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ORIGINAL RESEARCH

Thermodynamics of electrochemical reaction in Lead-acid Battery

Isaac Adebayo Akinbulu 1[1] and Babatunde Taofeek Ogunbayo 2[2]

1Department of Chemistry, University of Lagos, Lagos, Nigeria

2Department of Chemistry, University of Lagos, Lagos, Nigeria

Correspondence
Isaac Adebayo Akinbulu, Department of Chemistry, University of Lagos, Lagos, Nigeria
Email: iakinbulu@unilag.edu.ng

Abstract:
Introduction: The quest to construct efficient and reliable electric cars can be achieved with the use of highly efficient and dependable batteries. Electric cars are projected to replace the current petrol-powered automobiles. The debilitating effects of global warming have made this task more imperative. The design of such batteries requires broad understanding of their operations; in order to optimize their outputs. The study of the thermodynamics of the electrochemical reactions occurring in these batteries offers a veritable platform to achieving this aim.
Materials and Methods: In this study, thermodynamics of electrochemical reaction in a Lead-acid battery was investigated. Electromotive force (e.m.f.) of the battery, containing sulphuric acid electrolyte of known concentration, was measured at different temperatures (303, 308, 313, 318 and 323 K).
Results: Necessary thermodynamic parameters were determined from the measured e.m.fs. A negative value of change in Gibbs' free energy, ΔG, and positive entropy change, ΔS, were obtained for the reaction. ΔG was more negative at increased temperature. The reaction was exothermic, with a negative value of enthalpy change, ΔH. A relatively small value of temperature coefficient of the electromotive force of the cell, $\left(\frac{\partial E}{\partial T}\right)_p$, was also obtained. Values of these thermodynamic parameters indicate that reaction in the Lead-acid battery is thermodynamically feasible
Conclusion: Variation in the value of ΔG, with varying temperature, suggests that electrical work obtainable from the battery may be varied, by controlling temperature. Specifically, decrease in ΔG, with moderate increase in temperature, offers the prospect of enhanced efficiency, at moderately high temperature. Therefore, operation of the battery may be optimized, with an in-built temperature-control device

Keywords: Thermodynamics parameters, electrochemical reaction, temperature coefficient, electromotive force and Lead-acid battery.

All co-authors agreed to have their names listed as authors.

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1. INTRODUCTION (

Batteries are made from electrochemical cells, connected in series, to achieve maximum power output to weight ratio. The electrochemical reaction associated with a battery is characteristic of the electrolyte and the electrodes that make up the battery. The overall electrochemical reactions are the combined half-cell reactions at the respective anodes and cathodes. The lead-acid battery, alkaline cell, and nickel metal hydride are examples of frequently used batteries.

The lead-acid battery was invented in 1859 [1] and is widely used in automobiles. Its use in automobile, in preference to other batteries, can be attributed to its high current capacity and reasonably high recharging cycles [2]. The electrodes in the lead-acid battery consist of Pb powder (anode) and finely divided PbO2 and PbSO4 (cathode) supported on a Pb frame. These electrodes are supported in a container containing concentrated H2SO4 (electrolyte).

The half-cell reaction at the anode is:

Pb(s) + SO42-(aq) ⇌ PbSO4(s) + 2e- 1

The half-cell reaction at the cathode is:

PbO2(s) + 4H+(aq) + SO42-(aq) + 2e- ⇌ PbSO4(s) + 2H2O(l) 2

The overall cell reaction is the combined half-cell reactions:

PbO2(s) + Pb(s) + 2H2SO4(aq) ⇌ 2PbSO4(s) + 2H2O(l) 3

In the overall equation, the arrows pointing to the right and left denote the reactions associated with discharging and charging of the battery, respectively. The focus of the present work is to study the thermodynamics of this cell reaction and determine the values of associated thermodynamic parameters.

