BATTERY STUDIES WITH PARTICULAR REFERENCE TO ORGANIC DEPOLARIZERS

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Battery Studies with Particular Reference to
Organic Depolarizers

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ABSTRACT

Since Volta's invention of the first primary cell, using silver and zinc, numerous other cell combinations have been studied, covering a wide variety of anode and cathode materials. The latter have included both inorganic and organic substances capable of electrochemical reduction, although, historically, organic cathode materials have received very much less attention than the inorganic.

It was the purpose of this investigation to study the actual behavior of a selected number of quinones as depolarizers in primary cells. Performance of experimental cells was compared with cells of the usual dry cell composition but of the same size and construction as cells of experimental composition.

The results show that certain substituted anthraquinones possess good depolarizing ability as measured by discharge voltage and coulombic capacity. Energy output in some cases was higher than that of the manganese dioxide control cells (zinc anodes in all cases) because of higher effective coulombic capacities.

A qualitative study of the effect of substituents on the discharge voltages of various quinones showed that cell

working voltages were much more sensitive to quinone substitution than were the calculated reversible potentials. Also, in the case of nitro- substituted anthraquinones more coulombic capacity was obtained than could be accounted for by the simple reduction to the corresponding hydroquinone. The possibility of a reduction of the nitro- group of this compound was considered.

Substances investigated were benzoquinone, naphthoquinone, anthraquinone, and certain of their derivatives, using various electrolytes.

The size of the experimental cells was such that about 0.2 gram of the various depolarizers could be studied conveniently.

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HISTORICAL

CHAPTER I

EARLY HISTORY OF ELECTRIC CELLS

As early as 1767 Sulzer announced the discovery that a peculiar taste is perceived when two different metals are placed together on the tongue and brought into contact at their edges (7). Such a combination of two metals, as copper and silver, and the saline saliva constitutes, as we now know, a voltaic couple. But the significance of Sulzer's observation was not appreciated until more than thirty years later, after Galvani had made his discovery (1786) that freshly prepared frog legs, hung by a copper wire on an iron balcony railing, twitched convulsively whenever the frog touched the iron; and after Volta had demonstrated that the effect was not due to "animal electricity", but to the two metals, and that electricity, identical with that excited by friction, could be produced by means of the metals without the agency of animal tissues, nerves, or muscles.

In order to increase the electrical action, Volta constructed a chain of elements to which he gave the name "artificial electric organ" but which since has become known as the Voltaic pile. Volta's pile was the immediate forerunner of his "crown of cups", which was the first real voltaic battery. Each element of it was called a galvanic element. Thus the name of both Galvani and Volta became inseparably associated with this earliest device to

produce a continuous flow of electricity.

As described in a letter to the Royal Society of London, in 1800, Volta built his pile of silver, brass or copper against tin or zinc but stated repeatedly that silver and zinc were better than the others. Discs of silver and zinc were placed back to back, and between adjacent pairs of dissimilar metals was put porous material soaked in salt water. He mentions as many as sixty couples combined into a single battery.

Although Volta recognized the superiority of certain couples over others, he did not relate the chemical action occurring at the electrodes to the electricity produced. In fact, it was not recognized that chemical action necessarily occurred at all, by the early experimenters, in spite of the obvious corrosion of the zinc. The exact relationship was later elucidated by Faraday. Volta himself was not certain whether the voltage arose at the junction of the two metals or at the liquid-metal interfaces, and this question was not resolved for many years (8).

In spite of its limitations, which were numerous, Volta's pile enabled experimenters to enter a new era in research on electricity. Cells essentially of the type as described by Volta were the only ones known until the invention of the two-fluid cell by Daniell in 1836.

The principal difficulty with Voltaic cells, of course, was polarization of the positive electrode. Some progress was made toward alleviating this condition by increasing the

size of the positive electrode, (Wollaston's cell) but it remained for Daniell to initiate a new era in cell design.

The construction described by Daniell consisted of the hollow gullet of an ox, in the axis of which was placed a cylindrical rod of zinc immersed in dilute sulphuric acid. Surrounding this was a copper cylinder filled with a saturated solution of copper sulphate. Hydrogen evolution was prevented and a copper deposit appeared as a pink coating on the copper electrode (41).

The tremendous influence of Daniell's cell on the subsequent progress of battery development is shown by the many variations in construction and materials in batteries of the Daniell type. The best known of the various forms and the only one which has survived to the present time is the "gravity cell", which was patented by Varley in England in 1854.

Table I lists a few of the more prominent cells which resulted from early battery development.

Grove's cell (1839) had an electromotive force of from 1.9 to 2.0 volts, considerably higher than the earlier cells. The nitric acid was reduced to nitric oxide, which was oxidized to the dioxide on coming into contact with the air. Grove mentioned that a cover containing lime should be provided to absorb the liberated gases.

The cost of the platinum for Grove's cell was probably a factor that led to Bunsen's cell. Bunsen (1840) substituted carbon for platinum and produced a cell which came into wide use. The reactions and the voltage are essentially

TABLE I

SOME EARLY PRIMARY CELLS

Inventor	Year	Anode	Anolyte	Catholyte	Cathode	Voltage
Daniell	1836	Zinc	$ZnSO_4$	$CuSO_4$	Copper	1.07
Grove	1839	Zinc (amalg.)	HCl or H_2SO_4	HNO_3 and H_2SO_4	Platinum	1.9 - 2.0
Bunsen	1840	Zinc (amalg.)	H_2SO_4	HNO_3 and H_2SO_4	Carbon (gas coke)	1.94
Smee	1840	Zinc (amalg.)	1:7 Sulphuric acid (single fluid cell)		Platinized Platinum or Silver	0.5
Walker	1842	Zinc (amalg.)	1:7 Sulphuric acid (single fluid cell)		Platinized Carbon	0.4
Poggendorff	1857	Zinc (amalg.)	1:5 Sulphuric acid sat'd with $Na_2Cr_2O_7$. (single fluid cell)		Carbon	2.0
Leclanche	1868	Zinc (amalg.)	Saturated NH_4Cl		MnO_2 and retort carbon	1.5
De laRue	1880	Zinc	2.5% NH_4Cl		Silver chloride on silver	1.03

the same as for Grove's cell.

Smee (1840) developed a cell of low voltage which overcame, to a degree, the difficulty of polarization encountered with previous single fluid cells. His cell used a sulphuric acid electrolyte and a cathode of platinized platinum.

Walker (1857) modified Smee's cell by substituting platinized carbon for platinum. Walker's cell found extensive use on railroads for very light work and it is reported that such cells would stand without attention for a year or two and that upkeep was as little as 25 cents per year (41).

The bichromate cell was invented by Johann Poggendorff in 1842, and became widely used in laboratories. In various modifications it was either a one- or two-fluid cell. The cell reaction is (41):

$$3Zn + 7H_2SO_4 + Na_2CrO_7 = 3ZnSO_4 + Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

De laRue's cell (about 1880) was the most notable of the early silver chloride types. The soluble electrode was unamalgamated zinc, and the positive electrode consisted of silver chloride cast around a strip of silver. The electrolyte was dilute ammonium chloride and the e.m.f. was 1.03 volts.

Georges Leclanche first published a description of his now famous cell in 1868. The fact that manganese dioxide was a conductor of electricity and was at the same time a strong oxidizing agent led him to the conclusion that

he could construct a cell of constant voltage with this material. Leclanche apparently believed that ammonium chloride was used in the cell reaction and advocated using an excess amount of the salt. His first cells utilized a porous cup to contain the mixture of coarse manganese dioxide and retort carbon. The anode was amalgamated zinc. The beneficial effects of amalgamation had first been discovered as early as 1836 (41).

Leclanche's cell enjoyed wide popularity and many thousands of his cells were made and used during his lifetime. His same cell system is preeminent today in terms of production numbers in the form of the "dry cell".

Vinal (41) calls the years 1800 to 1900 the period of historical development. In these years, most of the cell couples still in the foremost use today (with improvements) were discovered, mostly by trial and error. By 1900 electrochemical theory had become well advanced and much subsequent battery development has been along the lines of improving the performance of existing cells with regard to overcoming difficulties such as anode corrosion and self discharge of the positive electrode. Better battery design and the use of higher purity material has contributed to increasing the output of the dry cell, for example, by a factor of five. (17).

CHAPTER II

THEORY OF VOLTAIC CELLS

1. Role of Primary Cells as Energy Sources.

It is customary to regard the difference between a secondary and a primary cell as resting upon whether the cell is an accumulator, that is, one which stores electrical energy primarily produced outside the cell, usually from a mechanical source, or whether the cell is immediately utilizable in producing electricity. A primary cell, being generally considerably less reversible than a typical secondary cell, is rarely recharged and is sometimes thought of as a primary energy source, in that it possesses available energy due to its construction and composition alone and not as a result of prior charging.

In another sense, a primary cell is not a primary energy source at all, but is a special type of accumulator, in that at least as much energy is expended in obtaining its component parts and in its fabrication as is obtained by discharging it. This statement is true of all primary cells in common use today, although it would not be true for the so-called "fuel cell", the object of which is to serve as a primary energy source using carbon fuels. The reason for this is that cell elements, anode materials particularly, do not occur as such in nature, with the exception noted above. An example would be the reduction of zinc ore to the metal to provide the most common anode

material, and the subsequent (less than reversible) work obtained from its oxidation in a primary cell.

These facts lead to the conclusion that primary cells would be useful only as highly specialized sources of electrical energy, and this is actually the case. Primary cells serve where it is inconvenient to use mechanical generators or where the amount or rate of electrical energy required is too small to justify mechanical equipment. Other properties of primary cells indicating their use are portability (as for flashlight cells) and steadiness of current (as for potentiometer slide wires). Primary cells show favorable watt-hour output per unit weight and volume when compared with mechanical generation and their dependability is often a factor in their choice. They are a very expensive source of energy, however, and this factor is usually overriding.

2. Thermodynamic Basis of Energy Release.

The electrical anergy obtainable from a voltaic cell derives from the free energy of the chemical reaction taking place in the cell (37). Voltaic cells are characterized by a tendency for the cell reaction to take place spontaneously to a point of equilibrium. This is paralleled by a potential difference between the electrodes which is initially a maximum and gradually approaches zero as chemical equilibrium is approached.

For any process taking place in a galvanic cell operating reversibly at constant temperature and pressure, the maximum useful work obtainable from the system is, as for any reversible process at constant temperature and pressure,

$$W_{net} = -\Delta(U + PV - TS) = -\Delta H - T\Delta S = -\Delta F.$$

In the above equation, W net is all work other than the (useless) work of expansion against atmospheric pressure, and the other terms have their customary thermodynamic significance.

The volume change in most practical primary cells is negligibly small; it is due only to changes in volume of (solid) electrodes, and to changes in concentration of the liquid electrolyte. Consequently, the net work is practically equal to the total work. Only rarely do gases take part in the reaction of a primary cell.

The maximum useful work obtainable from such a galvanic cell, however, is also equal to the quantity of electricity transferred through the cell multiplied by the potential difference through which the electricity is carried. It follows, therefore, that:

$$W_{net} = n\mathcal{F}E.$$

Here, n is the number of chemical equivalents per mole of reaction in the cell, $\mathcal{F}$ is the Faraday constant, giving the quantity of electricity associated with one chemical equivalent, and E is the electromotive force of the cell. It follows from the preceding two equations that:

$$-\Delta F = n\mathcal{F}E.$$

For any galvanic cell to be significant thermodynamically, its e.m.f. must be constant and reproducible and the reaction actually taking place in the cell must be identified (37).

It can be shown that, for the reaction actually taking

place in the cell,

$$\Delta S = n \mathcal{F} (dE)/(dT) \quad \text{at constant pressure.}$$

For cells, therefore, which have zero or negligible temperature coefficients, the net work obtainable from the cell is equal to the heat of reaction at constant pressure.

A given quantity of reactants in a primary cell, however, react under conditions of varying composition, so that the free energy change per mole of reactant, and hence, the potential difference between the electrodes, tends to become smaller as the reaction proceeds. The point of equilibrium itself, and the manner of reaching it are both complicated functions of the construction and composition of the cell.

Although the free energy change for the reaction taking place in a galvanic cell is a perfectly definite quantity which is quite independent of the path followed between the initial and final states, the actual net electrical work obtained is only a definite quantity when the reaction is taking place reversibly, which is to say, from a practical point of view, when it is not taking place at all. Furthermore, the reversible net work is the maximum obtainable from a given cell.

Applied to a discharging cell this means that the terminal voltage is a quantity which can only approach, and never equal, the reversible potential, since the quantity n, the number of equivalents per mole of reaction, like the free energy change, is independent of the degree of irreversibility, and $\mathcal{F}$ is a fundamental constant.

Algebraically,

$$W_{net,\ irr.} = n \mathcal{F} V,$$

where V is the terminal voltage of the cell, less than the reversible potential by an amount which depends on the rate of discharge, the history and geometry of the cell, and other non-thermodynamic factors. Irreversible processes are inherently not susceptible to thermodynamic analysis (29).

It will be apparent that the coulombic capacity of a given cell, the quantity $n \mathcal{F}$, can be predicted with certainty, in the absence of side reactions, in that it must follow from Faraday's laws.

3. Sources of E.M.F. and Polarization.

In the widest sense, any two different electrodes in contact with a common electrolyte constitute a Voltaic cell, since they will, in general, posess different potentials with respect to the electrolyte (42). These electrode, or "half-cell" potentials arise as a consequence of the tendency for the respective half-cell reactions to take place under the given conditions. The physical basis for the dependency of electrode potential on the chemical reaction occurring at that electrode lies in the fact that electrons are either reactants or products of those same reactions. All conceivable electrodes can be arranged in order of their tendency to undergo oxidation (or reduction). The electrode in a Voltaic cell having the greater tendency to oxidize becomes anodic with respect to the other electrode. Under open circuit conditions, the tendency for the individual electrode reactions

to occur is exactly counter-balanced by the potentials between electrodes and electrolyte. If external connection of the electrodes is made through a resistance, the electrode potentials assume values which more nearly approach each other and the potential difference becomes equal to the value of the ohmic drop through the external and internal resistances. This is illustrated by the polarization curves in Figure 1 for a hypothetical cell.

The curves are reversed with respect to each other since the same current which is anodic for one electrode (an anodic current tends to make the electrode more positive) is cathodic for the other. The quantities Δe_a and Δe_c are the anode and cathode polarizations, respectively.

In the case of hydrogen evolution, at least, the polarization, other than that due to concentration gradients, is dependent on the current density at the electrode in the following manner:

$$\Delta e = a - b \log i \ ,$$

where i is the current density and the quantities a and b are constants. This equation (the Tafel equation) is only valid at potentials not too near the reversible potential. When Δe becomes very small the reverse reaction rate (oxidation of hydrogen) becomes appreciable and a wholly different equation is followed.

Most cathodic and anodic processes behave similarly in that the polarization is a logarithmic function of current

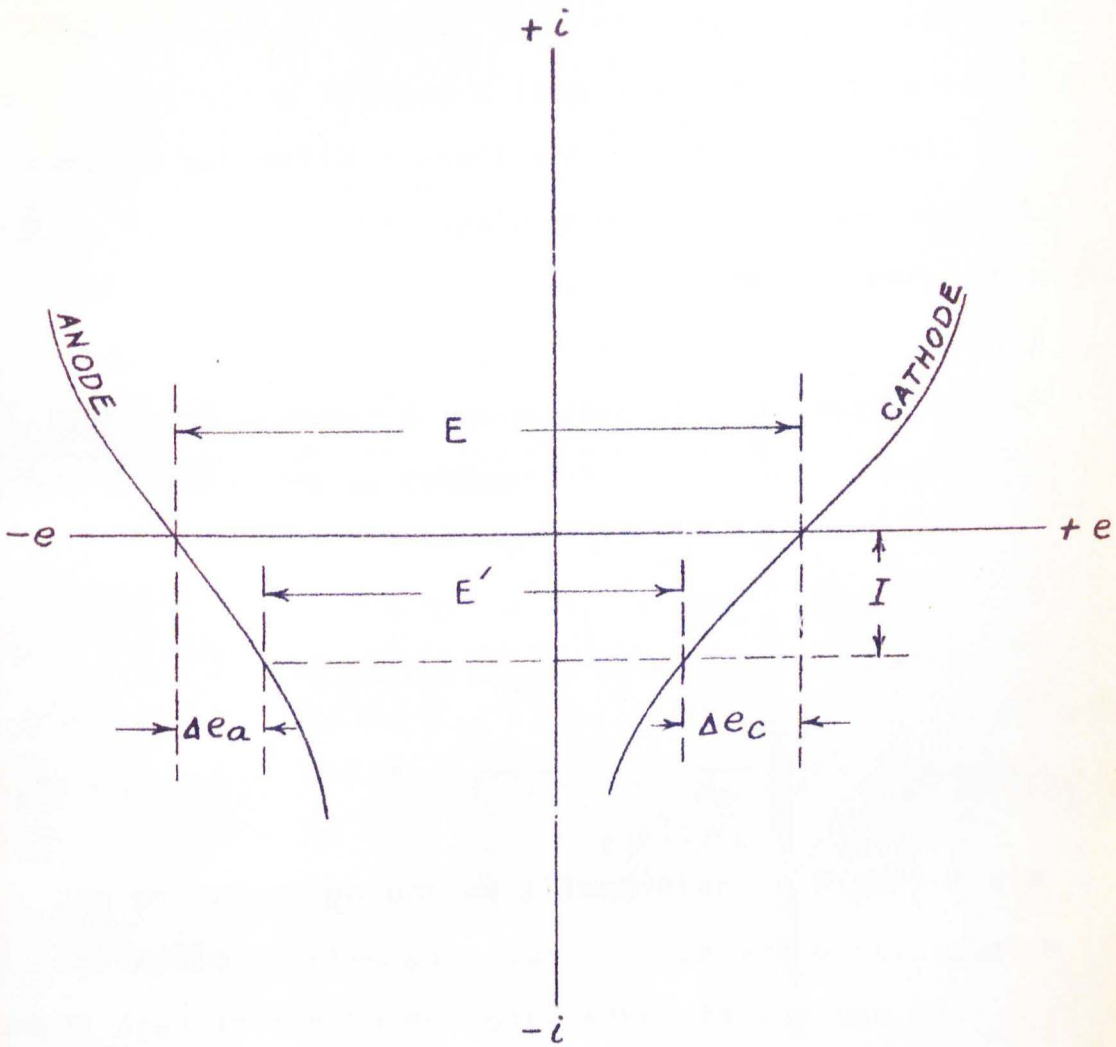


FIGURE 1. ELECTRODE POLARIZATION IN A HYPOTHETICAL PRIMARY CELL.

density. The particular polarization curve followed by an electrode in a primary cell, however, depends strongly on the sometimes considerable concentration gradients established in that cell.

The ohmic drop through the cell due to the resistance of the electrolyte is also a loss with regard to available voltage. A schematic circuit for a discharging cell is shown in Figure 2. The terminal voltage, V, and also the potential E' depend on the circuit current I, which in turn depends on the internal and external resistances, R_i and R_e.

