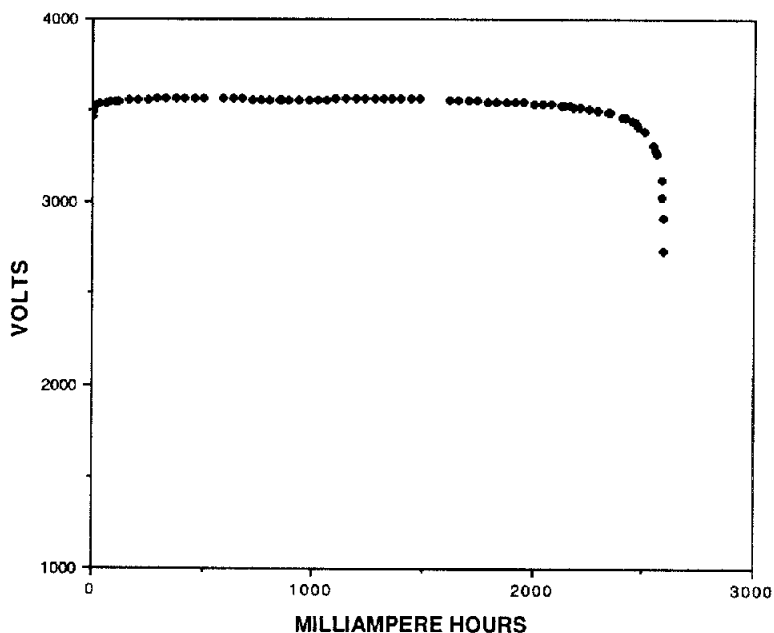


Fig 1 Discharge curve of lithium/thionyl chloride cell at 37 °C under a 2 k $\Omega$  load

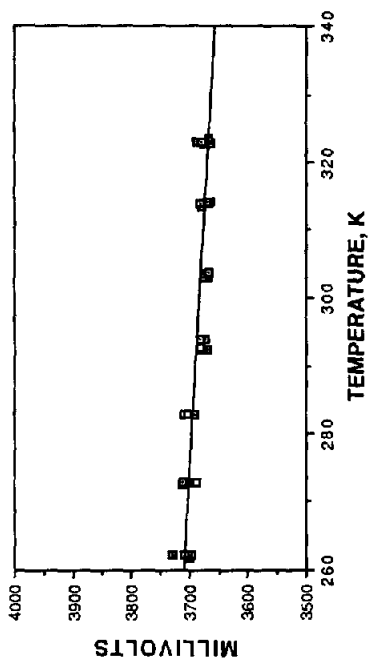
TABLE 1

Voltage *versus* temperature response of thionyl chloride cells

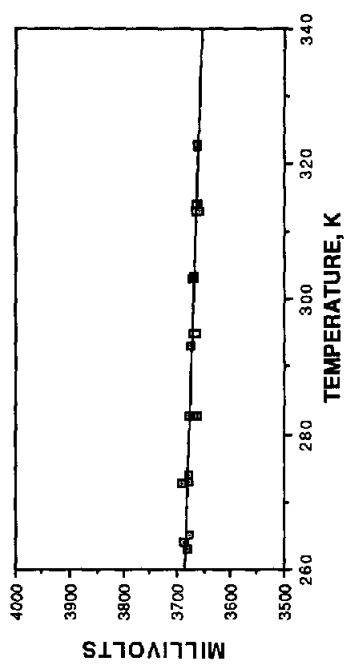
mA h discharged	$\partial E/\partial T$ (mV K <sup>-1</sup> )	95% confidence limits ( $\pm$ )
0 0	0 65	0 15
210	0 37	0 10
390	0 47	0 03
800	0 50	0 03
1200	0 44	0 05
1690	0 54	0 05
2600	0 58	0 14

value of the change in voltage with temperature at all depths of discharge is 0.50 mV K<sup>-1</sup>. At five out of seven depths of discharge the change in voltage with temperature is within 95% confidence of the overall mean. Apparently, there is little change in the voltage *versus* temperature dependence of these cells at different depths of discharge.