This study will provide a better understanding of the operation of the lead-acid battery. The change in Gibbs free energy (ΔG), enthalpy change, ΔH, and entropy change, ΔS, are the thermodynamic parameters of interest. ΔG and ΔH measure the maximum electrical work obtainable from a battery, while ΔS is a measure of the temperature coefficient of the electromotive force (e.m.f.) of the battery. Therefore, a comprehensive understanding of the thermodynamics of the electrochemical reaction in the lead-acid battery could serve as a template for designing more efficient batteries. The design of electric cars, powered by batteries, demands better understanding of the operations of batteries and makes the construction of highly efficient batteries a necessity. This underscores the relevance of this study.

2. MATERIAL AND METHODS

2.1 Material

Lead-acid battery, distilled water and sulphuric acid (98%)

2.2 Equipment

Water-bath, galvanometer, connecting wire and crocodile clip

2.3 Measurement of electromotive force

Sulphuric acid solution (4.0 M) was prepared. 200 cm^3 of the solution were measured into a 250 cm^3 beaker and placed in a water-bath. At the desired temperature (303 K), the solution was poured into an emptied lead-acid battery. The system was left for five minutes, for equilibrium to be established, and the electromotive force/voltage of the battery measured, with the aid of a galvanometer. At this temperature (303 K), five readings were taken and the average voltage calculated. This procedure was repeated at temperatures of 308, 313, 318 and 323 K.

3. RESULTS AND DISCUSSION

3.1 Variation of electromotive force with temperature

Table I shows the variation of electromotive force (e.m.f.) with temperature. Five readings were taken for each temperature and the average e.m.f. calculated. Table I shows that e.m.f. increases marginally as temperature increases. This relationship can be justified from the Nernst equation for the cell reaction. The Nernst equation is expressed in equation 4, and further simplified as shown in equation 5.

as separate, if appropriate.

$$E = E^\circ - \frac{2.303RT}{2F}\log\frac{1}{a^2_{H_2SO_4}} \qquad 4$$

$$E = E^\circ + \frac{2.303RT}{2F}\log a^2_{H_2SO_4} \qquad 5$$

R = molar gas constant

T = temperature in Kelvin

F = Faraday's constant

$a_{H_2SO_4}$ = Activity of solution of sulphuric acid

E = Electromotive force of the battery

E^o = Standard electromotive force of the battery

Equation 5 shows that electromotive force and temperature are linearly related, which justifies the results shown in Table 1.

Table 1: Dependence of electromotive force on temperature

T/K	E_1/V	E_2/V	E_3/V	E_4/V	E_5/V	Average/V
303	12.04	12.04	12.02	12.03	12.02	12.03
308	12.06	12.05	12.06	12.05	12.05	12.05
313	12.07	12.07	12.06	12.08	12.07	12.07
318	12.08	12.08	12.09	2.09	12.08	12.08
323	12.10	12.09	12.08	12.10	12.09	12.09

3.2 Variation of change in Gibbs' free energy with temperature

The change in Gibbs' free energy, ΔG, for any cell reaction, involving n number of electron, is defined by equation 6

$$\Delta G = -nFE \qquad 6$$

where F and E are as defined previously.

Table 2: Change in Gibbs' free energy and temperature

T/K	Average E/V	ΔG/kJ mol^{-1}
303	12.03	-2,321.79
308	12.05	-2,325.65
313	12.07	-2,329.51
318	12.08	-2,331.44
323	12.09	2,333.37

Table 2 shows the variation of change in Gibbs' free energy with temperature. At each temperature, ΔG is negative, which shows that the overall reaction in equation 3 is thermodynamically feasible. Since ΔG measures the amount of electrical work obtainable from a battery, the results in Table 2 shows that more electrical work can be obtained from the battery at increased temperature. This implies that efficiency of the battery can be enhanced by deliberately increasing the temperature of the associated cell reaction. This may be achieved by designing a battery with an in-built thermostat, in order to effectively control the temperature of the cell reaction.