The relationships between the various quantities of Figures 1 and 2 are as follows:

$$E = E' + (\Delta e_a + \Delta e_c)$$

$$V = E' - IR_i = IR_e$$

$$E' = I (R_e + R_i)$$

$$I = \frac{E'}{R_e + R_i} = \frac{V}{R_e}$$

The polarization curves illustrated in Figure 1 are for reversible electrodes. Such curves are continuous in passing from anodic to cathodic currents through the reversible potential. In connection with these electrodes, chemical reversibility should be distinguished from thermodynamic reversibility. For example, the Daniell cell

$$Zn \;/\; ZnSO_4 \;/\; CuSO_4 / \; Cu$$

is chemically reversible (10) in that current flow in one direction through the cell causes the solution of zinc and the deposition of copper, while the reverse current causes

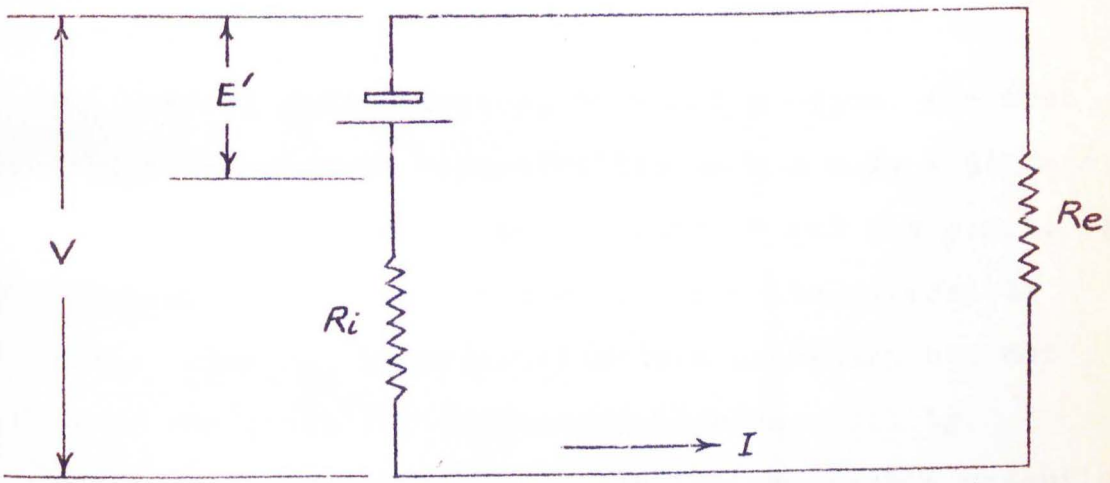


FIGURE 2. EQUIVALENT CIRCUIT OF DISCHARGING CELL.

exactly the opposite effect, that is, the solution of copper and the deposition of zinc. On the other hand, in the cell

$$Zn \ / \ H_2SO_4 \ / \ Cu$$

the spontaneous reaction (current flow from copper to zinc in the external circuit) allows the solution of zinc and the liberation of hydrogen at the copper electrode, while a reverse current causes the solution of copper and the liberation of hydrogen at the zinc. This cell is chemically irreversible.

The Daniell cell, however, does not achieve, nor even approach, thermodynamic reversibility unless only a differentially small current is flowing through it and its e.m.f. is only differentially less, or greater than its reversible potential. Chemical reversibility is a necessary but not sufficient condition for thermodynamic reversibility.

For cathodes which do not establish reversible potentials the polarization curve may show an apparent discontinuity when passing from anodic to cathodic currents and may not pass through a reproducible, reversible potential. An irreversible anodic effect is passivity, in which the electrode may suddenly assume a more noble potential after having undergone oxidation near its reversible potential.

4. Mechanism of Depolarization in Primary Cells.

Primary cells using aqueous electrolytes often present the possibility of hydrogen ion discharge as the cathode reaction since anodes of metals higher in the e.m.f. series

than hydrogen are usually provided. It will be recalled that Volta's original pile was built of zinc and silver using a common salt electrolyte. The reaction taking place in this cell, of course, is:

$$Zn + H_2O = ZnO + H_2$$

The anodic reaction:

$$Zn = Zn^{++} + 2e ,$$

takes place with little polarization under these conditions, but the cathodic reaction:

$$2e + 2H^{+} (aq.) = H_2 (g.),$$

taking place on the surface of the silver electrode, is subject to considerable polarization so that the electrode becomes nearly saturated with gas and only feeble currents may be drawn from a cell which has been in continuous operation. Daniell's cell, the first improvement of Volta's invention, substituted the nearly non-polarizable deposition of copper for hydrogen evolution.

The term depolarizer, in connection with primary cells, is now used loosely in the literature of battery technology to describe any substance, other than hydrogen, taking part in the cathode reaction. Two conflicting points of view are put forward today as to the mechanism of depolarization in primary cells, particularly in the Leclanche dry cell.

The older view is that the only function of the depolarizer (such as manganese dioxide) is to react with liberated hydrogen at the cathode and thus maintain the operating

voltage of the cell. That is, the reaction of the depolarizer is only a secondary reaction, and the primary, and therefore potential determining reaction, is the discharge of hydrogen ions in all cases. Such an explanation is given in most older texts and articles.

This view was developed clearly in connection with dry cells by MacInnes (31). His contention was based on e.m.f. measurements and on the Nernst equation. Hydrogen will be evolved at the cathode only when its pressure reaches one atmosphere. The action of the MnO_2 is to keep its pressure far below this. According to MacInnes, the system MnO_2 - Mn_2O_3 - H_2O - H_2 is univariant and will have a small, though definite, hydrogen pressure for each temperature. If allowed to stand on open circuit, the positive electrode (cathode) of the Leclanche cell will reach a voltage corresponding to that for hydrogen at this equilibrium pressure.

MacInnes regards the cell as a double one:

$Zn/\ NH_4Cl + ZnCl_2/\ H_2(1\ Atm.)/\ NH_4Cl + ZnCl_2/\ H_2\ (p\ Atm.)$.

He measured the e.m.f. of the left half of this double cell at 25°C., and found -0.514 volts. If the e.m.f. of the Leclanche cell on open circuit be taken as -1.50 volts, then the e.m.f. of the cell on the right has the average value -0.986 volts. With the aid of the Nernst equation, p is then found to be 4×10^{-34} Atm. A drop in voltage from -1.50 to -1.20 volts corresponds to a rise in the hydrogen pressure to 10^{-24} Atm.

Farrington Daniels (11) found that the rate of evolution of hydrogen from dry cells was the same on closed as on open circuit. He stated that this was due to the ready oxidation by MnO_2 of the additional quantities of hydrogen liberated during discharge.

Koehler (24) states that the function of the manganese dioxide in dry cells is to oxidize the liberated hydrogen. He also states that the cathode reaction in dry cells is:

$$2\ NH_4^+\ (aq.) + 2e = 2\ NH_{3(g)} + H_{2(g)}.$$

The more recent point of view is also implied by Koehler. He says that ". . . . the manganese dioxide must be considered as an energy producing material of definite cathodic potential."

According to G. W. Vinal (43), there are several possible cathode reactions in dry cells, depending on composition, pH, and current density but the one to be expected under usual conditions of operation is:

$$2MnO_2 + 2H^+ + 2e = Mn_2O_3 \cdot H_2O$$

(Strictly speaking, this reaction takes place in the absence of zinc. Under the usual dry cell conditions the final product of the cell reaction is hetaerolite, $Mn_2O_3 \cdot ZnO$).

Heise and Cahoon are most emphatic in their criticism of the older idea and include the following preface to a review (in 1952) of the general theory of the Leclanche cell (17):

> Electrochemical theory, particularly as regards the development of electromotive force, was well advanced by 1900, yet the early battery technologists were slow to apply its teachings to the

Leclanche system. Polarization was frequently considered loosely in terms of the cathodic liberation of hydrogen, though how the latter could be visualized as proceeding at the potential of the MnO_2 electrode or the operating voltage of the cell is not immediately clear. Depolarization, a term which we could well do without, is at best, as defined by LeBlanc, only a means of preventing evolution of hydrogen or oxygen; it has all too often been considered, not as the primary electrode process, but as a chemical reaction between MnO_2 and previously liberated hydrogen. There was little basis for this view, which regrettably is still found in many books on general chemistry and even in some electrochemical texts.

5. Reactions in Primary Cells.

Although it is true, as stated previously, that for a cell to be significant thermodynamically, it must exhibit a reversible, reproducible potential, and the cell reaction must be known, it is also true that at least two of the most important modern primary cells (the dry cell and the air depolarized cell, for example) do not exhibit reproducible, reversible potentials, and the exact cell reactions have only been recently determined in both cases. Primary cells, obviously, need not be significant in the rigorous thermodynamic sense to come into wide use.

If the performance of a particular cell is to be determined, however, the cell reaction taking place must be identified so that the theoretical output may be compared with the actual.

It frequently happens that the decision as to what reaction is actually taking place in a primary cell turns on the choice of one of several alternative cathode reactions, as the usual anodic process is the simple ionization

and dissolution of a metal such as zinc, about the reaction of which there can be little doubt.

Recent work in connection with the Leclanche cell illustrates some techniques used in elucidating the reactions.

Examination of crystals from spent cells shows (42) the presence, among other substances, of hetaerolite, $ZnO \cdot Mn_2O_3$. One would infer, on this evidence, that the overall cell reaction could be adequately represented by the equation:

$$Zn + 2MnO_2 = ZnO \cdot Mn_2O_3 ,$$

and the cathode reaction by the equation:

$$2e + 2MnO_2(s.) + 2H^+(aq.) = Mn_2O_3 \cdot H_2O\ (s.).$$

In this case the manganese dioxide would undergo a valence change of one, and the electrode potential would obey the following equation:

$$e = e_0 + RT/2\mathcal{F} \ln a^2(MnO_2)\ a^2(H+)/a\ (Mn_2O_3 \cdot H_2O).$$

If the activities of the solids remain constant as unity, the pH - potential relationship follows immediately:

$$e = e_0 - 2.3RT/\mathcal{F}\ (pH)$$

At 30° C., the slope of the line showing the pH - potential relationship should have a slope of -0.06 volts per pH unit.

Various investigators (6) (32) have studied the matter and values for the slope of this curve ranging from -0.06 to -0.12 volt per pH unit have been obtained.

McMurdie, Craig and Vinal (32) found that, in acid

solutions, the manganese dioxide electrode is in equilibrium with divalent manganese, but that at a pH of 4.5 or higher, the divalent manganese ion is largely removed from solution. This was explained by postulating the following equilibrium:

$$MnO_2(s.) + MnCl_2(aq.) + 2H_2O = Mn_2O_3 \cdot H_2O(s.) + 2HCl.(aq.)$$

The forward reaction is favored, of course, by an increase in pH. If manganese undergoes a divalent change, the cathode reaction to be expected is:

$$2e + MnO_2(s.) + 4H^+(aq.) = Mn^{++}(aq.) + 2H_2O,$$

and the pH - potential relationship would be as follows:

$$e = e_0 + RT/2\mathcal{F} \ln a^4(H^+) = e_0 - (2.3)2RT/\mathcal{F} (pH),$$

which has a slope twice as great (-0.12) as that corresponding to the univalent reaction.

Craig studied the pH - potential relation in the absence of zinc over a wider range of pH values than is normally encountered in dry cells and his results are illustrated in Figure 3. It is apparent that between a pH of 5 and 7 there is a region where it is particularly difficult to determine the change in potential per unit pH, which may account for the various values reported previously in the literature. In Figure 3 the slope of the lines is fixed definitely by the more strongly acid and alkaline regions. These slopes agree also with what would be expected from the theoretical considerations just presented. However, Cahoon (6) believes the reactions differ when zinc chloride is the acidifying agent, and that the slope in that case is -0.06 over the pH range 1-12. The actual amount of manganous ion

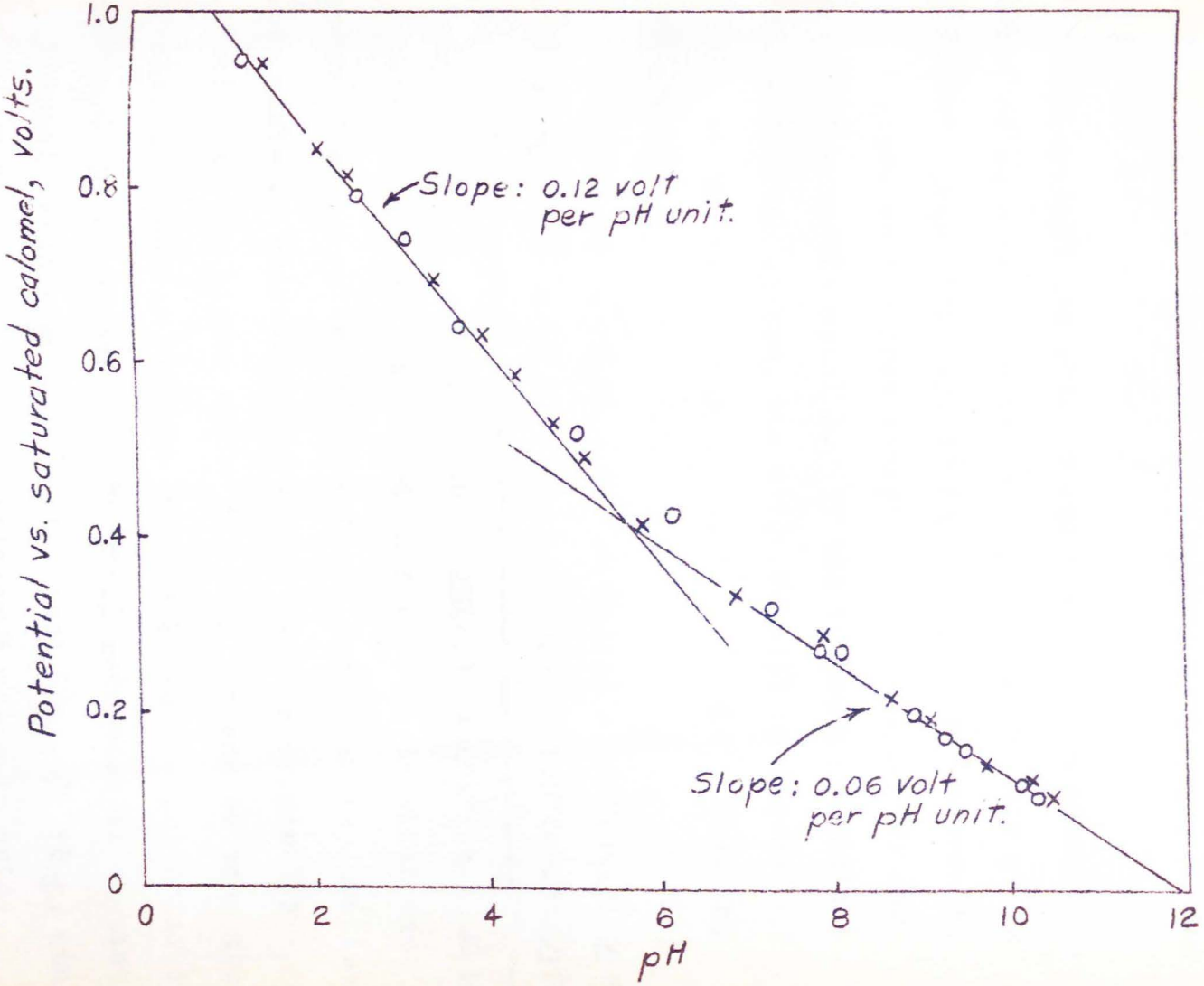


FIGURE 3 . RELATION BETWEEN pH AND POTENTIAL OF MnO_2 AS DETERMINED BY CRAIG.

which can exist in a dry cell is very small, because the pH of the electrolyte is higher than that at which any appreciable amount is possible. Under equilibrium conditions in a dry cell, then, the chief reaction to be expected at the manganese dioxide electrode is a univalent change, in any event.

Walkley (45) has pointed out that when an oxide is capable of more than one stage of reduction it may go to the lowest stage directly, or in steps. Which course it takes depends on the free energies of the oxides MO and M_2O relative to the metal M. If the following reactions characterize the system, the oxide MO will be reduced directly to the metal only if $\Delta F_1^0 < \Delta F_2^0$, that is, if $F^0_{M_2O} > F^0_{MO}$.

(1) $2MO(s.) + H_2O + 2e = M_2O(s.) + 2OH^-(aq.)$ ΔF_1°

(2) $M_2O(s.) + H_2O + 2e = 2M(s.) + 2OH^-(aq.)$ ΔF_2°

(3) $2MO(s.) + 2H_2O + 4e = 2M(s.) + 4OH^-(aq.)$ ΔF_3°

Both cases are illustrated in Figure 4, in which the standard free energies and potentials are shown as functions of the state of reduction of cathode systems originally consisting of the higher oxide MO only. It can be seen that a practical advantage accrues in Case I, as the potential is determined by the presence of MO until reduction is complete.

Thermal measurements (45) show that $F^\circ_{Hg_2O} > F^\circ_{HgO}$, and the Ruben-Mallory cell, which utilizes a mercuric oxide depolarizer has a notably constant discharge voltage. On the other hand $F^\circ_{Cu_2O} < F^\circ_{CuO}$, and the Lalande cell, using

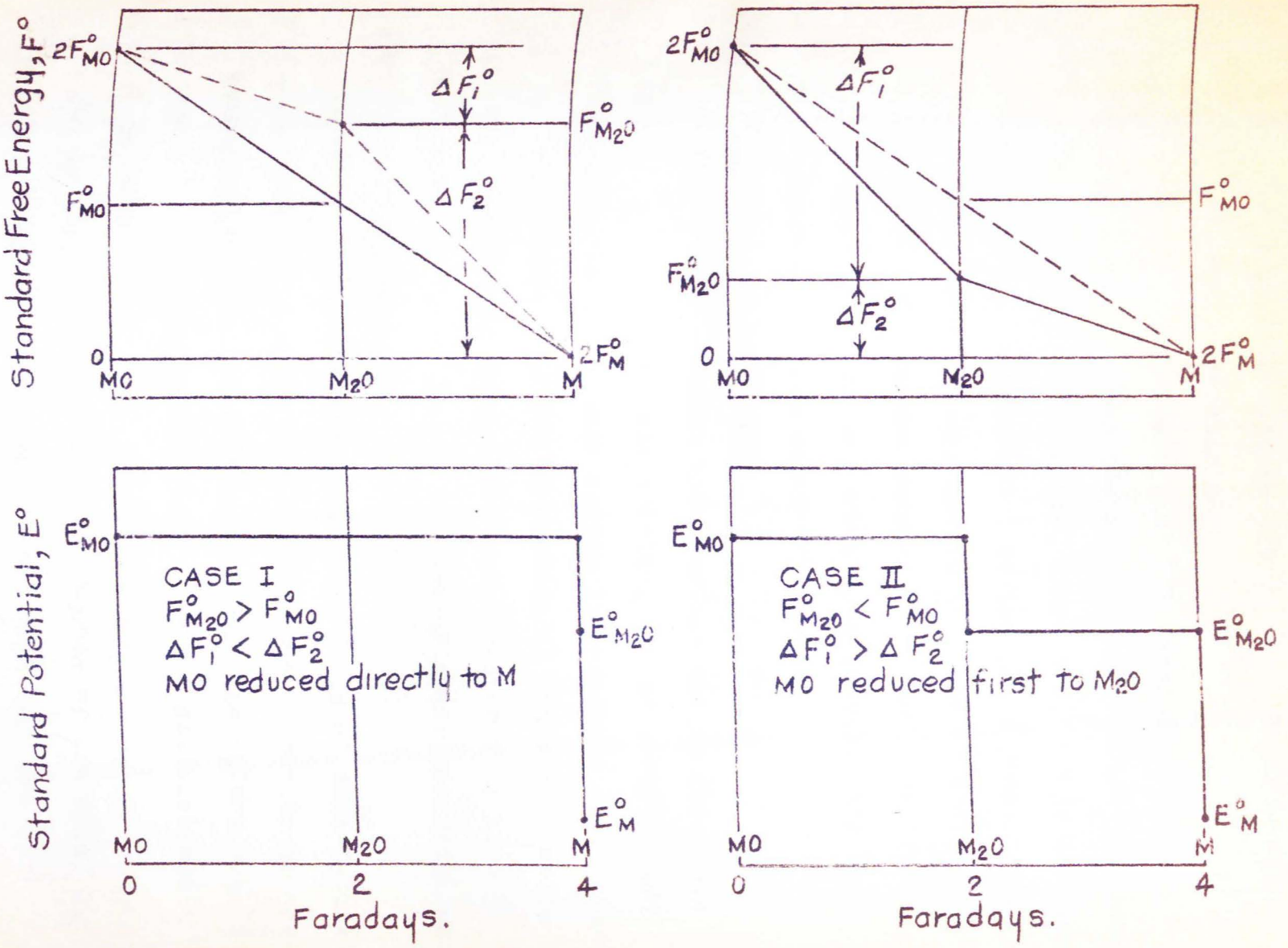


FIGURE 4. POSSIBLE MODES OF REDUCTION OF HIGHER OXIDE OF METAL HAVING TWO OXIDATION STATES.