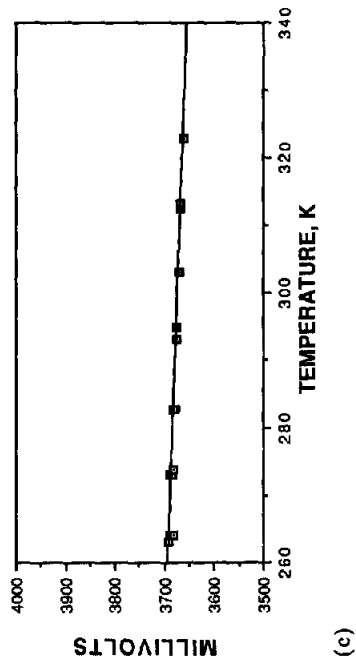
The voltage *versus* temperature dependence was used to determine internal energy and entropy values, summarized in Table 2. The entropy is negative at all depths of discharge and ranges from -15 cal/K-eq. to -8.6 cal/K-eq. The internal energy was calculated at 273 and 293 K. At 273 K, the internal energy ranges from -90.1 to -86.9 Kcal/eq., while at 293 K the internal energy ranges from -89.2 to -87.1 kcal/eq. As the free energy,

*(continued)*

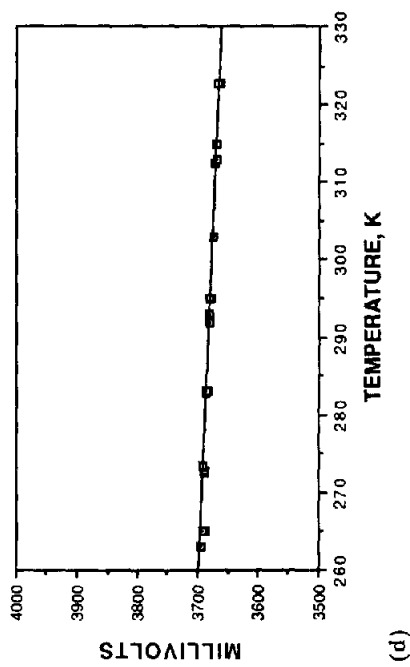
(a)



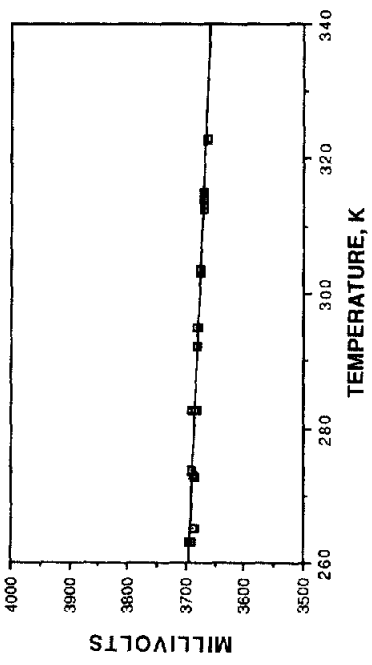
(b)



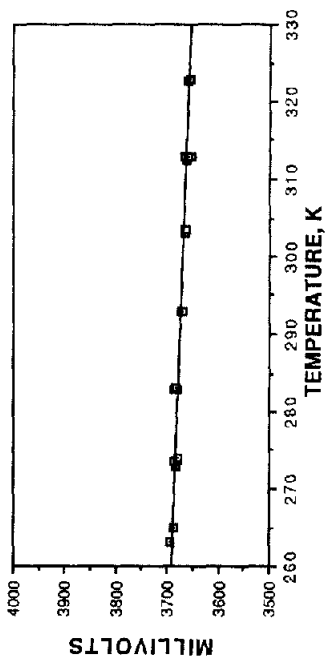
(c)