3.3 Determination of other thermodynamic parameters

Apart from ΔG, other thermodynamic parameters, such as ΔH and ΔS, were also determined. The change in Gibbs' free energy is related to enthalpy change by the expression in equation 7

$$\Delta G = \Delta H - T\Delta S \qquad 7$$

where T is temperature in Kelvin

The plot of ΔG versus T (Figure 1) is linear, with ΔH and ΔS as intercept and slope, respectively. The data in Table 2 were used for the plot in Figure 1. From the plot, the relationship between ΔG and T is expressed as equation 8.

$$\Delta G = -0.579T - 2147 \qquad 8$$

Equation 7 and 8 are similar, hence the intercept of the plot (-2147 kJ mol^{-1}) is ΔH. Negative value of ΔH shows that the reaction in the Lead-acid battery is exothermic. The energy released is electrical energy, which is the source of the energy needed for effective functioning of the major components of automobiles that make use of this battery.

The slope of the plot (-0.579) is similar to $-\Delta S$ in equation 7. Therefore, the entropy change for the cell reaction in the Lead-acid battery is +579 J mol^{-1} K^{-1}. The entropy change is positive, which implies the reaction is spontaneous and thermodynamically feasible. The temperature coefficient of electromotive force of the cell in the battery was calculated from entropy change.

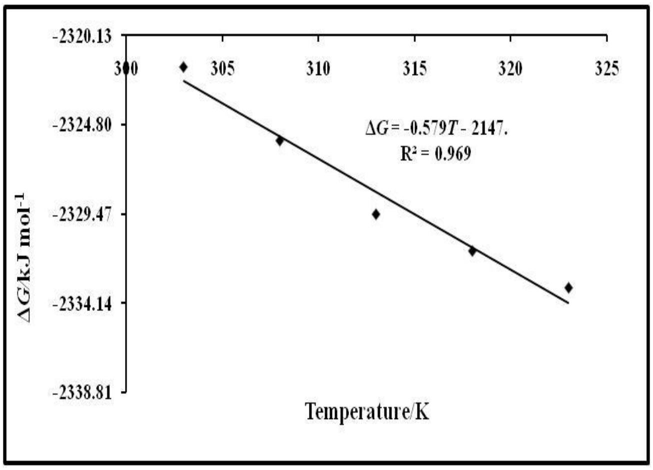

Fig. 1: Plot of ΔG versus Temperature

3.4 Determination of temperature coefficient of electromotive force of the cell

Differentiation of equation 6 with respect to temperature, at constant pressure, gives equation 9

$$nF\left(\frac{\partial E}{\partial T}\right)_P = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad 9$$

The fundamental equation of thermodynamics is expressed as equation 10

$$\Delta G = V\Delta P - T\Delta S \qquad 10$$

where V and P represent volume and pressure respectively, while other quantities are as defined previously. Differentiation of equation 10 with respect to temperature, at constant pressure, gives equation 11.

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad 11$$

Substitution of ΔS in equation 11 into equation 9 gives equation 12

$$nF\left(\frac{\partial E}{\partial T}\right)_P = \Delta S \qquad 12$$

From equation 12, the quantity $\left(\frac{\partial E}{\partial T}\right)_P$ can be defined, as indicated in equation 13

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF} \qquad 13$$

The quantity $\left(\frac{\partial E}{\partial T}\right)_P$ is the temperature coefficient of the electromotive force of the cell in the Lead-acid battery. From the value of ΔS (+579 J mol^{-1} K^{-1}) obtained previously, value of $\left(\frac{\partial E}{\partial T}\right)_P$ was calculated. A value of 3.52×10^{-3} V K^{-1} was obtained. This is not substantially different from the value, in the order of 10^{-4} or 10^{-5} V K^{-1}, usually obtained for electrochemical cell, such as that in the Lead-acid battery [3]. The small value of temperature coefficient can be attributed to the absence of a gas electrode in the Lead-acid battery [3]. The relatively small value of $\left(\frac{\partial E}{\partial T}\right)_P$ implies that e.m.f. of the cell in the Lead-acid battery can be measured within a wide range of temperature.