CuO, shows a decreased voltage after the loss of one-half of the oxygen of the depolarizer.

It should be understood that the foregoing analysis applies only where all the components involved are separate solid phases whose free energies, therefore, remain constant.

The potential is determined by the phase present which has the highest free energy, and in the case of oxidation-reduction electrodes, phase composition (and hence, free energy and potential) often varies continuously with the state of reduction of the electrode system.

6. Practical Considerations.

Although primary cells have certain unique favorable properties as sources of electricity, one property common to all of them is that their energy is available at a relatively low voltage. Series connection of individual cells overcomes this disadvantage, so that a property of more fundamental importance is the product of their potential and their coulombic capacity.

Table II lists the pertinent properties of some typical electrode materials which have either been proposed, or are in use, as materials for galvanic cells. The values are from some recent compilations (34) (45) and calculations by the author.

According to Walkley (45), the number of coulombs, C, of current produced by the anodic solution of 1 cc. of a metal is given by:

$$C = z \mathcal{F} d/A$$

where d is the specific gravity of the metal, A its atomic

weight, z is the valence change, and $\mathcal{F}$ is the Faraday constant.

If E is the reversible cell potential, the product EC has the units of watt-seconds per cc. of anode material. It often happens that the cathode is more bulky than the anode, so that the packing of as much cathode material as possible into a given space is an important factor in performance. Neglecting pore space, the equation for the specific coulombic capacity of cathode materials is exactly similar to the above equation for anodes, substituting the molecular volume for the factor d/A. Capacities for typical electrode materials are included in Table II.

The full coulombic capacity of a voltaic cell is seldom realized, however, for the reason that it is discharged only to a practical "cut-off" voltage and not to the point of chemical equilibrium.

It is, of course, desirable that cells be free from local action which would result in self-discharge. All known cells suffer from this effect, however, to one degree or another. It is on this account that many types of cells are normally stored in the dry state, and activated just before use by the addition of electrolyte or water.

Balanced cells, that is cells in which the coulombic capacities of the anode and cathode are equal, are obviously desirable for economic reasons. They also offer another advantage. Cells in which there is an excess of anode material may begin liberating hydrogen at the positive

TABLE II

PROPERTIES OF SOME GALVANIC ELEMENTS

Electrode	Reaction	Reversible Potential, 25°C.	Gram - Equivalent Weight	Specific Coulombic Capacity	Mat'l. req'd. per watt-hr., grams
Anodes				(zd/A)	*
K	$K^+ + e = K$	-2.92	39.10	0.022	0.50
Na	$Na^+ + e = Na$	-2.71	22.99	0.042	0.31
Mg	$Mg^{++} + 2e = Mg$	-2.36	12.16	0.143	0.19
Al	$Al^{+++} + 3e = Al$	-1.67	8.99	0.301	0.20
Zn	$ZnO_2 + 2H_2O + 2e = Zn + 4OH^-$	-1.32	32.69	0.218	1.0
Zn	$Zn^{++} + 2e = Zn$	-0.76	32.69	0.218	1.6
Cd	$Cd^{++} + 2e = Cd$	-0.40	56.20	0.154	5.2
Pb	$Pb^{++} + 2e = Pb$	-0.13	103.60	0.109	30.5
Cathodes				(zd/M)	***
Cu_2O	$Cu_2O+H_2O+2e = 2Cu+2OH^-$	-0.36	71.54	0.084	2.8
HgO	$HgO+H_2O+2e = Hg+2OH^-$	+0.10	108.80	0.102	0.49
O_2	$O_2+H_2O+2e = OH^-+HO_2^-$	+0.15**	8.00		0.20
MnO_2	$MnO_2+H_2O+e = MnOOH+OH^-$	+0.17	86.90	0.058	0.22
AgCl	$AgCl+e = Ag+Cl^-$	+0.22	143.30	0.039	3.5
Ag_2O_2	$Ag_2O_2+2H_2O+4e = 2Ag+4OH^-$	+1.07**	61.94	0.120	0.94
MnO_2	$MnO_2+4H^++2e = Mn^{++}+2H_2O$	+1.23	43.45	0.116	0.82

* H_2 cathode. ** Refs. (34) (45). ***Zn anode.

terminal on exhaustion of the cathode material, thus generating pressure which could rupture the cell.

CHAPTER III

MODERN PRIMARY CELLS

There are a wide variety of modern types of primary cells available today. World War II acted as a stimulus to battery research, resulting in the development of fundamentally new types as well as the redesign of cell combinations known for many years. Particular emphasis was placed during the war on types giving high output per unit weight and volume. Considerable development of low-temperature types took place also.

1. The Leclanche Dry Cell.

Much has already been said about the dry cell by way of illustration of the theory and the reactions taking place in voltaic cells in general.

Although the modern product utilizes the Leclanche couple, Gassner is generally credited with producing the first successful dry cell (about 1888). According to Vinal (41), Gassner's positive electrode consisted only of carbon, however. His cell climaxed the work of a number of inventors, of which the primary object was making the electrolyte unspillable.

In regard to the modern cell, the important ingredients are zinc, manganese dioxide, graphite, acetylene black, a gel of starch and flour which acts as a medium to hold the electrolyte and also serves as a separator for the electrodes,

and the electrolyte itself which typically consists of ammonium chloride, about 26%, zinc chloride, about 9%, and water, about 65%. In its conventional form, zinc is drawn into a can which serves as the anode, or negative electrode. Manganese dioxide and about twice its weight of carbon, as a mixture of various proportion of graphite and acetylene black is milled together to extreme fineness and the mixture, dampened with the proper amount of electrolyte, is molded under pressure into a bobbin of the height and diameter required to fit the zinc can. These cells typically show an open circuit voltage of 1.50 to 1.54 volts. They are manufactured in a wide variety of sizes, of which the "D" size (the flashlight battery) is perhaps best known. This size, according to Farrington Daniels (11), has a useful energy output of about 13000 watt-seconds. Heise and Cahoon (17) state that in actual service, as much as 50% of the zinc is wasted due to corrosion. This corrosion is believed (42) to be due principally to the following reaction:

$$Zn + 2NH_4Cl = Zn(NH_3)_2Cl_2 + H_2$$

and the crystals of diammine zinc chloride which form are known as "shelf-life" crystals.

In 1949 alkaline manganese dioxide dry cells were first placed on the market. The aqueous electrolyte is 30% sodium hydroxide. The advantage claimed for these cells is their excellent shelf life. The cell reactions are somewhat less complex than in the conventional dry cell, and in particular, there is less corrosion of the zinc on standing. These cells have a potential of about 1.52 volts. The ones now being

produced were designed for low drain applications.

2. Alkaline Cells with Copper Oxide Depolarization.

The alkaline elements have become the most important of present day primary wet cells. Their greatest usefulness is found in applications in which large capacity, ability to deliver moderately large currents at constant voltage, and long life are the dominant service requirements. They are used for mine, highway, railway, and marine signalling installations, for telephone and telegraph circuits, for radio "A", and various other uses.

The cell with copper oxide depolarizer was invented by Lalande. The overall cell reaction can be written as:

$$3Zn + 3CuO + 2NaOH = Na_2Zn_2O_3 + 3Cu + Zn(OH)_2.$$

The electrolyte is 5N to 6N caustic soda which is in the region of maximum conductivity and minimum freezing point. The open circuit potential of these cells is 1.06 volt, but the operating voltage is only 0.5 to 0.7 volt. Because the electrolyte takes part in the cell reaction, the amount of sodium hydroxide present is a limiting factor in cell operation. On saturation of the electrolyte with zinc, crystals of octahedral zinc oxide form on the electrodes and container walls, usually in adherent, impervious layers and thus terminate cell operation. Recent practice is to add a small quantity of lime to the cell, which is nearly insoluble, but reacts with the dissolved zinc to regenerate the sodium hydroxide, according to the equation:

$$Ca(OH)_2 + 2ZnO \cdot NaOH = Ca(HZnO_2)_2 + 2NaOH .$$

In the form of the Wedekind element (39) a Lalande cell was so designed that the copper oxide cathode of an exhausted cell could be removed and regenerated by heating in air. This might perhaps also be considered a form of air depolarization, though, of course, neither continuous, nor effective at the voltage of the oxygen electrode.

3. Air Depolarized ("AD") Cells.

Though long sought, the substitution of an air depolarized cathode for the copper oxide of the Lalande cell, whereby operating voltage was approximately doubled, was not successfully accomplished until some forty years after the introduction of the Lalande element. The electrochemical behavior of the carbon cathodes is complex. Depending on their thermal treatment, the formation of definite carbon: oxygen surface complexes having various properties have been reported (39). Exposed to air, these active carbons acquire various amounts of both physically and chemically sorbed oxygen and, in contact with aqueous electrolyte, they develop reproducible potentials and have marked oxidizing properties. According to Schumacher and Heiss (39) and also Berl (3), oxygen, at these electrodes, in alkaline electrolytes, establishes a reversible equilibrium with peroxyl ion:

$$O_2 + H_2O + 2e = OH^- + HO^-_2$$

and the final reaction product in air depolarized cells is peroxide:

$$OH^- + HO^-_2 + 2Na^+ = Na_2O_2 + H_2O \ .$$

These equations indicate the consumption of twice as

much oxygen per Faraday as is actually observed. This apparent contradiction is explained by the known instability of peroxide in the presence of the active carbon, and in fact, at low temperatures, where the decomposition of the peroxide is less, and at high current drains, where the rate of formation of peroxide is greater than its decomposition, oxygen consumption approaches the theoretical value (43).

The cathodes now in general use are made of agglomerated, amorphous carbon. The finished electrode must be permeable to air, but substantially impervious to electrolyte. It is stated (18) that the penetration of caustic electrolyte is reduced to a few millimeters per year by a mild water proofing treatment of the electrode.

Cells of the type just described find the same use as the conventional Lalande cells, with the following advantages: freedom from the limitations of a solid chemical depolarizer, an operating voltage of about 1.52 volts, compared with the Lalande 0.7, lighter weight, and easier maintenance. Recently, miniature air depolarized cells with an immobilized electrolyte have appeared on the market for use as "A" supply for portable hearing-aid sets. In these cells, the electrolyte is 9N caustic soda containing dissolved zinc. In electrolyte of this composition, zinc oxide is the anode product, which precipitates in porous form, and the electrolyte is substantially nonvariant in composition, giving a greater uniformity of discharge voltage through its useful life.

4. Other Alkaline Cells.

Two new couples have come into commercial development as a result of intensive research and development connected with World War II.

The "RM" cell utilizes a cathode-depolarizer of mercuric oxide and finely divided graphite compressed into a hard pellet, an amalgamated zinc anode, and an electrolyte of potassium hydroxide substantially saturated with potassium zincate. The electrolyte is held in an absorbent spacer-barrier interposed between the two electrodes, the cell elements being housed under compression in an air-tight sealed steel case. These cells are characterized by their high ratio of energy to volume, long shelf life, uniform discharge potential, resistance to environmental conditions of corrosion, temperature and pressure, and are mechanically rugged and stable. The theoretical voltage of this system is in close agreement with the measured value of stabilized cells, that is 1.345 volts. The uniformity of this value of open circuit voltage makes it applicable as a secondary standard of potential where extreme precision is not required. The ratio of energy to volume, as reported by Booe (4) approaches 30 watt-min. per cubic cm. at the lowest current drains which is three times as high as the air depolarized cell, for example, and five times as high as the Leclanche dry cell. The electrode reaction is:

$$Zn + HgO = ZnO + Hg$$

The presence of zincate in substantially saturated concentration tends to inhibit corrosion of the zinc by a mass

action effect. The zinc oxide formed as a result of electrochemical action precipitates, and thereby maintains the electrolyte composition, as in the alkaline Leclanche cell.

The silver peroxide-zinc couple has been the subject of numerous investigations with regard to its possibilities as a secondary battery. A practical, reserve type, high rate primary battery, using this couple was developed during World War II for military use. This battery has a cathode consisting of a coating of silver oxide or silver chloride on a grid material such as silver-plated copper, nickel or silver wire or screen, subsequently reduced to silver and electrolytically formed to silver peroxide. The anode is of sheet zinc, zinc plated or zinc dust pasted on copper, nickel, or silver wire or screen. The electrolyte is 25 to 35 percent potassium hydroxide solution.

The outstanding characteristic of this cell, which is really a characteristic of the cathode, is its ability to operate at very high current densities. It will deliver current at the rate of 1.0 amperes per sq. cm. of cathode superficial area for periods up to several hours. Because the silver oxides are soluble in the electrolyte, this cell is normally stored in the dry state and is limited to 24 to 72 hours activated stand life before use.

The electrochemical behavior of the oxide plate is unusual. Silver forms two oxides, Ag_2O and Ag_2O_2. In the plate forming process, the charge is carried past the voltage corresponding to the higher oxide, to the point of oxygen evolution. There are significant differences in the discharge

characteristics of the two oxides. The univalent oxide gives a coulombic output which is 100 percent of the theoretical and is not affected by the rate at which the oxide is formed. The peroxide, Ag_2O_2, on the other hand, approaches this ideal efficiency only when it is formed at a very low current density. Both oxides are ultimately reduced to silver as a result of the discharge. The two states of oxidation of the silver would indicate two states of discharge at different potentials; however, at high discharge rates the higher potential, 1.90 v., is not always observed, and the operating voltage falls quickly to a value of about 1.45 volt.

5. Cells with Magnesium Anodes.

Magnesium has certain outstanding qualities which recommend its use as a galvanic anode. Its gram-equivalent weight is 12.16 compared with 32.69 for zinc, and its reversible electrode potential is -2.34 compared with -0.761 for zinc.

In spite of these real advantages, magnesium has found little use as an anodic material in voltaic cells, because it is corroded rapidly in electrolytes. Chromates have been used to inhibit its great activity but no really stable cell using magnesium has been reported yet.

A reserve-type cell utilizing a magnesium anode has been developed for use in pilot balloons for meteorological work, however. It consisted of a foil of high purity magnesium separated by a thin layer of absorbent paper from a cathode

of silver foil upon which a layer of silver chloride was electroformed. The foil electrodes were one to three mils in thickness. The foil-paper strip was wound spirally into the shape of a cylinder. This design allowed discharge at extremely high rates. It was reported that one such cell approximately the size of a flashlight cell could discharge at 100 amperes for a few seconds (33). Sea water, tap water and even distilled water served to activate the cell.

6. Chlorine Depolarized Cells.

Porous carbon of the type used in air-depolarized cells attains the theoretical potential of 1.358 volts when exposed to chlorine at atmospheric pressure.

Cells using chlorine as depolarizer make provision for the gas to be admitted only as needed on closed circuit, but great anode wastage occurs with even the least active anode materials. Chlorine has been coupled with iron, zinc, aluminum and magnesium in such cells. With zinc the cell voltage is 2.05 volts. Although the open-circuit voltage of such cells is only slightly increased by moderate increases (up to 80 psi) in gas pressure, the operating voltage is raised considerably (43).

7. Cells Using Non-Aqueous Electrolytes.

It was mentioned that considerable difficulty has been experienced in various attempts to construct stable primary cells using magnesium. Sodium and potassium, which appear even more attractive from the point of view of potential, are, of course, altogether incompatible with aqueous solutions.

The attention of various investigators (30) (40) has therefore been turned to the possibilities that lie in the use of non-aqueous electrolytes. Two examples are the use of liquid sulfur dioxide and liquid ammonia. Both of these compounds are liquid under moderate pressure at normal temperatures, and both have the property of dissolving various salts to form conducting solutions.

McDonald (30) has constructed experimental cells using both of these solvents. A cell with a magnesium anode, a carbon cathode, and an electrolyte of liquid ammonia containing magnesium nitrate and potassium persulfate had an open circuit voltage of 1.3 volts. This cell could be shorted for 100 hours and would recover its voltage quickly. A short circuit current density based on the area of the magnesium was 1 milliampere per sq. cm. This low value was attributed to insufficient wetting of all the magnesium and carbon surface. A similar cell using a sodium anode gave 3.5 volts on open circuit, with 120 ma. per sq. cm. maximum current density. Sodium was corroded rapidly in the solution, however.

The best of the sulfur dioxide cells studied by McDonald utilized sodium as the anode and an inert iron positive electrode. The electrolyte was liquid sulfur dioxide with iodine tribromide and ferric chloride dissolved in it. The open circuit voltage varied from 3.5 volts at room temperature to 2.7 volts at -60°C.

8. <u>Cells Using Organic Depolarizers.</u>

W. C. Bauer (2) described several types of primary cells in which use was made of nitrobenzene and other organic nitro compounds as the depolarizing agent. Bauer did not state what cell voltages or other operating characteristics were obtained in his cells, but discussed, at some length, the electrochemical action occurring on discharge.

Bauer apparently shared the belief, previously widely held, (see Ch. II) that the function of a depolarizer is to react with nascent, or molecular hydrogen after it is liberated at the cathode. To illustrate the sequence of reactions taking place in his cells, for example with nitrobenzene, he cited the well known (25) reduction scheme followed by that, and related compounds, in electrolysis cells:

Nitrobenzene = Nitrosobenzene =

Phenylhydroxylamine = Aniline.

According to this scheme, a given amount of oxygen, present originally in the depolarizer combined in a nitro group, is ultimately found in the form of water as a result of the reduction, thus:

$$R(NO_2)_x + 6xH = R(NH_2)_x + 2xH_2O.$$

Bauer recommended the employment of alkaline electrolytes, especially the hydroxides of the alkali metals and stated that a zinc anode could be used with copper, iron, nickel, or carbon as the cathode element. He stated that the value of the nitro compounds was largely enhanced when used mixed with, or in the presence of a metal in a finely divided

state, or in the presence of a reducible metallic oxide. It was explained that this was probably due to alternate oxidation and reduction of the metal at the expense of the nitro group. Thus the metal acted not merely as the collector of current, but also as a catalyst, by drawing the nitro compound into reaction.

Bauer pointed out that the nitro compounds are either solids or oily liquids and are generally poor conductors of electricity. In some forms of his battery they were used mixed with a conducting substance like retort carbon or graphite. It was suggested that solids be melted and mixed with the conducting substance, then broken up into granules when cold. In particular, in one form of his battery, the nitro compound floated on top of the electrolyte exposed to the air. Bauer stated that reoxidation of the nitro compound by atmospheric oxygen took place in the presence of the alkaline electrolyte. Thus only a fraction of the theoretical amount of depolarizer would be needed for a given ampere-hour capacity. The suggestion was made further, that since the nitro reduction products are readily oxidized, they may be used in secondary, or storage batteries. In this case, according to the patent specification, the electrolytic oxygen liberated on charge effects the reoxidation.

The nitro derivatives of benzene, toluene, xylene and naphthalene were especially preferred.

In 1942 W. C. Arsem (1) described the invention of a voltaic cell which used "a novel depolarizing system".