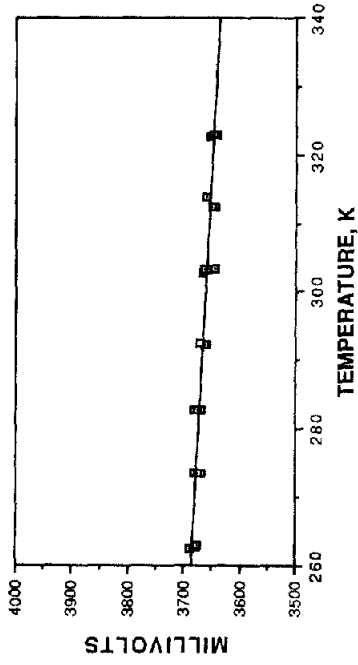
(d)



(e)



(f)



(g)

Fig 2 Plot of open circuit voltage vs temperature for thionyl chloride cells discharged at (a) 0.0, (b) 210, (c) 390, (d) 800, (e) 1200, (f) 1690, (g) 2600 mA h prior to test.

TABLE 2

Entropy and internal energy of thionyl chloride cells

mA h discharged	$\Delta S$ (cal/K eq)	$\Delta U$ (kcal/eq)	
		273 K	293 K
0 0	-15	-90 1	-89 2
210	-8 6	-86.9	-87 1
390	-11	-87.9	-87 9
800	-11	-88 2	-88 2
1200	-10	-87 8	-87 8
1690	-12	-88 3	-88 3
2600	-13	-88 4	-88 4

$\Delta A$ , must be negative for a thermodynamically favorable reaction, it can be seen that the negative internal energy favors the reaction while the negative entropy does not. The relative contributions of entropy and internal energy to the free energy do not change significantly with depth of discharge.

Other reports of entropy and internal energy determinations of lithium/thionyl chloride cells exist in the literature and have been recently summarized [9]. Three methods have been used in the past to determine the internal energy and entropy of thionyl chloride cells open circuit voltage *versus* temperature; open circuit voltage *versus* temperature as extrapolated from low rate discharge, and calorimetry. The entropy was reported as positive when the voltage extrapolation method was used [10]. Other reports of the entropy have ranged from -4.64 to -20.8 cal/K -eq. [9, 11 - 13] The internal energy values reported have ranged from -90.4 to -77 kcal/eq. Thus, the values found here are within the range of values previously reported. The literature reports present data based on limited numbers of cells, in most cases a sample size of two or three cells, at only one or two depths of discharge. What distinguishes the work here is the large number of cells measured, which allows significant statistical analyses to be done, plus the multiple depths of discharge which present data for the entire cell life.

#### *BrCl-thionyl chloride cells*

The voltage *versus* temperature response of thirty-two lithium/BrCl-thionyl chloride cells was tested. Six cells were tested undischarged, six cells were tested fully discharged (2.1 A h delivered capacity) and five groups of four cells each were discharged 220, 400, 800, 1180 and 1690 mA h before test. A typical discharge curve of a lithium/BrCl in thionyl chloride cell is shown in Fig. 3.

The voltage *versus* temperature response of the BrCl-thionyl chloride cells is shown graphically in Fig. 4. The dependence of voltage on temperature is summarized in Table 3. The change in voltage with temperature is 0.25 mV K<sup>-1</sup> for undischarged cells. The dependence of voltage on temperature steadily increases as the cells are discharged and reaches a value of 1.02 mV K<sup>-1</sup> for discharged cells.

