A Microcalorimeter for Measuring Self-Discharge of Pacemakers and Pacemaker Power Cells

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The self-discharge heat losses of cardiac pacemaker power cells and pacemakers were investigated by microcalorimetry. Results were obtained with small alkaline, mercury and lithium-iodine batteries under opencircuit and external load conditions to monitor their heat loss characteristics and to gather information on the self-discharge mechanism. Results obtained with "complete pacemakers" are also reported.

Key words: Battery; microcalorimeter; pacemaker; power cell; self-discharge.

1. Introduction

We have developed a microcalorimeter capable of measuring the small heat losses occurring in pacemaker batteries, small camera and watch batteries and the "complete pacemaker." The small heat loss or self-discharge is a contributing factor in shortening the shelf life of the battery and finally the-useable life of the pacemaker. Under ideal conditions, the pacemaker microcalorimeter is capable of detecting as little as $0.1 \ \mu$ W. It has been used for obtaining information on the self-discharge mechanism and is being used by the battery and pacemaker industry to develop a non-destructive test for the complete pacemaker.

Self-discharge can be defined as the gradual loss of deliverable energy when a power cell is stored open-circuit. Hence, self-discharge can limit the time that a power cell will be able to provide power for a pacemaker. The self-discharge mechanism is not completely understood, also the self-discharge rate varies for different power cells and for different manufacturing conditions. Therefore, it would be expected that measurement of the self-discharge heat of batteries manufactured under known conditions could help to obtain a better understanding of its causes.

Microcalorimetry can measure open-circuit self-discharge heat losses and therefore can non-destructively discover batteries with inordinately large self-discharge heats; and, using such data, limits can be set on the time a battery can be stored before usage without undue power loss. Measurements on the complete pacemaker constitute a non-destructive test which can help detect any pacemaker that draws too much power. This would be a useful test that can be performed *after* the hermetic sealing of the unit.

The measurement of these small heat losses was undertaken first in a feasibility study with small camera and watch batteries which could fit easily into the existing NBS Batch Microcalorimeter [1].¹

2. Design of Batch Microcalorimeter

The Batch Microcalorimeter, sketched in figure 1, is a heat-conduction microcalorimeter. An aluminum block or



NBS Microcalorimeter

' Figures in brackets indicate literature references at the end of this paper.

FIGURE 1. Schematic of NBS Conduction Microcalorimeter

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heat sink is centered inside an inner aluminum can which in turn is surrounded by a larger aluminum can. The two aluminum cans protect the heat sink from any sudden changes in room temperature. Polyurethane foam insulates the air space between the inner and outer cans. A heating wire and wires of a Wheatstone bridge were wrapped around the inner can to control its temperature to within \pm 0.001 °C. All measurements are made inside the heat sink which contains a calorimeter compartment or sample box into which microcalorimeter vessels with sample material are placed. The heat flow detector surrounds the outer sample box. The detector consists of multiple-junction thermocouples with its inner face in good contact with the calorimeter and its outer face in good contact with the aluminum block.

The detectors are N-type and P-type solid state thermopiles (Metal Specialties Company)² with an output of 1 μ V for every 4.90 μ W of power generated within the sample box. An operational amplifier (Analog Device 261 K), kept at a constant temperature (±0.001 °C) within the calorimeter shield, amplifies the output by 1000. The output voltage is recorded by a millivolt potentiometer recorder or read by a digital voltmeter. The data are recorded on magnetic tape cassettes, and plotted during the experiment.

The noise level and stability of the microcalorimeter are within a few tenths of a microwatt. The calibration factor of 4.90 μ W/ μ V was determined by using a four lead electrical heater in the sample box and is the value used to convert signal output in μ V to power in μ W.

The microcalorimetric sample box measured 3.8 by 2.8 by 0.8 cm. Because of its small size, the larger pacemaker power cells could not be used; therefore, small camera and watch power cells were used to test the feasibility of the microcalorimetric method.