The cathode depolarizing assembly was described as being made up of the following elements:

a. A depolarizing agent which is an organic substance capable of electrolytic reduction.

b. An acid substance having a low ionization constant, or low solubility.

c. A highly conducting form of carbon.

d. A form of carbon having a high specific surface.

e. A solution of an electrolyte.

As examples of the depolarizing agent, Arsem mentioned substances in which the oxidizing properties are due to a grouping containing nitrogen attached to a halogen or oxygen, as well as other reducible organic compounds. Specifically, the following substances were claimed: N-chloramides such as p-toluene sulfonyl dichloramide, p-toluene sulfonyl sodio-chloramide, and N-chlorbenzamide; N-chlorimides, such as N-chlorphthalimide; and in general, substances containing the groups R - X - NCl_2 or $(RX)_2$ - N - Cl, in which X is an acidic radical, such as - CO - or - SO_2 - and also substances containing other halogens in place of chlorine. Other compounds claimed were Nitro-compounds such as alpha-nitronaphthalene, 2,4, dinitrophenol and dinitrotoluene, as well as nitroso and azoxy compounds. Finally, quinones, such as benzoquinone and chloranil, were mentioned. Arsem also states that the reaction of the depolarizer is with molecular hydrogen. With the chlorine containing compounds, the reaction products are given as the corresponding amide and hydrochloric acid. In the case

of nitro-compounds, the products are shown as the corresponding hydroxylamine and water. No reaction for quinones was indicated.

The purpose of the acid ingredient was stated to be to prevent the cathode liquid from becoming strongly alkaline, thereby lowering the cathode potential.

Arsem gave data to show the performance of one of his cells in which the depolarizing assembly weighed twenty-five grams and contained ingredients in the proportions: p-toluene sulfonyl dichloramide, 500 parts; boric acid, 500 parts; carbon black, calcined out of contact with air, 55 parts; artificial graphite, 1045 parts; sodium chloride solution, 5%, 800 parts. The following table was presented to show the results of an experiment which compares Arsem's cell with two dry cells of the usual composition. All the cells were of the "D" size commonly used in flashlights, and were discharged through 4 ohms.

TABLE III

DISCHARGE CHARACTERISTICS OF ARSEM'S CELL AS COMPARED WITH COMMERCIAL DRY CELLS.

Minutes	Volts		
	Arsem Cell	Cell A	Cell B
0	1.65	1.40	1.38
20	1.39	1.18	1.21
60	1.32	1.06	1.10
120	1.29	0.93	1.02
180	1.18	0.77	0.88
195	1.17	0.75	0.80
205	1.15		0.75
240	1.08		
300	0.83		
310	0.75		

Data on cells with nitro-compounds or quinones was not given. Schauli (38) described a modified dry cell, (in 1908) in which was made of "phloridzin", a naturally occurring substance which is glucoside of phloretin (c.f. Merck's Index) and has the empirical formula $C_{21}H_{24}O_{10}$.

According to Schauli, this material has the property of absorbing ammonia and ammonium salts and also ". . . . gives up and takes in oxygen without any change in temperature and considerably increases the capacity and also the recuperative power of the battery."

In 1927, I. Estermann was granted a German patent (12) for an "Electrolyte for a Galvanic Element of the Leclanche Type." Estermann called attention to the well recognized fact that many dry cell failures were the result of anode corrosion with subsequent bursting of the zinc can due to hydrogen pressure. He therefore added a material such as benzoquinone or methylene blue to the electrolyte to function as an additional depolarizer. It was claimed that these materials oxidized any hydrogen which might be liberated at the anode.

Sullivan (40) constructed a number of primary cells in which use was made of various quinones and other organic oxidizing compounds as depolarizers with methyl and ethyl alcohol electrolytes. The results showed that azoxybenzene, p-aminoazobenzene, anthraquinone, quinhydrone, and benzoquinone all gave promising discharge characteristics. The effect of temperature was the primary object of investigation

and it was shown that at -30°C., the cell using benzoquinone with the methyl alcohol electrolyte was the best with regard to height and uniformity of discharge voltage. It was found also that, at -30°C., in both electrolyte solvents, solid inorganic depolarizers, like MnO_2 and V_2O_5, although giving initially higher voltages, became polarized more quickly and soon dropped to voltages lower than benzoquinone.

CHAPTER IV

THE ELECTROCHEMICAL BEHAVIOR OF QUINONES

1. Standard Oxidation-Reduction Potentials.

An inert electrode, such as platinum, immersed in a medium which contains an oxidizing agent and a reducing agent which will react reversibly with each other will come to a definite potential with respect to some standard electrode. That potential follows from the thermodynamic expression:

$$E = - \Delta F/n\mathcal{F}.$$

When the reactants and products are all at unit activities, the potential is called the standard potential, E°, which is thus a measure of the standard free energy change, ΔF°, of the reaction.

One such system, which is very common in organic chemistry, is the reduction of a quinone to its hydroquinone at a platinum electrode.

Generally, the potential for this type of reaction is given by:

$$E = E^\circ + 0.06 \log(H^+) + 0.03 \log \text{(Quinone)}/\text{(Hydroquinone)}$$

at 30°C.

Each quinone has a characteristic oxidation-reduction potential which is a measure of its oxidizing power. The more positive the potential, the stronger is the quinone as an oxidizing agent. Also, since these potentials are measured against a hydrogen electrode, a positive potential indicates

a quinone which is a stronger oxidizing agent than H^+ and a hydroquinone which is a weaker reducing agent than H_2. A negative potential indicates the contrary. If the standard potentials of a series of quinones is compared, the change from compound to compound represents the change in the relative stability of the quinone as compared with its corresponding hydroquinone.

It has been found that the temperature coefficient of the standard potential is about the same for a large number of quinones, and is equal to about 0.7 millivolt per °C. Thus, the change in potential in a series of quinones is a measure of the change in the relative heat contents of the quinone and hydroquinone throughout the series.

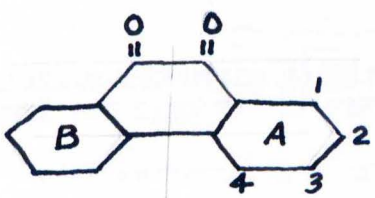
It is also found experimentally that compounds such as diphenoquinone, stilbenequinone, and amphinaphthoquinone have very high standard potentials, whereas anthraquinone and other linear condensed-ring systems exhibit relatively low potentials. Branch and Calvin (5) explain this on the basis of the relative number of valence bond resonance forms found in the quinone and hydroquinone, respectively. They found nearly a straight line relationship between the standard potential of para-quinones and the ratio of the number of these forms as is illustrated in Figure 5. Ortho-quinones have higher energy contents than para-quinones, and hence, slightly (about 0.1 v.) higher potentials.

2. Effect of Ring Substitution on the Standard Potentials.

Fieser (13) has studied the effect of substituents in

the 1 or 3 position on the potential of phenanthraquinone, and Fieser and Fieser (14) studied the effect of substitution on the potential of both 1, 2, and 1, 4 naphthoquinones. Most of the determinations were carried out in alcoholic solution, but the results would be expected to apply closely to aqueous solutions. In general, the conclusions were that acid-strengthening groups increase the potential and acid-weakening ones decrease it. For example, a 2 substituted NH_2 group lowered the standard potential of 1,4 naphthoquinone by 210 millivolts (E° unsubstituted = 0.48 volt), whereas an SO_3Na group in the same position increased the potential by 69 millivolts. The effects with 1,2 naphthoquinone substituted in the 4 position were -251 and +60 millivolts, respectively.

When substitution is not in the quinone ring, the magnitude of the effect is smaller, but the order is again the usual one. An NH_2 group in either the 1 or 3 position of phenanthraquinone lowers the potential by 98 millivolts (E° unsubstituted = 0.460 v.) whereas the SO_3H group (data for SO_3Na not given) increases it by 23 to 30 millivolts. An NO_2 group, incidentally, raised the potential by 91 millivolts in the 1 or 3 position. Comparative data for the effect of the nitro group on naphthoquinones was not given, but should be considerably larger.



PHENANTHRAQUINONE

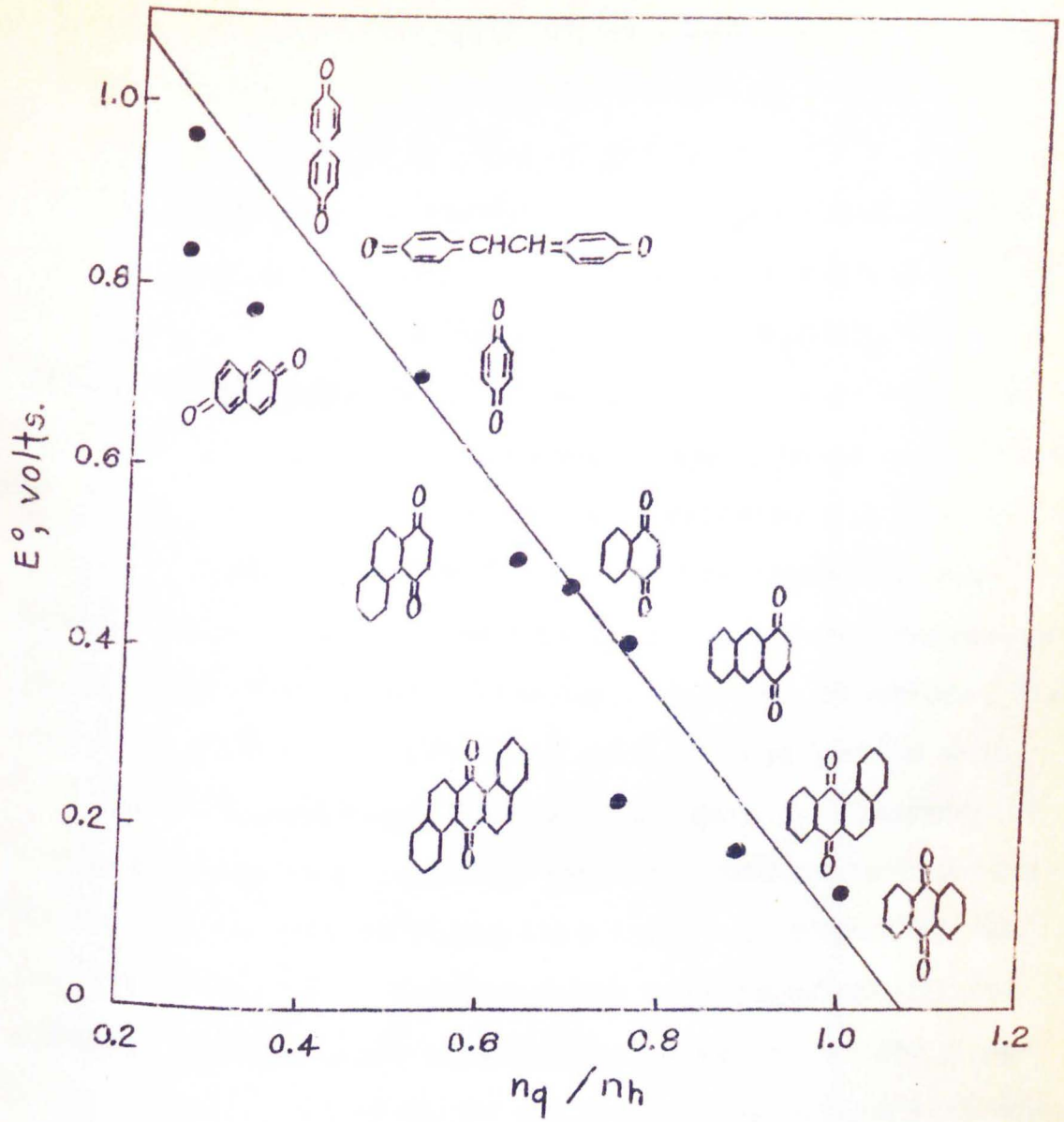


FIGURE 5 . THE OXIDATION-REDUCTION POTENTIALS OF CERTAIN CONDENSED RING SYSTEM PARA QUINONES

(After Branch and Calvin).

Also, when the substituent is not in the quinoid ring its effect depends very critically upon its position with respect to the quinoid ring. Substituents in the 2 or 4 position of phenanthraquinone, for example, are practically without effect on the standard potential.

3. The Electrode Reactions of Quinones.

It is generally stated (28) that the reaction at a benzoquinone-hydroquinone electrode is as follows:

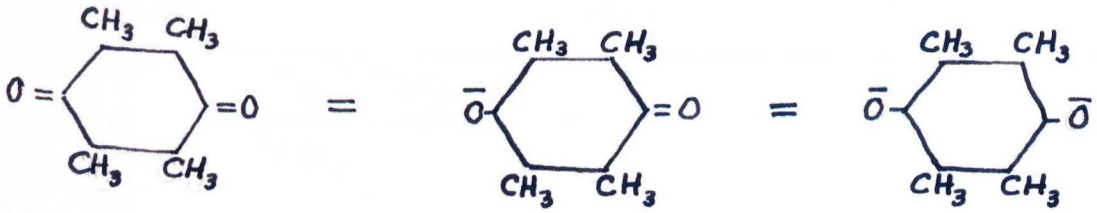
$$C_6H_4O_2(aq.) + 2H^+(aq.) + 2e = C_6H_4(OH)_2\ (aq.)$$

If, as is customarily the case when this electrode is being used for pH measurement, the concentrations of quinone and hydroquinone are fixed at the same value by the use of the molecular compound quinhydrone, and both these values remain constant, the electrode will respond to changes in pH in exactly the same manner as a hydrogen electrode, that is, by a decrease in potential of 0.06 volt per pH unit.

On the other hand, if the pH of such an electrode is maintained constant, and the ratio of quinone to hydroquinone is varied, it is found that a plot of potential vs. the log of the ratio $(Q)/(QH_2)$ has a slope of +0.03, as would be expected from writing the equation for the electrode potential in terms of the activities of the reactants and products. This fact supports the proposed electrode reaction because it shows that two electrons take part in the reaction per mole of quinone (28). All quinones, however, do not react in the same manner. With certain compounds, there is a possibility of semi-quinone formation. For example, tetramethylquinone reacts in two stages

as follows (28):

TMQ SEMIQUINONE HYDRO-TMQ ION



Each stage of the reduction involves only one electron per mole of TMQ. The slope of the potential - log Ox./Red. plot is twice as great in this case, but the pH - potential relation remains the same, -0.06 volt per pH unit.

Often, the hydroquinone of the compound in question has a tendency toward acidity and undergoes dissociation in alkaline solution according to the following reactions:

$QH_2 = QH^- + H^+$ and $QH^- = Q^= + H^+$.

In a case of this sort, the normal pH - potential slope would shift to a smaller value at high alkalinities, with a given initial ratio of oxidized to reduced substances, since the actual amount of reduced material (hydroquinone) present in solution would decrease with alkalinity, thus partially counterbalancing the potential change due to increase in pH. (27)

An electrode sometimes used in pH measurement is the "quino-quinhydrone electrode" in which a solution saturated with both quinone and quinhydrone is used. This electrode has the advantage that it is free from salt effects on the

activity coefficients of the quinone and hydroquinone. The equilibrium constant for the reaction

Quinone + Hydroquinone = Quinhydrone

is given by

$$\frac{a_Q \cdot a_{QH_2}}{a_{QQH_2}} = K$$

where K depends only on temperature and pressure. Consequently it follows that if any two of the activities in K are fixed by saturation, the ratio a_Q/a_{QH_2} is fixed and hence the electrode potential will remain constant as the electrode is reduced, until unsaturation occurs with respect to quinone. Such an oxidation-reduction electrode is similar in this respect to the metal oxide electrodes referred to in Chapter II.

4. Mechanism and Kinetics of the Electrode Reaction.

Rosenthal, Lorch, and Hammet (36) studied the kinetics of the reduction of benzoquinone to hydroquinone at platinum electrodes. They found an extreme dependence of the electrochemical reaction rate on the nature and history of the cathode surface. For example, the initial catalytic activity of various metal surfaces was approximately as follows:

Blank platinum	1
Gray platinum on gold	10
Bright platinum on gold	80
Bright gold on platinum	3
Blank gold	0.5
Mercury	0.3
Bright palladium on gold	1

Any one metal surface, however, given various pretreatments, such as heating in air or nitrogen or soaking in cleaning

solution, gained catalytic activity by a factor of ten or twenty. This initial catalytic activity decreased, moreover, with time, whether the cathode was in use or not and leveled off to a more or less steady value, in ten to thirty hours.

Even under the most precisely defined conditions the rate of reduction of quinone, as measured by the cathodic current at a given potential, decreased rapidly for from thirty seconds to two minutes and then continued a slow downward drift indefinitely. Thus it can be seen that the reduction rate of quinone is an extremely variable and indefinite quantity.

Nevertheless, the above mentioned authors were able to calculate specific rate constants for the electrochemical reaction at a blank platinum electrode and show that, under conditions such that concentration overpotential and side reactions can be neglected, the current was an exponential function of the potential and to determine the order of the reaction with respect to quinone, hydroquinone and hydrogen ion.

As in the case of inorganic depolarizers, already discussed, the reduction of quinone had previously been stated by Glasstone and Hickling (16) to occur through the primary formation of hydrogen atoms at the electrode, thus:

$$Q + 2H^{\circ} = QH_2 .$$

Rosenthal et al showed that this view was untenable in this case, at least, since the reduction of quinone was rapid even at a positive potential of 0.65 volt with respect to the

reversible hydrogen electrode, whereas the deposition of hydrogen would be completely negligible at this potential on the same cathode surface or even on one much more active.

The mechanism postulated for the reaction was as follows: the reaction of a molecule of quinone with either two, one, or no hydrogen ions simultaneously with two or one electrons. Kortum and Bockris (26) agree with this postulated mechanism. This indicates six possible parallel reaction paths with the formation of the six following intermediate or final products: $Q^{=}$, Q^{-}, QH^{-}, QH (Michaelis' semiquinone), QH_2 and QH_2^{+}. Which path predominates depends on composition and potential. It was noted that the reaction was zero order with respect to hydrogen ions in slightly alkaline solutions (pH > 8) and first order from 0-6 pH, with a trend to higher order at very low pH values.

Comparable mechanisms for the reduction of other quinones were not suggested. However, inasmuch as all quinones establish reversible oxidation-reduction potentials with their hydroquinones, such mechanisms would not seem unlikely.

5. Relative Depolarizing Abilities of Various Organic Materials.

Organic materials, other than quinones, which are capable of electrolytic oxidation and reduction do not, as a general rule, establish reversible oxidation-reduction potentials (26). Rather, the process of reduction, for example, requires a definite hydrogen overvoltage. In electrolytic reduction processes the desired hydrogen overvoltage is controlled by the choice of cathode metal and by variations in current

density, temperature, and pH.

Compounds such as ketones and oximes, which are difficult to reduce, undergo reduction only at metals at which the hydrogen overvoltage is relatively high (lead, mercury, cadmium, etc.) while compounds containing the more easily reducible nitro groups are readily reduced at platinum, copper and nickel electrodes.

Stone and Hunter (22) studied the "single potentials" of various cathode metals versus a number of "depolarizers". They found the relative order of the potentials on the e.m.f. scale the same regardless of the cathode material, although the absolute value was different. The most positive potentials were obtained with the first, the least positive with the last, in the following list.

1. Quinone - Hydroquinone.
2. Quinone.
3. Fe^{++}, Fe^{+++}.
4. I^-, I_2.
5. OH^-, O_2.
6. m - Nitroaniline.
7. Acetaldehyde.
8. Formaldehyde.
9. Azobenzene Sulfonic acid.
10. Acetone.
11. 3,3' Diaminoazoxybenzene.
12. H^+, H_2.