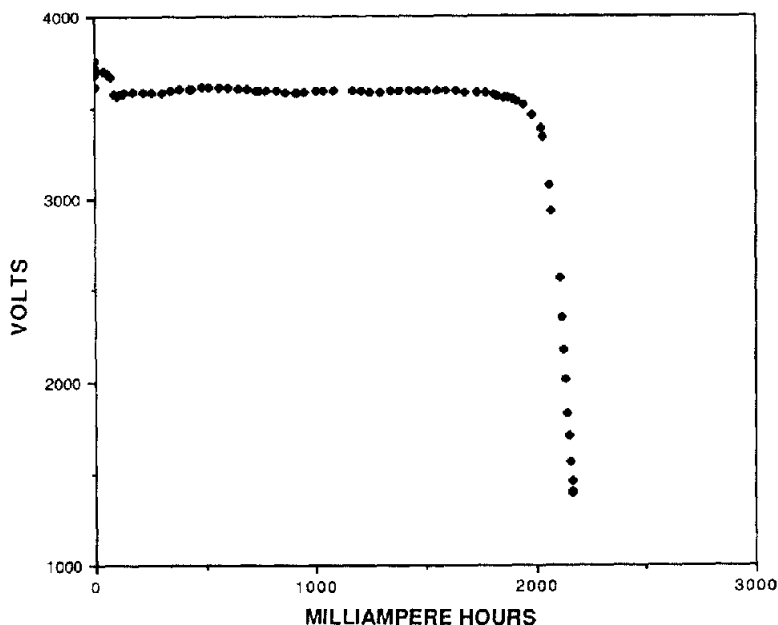


Fig 3 Discharge curve of lithium/BrCl-thionyl chloride cell at 37 °C under a 2 k $\Omega$  load

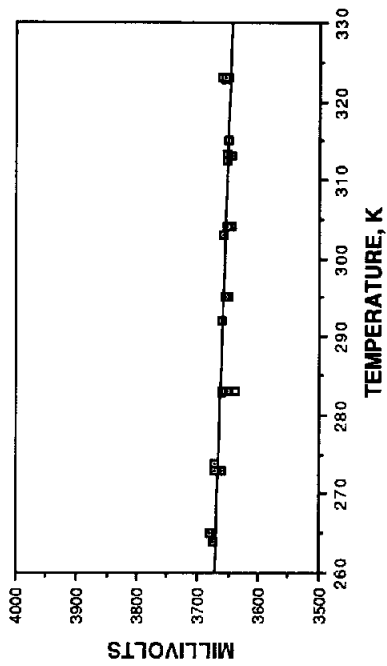
TABLE 3

Voltage *versus* temperature dependence of BrCl-thionyl chloride cells

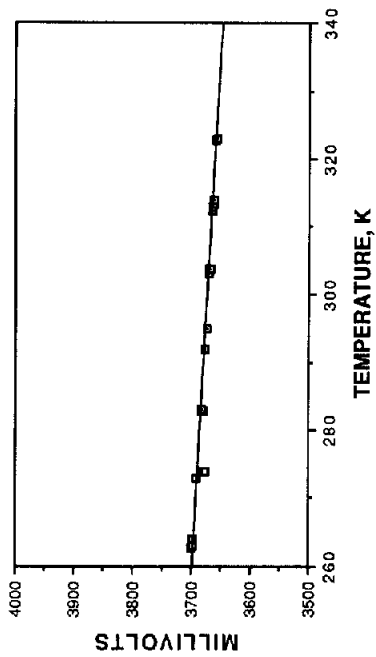
mA h discharged	$\partial E/\partial T$ (mV K <sup>-1</sup> )	95% confidence limits ( $\pm$ )
0 0	0.25	0 20
210	0 38	0 16
400	0 58	0 09
800	0 63	0 06
1180	0 66	0 10
1690	0 83	0 13
2100	1 02	0 19

The voltage to temperature relationship was used to determine the thermodynamic properties of the cells. Table 4 summarizes the entropy and the internal energy at 273 and 293 K for the BrCl-thionyl chloride system. The internal energy is negative and ranges from -89.6 to -86.2 kcal/eq. The entropy was found to be negative and becomes increasingly more negative as the cells are discharged. Figure 5 shows the entropy *versus* depth of discharge for the BrCl-thionyl chloride cells. At beginning of life the entropy was determined as -5.7 cal/K-eq., after 800 mA h of discharge the value is -14.5 cal/K-eq., while for discharged cells the value is -23.5 cal/K-eq. The increasing dependence of voltage on temperature with discharge is not due to changes in internal energy,  $\Delta U$ , but rather to changes in entropy,  $\Delta S$ . The