3. Experimental Data on camera and watch batteries

The batteries used in the feasibility study are described in table 1. To improve the thermal contact between the power cell and sample box, an electrically non-conducting hydrocarbon oil (Cenco Hyvac Oil) was added to the sample box to just cover the power cell. We placed transparent adhesive tape over one battery terminal to prevent shorting to the box and used a string to lower the battery into the oil filled sample box.

Figure 2 shows a recording of the self-discharge of power cell X-5, a mercury watch battery. The initial portion of the plot is the calorimeter baseline without any power cell in the sample box. When the power cell was inserted, the output

Battery			Size, cm
No.	Type	Use	$Diameter \times Thickness$
X-2	alkaline	camera	2.3×0.6
X-3	mercury	camera	1.55×0.6
X-4	alkaline	camera	2.3×0.6
X-5	mercury	watch	1.15×0.35
X-6	mercury	camera	1.55×0.6

increased (the exothermic direction is downward on the plot.) Since the power cell was not initially very close in temperature to the calorimeter block, a large offset was first observed and the block temperature was somewhat changed. A more reliable effect was observed when the power cell was removed from the sample box. The thermopile output is shown to be 0.4 μ V, the vertical height indicated in figure 2. This corresponds to a self-discharge power of 1.96 μ W for the battery (0.4 μ V × 4.90 μ W/ μ V = 1.96 μ W).

Table 2 lists the self-discharge results found for four power cells. The alkaline cells emit approximately 4 to $5 \mu W$ of self-discharge and the mercury power cells emit 1.5 to 2 μW .

Since only a few measurements were made, these results are not conclusive and perhaps uncertain by ± 1 or $2 \mu W$. No attempt was made to obtain typical or representative samples.

The result of additional tests with battery X-3 connected to a 110 k Ω load in the calorimeter is shown in figure 3. There were two insertions and removals of the unit from the calorimeter. The second removal in figure 3 was made after the unit had been in the calorimeter for several hours. The bottom portion of table 2 gives the experimental and calculated value of the battery output under a 110 k Ω load. The calculated power that is dissipated in the 110 k Ω external resistor is 15.4 μ W [(1.30 v)²/(1.1 × 10⁵ Ω)], leaving 2.2 μ W unaccounted for. This difference may be leakage or self-discharge. However, no great significance can be attached to this difference since only one experiment was performed with one rough measurement being made of the power cell voltage before and after the experiment. The 15.4 μ W corresponds to the enthalpy of the cell reaction per unit time, when both the battery and resistor were in the calorimeter. This experiment illustrates that power can be measured in the calorimeter with a complete pacemaker and that the measured value for the load plus leakage or self-discharge is near the *calculated* value for power with the battery under external load.

The results of the measurements with several resistors of different values outside the calorimeter and the power cell inside the calorimeter are shown in figure 4. By measuring the voltage and resistance across the external resistor with a

² The commercial items or products identified in this paper are included to adequately describe the instrumentation and experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.



FIGURE 2. Battery X-5 Self-Discharge

TABLE 2. Microcalorimetric Determination of Self-Discharge

Battery	Self-Discharge,	μW
X-2 ALK(Camera)	4.9	
X-4 ALK(Camera)	3.9	
X-5 Hg(Watch)	2.0	
X–6 Hg(Camera)	1.5	
Battery Under Load in Microcalorimeter		μW
X-3 Hg(Camera) with 110 kΩ load in calori	imeter	17.6
Calculated value: $W = E^2/R$, $(1.30)^2/1.1 \times 1$	0⁵Ω	15.4
	Difference	2.2