6. Oxidation and Reduction of Anthraquinones.

According to Fieser and Fieser (15), when a suspension of anthraquinone in aqueous alkali is treated with a reducing agent of suitable potential, such as sodium hydrosulfite or zinc dust, the material dissolves to give a rich blood red solution of the sodium salt of anthrahydroquinone. On contact with air, the red color is discharged from the solution and anthraquinone is reprecipitated. This sequence of reactions is the basis for an oxygen reagent developed by Fieser in 1924 (15). This reagent is made by dissolving sodium hydrosulfite in alkali and adding a small amount of sodium anthraquinone-beta-sulfonate. The organic reductant absorbs oxygen much more rapidly than the hydrosulfite, but is kept in the reduced state by the inorganic reagent and functions as a catalyst for the eventual utilization of the hydrosulfite. Fieser states that the organic reductant has a powerful affinity for oxygen.

In the course of research looking toward the development of a liquid absorption reagent for hydrogen, several investigators (23) (35) had found that soluble organic nitro compounds were quantitatively reduced by hydrogen in the presence of a palladium colloid catalyst. The rate of absorption became slow after only a fraction of the stoichiometric amount of hydrogen had been absorbed, however.

An improved hydrogen reagent (23) was developed by Huff and Bonney using various substitution products of anthraquinone in the presence of a stabilized palladium colloid. This solution could function either as an oxygen or as a

hydrogen reagent, depending on the state of oxidation or reduction of the anthraquinone and on the pH. Further, oxygen and hydrogen could be absorbed rapidly and simultaneously in stoichiometric amounts, or alternately, the solution could be regenerated by air after absorption of hydrogen alone. The following compounds were found to possess considerable activity: 2,7 sodium anthraquinone disulfonate and sodium, 1-nitro anthraquinone 8-sulfonate. Sodium beta-anthraquinone sulfonate also possessed fair activity.

It seems likely that all the above mentioned reactions are fundamentally electrochemical in nature, especially in view of the increased activity in the presence of a finely divided metal having a low hydrogen overvoltage, and could be caused to take place in a voltaic cell under suitable conditions.

CHAPTER V

SUMMARY OF FOREGOING AND STATEMENT OF PROBLEM

1. Use of Organic Compounds as Depolarizers in Primary Cells.

Although, as has been described, a number of investigators have constructed primary cells in which use was made of various organic compounds (1) (2) (12) (38) (40), and certain of them, as quinones, establish reversible oxidation-reduction potentials (5); and although various organic compounds, particularly nitro compounds and anthraquinones, are known to possess the ability to absorb hydrogen and oxygen, in the presence of metal catalysts, by reactions which can be stated, at least formally, to be electrochemical in nature (23) (35); it has not yet been shown what relation the discharge characteristics of primary cells using these materials bears to their theoretical potential and coulombic capacity, nor under what conditions their most effective use could be realized.

2. Research Objectives.

It was the purpose of this research, therefore, to study the complete discharge characteristics of a number of organic compounds, principally quinones, to determine the discharge voltage and actual coulombic capacity as affected by variations in discharge rate, electrolyte base, pH, access of oxygen and also as affected by the nature of the compound itself and by any substituent groups.

PART II

EXPERIMENTAL

CHAPTER VI

INTRODUCTION

1. Program.

In contrast to the field of inorganic depolarizers, there are a wide variety of organic substances which could conceivably act as depolarizing materials. Considering only those classed as quinones, there are a great many quinone derivatives of benzene, naphthalene, anthracene, phenanthrene and other polynuclear hydrocarbons as well as all the possible substitution products and their isomers, not to mention heterocyclic analogs of these. Each can be regarded as probably different with regard to solubility and stability in various solvents, standard oxidation-reduction potential, equivalent weight, and, undoubtedly, reduction rate at various inert electrodes. It was clearly impossible to attempt a quantitative study of the behavior of even most types of quinones, let alone organic depolarizers in general, within the scope of this type of investigation.

It was necessary, therefore, to delimit the area of more detailed study by a preliminary qualitative survey of some representative compounds of various types. It was decided also that these preliminary tests should be carried out in several electrolytes. The more promising materials were then to be studied as to coulombic capacity

and voltage under various conditions and, if possible, as to the reactions actually occurring.

Factors such as availability and cost in part determined what particular materials were selected for investigation. Quinones were considered more likely to have desirable properties as depolarizers than other reducible organic materials, such as nitro compounds, principally because quinones establish reversible potentials while nitro compounds, for example, as a general rule do not. As it happened, two quinones selected for study were nitro-substituted. The two compounds in question, therefore, served to illustrate the possibilities of nitro-compounds as well as those of quinones.

2. Apparatus.

The discharge of various experimental cells was followed with the apparatus shown in Figure 6. The voltmeter was constructed from a Leeds and Northrup moving coil, reflecting-type galvanometer in which a lens having negative curvature was interposed between the hair line and scale to increase the focal length of the optical system, thus increasing the sensitivity of the meter. A five-hundred thousand ohm resistance was included in series with the galvanometer to give, in effect, a very high resistance voltage measuring system. Readings taken with this instrument are referred to as "terminal voltage" or "open circuit voltage".

When not in use, the galvanometer was protected with a heavy shunting switch. The focal length of the lens and the resistance were selected so that a one millimeter deflection of the hair line image on the scale corresponded to

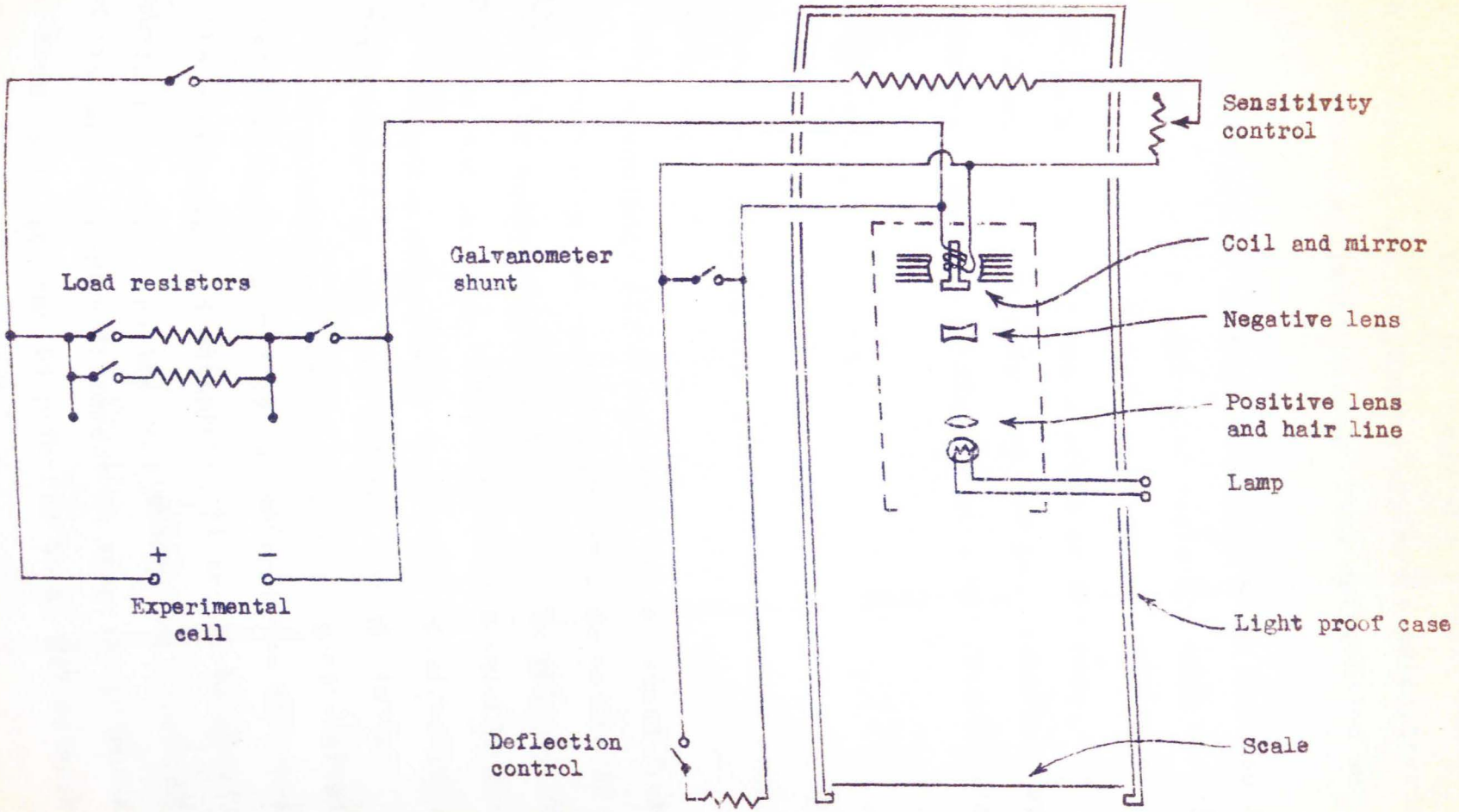


FIGURE 6. SCHEMATIC DISCHARGE AND MEASURING CIRCUIT.

0.02 volt and so that the range 0 - 3 volts could be measured. The instrument was calibrated against a potentiometer and was found to have a linear scale. This calibration was rechecked at intervals.

A cell placed in the rack could be discharged through one or a combination of calibrated resistors with or without simultaneous measurement of cell voltage. A milliameter could be switched in or out of the circuit as desired. Discharge times were measured with a stopwatch for the first few hours of discharge; then time readings were taken from an electric wall clock.

3. Chemicals.

All of the organic compounds (except one) used in this research were Eastman c.p. grade and were used without further purification.

Anthraquinone disulfonic acid was obtained from a neutralized mixture of mono- and di-sulfonates as occurs in the sulfonation of anthraquinone with oleum. In this mixture the 2:7 disulfonic acid is considerably more soluble than the mono sulfonates and more so than other disulfonated isomers. A small amount of the more soluble components was dissolved from this mixture and recrystallized without analysis. It is believed that the 2:7 isomer constitutes the major portion of the recrystallized material. It should be noted that all disulfonates will have the same theoretical coulombic capacity and are not very much different in standard potential. In any event this quinone is referred to as 2:7 anthraquinone disulfonic acid in the data.

Several forms of carbon were used in the various experiments: Acheson graphite in the form of extruded rods from which inert electrodes were machined (this is a relatively non-porous form of graphite); Statex carbon black, a battery-grade carbon black having pronounced absorption properties and a high surface area per unit weight; finally, graphite powder, approximately 200 mesh, used to increase the conductivity of the cathode mix. The zinc was in the form of commercially pure rolled strip, 0.010 inches thick. All other chemicals used were of reagent grade.

Table IV compares the properties of the various experimental cathode materials. The coulombic capacity is calculated on the assumption that the only reaction occurring is the complete reduction of the quinone to the corresponding hydroquinone.

4. Cell Design and Assembly.

The cell design arrived at after various trials was that shown in Figure 7. A graphite plug sealed into a glass cylinder with parrafin wax constituted the empty cell. This construction was desirable because the cell was small enough and light enough to allow the depolarizing mix to be conveniently weighed into it on an analytical balance, when desired; the cell contents could be observed through the glass tube; and the graphite plug, acting as an inert conductor, allowed electrical contact with the depolarizing mix without contamination. Also the cell was of such a size and design that small amounts of materials could be utilized effectively in runs of reasonable length.

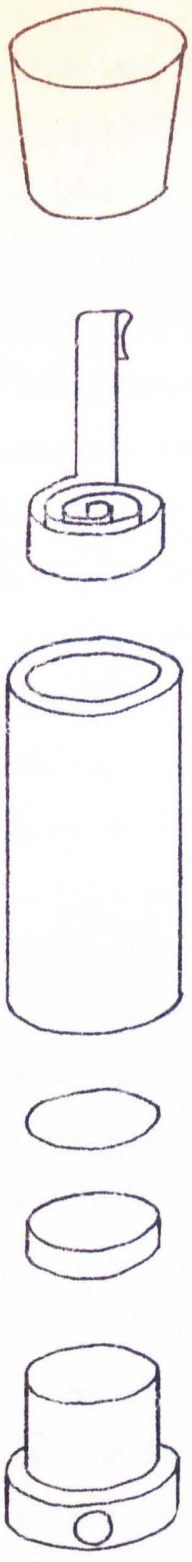
TABLE IV

PROPERTIES OF EXPERIMENTAL GALVANIC CATHODE MATERIALS

Depolarizer	Standard Oxidation/Reduction Potential, E°, 25°C	Coulombic Capacity amp-min/gm.
Benzoquinone	0.699	29.8
2,5 Diphenyl-p-quinone	* 0.635	12.25
Quinhydrone	0.613	14.75
1,2 Naphthoquinone	0.555	20.3
1,4 Naphthoquinone	0.470	20.3
Anthraquinone	0.154	15.45
Na-Anthraquinone-β-Sulfonic Acid	0.187	10.35
K-Anthraquinone-α-Sulfonic Acid	0.195	9.88
2,7 Anthraquinone-Disulfonic Acid	0.229	8.73
2,7 Anthraquinone-Disodium Sulfonate	0.229	7.05
2,6 Anthraquinone-Disulfonic Acid	0.228	8.73
5-Nitro-Anthraquinone-1-Sulfonic Acid	** 0.270	9.65
1-Nitro-Anthraquinone-8-Sulfonic Acid	** 0.270	9.65

* Estimated from effects of o-substitution in 1,4 Naphthoquinone. (Fieser and Fieser).

** Estimated from effects of 1 or 3 substitution in Phenanthraquinone. (Fieser and Fieser).



Scale: 1/1

FIGURE 7 . EXPLODED VIEW OF CELL AND COMPONENTS.

The cathode mix, after being weighed out into the empty cell, and wet with a small quantity of electrolyte, was pressed into a coherent cake at any desired pressure with a cylindrical graphite plunger. An asbestos diaphragm (circle cut from asbestos paper) which fit snugly into the glass cylinder was pushed into the cell on top of the mix, before pressing. This procedure served to carry down any mix particles, which might have tended to cling to the sides of the tube, to the bottom of the cell, and subsequently prevented any graphite or carbon particles from becoming disengaged from the mix, thereby allowing the possibility of an internal short circuit in the cell.

The glass cylinder was of a length such that as much as eight milliliters of electrolyte could be introduced into the cell. In many runs, only three and one-half milliliters sufficed to activate the cell under study.

The zinc anodes were carefully cut into an L - shape, with legs of two and five inch lengths respectively, both legs one-quarter of an inch wide. The five inch leg was coiled into a spiral having an outer circumference nearly equal to that of the inside of the glass tube. This anode coil was suspended from the top of the glass tube. The anodes were cut from fresh stock for every cell, cleaned with abrasive and coiled; cleaned again in dilute HCl and rinsed, just before use.

The cell was easily disassembled after each run and the parts cleaned before reassembly. Cells were sealed with

corks to prevent evaporation and electrolyte creepage and were activated by filling with the desired quantity of electrolyte at the start of a test.

CHAPTER VII

INITIAL CELLS: VARIOUS DEPOLARIZERS AND ELECTROLYTES

1. Control Cells.

In order to judge the performance of an experimental cell, it is desirable that it be compared with some cell of known behavior. The Leclanche system, used in the familiar dry cell, serves as the "control" comparison in this research. A fair comparison would be between control and experimental cells of the same size (or weight) and design. Accordingly, Leclanche cells were constructed in exactly the same manner as the experimental cells and subjected to several types of discharge.

As with later experimental cells, each ingredient of the cathode mix was weighed out separately to 0.1 milligram, and the weighed materials then ground together in a mortar. An amount of mix containing the desired quantity of depolarizer was afterwards weighed directly into the cell. After the cell was assembled and the electrolyte was introduced, the open circuit voltage was measured and the cell was put on discharge immediately.

The calculations for these control cells also illustrates the method of calculation used for the experimental cells discussed in chapters VIII and IX. The data for all cells is given in the appendix.

The quantities V (terminal voltage) and θ (time, minutes)

were measured. W, the net electrical work, was calculated as follows.

W is equal to the product of voltage, current, and time:

$$W = 60\ V\ I\ \theta \qquad \text{(VII - 1)}$$

W = watt - seconds

V = volts

I = amperes

θ = minutes

However, $I = \frac{V}{R}$,

where R = external resistance (ohms).

Therefore,

$$W = (60/R)\ V^2\theta \qquad \text{(VII - 2)}$$

In a discharge through a fixed resistance, voltage, V varies (decreases) with time, θ.

$$\text{i.e., } W = 60/R \int_0^{\theta} V^2\, d\theta \qquad \text{(VII - 3)}$$

The quantity W was calculated for every value of θ by a process of numerical integration from the start of discharge, using equation (VII - 3) and the appropriate value of R.

The theoretical fractional reduction, X, was calculated also, using an equivalent weight equal to one-half the molecular weight for every quinone and equal to the molecular weight for manganese dioxide.

Algebraically,

$$X = \frac{\text{Number of coulombs passed}}{\text{Coulombic capacity of cathode.}} \qquad \text{(VII - 4)}$$

Therefore;

$$X = \frac{60/R \int_0^{\theta} V d\theta}{(\text{M/Equiv. wt. })\ (96500).} \qquad \text{(VII - 5)}$$

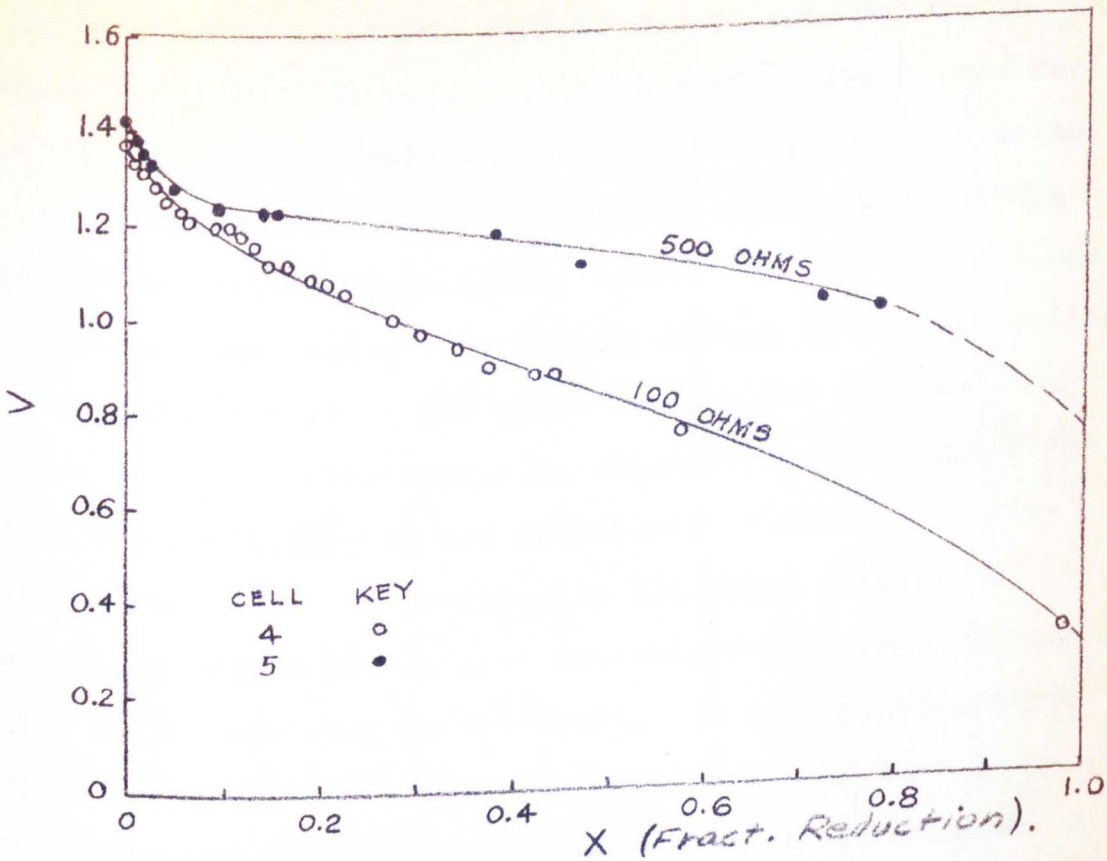
where M = weight of active material in cathode.

