Effect of Temperature on Dry Cell Life Span: A Case Study

R. Radharamanan[1] and Jeng-Nan Juang[2]

Abstract – In this paper, the life of dry cells using a flashlight at different temperatures were tested. The dry cells used were heavy-duty (non-alkaline) batteries using zinc and carbon electrodes. The objective is to see whether a dry cell's life span is affected by temperature because the dry cell relies on a chemical reaction to generate its energy, and typically, as temperature increases, the rate of chemical reaction also increases. The batteries were subjected to a specific temperature, 72^{o}F and 170^{o}F, for 15 minutes and then ran until the light emitted by the flashlight was determined not visible anymore. Once the tests were completed, the data were analyzed and the results indicated that temperature has a significant effect on the life span of dry cell batteries. Finally, the chemical reaction's overall activation energy equation was solved using the average life spans of batteries measured.

Keywords: Life of a dry cell, statistical analysis, Tukey's test, ANOVA, and temperature effect.

INTRODUCTION

The interest for this experiment came as a result of a desire for practical application. If one is using a piece of battery-operated equipment in a high-temperature environment (such as the troops using hand-held radios in the in the deserts of Iraq at >130°F), it would be good to know how long one can expect the equipment to last versus assuming it would be the same while using it at room temperatures (~72°F). The life spans would be different at different operating temperature conditions since (a) a battery relies on chemical reaction to make its energy [3] and (b) temperature affects the rate at which the chemical reaction takes place [8].

In today's market there are several different types of batteries. For this experiment, AA-sized batteries were chosen. There are two types of AA batteries: primary and secondary. Non-alkaline and alkaline batteries are known as primary [4] batteries because after their first use, they must be replaced or discarded. Rechargeable batteries are referred to as secondary batteries since their chemical makeup allows them to be recharged, and thus, reused. Only primary batteries were tested in this study.

Primary batteries are very popular in industry, despite their one-time use. The alkaline battery, specifically, though it must be discarded after its first use, tends to be cheaper, more efficient, and longer lasting than the current rechargeable batteries available [6]. The focus for this experiment, however, was on the weaker of the two primary battery types, the non-alkaline battery. The two main advantages that the non-alkaline used to have over the alkaline battery were that it was much cheaper and was also less likely to leak its internal chemicals [5]. Recently, however, due to advances in manufacturing and technology, the price and stability of alkaline batteries are closely matching non-alkaline, thus driving the non-alkaline to extinction.

[1] Mercer University School of Engineering, 1400 Coleman Ave., Macon, GA 31207, radharaman_r@mercer.edu

[2] Mercer University School of Engineering, 1400 Colman Ave., Macon, GA 31207, juang_jn@mercer.edu

So why test the weakest battery? Two reasons – it's cheaper and it takes less time. In a recent study of the life span of various AA batteries, it was shown that an alkaline battery lasted 4.3 times longer than a heavy duty (non-alkaline) battery [5] for a flashlight test. As for pricing, a simple internet search revealed that when buying in bulk (1000+ batteries) the cheapest price per battery for non-alkaline was 8¢ /battery, whereas the cheapest for alkaline was 11¢ /battery.

As stated previously, the driving force behind a battery is the internal chemical reaction taking place. The batteries tested undergo what is called an oxidation-reduction reaction. To better understand this reaction, look at Figure 1 [10].

In Figure 1, it is seen that a battery has a positive terminal and a negative terminal. The positive terminal functions as the electric focal point for the carbon rod, which serves to carry electrons to the manganese dioxide mix. The negative terminal serves as the electric focal point for the zinc. Ultimately, a battery functions by allowing electrons to flow from the negative terminal to the positive terminal, as shown in Figure 2 [7].