digital voltmeter, the value Wx, was calculated as the power dissipated in the resistor *outside* the calorimeter. The external resistors were connected to the battery with copper leads of 0.02019 cm (No. 32 AWG) diameter and about 40 cm in length. Resistors of 5 k Ω , 10 k Ω and 3 k Ω values were connected and disconnected to battery X-2, as shown in figure 4. Similar experiments were also run on the power cell X-4. Table 3 lists the results of the alkaline power cells X-2 and X-4 under external load conditions. Table 4 lists the results for the mercury battery with external load. Figure 5 is a plot of the internal power versus the external power, Wi versus Wx, for the three power cells. Wi is a linear function of Wx and the slope or the ratio Wi/Wx corresponds to about 4 percent (Wi is 4 percent of Wx) for the alkaline cells and about 1 percent for the mercury cell. The larger Wi for the alkaline cell suggests that it has a shorter shelf life than the mercury cell. The points plotted in figure 5 produce lines which extrapolate to near zero Wi for zero Wx (or open-circuit). Some curvature is evident which is due to the finite internal resistance of the power cell. The method used for measuring Wi excluded any open circuit power, because Wi was obtained in these external load experiments from the vertical height of the shift in output (for example, A in fig. 4) when the external load was connected and disconnected.

The ratio Wi/Wx does not indicate any additional lost power above what would be obtained if the cell reaction were ideal. Each type of cell reaction has a characteristic Wiwhich is dissipated. The Wi can be calculated from the thermodynamics of the cell reaction if all the thermodynamic quantities are known. The measurements that were made could help to obtain these thermodynamic properties. Theoretically, Wi should be a linear function of Wx since both are proportional to the number of moles of cell constituents that are reacting. Variation from strict linearity may



FIGURE 3. Battery X-3 with 110 k Ω Load in Calorimeter



FIGURE 4. Battery X-2 with $5 k\Omega$, $10 k\Omega$ and $3 k\Omega$ External Load

Table 3	3.	Alkaline	Batteries	With	External	Load
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	X-2 ALK(camera)					
$Rx/(\Omega)^{a}$	<i>I/(</i> µА) ^b	$Wi/(\mu W)^{c}$	$Wx/(\mu W)^{d}$	Wi/Wx ^e		
10010	146	8.3	213	0.0390		
4996	292	17.2	426	0.0404		
3005	484	29.4	703	0.0418		
	Х	4-4 ALK(camera	a)			
9999	144	8.8	207	0.0425		
5003	285	18.1	405	0.0447		
3005	476	29.9	681	0.0439		

(a) $Rx/(\Omega)$, value of the external resistor

' (b) $I/(\mu A)$, current through the external resistor

(c) $Wi/(\mu W)$, power dissipated internally in battery

(d) $Wx/(\mu W)$, power dissipated externally in resistor

(e) Wi/Wx, ratio of internal power to external power

TABLE 4. Mercury Battery with External Load

X-3 Hg(camera) ^a					
$Rx/(\Omega)$	Ι/(μΑ)	$Wi/(\mu W)$	$Wx/(\mu W)$	Wi/Wx	
4996	269	2.1	361	0.0058	
3005	445	6.6	596	0.0111	
2005	666	10.8	889	0.0121	
1001	1329	27.0	1767	0.0153	

(a) For description of column notations, see table 3.

be due to the effect of self-discharge, leakage or high internal resistance of the power cell or other non-ideal effects. Such self-discharge or non-ideal effects have not been considered in these calculations.

The data demonstrated that useful measurements of selfdischarge of small power cells could be made with an NBS microcalorimeter [2] or other microcalorimeter of comparable sensitivity. These preliminary results lead to the construction of a larger microcalorimeter that could accomodate the larger pacemaker batteries and pacemaker.

4. Design and construction of pacemaker microcalorimeter

This calorimeter is also based on the heat conduction principle [2]. It employs a substitution and guarding principle; that is, dummy vessels can be substituted in the measuring compartment in place of vessels containing active samples. The two additional aluminum blocks act to guard or protect the central measuring compartment from sudden changes in room temperature and serve as sample pre-equilibration chambers. Three solid aluminium blocks, (instead of one), horizontal positioning of the calorimeter, and larger size are features that make this calorimeter different from the NBS Batch Microcalorimeter of figure 1. The three block sections with total dimensions of 28.6 cm in length by 20.3 cm in diameter are illustrated in the schematic



FIGURE 5. Internal Power vs. External Power

diagram of figure 6. The blocks are in good thermal contact with each other and each has a tunnel-like chamber in which reaction vessels are inserted snugly. Each chamber can contain an aluminum reaction vessel of size 7.93 by 6.66 by 2.85 cm. The vessels can contain a battery or a pacemaker or can serve as empty "dummy" vessels.