In these control cells, as in all subsequent experimental cells, the amount of zinc present is large enough that the coulombic capacity of the anode is greatly in excess of that of the cathode. Further, the composition and quantity of the Leclanche electrolyte are such that very little change takes place in the zinc ion concentration during discharge. Also, the surface area of the anode is deliberately designed to be so large that little polarization of the anode takes place. Thus, changes in cell voltage as discharge progresses should be for the most part due to changes in composition of the cathode and in cathode polarization.

Cells 4 and 5 are compared in Figure 8 on the comparable basis of fractional reduction of the MnO_2 to Mn_2O_3. The corresponding data is given in the tables in the appendix. Comparable data on the performance of commercial "dry" cells are not available in the literature but it is estimated that the performance of this cell when discharged through 100 ohms corresponds roughly to the performance of a dry cell on a moderately heavy drain. The 500 ohm load, then, corresponds to a relatively light drain for this type of cell. The results for these control cells are more directly comparable to the cells discussed in later chapters in which capacities were studied, than to the initial studies discussed in this chapter.

2. Electrolytes.

Various properties of the electrolyte would be expected to have effect on not only the reversible cell potential but also



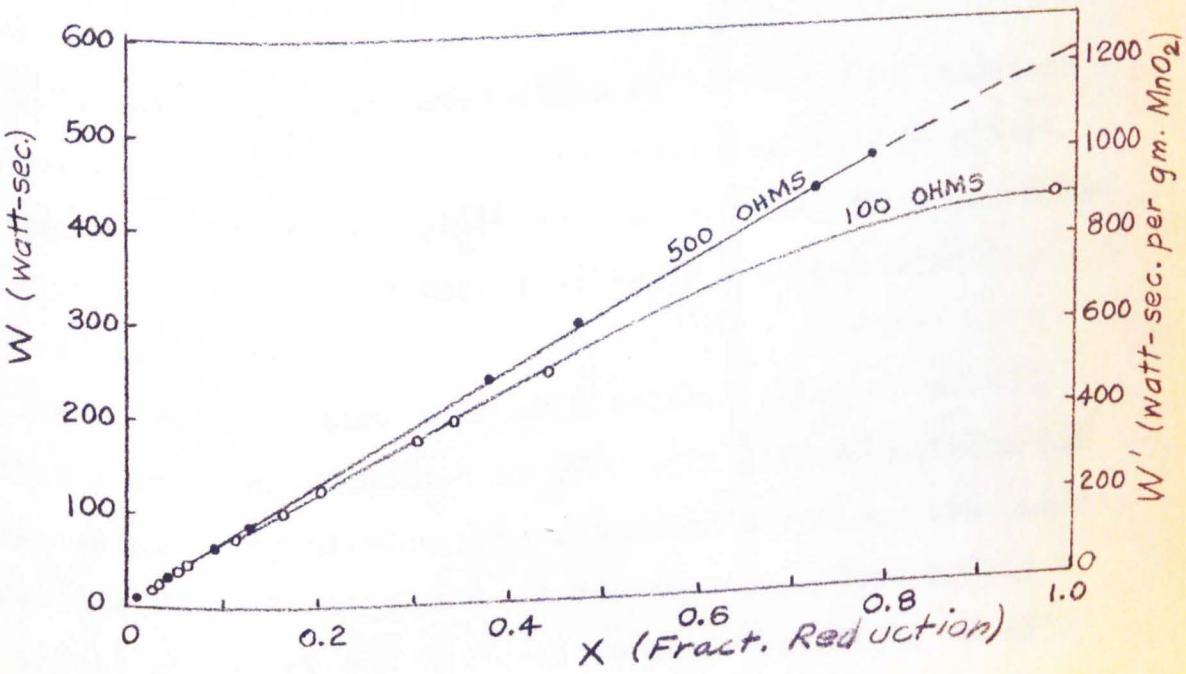


FIGURE 8. DISCHARGE CHARACTERISTICS OF CONTROL CELLS.

on the cathode polarization on drain. The reversible potential of quinones has been shown (13) to depend somewhat on the intrinsic nature of the solvent, as well as on the pH and concentration ratio of the oxidized and reduced forms. The presence of dissolved substances other than the quinone will affect (usually unequally) the activity coefficients of the quinone and hydroquinone forms. The actual working cathode potential will depend not only on the above factors but also on such properties of the electrolyte as viscosity and conductivity, and on the solubility of the individual reactants and products of reaction. In addition to all these effects, the electrolyte resistance in part determines the terminal voltage of the cell, depending on the drain. It is impractical or impossible to eliminate this IR drop completely in a cell modelled on the usual battery design as it is eliminated (or nearly so) in simple polarization studies by the use of a capillary tip electrode.

In the preliminary evaluation of various cell combinations, the three electrolytes used were chosen with a view to ascertaining the effect of alcohol content, if any, on the relative and absolute terminal voltages obtained with the various depolarizers.

Electrolyte A consisted of a solvent composed of 40% methanol in water saturated at 25°C with lithium nitrate and methylamine hydrochloride, the saturated solution subsequently diluted with an equal volume of the solvent. Electrolyte B consisted simply of 60% methanol in water saturated at 25°C

with lithium nitrate. The third electrolyte corresponded to a formulation stated (44) to be typical of Leclanche cells. It was composed only of ammonium chloride, zinc chloride, and water. This electrolyte is identified in the data simply as L.

In general quinones are somewhat more soluble in alcohols than in water. The Leclanche electrolyte, however, has considerably higher conductivity at room temperature than either A or B or probably any other alcohol-containing electrolyte. The composition, resistivity and pH of these electrolytes are compared in Table V, along with those of the electrolytes used in some later cells. From the results obtained in the preliminary testing of various cell combinations it was concluded that the Leclanche electrolyte, using an aqueous solvent, was the most desirable one for experimental purposes, and most subsequent cells used this component.

3. Various Cell Combinations.

The discharge curves shown in Figure 9 indicate the extremes of terminal voltage encountered with zinc couples. However, these results do not indicate quantitatively the differences in the various cell combinations, because not all of these preliminary cells were fabricated with foreknowledge of what factors were most likely to lead to irreproducible results, nor was the discharge allowed to proceed to the same relative degree as with later cells. The cathode mix was accurately proportioned as between carbon and active material, but the weight of total cathode mix was measured only to 0.1 gram (about $\pm$ 7%). Furthermore, the discharge

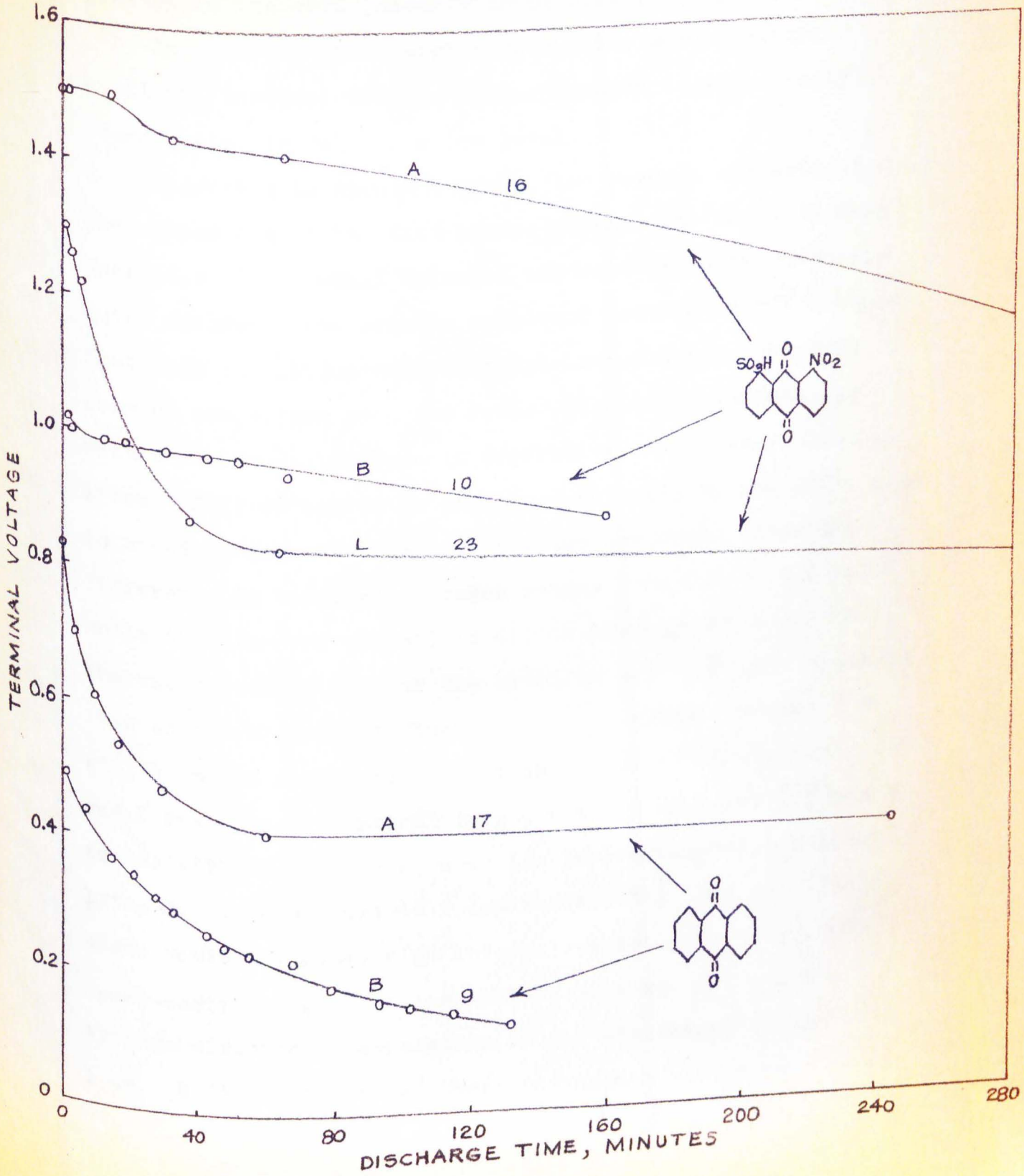
TABLE V

PROPERTIES OF EXPERIMENTAL ELECTROLYTES

Electrolyte	Composition		Resistivity ohm-cm. 25°C.	pH, 25°C.
A	CH_3OH	18.4%	8.11	4.50
	H_2O	27.5%		
	$LiNO_3$	16.7%		
	CH_3NH_3Cl	37.4%		
B	CH_3OH	34.8%	27.0	4.50
	H_2O	23.2%		
	$LiNO_3$	42.0%		
L	H_2O	65.0%	2.28	4.44
	NH_4Cl	26.0%		
	$ZnCl_2$	9.0%		
Sat'd. NH_4Cl	H_2O	70.8%	2.10	5.45
	NH_4Cl	29.2%		
Sat'd. NaCl	H_2O	73.2%	4.68	6.18
	NaCl	26.8%		
20% NaOH	H_2O	80.0%	2.62	-
	NaOH	20.0%		

FIGURE 9 .

DISCHARGE OF CELLS IN VARIOUS ELECTROLYTES.



was carried only to from 5 to 20% of the theoretical maximum based on the equivalent weight of the quinone and the amount present in the cell (usually about 0.46 grams per cell).

In general, these exploratory cells were discharged until the terminal voltage either dropped to some fairly steady value or fell to a low level.

Referring to Figure 9 again, two results are evident from the comparison of the five curves shown. The first is that decidedly low terminal voltages are obtained with unsubstituted anthraquinone even in a solvent containing 60% methanol. That this is not due to electrolyte conductivity or pH is seen by comparison with the rather high voltages obtained with the nitro-sulfonic acid derivative in the same electrolytes. Neither can it be explained entirely by the difference in standard potential between the two compounds since the difference in terminal voltages ranges from 0.8 to 1.2 volts while the standard potentials differ by only about 0.1 volt. The second result is that the specific nature of the electrolyte exerts a strong influence on the terminal voltage. It will be noted from Table V that the three electrolytes A, B and L are almost identical in pH, but are somewhat different in resistivity. However, even the least conductive electrolyte, B, had a sufficiently low resistivity that this factor alone would not cause high internal resistance. Thus, the cross-sectional area of the cell is 3.46 sq. cm. and the average distance of separation of the electrodes is about 1 cm. A liquid column of these dimensions having the

resistivity of electrolyte B would therefore add only 7.8 ohms to the internal cell resistance. This resistance, alone, is small compared with the external load of 500 ohms.

In general, it appears that it can only be said of the effect of a given electrolyte on the discharge behavior of a depolarizer that it is the result of the interrelated and mostly unknown effects on:

(a) Depolarizer standard (or reversible) potential.

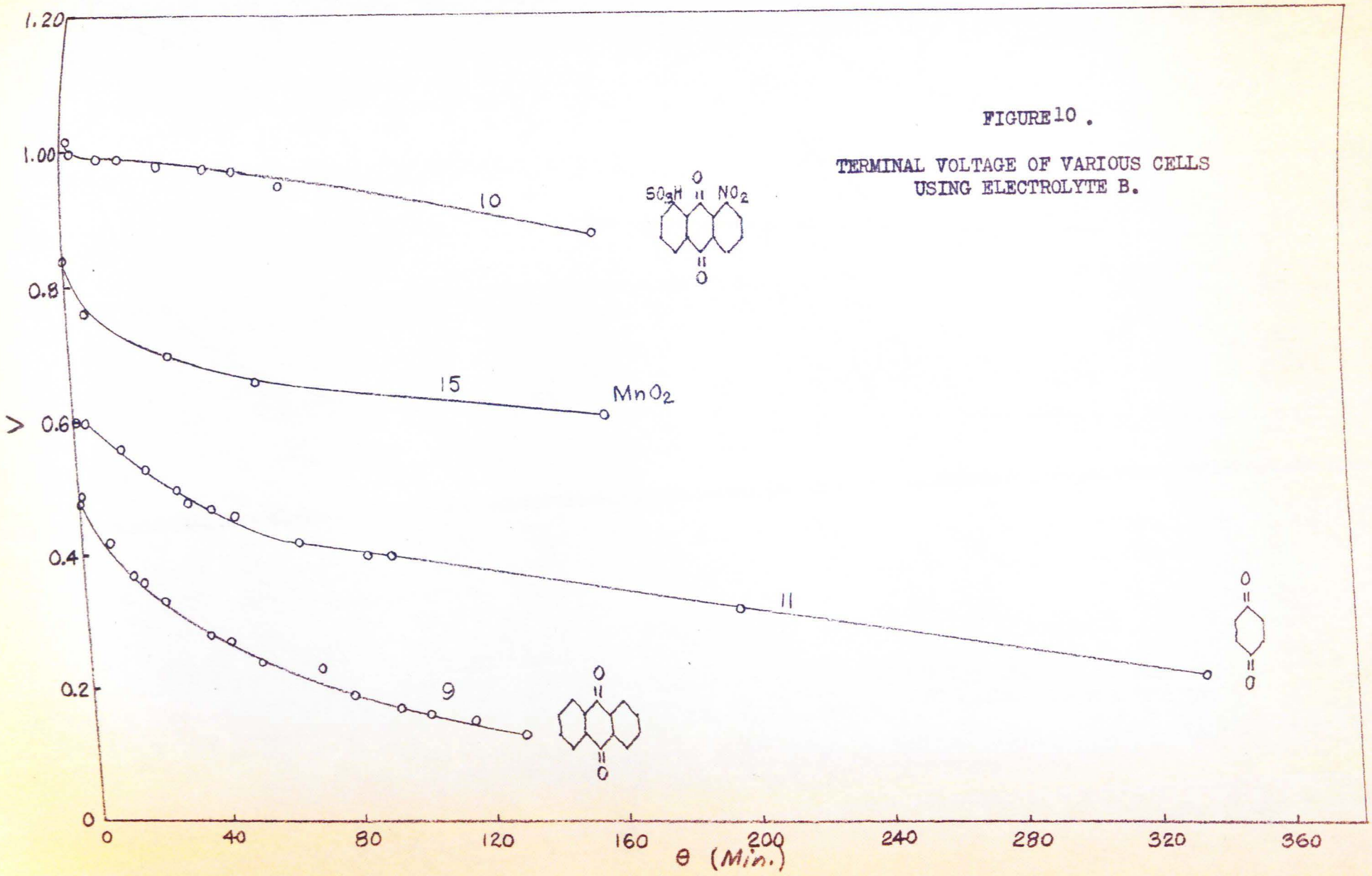
(b) Cathode polarization (resulting from solubility, diffusivity, and reaction rate in the solvent.)

(c) Internal cell resistance due to electrolyte resistivity.

In Figure 10 benzoquinone is compared with the two anthraquinones and manganese dioxide in electrolyte B. The same three organic depolarizers are compared in Figure 11 in the Leclanche electrolyte. Curiously, the relative positions of benzoquinone and the substituted anthraquinone are reversed in the two solvents. Again, it is not possible to explain this on the basis of pH of the two solvents since that difference is relatively slight and in any event would alter the reversible potential of both compounds by the same amount in the same direction. The effect of an increase in resistivity on the terminal voltage of the cells is also slight, and furthermore should simply decrease the terminal voltage obtained with both compounds, without affecting their relative order. Although the reversible potentials do depend somewhat on the nature of the solvent, the possible difference is too small to account for the observed effect. Finally, whatever

FIGURE 10.

TERMINAL VOLTAGE OF VARIOUS CELLS USING ELECTROLYTE B.