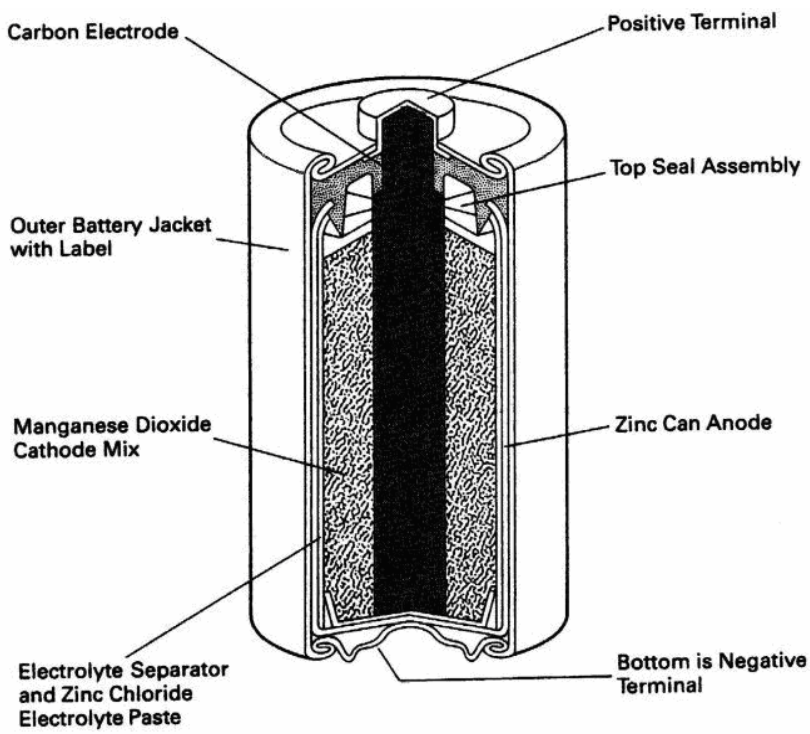

Figure 1: Battery with positive and negative terminals

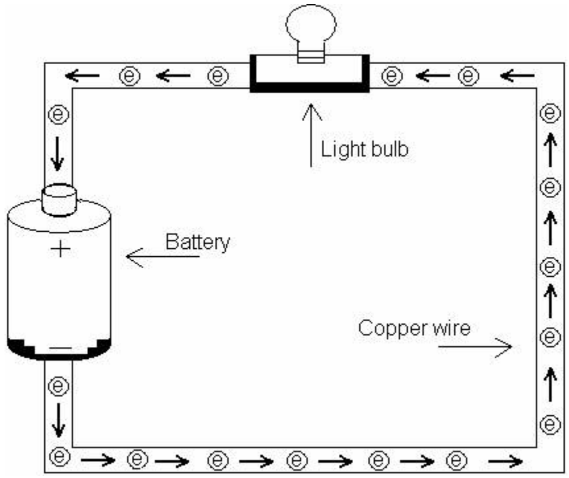

Figure 2: Flow of electrons from negative to positive terminal

The driving force behind the electrons 'wanting to go' from one terminal to the other is from these two half-reactions:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^- \tag{1}$$

$$MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq) \tag{2}$$

Equation (1) is the oxidation reaction because zinc is oxidized from Zn^0 to Zn^{2+}. Equation (2) is the reduction reaction because Mn^{4+} is reduced to Mn^{3+}. From Figure 1, it is seen that there is an electrolyte separator between the zinc and the manganese dioxide, otherwise a reaction would take place internally between the solids and chemicals and the battery would quickly lose all its electrical power. Equation (2) can only take place if there is a flow of electrons to come into contact with the MnO_2, and the separator prevents this from occurring. The only way for this to occur is to run a wire between the two electrodes (Fig. 2).