FIGURE 6. Cross-Sectional Schematic of Pacemaker Calorimeter

As in the smaller calorimeter, the blocks are surrounded by an inner and an outer aluminum can or shield. The inner can measures 31.8 cm in length by 24.2 cm in O.D. and the outer can 43.2 cm in length by 30.4 cm in O.D. A heating wire and wires of a Wheatstone bridge were wrapped around the inner can to control the can temperature to \pm 0.001 °C. The temperature of the blocks, which are separated from the inner can by a 1.0 cm air-space has been found to be constant to about 1μ °C after an overnight equilibration period. Polyurethane foam fills the 5 cm space between the inner and outer shield.

A temperature controlled air bath encloses the entire microcalorimeter. For initial experiments on the lithiumiodine power cells, the air bath was maintained at 30 ± 0.02 °C. The block temperature was held at 32 °C. For measurements on the cardiac pacemaker, the block temperature was controlled at 37 °C. The block temperature can be anywhere between 20 and 40 °C. Under ideal conditions the sensitivity of the instrument is expected to be 0.1 μ W, but it has not yet been attained on active samples.

The microcalorimeter always contains three vessels, one in each block. Initially, the vessel in the heat sensing chamber is empty and the vessels in the two guarding chambers

GABLE 5. Alkaline and Mercury Batteries—Self-Dis	charge
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Battery			×	
Description	Exp. No.	μV total	µW total	µW/battery
16 Mercury, 1.35 v open-circuit	0615	14	69	4.3
(1.6 cm, diam. x 1.7 cm, ht)	0616	20	98	6.1
	0618	24	118	7.4
	0620	20	98	6.1
	0621	20	98	6.1
	0621	22	108	6.7
	0622	24	120	7.5
				AVG 6.31
				SD 1.07
16 Mercury, 1.35 v open-circuit (new set)	0712	40	196	12.3
(1.6 cm, diam. x 1.7 cm, ht)	0713	32	157	9.8
	0713	33	162	10.1
	0719	30	147	9.2
	0725	26	127	8.0
				AVG 9.88
				SD 1.57
8 Alkaline, 1.57v open-circuit	0623	95	465.5	58.2
(1.4 cm, diam. x 4.9 cm, ht)	0624	95	465.5	58.2
	0627	104	509.6	63.7
	0628	94	460.6	57.6
	0629	92	450.8	56.4
				AVG 58.82
				SD 2.83
8 Alkaline, 1.57v open-circuit (new set)	0630	96	470.4	58.8
(1.4 cm, diam. x 4.9 cm, ht)	0705	92	450.8	56.4
	0705	94	460.6	57.6
				AVG 57.60
				SD 1.20

contain power cells or pacemakers. A thin layer of mica lines each vessel to prevent any shorting of power cells to the metal. About 35 ml of hydrocarbon oil is also added to improve thermal contact between the sample and vessel.

Before an experiment, the two vessels containing the test batteries are placed in the guarding chambers and an empty vessel is placed in the heat sensing chamber. About 4 hours are required to reach proper temperature equilibrium. A longer overnight equilibration was found to be better and more convenient. Once equilibrium is attained, the vessels are pushed to new positions in the blocks. For example, the vessel containing the active sample in the first guard chamber is pushed into the heat sensing chamber. In the process, the empty vessel is pushed into the second guard chamber; the second vessel containing an active sample is then placed in the first guard chamber. Differences in signal output are a measure of the power output from the active sample. This arrangement has minimized shifts due to temperature differences in the vessels and resulted in a highly stable baseline.

Commercial alkaline and mercury-zinc batteries were tested for their self-discharge characteristics and the results are listed in table 5. An example of a plot of 8 alkaline batteries undergoing self-discharge is shown in figure 7. The 92 μ V corresponds to 451 μ W or 56 μ W self-discharge for each battery. The self-discharge of 16 mercury batteries is shown in figure 8; each battery dissipates about 5.8 μ W.