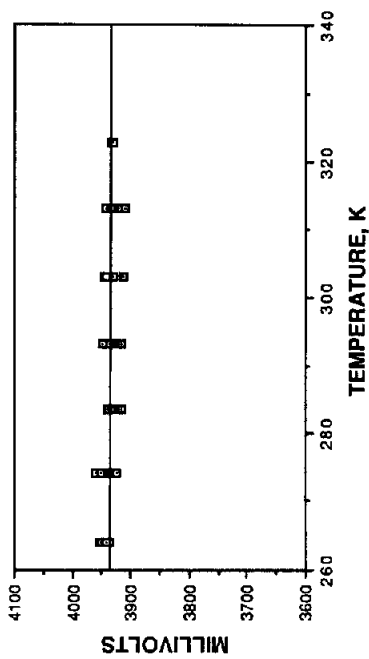


*(continued)*

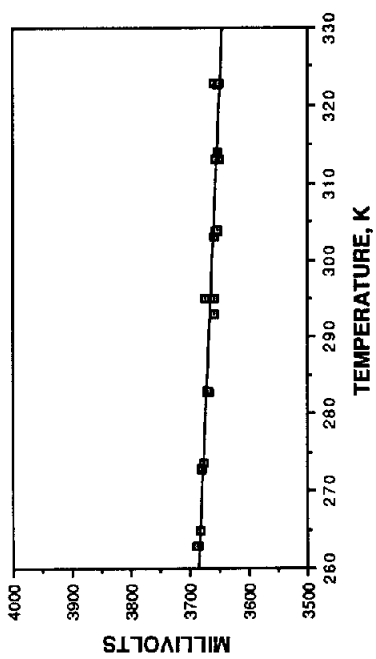
(b)



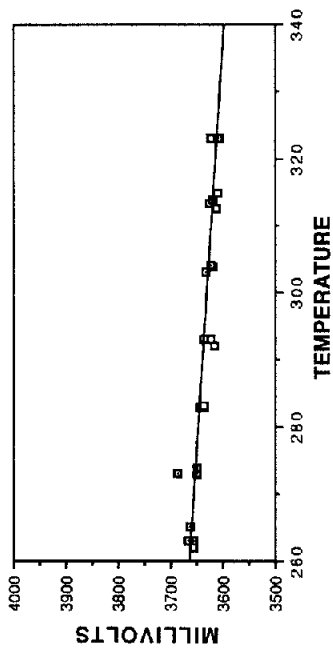
(d)



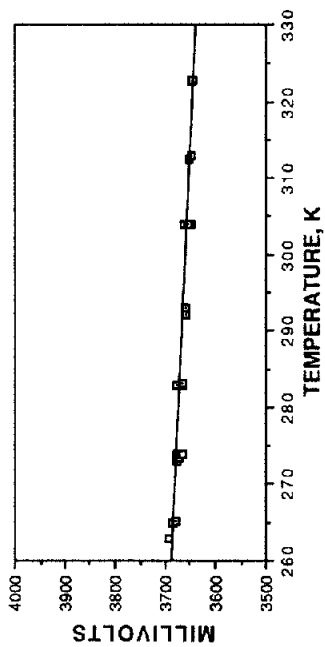
(a)



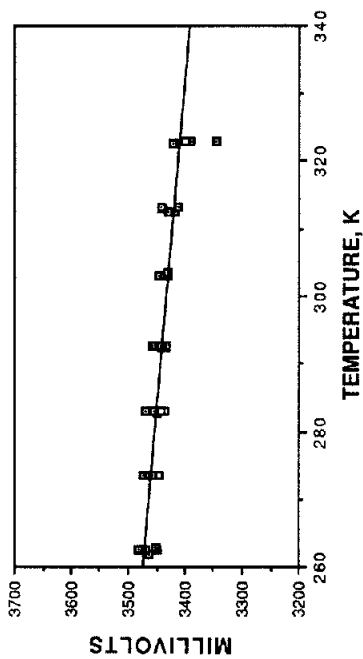
(c)