As for measuring the strength of the battery, voltage is the battery's driving force to push electrons through a circuit. It is the change in potential energy when a reaction occurs. Equations (1) and (2) have specific voltages associated with each of them and when combined, equation (3) is the overall chemical reaction, where the voltages add up to 1.5V (the standard voltage for an AA battery):

$$8MnO_2 + 4Zn + ZnCl_2 + 9H_2O \rightarrow 8MnOOH + ZnCl_2 \cdot 4ZnO \cdot 5H_2O \tag{3}$$

Understanding how a battery works internally, now one can briefly analyze a chemical reaction's temperature dependence. Temperature is the measure of a substance's average molecular kinetic energy. Kinetic energy is equal to $\frac{1}{2}mv^2$, where m is the mass of the molecule and v is the average velocity of the molecule based either on the molecule moving through space (gas or liquid) or vibrating in place (solid). In order for a reaction to take place, molecules must be interacting and coming into contact to share electrons. The more that molecules move around, the more these reactions occur. A general rule of thumb is that for every 10°C rise in temperature, the rate of the reaction doubles [2]. This loosely-followed rule is derived from the Arrhenius equation (eq. 4). This equation can be rearranged to compare reaction rates at two different temperatures (eq. 5):

$$k = A\ e\ (-\ E_a/RT) \tag{4}$$

$$\frac{k_2}{k_1} = e\left(-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \tag{5}$$

where E_a is the activation energy, the minimum energy required to get the reaction to take place, expressed in J/mol of reactant; R is the universal gas constant (in this case, 8.3145 $J \cdot mol^{-1} \cdot K^{-1}$); k is the rate of the reaction; and T is the temperature. The E_a value in equation (3) is not known otherwise one could directly estimate a battery's life span for a given temperature if the life span at the room temperature is known. This can be solved once the data to estimate the reaction rates at the two temperatures are known.

METHODOLOGY

Having analyzed the chemistry and the potential temperature dependence for the life of a battery, one can look at the methods of analyzing this phenomenon. The method for testing the life of a battery was to use a flashlight at two different temperatures and observe it from the initial start time until it was no longer bright enough to be of any use. This could be a significant source of error since it is difficult to define exactly when the flashlight was 'dead'. As the battery's power decreases, the light of the flashlight does not stay at a constant brightness, but instead becomes dimmer. So, while the power may be diminishing, its output also diminishes, thus the flashlight could be deemed as functioning almost indefinitely.

The equipment used for this experiment was two Rayovac® Industrial AA flashlights and 28 GI Super Heavy Duty Batteries. The two flashlights required two AA batteries for operation, and with seven runs per flashlight at two separate temperatures, 28 batteries were used. The flashlights were purchased from Lowes® and the batteries were ordered from www.batteriesandbutter.com.

The flashlights were tested at 72°F and 170°F, which translates to 295°K and 350°K respectively. Conversion to Kelvin temperatures is needed because equations (4) and (5) require an absolute scale. 295°K was achieved by testing at room temperature, while 350°K was achieved using a kitchen oven. To ensure that each battery was at the right temperature prior to testing, both the battery and the flashlight were required to be in the testing environment for at least 15 minutes. Both the oven and the ambient environments could be controlled by a temperature setting, but both were closely monitored using a separate thermometer to ensure that the thermal accuracy of at least ± 5°F was achieved.

As stated previously, judging when a flashlight is 'dead' is difficult. A method for better judging this was to set the flashlight approximately one foot from a white piece of paper in a dark environment. At initial operation, there was a bright white circle that appeared on the paper. As time increased, the circle became smaller and started to appear an amber color. The time when the flashlight was declared done was when that amber circle was no longer reasonably visible.

After observing and collecting the data for each of the 14 runs, statistical tests were carried out to determine if temperature did affect the life span of the batteries.