FIGURE 7. Microcalorimetric output voltage versus time for 8 separate open-circuit batteries in and out of the microcalorimeter. A sensor output voltage of 92 μ V is indicated which corresponds to 451 μ W or about 56 μ W for each battery.



FIGURE 8. Microcalorimetric output voltage versus time for 16 separate open-circuit mercury batteries in and out of the microcalorimeter.

A sensor output voltage of 19 μ V is indicated which corresponds to 93 μ W or about 5.8 μ W for each battery.

The results confirm that alkaline batteries have a larger self-discharge rate than mercury batteries as shown in table 2.

The results of measurements of open-circuit and load induced power losses in lithium-iodine cells, with three different histories, are listed in table 6. The batteries are of the same type but were stressed by the manufacturer by connecting a 100 k Ω resistor for different time periods: 60 days, 10 months and 18.7 months. Figure 9 shows examples of the open-circuit and load induced power loss measurements obtained with lithium-iodine batteries. Figure 9A shows a power loss of $0 \pm 5 \ \mu W$ for four lithium-iodine cells under open-circuit conditions. Figure 9B shows 15 μV or 73.5 μW of power that resulted when one lithium-iodine cell was placed under a 100 k Ω load in the microcalorimeter. The experimental value of 73.5 μW is approximately equal to the value 75.5 μW obtained by calculating the power dissipated in the load.

Lithium-iodine batteries from another manufacturer were also measured for their open-circuit self-discharge. One battery was placed in a microcalorimetric sample vessel and then two batteries to determine if twice the amount of self-

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Battery Description Exp. No. Load Size, ohms Power, μ W Total, eq. Power, μ W Per battery Total, eale. W(exp)-W(eale/ μ W) 4 open circuit 60 day, 2.8v 0831 44.1 1 1 1 1 60 day, 2.8v 0831 44.1 1 1 1 1 1 0912 34.3 8.6 7.4 8.6 7.4 8.6 1 </th <th>_</th> <th></th> <th></th> <th></th> <th></th> <th>W = E2/R</th> <th></th>	_					W = E2/R	
$ \begin{array}{ c c c c c c } \hline losed-circuit \\ 60 day, 2.8v \\ \hline 0011 \\ 0001 \\ 0012 \\ 0020 \\ 100 200 \\ 73.5 \\ 73.5 \\ 73.5 \\ 75.5 \\ 75.5 \\ 75.5 \\ 75.5 \\ 75.5 \\ -2.0 \\ AVG \\ 74.28 \\ SD \\ 100 \\ 200 \\ 73.5 \\ AVG \\ 74.28 \\ SD \\ 100 \\ 100 \\ 200 \\ 73.5 \\ AVG \\ 74.28 \\ SD \\ 100 \\ 100 \\ 100 \\ 200 \\ 73.5 \\ 100 \\ 100 \\ 200 \\ 73.5 \\ 100 \\ 100 \\ 200 \\ 73.5 \\ 100 \\ 100 \\ 200 \\ 73.5 \\ AVG \\ 74.28 \\ SD \\ 1.44 \\ 10 \\ 100 \\$	Battery	Exp.	Load Size,	Power, µW	Power, µW	Power, µW	
	Description	No.	ohms	Total, exp.	per battery	Total, calc.	$W(exp)-W(calc)(\mu W)$
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$ \begin{array}{ c c c c c c c } & 0913 & & 34.3 & 34.3 & 34.6 & 0 \\ & AVC & 9.52 & 50 & 1.91 & 000 & 000 & 73.5 & 73.5 & 75.5 & 2.9 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 73.5 & 73.5 & 75.5 & -2.0 & 74.5 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -2.0 & 74.5 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.8 & 75.5 & -3.5 & 75.5 & -3.5 & 75.5 & -3.5 & 75.5 & -1.0 & 74.5$		0912	·	29.4	7.4		
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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	10 mos, 2.8v	0907		34.3	8.6		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		0908		29.4	7.4		
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		0918		24.5	6.1		
0921 24.5 6.1 AVG 7.12 SD 1.05 1 closed-circuit 60 day, 2.75v		0920		29.4	7.4		
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1127 100 200 90.7 90.7 75.5 15.2 1128 100 200 75 75 75.5 -0.5 1129 100 200 85.8 85.8 75.5 10.0 1205 100 200 76 76 75.5 0.5 1212 100 200 76 76 75.5 0.5 SD 6.89 6.89 6.89 6.89 6.89		1125	100 200	72	72	75.5	-3.5
1128 100 200 75 75 75.5 -0.5 1129 100 200 85.8 85.8 75.5 10.0 1205 100 200 76 76 75.5 0.5 1212 100 200 76 76 75.5 0.5 200 76 76 75.5 0.5 1212 100 200 76 76 75.5 0.5 SD 6.89 5 5 5 5		1127	100 200	90.7	90.7	75.5	15.2
1129 100 200 85.8 85.8 75.5 10.0 1205 100 200 76 76 75.5 0.5 1212 100 200 76 76 75.5 0.5 1212 100 200 76 76 75.5 0.5 SD 6.89 5.0 5.5 0.5 0.5		1128	100 200	75	75	75.5	-0.5
1205 100 200 76 76 75.5 0.5 1212 100 200 76 76 75.5 0.5 1212 100 200 76 76 75.5 0.5 SD 6.89 0.5 0.5 0.5 0.5		1129	100 200	85.8	85.8	75.5	10.0
1212 100 200 76 76 75.5 0.5 AVG 78.57 SD 6.89		1205	100 200	76	76	75.5	0.5
AVG 78.57 SD 6.89		1212	100 200	76	76	75.5	0.5
SD 6.89					AVG 78.57		
					SD 6.89		