(f)



(e)



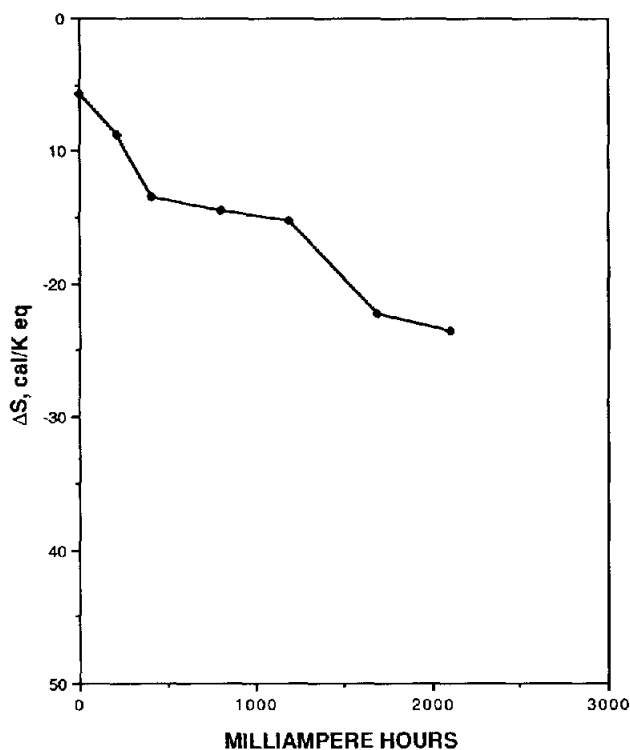
(g)

Fig 4 Plot of open circuit voltage vs temperature for BrCl-thionyl chloride cells discharged at (a) 0 0, (b) 210, (c) 400, (d) 800, (e) 1180, (f) 1690, (g) 2100 mA h prior to test

TABLE 4

Entropy and internal energy of BrCl-thionyl chloride cells

mA h discharged	$\Delta S$ (cal/K eq)	$\Delta U$ (kcal/eq.)	
		273 K	293 K
0 0	-5.7	-89.3	-89.0
210	-8.7	-87.0	-87.0
400	-13	-88.5	-88.4
800	-14	-88.9	-88.9
1180	-15	-88.8	-88.8
1690	-22	-89.6	-89.2
2100	-23	-86.2	-86.2

Fig. 5 Plot of entropy,  $\Delta S$ , vs capacity for the BrCl-thionyl chloride system

entropic contribution to the free energy increases as the cells are discharged.

A comparison of the thermodynamic values obtained for the thionyl chloride and the BrCl-thionyl chloride systems shows that they are not identical. The internal energy of the lithium/thionyl chloride system ranges from  $-90.1$  to  $-86.9$  kcal/eq. The internal energy of the lithium/BrCl in thionyl chloride system ranges from  $-89.6$  to  $-86.2$  kcal/eq, thus not

showing much difference between the two systems. The entropy for thionyl chloride cells ranges from  $-15$  to  $-8.6$  cal/K-eq, where the change in entropy is not a consistent trend with depth of discharge. The BrCl-thionyl chloride system has entropy values of  $-5.7$  cal/K-eq at the beginning of life which increase steadily to  $-23.5$  cal/K-eq for discharged cells. The relationship of entropy with depth of discharge is not linear for these cells as is shown in Fig. 5. The relative contribution of entropy to the free energy of the cells increases with depth of discharge much more for the BrCl-thionyl chloride cells than for thionyl chloride cells.