RESULTS AND DISCUSSIONS

In order to test the life span of batteries a method known as Analysis of Variance (ANOVA) was used. This type of testing is used to determine if there is a significant difference in the means of treatments [9]. Single factor treatments were used with temperature variability at 72°F and 170°F. Fourteen samples were taken, seven at both 72°F and 170°F. The data collected are presented in Table 1. The sample data is described by the linear statistical model for One-Way-Classification Fixed-Effects Model,

$$y_{ij} = \mu + \tau_i + \varepsilon_{ij} \quad \begin{cases} i = 1, 2 \\ j = 1, 2 \end{cases} \tag{6}$$

where μ is the overall mean, τ_i the *i*th treatment effect and ε_{ij} is the random error component [1]. For hypothesis testing, the model errors are assumed to be normally and independently distributed with mean zero and variance σ^2, and variance is considered constant at all levels [1]. The hypothesis used for testing:

$$\begin{gathered} H_0: \tau_{72} = \tau_{170} = 0 \\ H_1: \tau_i \neq 0 \text{ for at least one } i. \end{gathered} \tag{7}$$

The resulting ANOVA One-Way-Classification Fixed-Effects Model is shown in Table 2, where "DF" is Degrees of Freedom.

Table 1: Sample data collected at ambient and heated conditions

Temperature (^oF)	Battery Life (minutes)							$y_{i\cdot}$	$\overline{y}_{i.}$
	1	2	3	4	5	6	7		
Ambient (72^{o}F)	73	75	76	76	85	80	79	544	77.71
Heated (170^{o}F)	36	32	39	41	38	37	31	254	36.29

Table 2: ANOVA

Source of Variation	SS	DF	MS	F_0	F(.05,1,12)	S/NS
Temperature	6007.14	1	6007.14	412.25	4.75	S
Error	174.86	12	14.57			
Total	6182.00	13				

SS = Sum of Squares; DF = Degrees of Freedom; MS = Mean Square Error; S/NS = Significant/Not Significant.

Factors for the ANOVA model were determined from the following equations and processes [1, 12],

Temperature Sum of Squares ($SS_{Temperature}$) = $\sum \sum y_{ij}^{2} - y..^{2} / N$ (8)

Total Sum of Squares (SS_T) = $\sum y_{i.}^{2} - y..^{2} / N$ (9)

Error Sum of Squares (SS_E) = $SS_T - SS_{Temperature}$ (10)

Temperature Mean Square ($MS_{Temperature}$) = $SS_{Temperature}$ / DF (11)

Mean Square Error (MS_E) = SS_E / DF (12)

$F_0 = MS_{Temperature} / MS_E$ (13)

In order to test the null hypothesis the calculated F_0 from the ANOVA table is compared to $F_{.05,\,1,\,12}$. From the ANOVA table F_0 was found to be 412.25 and from F-Table $F_{.05,\,1,\,12}$ was found to be 4.75.

To check the model and affirm the assumption, that errors are normally and independently distributed with constant variance, residuals were used from the following equations [1, 12]:

Residual (e_{ij}) = $y_{ij} - \overline{y_i}$ (14)

$\overline{y_i} = 1/n \sum y_i$ where i = 1, 2 (15)

Normal Score = ((1 – .5) / N) * 100 (16)

Figures 3, 4, and 5 were made to visually and graphically determine the model adequacy to normality and constant variance. Figure 3 is the Normal Scores vs. the Residual; Figure 4 is Residuals vs. Fitted Values; Figure 5 is Residuals vs. Battery Life. These graphs and their significance are further explained below.