 TABLE 6. Lithium Iodine Batteries—Self-Discharge and Load Induced Power Loss

 Battery Dimensions (1.3 x 2.2 x 4.5 cm)



FIGURE 9. A) Microcalorimetric output voltage versus time for 4 Li/I batteries (open-circuit and previously discharged for 60 days through 100 k Ω).

A sensor output voltage of $\pm 1 \ \mu V$ is indicated which corresponds to $\pm 5 \ \mu W$ or $\pm 1 \ \mu W$ for each battery.

B) Microcalorimetric output voltage versus time for 1 Li/I battery (under load of 100 k Ω in the microcalorimeter.)

A sensor output voltage of $15 \,\mu\text{V}$ is indicated which corresponds to $73.5 \,\mu\text{W}$ of power.

discharge could be detected by the microcalorimeter. The results in table 7 show that about twice the power was indeed dissipated as self-discharge when two batteries were measured as compared to the power loss in one power cell.

Battery Description	Exp. No.	Power, µW Total
l open-circuit		
2.17v	T-52	17.2
2.17v	T-54	17.2
2.17v	T-66	14.7
2.15v	T-57	17.2
2.15v	T-58	17.2
2.15v	T-65	14.7
		AVG 16.37
		SD 1.29
2 open-circuit,	T-42	34.3
2.15 & 2.17v	T-43	27
	T-44	27
	T-47	32
		AVG 30.08
		SD 3.67

TABLE 7. Lithium Iodine Batteries

We also measured the heat loss from two different pulsing pacemakers; the heat loss rates for each pacemaker are listed in table 8. Pacemaker #1 contained two Li/I batteries and was losing an average of 45.7 μ W of power. Pacemaker #2 contained one Li/I battery and was losing an average of 28.4 μ W.