The BrCl in thionyl chloride cell system differs from plain thionyl chloride as there are at least four active components in the catholyte solution: thionyl chloride, bromine chloride, bromine, and chlorine [14]. The halogens and interhalogens discharge at higher potentials than thionyl chloride and are responsible for higher voltages early in the discharge of these cells, as is evident in Fig. 3. It is apparent from the change in entropy as a function of discharge, that the effect of the interhalogen addition on battery characteristics is not limited to the early stages of the discharge where the voltage is higher, but extends through the entire range of discharge.

## Conclusions

The voltage *versus* temperature response was measured for thirty-two lithium/thionyl chloride cells and thirty-two lithium/BrCl-thionyl chloride cells at seven depths of discharge. The measured values were used to determine entropy and internal energy for the two systems. The internal energy for the lithium/thionyl chloride cells ranged from  $-90.1$  to  $-86.9$  kcal/eq and was not strongly dependent on the depth of discharge. The entropy of the thionyl chloride cells ranged from  $-15$  to  $-8.6$  cal/K-eq. The enthalpy of the lithium/BrCl-thionyl chloride system ranged from  $-89.6$  to  $-86.2$  kcal/eq., while the entropy of the BrCl-thionyl chloride system depended on depth of discharge and increased steadily from  $-5.7$  cal/K-eq at the beginning of life to  $-23.5$  cal/K-eq. for discharged cells. The loss of free energy in the BCX system with discharge is due to entropic contributions. The internal energy and entropy values provided here should assist in more accurate interpretation of battery self-discharge when estimated by microcalorimetry.

## Acknowledgements

The authors express their gratitude to Ms. Gail M. Bergman for her assistance with the data reduction. Financial support for Mr. Eric Eads was received from the Minority High School Apprenticeship Program of the State University of New York at Buffalo.

## References

- 1 P. M Skarstad, in B B Owens (ed ), *Batteries for Implantable Biomedical Devices*, Plenum Press, New York, 1986, pp 215 - 259
- 2 D Untereker, *J Electrochem Soc* , 125 (1978) 1907 - 1912
- 3 M J Harney and S Brown, in B Owens and N Margalit (eds ), *Proc Symp on Power Sources for Biomedical Implantable Applications, and Ambient Temp Lithium Batteries* The Electrochemical Society, Princeton, NJ, 1980, pp 102 - 109
- 4 W G. Howard, R C Buchman, B B Owens and P M Skarstad, in L J Pearce (ed ), *Power Sources 10*, Academic Press, New York, 1985, pp 129 - 144
- 5 C F Holmes and P Keister, Abstr No 39, *Ext Abstr Fall, 1986, Electrochem Soc Meeting* The Electrochemical Society, Pennington, NJ, 1986, pp 61 - 62
- 6 C F Holmes, R L McLean and C C Liang, in G A Feruglio (ed ), *Cardiac Pacing*, Piccin Medical Books, Padua, Italy, 1982, pp 1193 - 1195
- 7 M J Brookman and R L McLean, Abstr No 303, *Ext. Abstr Fall, 1982 Electrochem Soc Meeting* The Electrochemical Society, Pennington, NJ, 1982, p 489
- 8 M J Brookman and R L McLean, Abstr No. 90, *Ext Abstr Fall, 1983 Electrochem Soc Meeting* The Electrochemical Society, Pennington, NJ, 1983, p 142
- 9 N. A Godshall and J R Driscoll, *J Electrochem Soc* , 131 (1984) 2221 - 2226
- 10 C R Schlaikjer, F Goebel and N Marincic, *J Electrochem Soc* , 126 (1979) 513 - 522
- 11 P Bro, in J Thompson (ed ), *Power Sources 7* Academic Press, New York, 1979, pp 571 - 582
- 12 H F Gibbard, in B B Owens and N Margalit (eds ), *Power Sources for Biomedical Applications and Ambient Temperature Lithium Batteries* The Electrochemical Society, Princeton, NJ, 1980, pp 510 - 525
- 13 L D Hansen and H A Frank, *J Electrochem Soc* , 134 (1987) 1 - 7
- 14 K M Abraham and M Alamgr, *J Electrochem Soc* , 134 (1987) 2112 - 2118