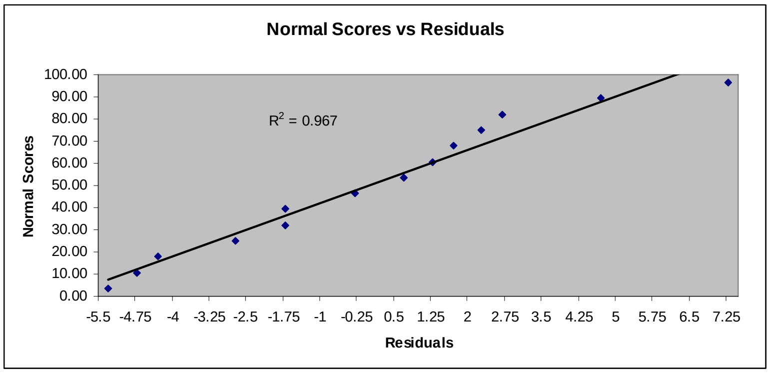

Figure 3: Normal scores vs residuals

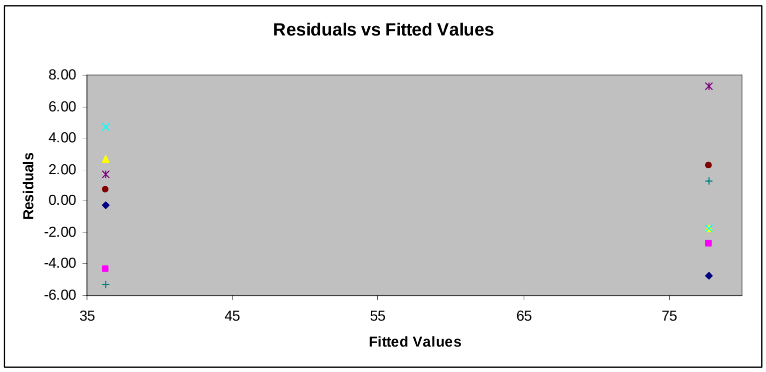

Figure 4: Residuals vs fitted values

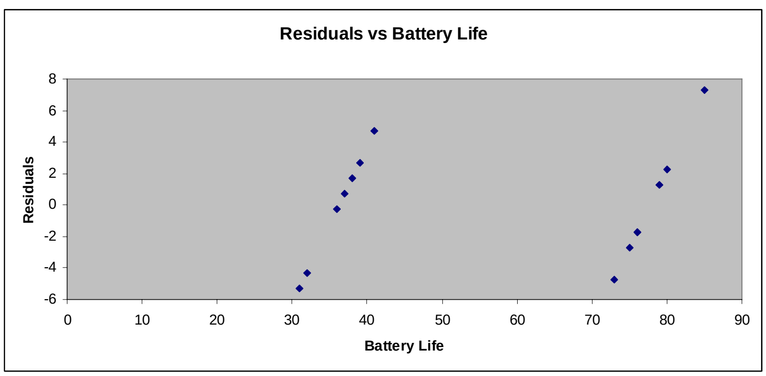

Figure 5: Residuals vs battery life

The 95% confidence interval on the difference between the two treatments was also determined to verify that zero does not lie within the interval. If zero lies within this interval the conclusion may be made that there is no difference in means. The equation used to calculate this is [1, 12]:

$$Y_{i.} - Y_{j.} \pm t_{.025,\,12} \sqrt{(2 * MS_E / n)} \tag{17}$$

It was found with 95% confidence that $38.276 \leq \mu_{72deg} - \mu_{170deg} \leq 44.564$.

One other method used to determine if there was a significant difference in sample means was Tukey's Test. This test analyzes the differences between means and compares it to a Studentized range statistic "q". The difference in means is considered significantly different if [1, 12]

$$|Y_i - Y_j| > T\alpha \tag{18}$$

where

$$T_\alpha = q_\alpha(a, f)\sqrt{(MS_E/n)} \tag{19}$$

From the data samples and treatment means $|Y_1 - Y_2|$ was found to be 41.42 and T_α to be $q_{.05}(2, 12)\sqrt{MS_E/n} = 4.44$.