Temperature coefficient was also measured by using the integrated form of equation 13. Integration of equation 13 between a reference temperature, T_o, and any temperature, T, gives

$$\int_{T_o}^{T}(\partial E) = \int_{T_o}^{T}\left(\frac{\Delta S}{nF}\right)\partial T$$

$$E_T - E_{T_o} = \frac{\Delta S}{nF}(T - T_o) \qquad 14$$

If E_T is expressed simply as E, while T_o equals 298 K, equation 14 becomes

$$E = E^{\circ} + \frac{\Delta S}{nF}(T - 298) \qquad 15$$

Table 3: Variation of Electromotive force with (T-298)

T/K	Average *E*/V	(*T*-298)/K
303	12.03	5
308	12.05	10
313	12.07	15
318	12.08	20
323	12.09	25

The quantities in equation 15 are as defined previously. The data in Table 3 were extracted from Table 1, and used for the plot in Figure 2. A plot of E versus (T-298), Figure 2, is linear, with E^o and $\frac{\Delta S}{nF}$ as intercept and slope, respectively.

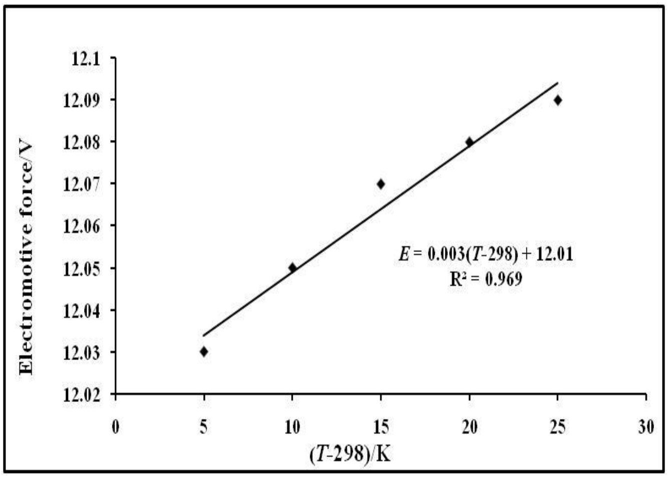

Fig. 2: Plot of Electromotive force with (*T*-298)

From the plot in Figure 2, the relationship between E and (T-298) is as indicated in equation 16

$$E = 0.003\,(T-298) + 12.01 \qquad 16$$

Equations 15 and 16 are similar; hence the slope (0.003) of the plot in Figure 2 is the value of $\frac{\Delta S}{nF}$, the temperature coefficient of the electromotive force of the cell in the Lead-acid battery, defined previously in equation 13. This value (3.0×10^{-3} V K^{-1}) is not significantly different from the value (3.52×10^{-3} V K^{-1}) calculated previously. The intercept (12.01) of the plot in Figure 2 is the value of the standard electromotive force (E^o) of the Lead-acid battery. This is the same as a value of approximately 12 V, the nominal voltage obtainable from a Lead-acid battery consisting of six cells connected in series [2].

4. CONCLUSION

Thermodynamics of the electrochemical reaction in Lead-acid battery was studied. The results of the study show that the electromotive force obtainable from the battery increases marginally with temperature. The values of thermodynamic parameters, such as ΔG, ΔH and ΔS suggest that the reaction in the Lead-acid battery is thermodynamically feasible. The value of ΔG was more negative with moderate increase in temperature. This suggests that more electrical work can be obtained from the battery at moderately high temperature. This offers the prospect of optimizing the efficiency of the battery, if an in-built temperature-control device can be incorporated into its architecture. The value of temperature coefficient of the electromotive force of the cell in the Lead-acid battery is very close to that for similar electrochemical cell. The relatively small value, obtained in this work, suggests the absence of a gas electrode, usually associated with high temperature coefficient. The value of standard electromotive force obtained is the same as that associated with a Lead-acid battery, consisting of six cells connected in series.

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