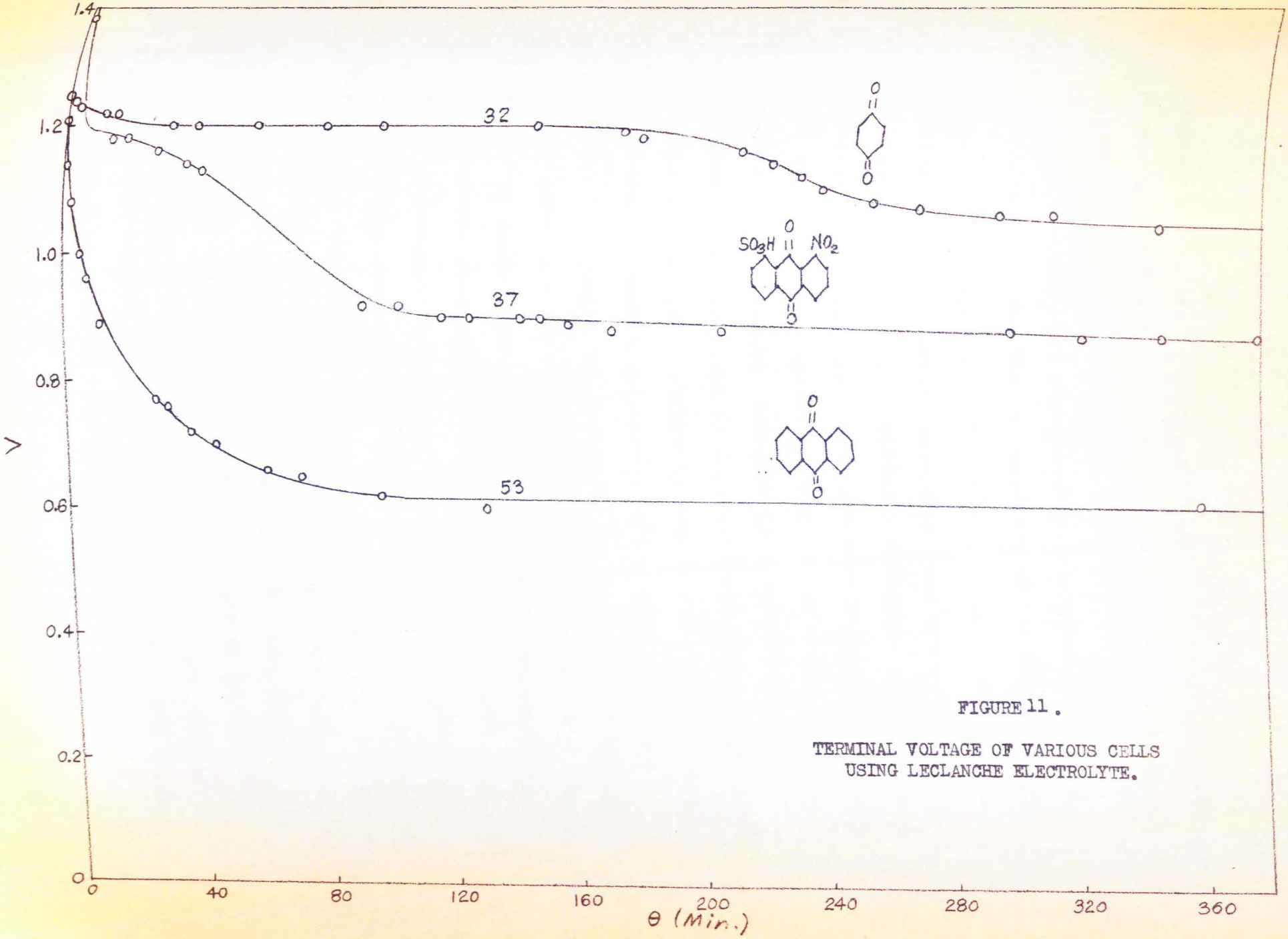


FIGURE 11.

TERMINAL VOLTAGE OF VARIOUS CELLS USING LECLANCHE ELECTROLYTE.

changes take place in anode potential and polarization should affect equally cells using both depolarizers regardless of the electrolyte.

The results must therefore be attributed to differential effects on the rate of reaction of the two compounds (i.e., on the polarization). Figure 12 shows the results obtained with the various anthraquinones using Electrolyte A. Increasing substitution apparently decreases polarization of the cathode, giving more favorable discharge characteristics. When the nitro-compound is present as the potassium salt, there is a considerable decrease in terminal voltage. Apparently the influence of depolarizer acidity is strong in this electrolyte. Figure 13 compares the two isomeric unsubstituted naphthoquinones with the alpha substituted anthraquinone using the Leclanche electrolyte. It is interesting to note that the steady voltage reached by cells 20 and 22 differ by approximately 0.28 volt while the standard potentials of the respective depolarizer differ by 0.275 volt. Also the terminal voltage of the ortho-naphthoquinone cell is initially about 0.08 volt higher than the cell containing the para compound. The standard potentials of the two stand in the same relative order and differ by 0.085 volt.

Figure 14 compares two disubstituted anthraquinones in cells using the Leclanche electrolyte. As in all other combinations, the nitro-derivative is superior. This superiority in terminal voltage is not due solely to the influence of depolarizer acidity on cathode potential, as seemed to be

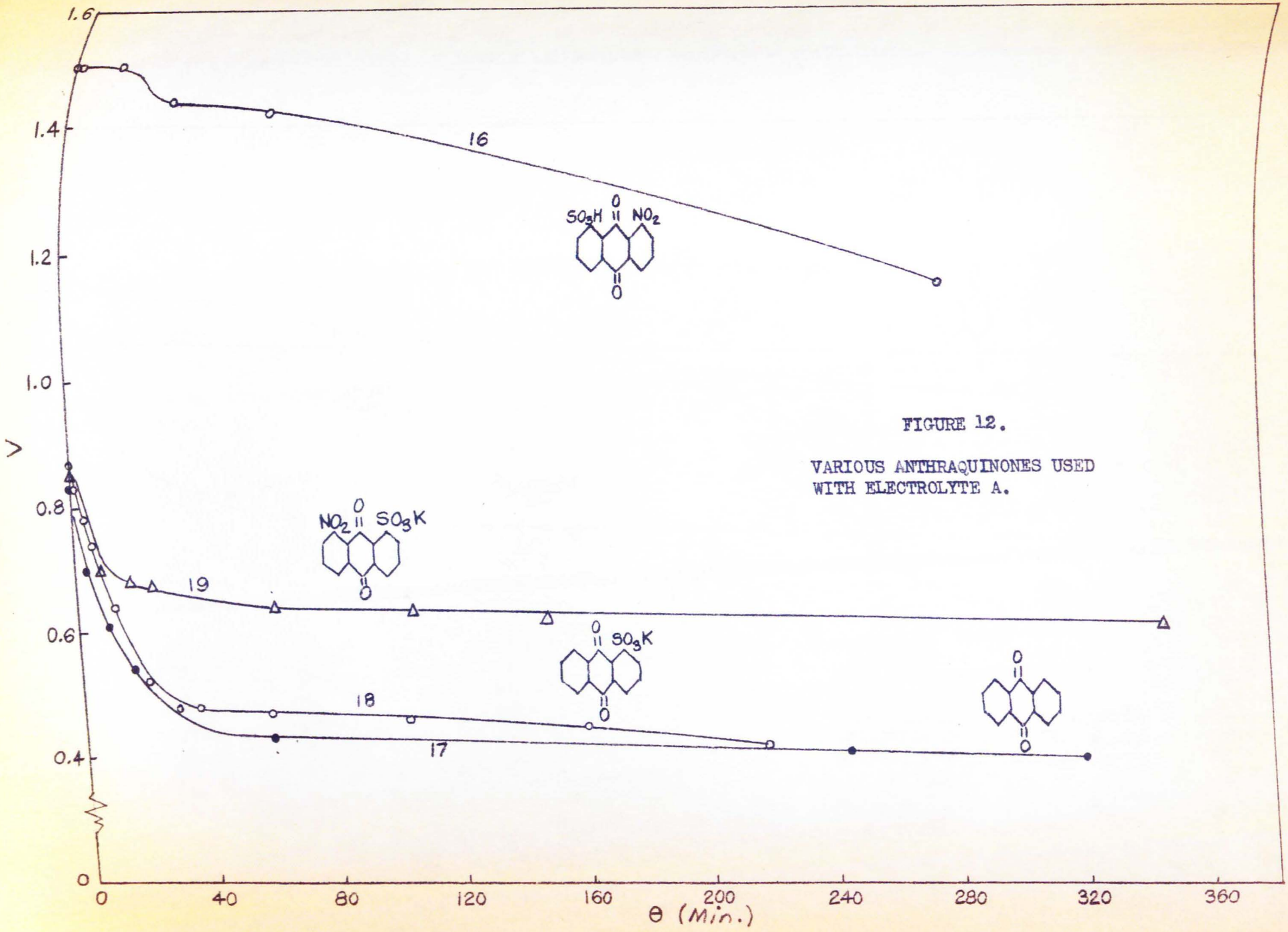


FIGURE 12.

VARIOUS ANTHRAQUINONES USED WITH ELECTROLYTE A.

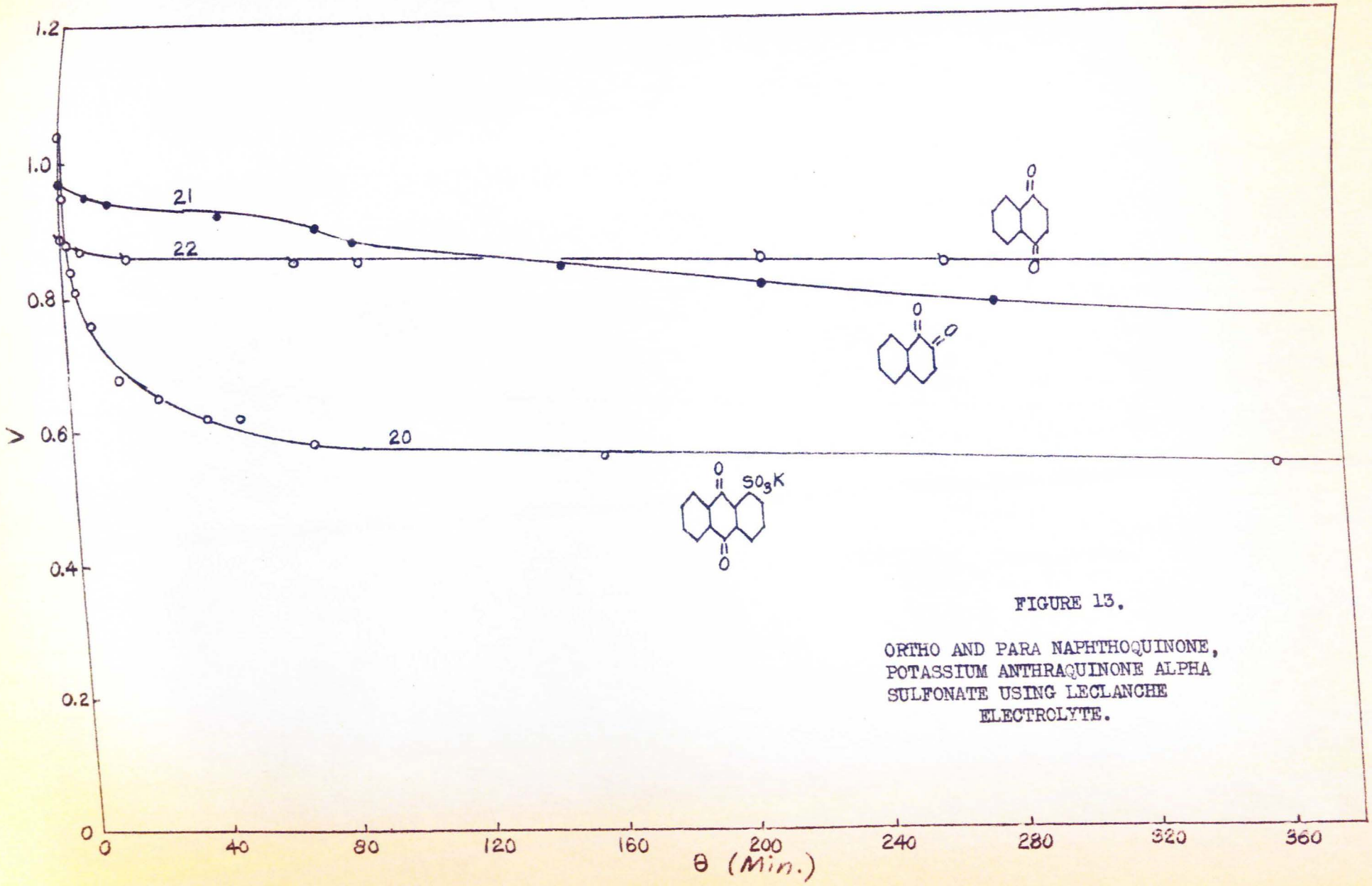


FIGURE 13.

ORTHO AND PARA NAPHTHOQUINONE, POTASSIUM ANTHRAQUINONE ALPHA SULFONATE USING LECLANCHE ELECTROLYTE.

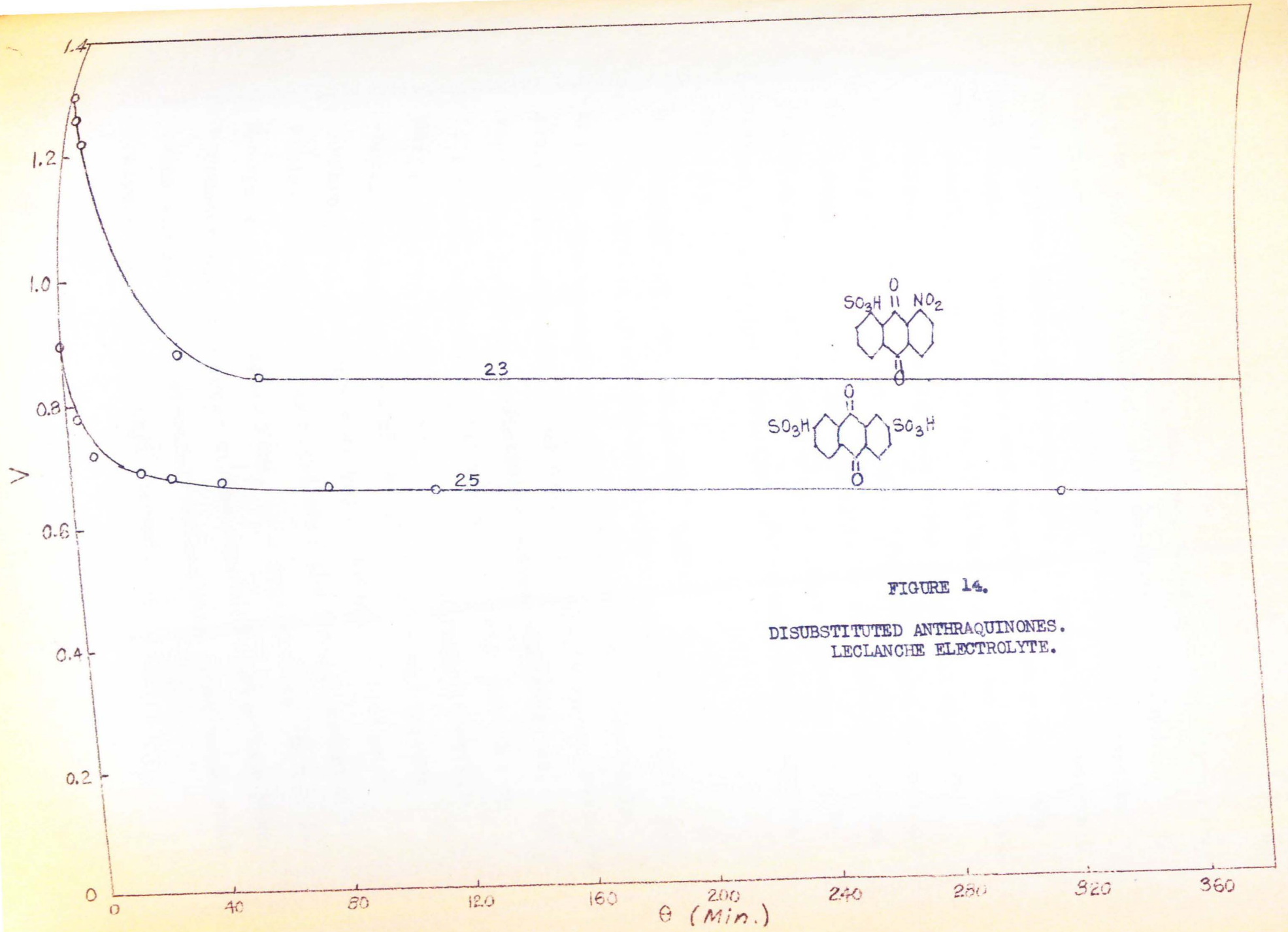


FIGURE 14.

DISUBSTITUTED ANTHRAQUINONES.
LECLANCHE ELECTROLYTE.

the case in electrolyte A, however, since the comparison here is with the free disulfonic acid derivative. Figure 15 illustrates what might be anticipated in regard to results obtained with diphenyl-benzoquinone. Although the reversible potentials of benzoquinone and its substitution product are not greatly different (Table V) it would be expected that the derivative compound would have lower solubility and diffusivity than the parent quinone. The difference between the two curves is much too pronounced to be accounted for by the relative equivalent weights since neither compound was discharged to more than a fraction of its theoretical coulombic capacity.

4. Conclusions From The Initial Runs.

The effect of electrolyte variation on the relative and absolute discharge characteristics of various quinones is pronounced and cannot be accounted for simply on the basis of variations in pH and resistivity between electrolytes. It is probable that the variations are in large part due to differences in relative solubilities, diffusivities and specific reduction rate of the quinones in the various electrolytes, although this point was not investigated experimentally. It was noted that the initial steady discharge voltages reached were, as a general rule, in better agreement with the order of the reversible potentials when using the Leclanche electrolyte than when using those electrolytes containing methyl alcohol.

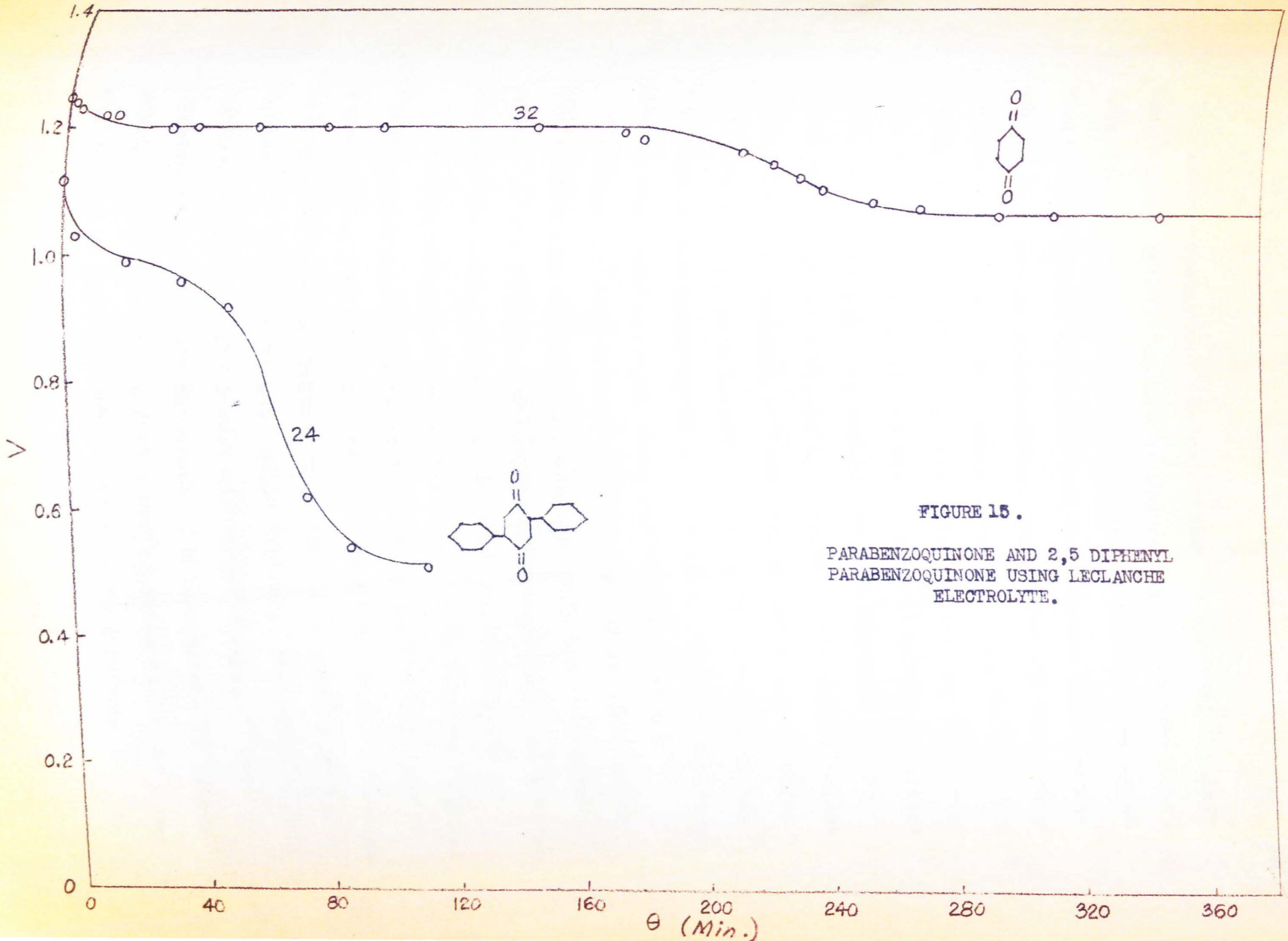


FIGURE 15.