Having demonstrated that the means are quite different, we now move on to estimating the activation energy for the chemical reaction is estimated. Referring back to equation (5), the values of T_1, T_2, and R are known, the ratio of the reaction rate constants, k_2/k_1 = 77.7 minutes / 36.3 minutes = 2.14. Though the reaction rate is expressed in more complicated units, those units cancel with the only remaining difference is the difference in times. Equation (20) solves for E_a.

$$\frac{k_2}{k_1} = e^{\left(\frac{-E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right)} = \frac{77.7}{36.3} = e^{\left(\frac{-E_a}{8.3145}\left(\frac{1}{350}-\frac{1}{295}\right)\right)} \Rightarrow E_a = 11.9 \text{ kJ/mol} \tag{20}$$

CONCLUSIONS

An analysis on the life span of dry cell batteries with temperature variability was conducted. The batteries were subjected to a specific temperature, 72°F and 170°F, for 15 minutes and then run until the light emitted by the flashlight was determined not visible anymore. Once the tests were completed, the data was analyzed and interpreted using ANOVA, residuals, confidence interval, and Tukey's Test to determine if temperature affects the life expectancy of dry cell batteries.

Analyzing the results from the ANOVA table allows the conclusion to be made that temperature has a significant effect on the life span of dry cell batteries since F_0 is greater than $F_{.05, 1, 12}$. This finding indicates the rejection of the original null hypothesis, H_0. The residuals found from the treatment means and individual samples were used to plot figures 3, 4, and 5. These plots indicate that the errors tend to follow a straight line indicating normality; the variance is constant between errors; and significant difference in mean battery life expectancy between 72°F and 170°F, respectively. The resulting 95% confidence interval found indicated that zero did not lie with in the interval, indicating that there is a significant difference between the means for battery life at different temperatures. Tukey's Test also indicated a significant difference in the means for battery life at different temperatures since $|Y_{72} - Y_{170}|$ was greater than T_α. However, Tukey's Test did not provide any value added information since only two treatment means were being compared. From these findings, it can be concluded that increased temperature decreases the life span of dry cell batteries by altering the rate at which the internal chemical reaction takes place; and many spares would be needed if the equipment being used was subject to high environmental temperatures. Finally, the chemical reaction's overall activation energy was calculated using the measured average life spans.

For future research and development, different brands of AA batteries could be tested and analyzed by measuring voltage, current, or power. The experiments could be run until the battery voltage reaches 5% of the starting voltage. This may also be applied to larger sized batteries. Studies may also be performed on different types of batteries such as lead-acid, lithium-ion, and zinc-air batteries as well as based on the user's environmental and situational needs.

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R. RADHARAMANAN

Dr. R. Radharamanan is a Professor of Industrial and Systems Engineering in the Department of Mechanical and Industrial Engineering at Mercer University in Macon, Georgia. He has twenty-eight years of teaching, research, and consulting experiences. His previous administrative experiences include: President of International Society for Productivity Enhancement (ISPE), Acting Director of Industrial Engineering as well as Director of Advanced Manufacturing Center at Marquette University, and Research Director of CAM and Robotics Center at San Diego State University. His primary research and teaching interests are in the areas of manufacturing systems, quality engineering, and product and process development. He has organized and chaired three international conferences, co-chaired two, and organized and chaired one regional seminar. He has received two teaching awards, several research and service awards in the United States and in Brazil. His professional affiliations include ASEE, IIE, ASQ, SME, ASME, and ISPE.

JENG-NAN JUANG

Dr. Dr. Juang received the B.S. degree in Electrical Engineering from National Taiwan Ocean University, Keelung, Taiwan and the M.S. and Ph.D. degrees from Tennessee Technological University, Tennessee. He has been a faculty member of the Electrical and Computer Engineering at Mercer University since 1987. He organized and chaired the "International Workshop on Future Aerospace Maintenance & Technology" at Taipei in Taiwan. He also served as a prime consultant for Fiber Optic Rate Gyroscope Development Program (A grant from Wright-Patterson Air Force Base, Ohio, and USA). He has received one teaching award, and two research fellow awards from NASA Langley Research Center, Virginia, USA. His professional affiliations include: ASEE, IEEE, AIAA, NATPA, NSPE, CAPASUS, and AAUP.