TABLE 8	. Self L	lischarge	of Pacemakers	5
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Pacemaker I.D.	No. of Li/I Batteries	Exp. No.	Output (µV)	Outpu	ıt (μW)
1	2	T-115-116	9		44.1
		T-121-122	9		44.1
		T-123-124	10		49
				AVG	45.73
				SD	2.8
2	1	T-127-128	5		24.5
		T-131-132	6.3		30.9
		T-134-136	5		24.5
		T-137-138	6.9		33.8
				AVG	28.43
				SD	4.6

5. Summary

We try to explain the quantities being measured per unit of time by using the following thermodynamic equation,

$$-\Delta G = -\Delta H + T\Delta S$$

where ΔG , ΔH , and ΔS are the changes of the Gibbs energy, enthalpy, and entropy, respectively, and T is the absolute temperature. A *negative* sign denotes an exothermic reaction, $-\Delta H$, or that heat is being given off by a battery to the calorimeter and $-\Delta G$ denotes the process tends to proceed spontaneously [3]. It is assumed that the reaction takes place at constant temperature and pressure. Each of the quantities in the equation has been measured in the present experiments; see figure 10.



FIGURE 10. Illustration of Thermodynamic Quantities measured.

(a) Battery in calorimeter with no load; self-discharge is measured by calorimeter.

b) Battery with load inside calorimeter; $-\Delta H$ measured by calorimeter.

c) Battery in calorimeter, load outside calorimeter; $-T\Delta S$ is measured by calorimeter, $-\Delta G$ is dissipated in the load outside the calorimeter.

When an open-circuited power cell is placed *alone* in the calorimeter, then the self-discharge power is measured by the calorimeter. Side reactions, such as corrosion of the metal components, may account for some of this self-heating.

When the power cell has a resistor placed across it and both the power cell and resistor are placed in the calorimeter, then the cell reaction corresponding to $q = -\Delta H$ is measured by the calorimeter. Self-discharge may also be occurring. When a power cell and resistor are connected with the resistor placed outside the calorimeter, then the heat corresponding to $q = T\Delta S$ is measured by the calorimeter. The useable energy, $-\Delta G$, is determined electrically by measuring the current and voltage across the external resistor. In each of these cases the measured quantity is power rather than energy.

Tests of internal power Wi as a function of external power Wx yielded results which are characteristic of the ideal cell reaction; that is, Wi is a linear function of Wx(within the precision of the measurements). This was found for both the alkaline and mercury cells.

For the kinds of cell reactions that take place in alkaline and mercury batteries, the $T\Delta S$ can be a large fraction of ΔH as in the silver-zinc battery. The literature value of the $T\Delta S$ quantity for the reaction Ag₂O(c) + Zn(c) + H₂O(liq) $\Rightarrow 2 \text{ Ag(c)} + \text{Zn}(\text{OH})_2 (c,\beta)$ [4], where (c) signifies condensed phase, is -19.859 kJ/mol [5] and ΔH is -325.034 kJ/mol [5]. The $T\Delta S$ is 6.11 percent of ΔH . On the other hand, the literature value of the $T\Delta S$ quantity for the reaction Li(c) + 1/2 I₂(c) \Rightarrow LiI(c) is very small, -0.22 kJ/mol compared to ΔH of -273.6 kJ/mol or only 0.08 percent of ΔH [6]. The small value for $T\Delta S$ is corroborated by our experimental data (see table 6 and fig. 9).

The pacemaker microcalorimeter is capable of nondestructively measuring small heat losses on the order of microwatts from a power cell or pacemaker. This instrument has already found many applications in the battery manufacturing industry as a repair check on faulty batteries in which measurements are made before and after repair to determine if the repairs made were correct. It can be used for testing the heat output of new batteries and pacemakers in a quality control test, for development of new power sources, and for determining the shelf-life of batteries. Greatbatch, et al [7], have reported detection of heat losses of 10-50 μ W in new pacemaker batteries which was traceable to the continuous curing of plastic materials in the battery. True internal shorts have produced 1000-2000 μ W of heat. They report also that the microcalorimeter should prove invaluable for early nondestructive identification of parasitic power losses in batteries and pacemakers.

The pacemaker microcalorimeter, with minor design modifications, is expected to have commercial and research applications beyond the study of self-discharge of power sources and pacemakers, such as, detection of bacterial contamination in dried food materials and the study of radiation effects on the metabolism of living cells as being undertaken by the Bureau of Radiological Health, Department of Health and Welfare.

6. References

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