PARABENZOQUINONE AND 2,5 DIPHENYL PARABENZOQUINONE USING LECLANCHE ELECTROLYTE.

Every depolarizer was not tested in every electrolyte because the initial objective was merely to discover suitable combinations for further study and to determine only qualitatively what effect on cell performance might be expected by changing electrolytes. As previously discussed, the Leclanche electrolyte seemed finally to be the most appropriate and suitable electrolyte considering all factors. From a theoretical point of view, since it already contains zinc, a smaller relative effect would be expected on the anode potential as a result of discharge with this electrolyte; also the presence of both zinc chloride and ammonium chloride acts as an acid-base buffer. In addition, it has the highest conductivity of those tested. From an experimental view good correspondence was observed between differences in cell voltage and depolarizer standard potentials with this electrolyte, compared with the unexplained effect on the relative potentials of benzoquinone and 1 Nitro anthraquinone-8-sulfonic acid obtained in electrolyte B.

One-Nitro anthraquinone-8-sulfonic acid gave the highest terminal voltage encountered in testing the various depolarizer-electrolyte combinations. Its terminal voltage was also the highest in each electrolyte, with the exception of the Leclanche, in which it was second highest. Unsubstituted anthraquinone gave the lowest discharge voltages in all electrolytes. The effectiveness of anthraquinone increases somewhat as solubilizing groups are substituted in the ring. The effect of diphenyl substitution on benzoquinone was to

decrease the performance considerably in the aqueous electrolyte. It was noted that in the electrolyte containing the most methanol (B), manganese dioxide was inferior in voltage to at least one organic depolarizer (Figure 10).

Because it has the highest possible theoretical coulombic capacity for a quinone, and because it apparently performed well in the initial tests, benzoquinone was selected for first capacity studies. Runs with this depolarizer are discussed in Chapter VIII. The results of further experiments with 1-Nitro anthraquinones are discussed in Chapter IX.

Although the preliminary results were essentially qualitative, since no exact measurement was made of the quantity of depolarizer used in every case, and the theoretical capacities could not therefore be compared with those actually obtained, it is beleived that the results served to show that reasonable working voltages could be obtained with these materials.

These voltages were maintained in many cases on fairly severe loads, when the very small size of the cell is taken into account, and this fact justified the extension of the study to capacities for the better materials. This extension of the study to coulombic capacities proved to be the most fruitful part of the work and although it was carried out entirely with aqueous electrolytes, there is little reason to believe that radically different relative capacities would be found with any of the electrolytes used

in the preliminary tests.

CHAPTER VIII

CELLS USING BENZOQUINONE

1. Theoretical Behavior of the Quino-Quinhydrone Electrode.

A known disadvantage in the use of the quinhydrone electrode in pH measurement is due to an effect termed the "salt error" (27). This results from the differential action of moderate to high concentrations of electrolytes on the activity coefficients of quinone and hydroquinone in the same solution. Because the potential of the quinhydrone electrode depends on the ratio of the activities of these two, as well as on the pH, an uncertainty arises as to the pH measurement in solutions of high ionic strength. The so-called "quino-quinhydrone" electrode does not suffer this disadvantage however. This electrode is saturated with both quinone and quinhydrone.

A thermodynamic equilibrium constant may be defined as follows for the dissociation of quinhydrone:

$$(a_Q)\ (a_{QH_2}) / (a_{QQH_2}) = K$$

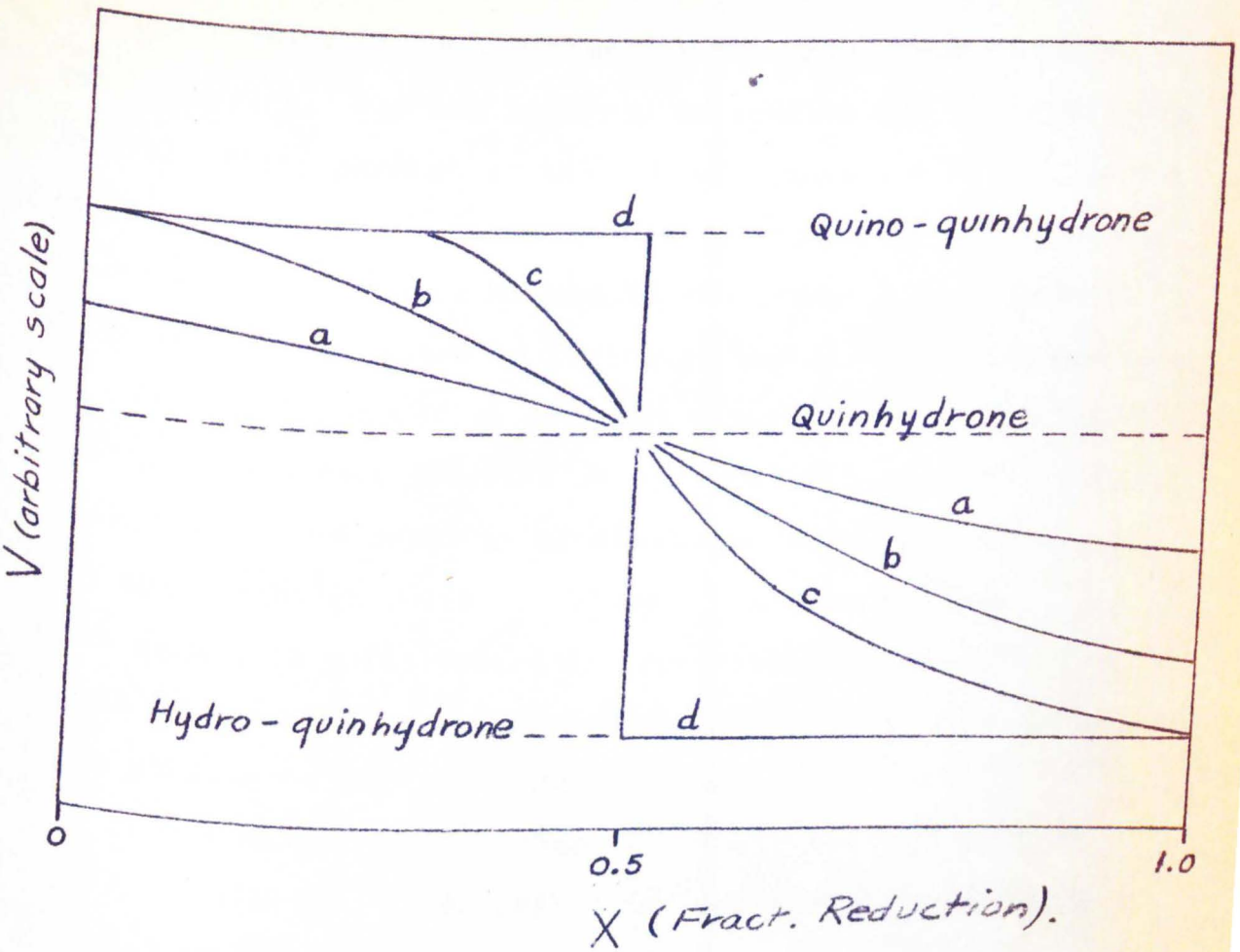
If the activities of both quinone and quinhydrone are fixed by saturation, the activity of the hydroquinone must also be fixed, and hence, the ratio of quinone to hydroquinone. There results an electrode potential different from that of quinhydrone alone, but which is constant, characteristic of of the electrode, independent of salt (or other) concentration, and dependent upon pH and temperature only.

This reversible potential must remain the same, furthermore, in various stages of reduction, until unsaturation takes place with respect to quinone.

If the reversible voltage of cells having quino-quinhydrone cathodes be measured and plotted as a function of the state of reduction of the cathode, and if the variations in cell voltage essentially reflect only variations in cathode potential, curves such as those shown in Figure 16 would be anticipated. These curves indicate that, under favorable conditions, 50% of the theoretical capacity of benzoquinone could be realized at a constant, and relatively high, potential. It is assumed that the electrode is initially saturated with a sufficient amount of quinhydrone, for which no coulombic capacity is assigned. This condition corresponds closely to practice, since the solubility of quinhydrone is very small, and an electrode consisting initially of only quinone should quickly become saturated with quinhydrone as reduction takes place.

2. Experimental Results with Benzoquinone.

As discussed in the preceding chapter, the high standard potential (0.699 volt) and high theoretical coulombic capacity (29.8 ampere-minutes per gram) of benzoquinone indicate that this compound might be a desirable depolarizer. Also the results observed in the preliminary testing of various cell combinations seemed to bear out the theoretical considerations of the preceding paragraph in that a remarkably steady voltage is observed with benzoquinone cells during the first few hours of discharge.



Curve a — Electrode initially unsaturated with quinone.

Curve b — Electrode initially just saturated with quinone.

Curve c — Excess quinone present initially.

Curve d — Limiting case of excess quinone.

FIGURE 16. THEORETICAL DISCHARGE CHARACTERISTICS OF BENZOQUINONE CELLS.

Unfortunately, an analysis of the actual coulombic capacity obtained with benzoquinone cells does not confirm all the possibilities indicated by the preliminary results and by theory. Various attempts to achieve the theoretically possible fifty percent of the ultimate capacity at a constant voltage were without success. In the following sections are discussed the results obtained in the study of the variables which might be expected to influence the discharge behavior.

It was the objective of these experiments to see what quantitative effect moderate changes in cell composition and construction or conditions of discharge would have on capacity and discharge voltage. Those directions of change which seemed to point toward an appreciable increase in the length of discharge at approximately constant voltage were to be pursued to find the optimum effect.

It was convenient to select a cut-off voltage of 0.75 volt for comparison of delivered coulombic capacities since at this voltage the rate of decrease of voltage with increasing fractional reduction of the depolarizer was found to be high. The actual capacity obtained therefore, does not depend critically on the chosen cut-off. An increase in length of the plateau should be reflected in a roughly proportional increase in coulombic capacity.

3. Effect of Discharge Rate.

Cells in which the amount of quinone present was known accurately to a milligram were discharged through 500, 150 and 75 ohms. The results are shown in Figure 17. Although

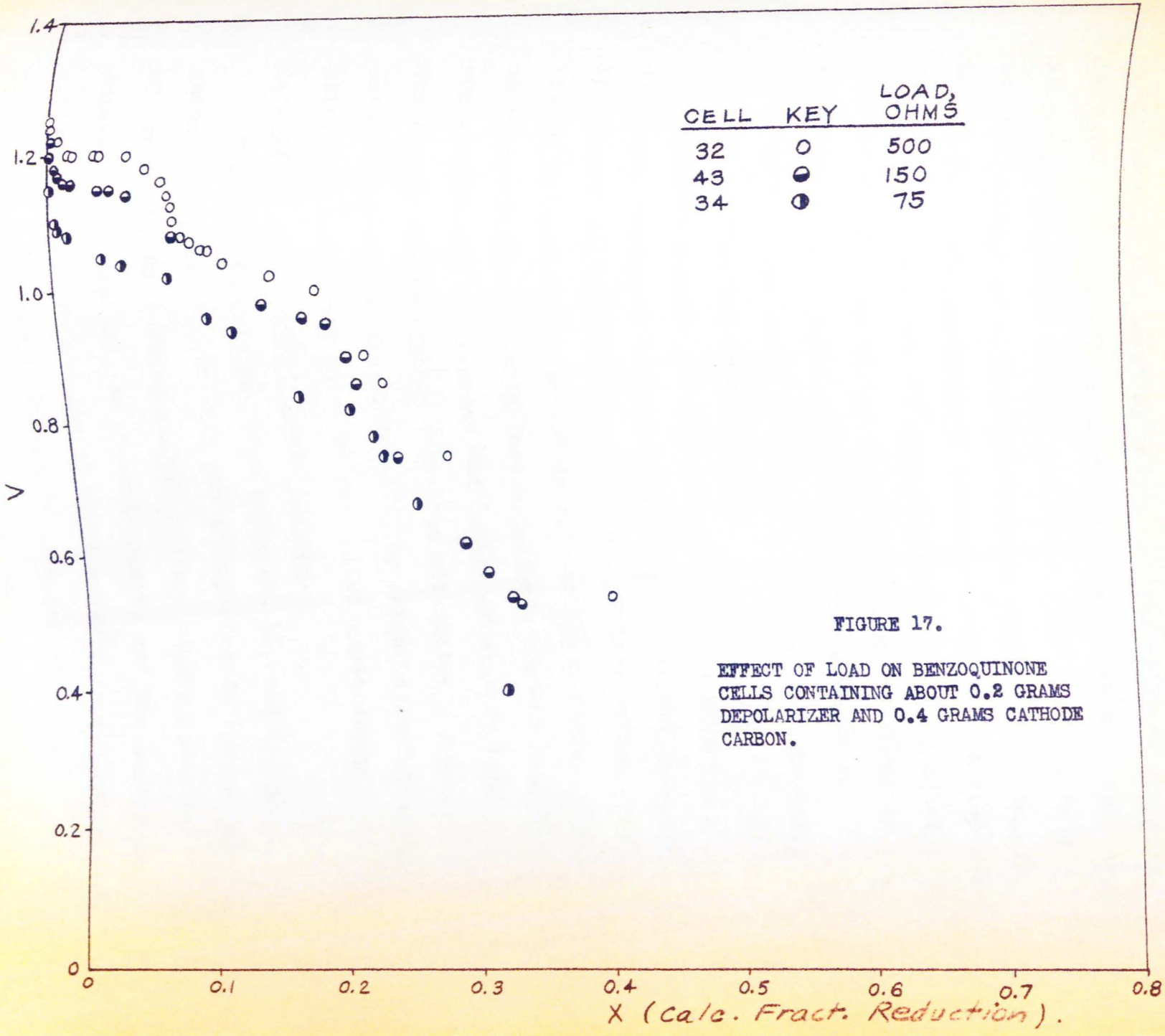


FIGURE 17.

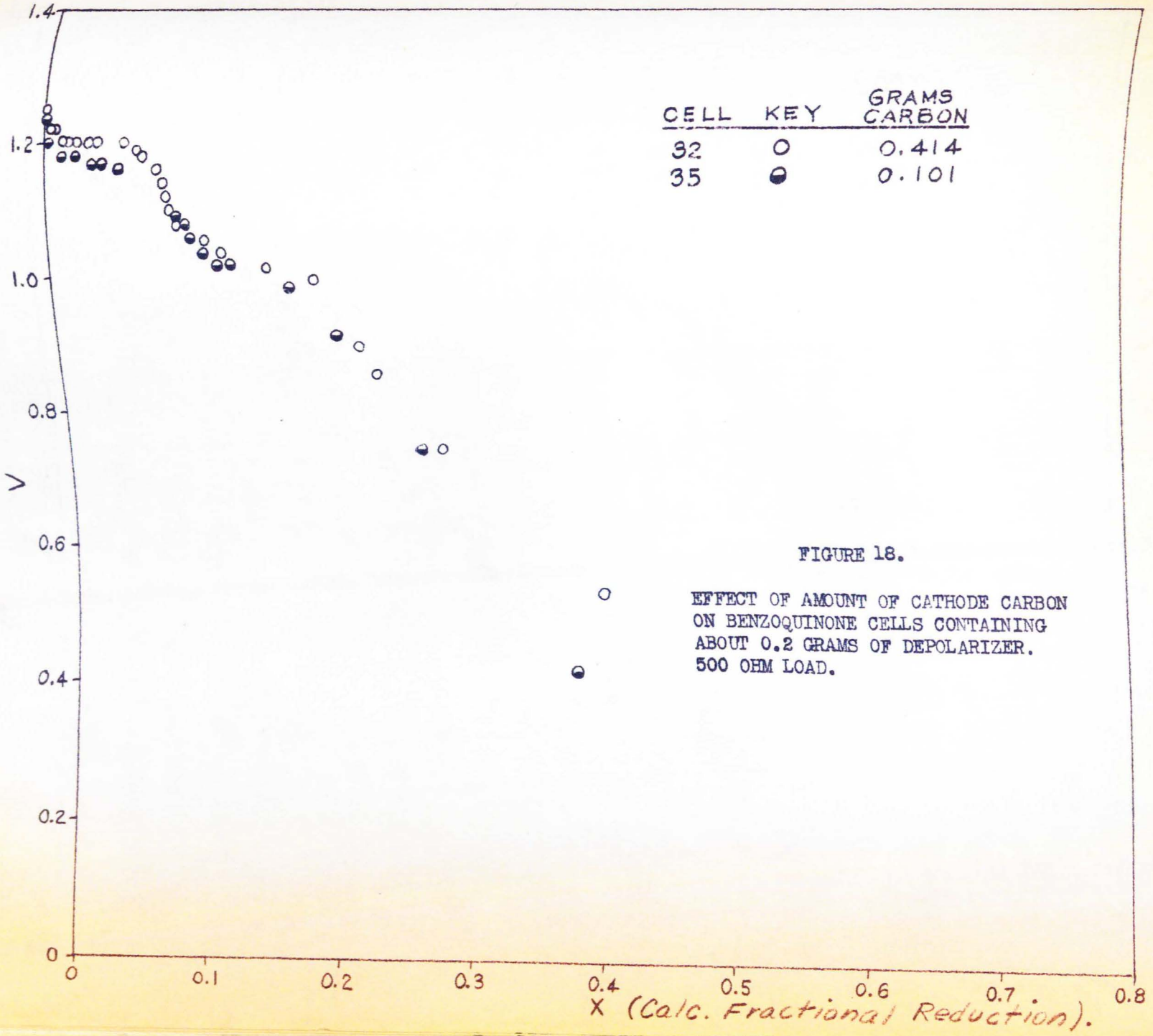
EFFECT OF LOAD ON BENZOQUINONE CELLS CONTAINING ABOUT 0.2 GRAMS DEPOLARIZER AND 0.4 GRAMS CATHODE CARBON.

there is a substantial increase in polarization, that is, a decrease in the terminal voltage of the cells as the load is increased, the effect is much more noticeable in the early stages of discharge than in the later. For example, to a cut-off voltage of 0.75 volt, there is realized only 24, 25, and 28.5% of the theoretical capacity of the depolarizer with loads of 75, 150, and 500 ohms respectively. Very likely, greater utilization of the depolarizer would be found if the load were smaller still. However, judging from these results, the load would necessarily be very small indeed, to show substantial improvement.

Similar results were obtained with cells in which a decreased amount of carbon was used in the cathode mix, as is illustrated in Figure 18. The use of less carbon effectively increases the current density at the cathode. Since no reasonable decrease in load or cathode current density appeared likely to increase the length of plateau (and therefore, the percentage effective utilization of the depolarizer to the chosen cut-off) by any substantial amount, attention was turned to other avenues of exploration.

4. Effect of Amount of Excess Quinone.

The results obtained with cells 44, 45, and 46 are shown in Figure 19. In this set of experiments the amount of carbon in the cathode mix was fixed at 1.813 grams to ensure a constant and low current density and the amount of active material (benzoquinone) was increased from 0.201 to 0.403 to 0.604 grams in the respective cells. It was necessary to use 5 milliliters of electrolyte in all these



CELL	KEY	GRAMS CARBON
32	○	0.414
35	◒	0.101

FIGURE 18.

EFFECT OF AMOUNT OF CATHODE CARBON ON BENZOQUINONE CELLS CONTAINING ABOUT 0.2 GRAMS OF DEPOLARIZER. 500 OHM LOAD.

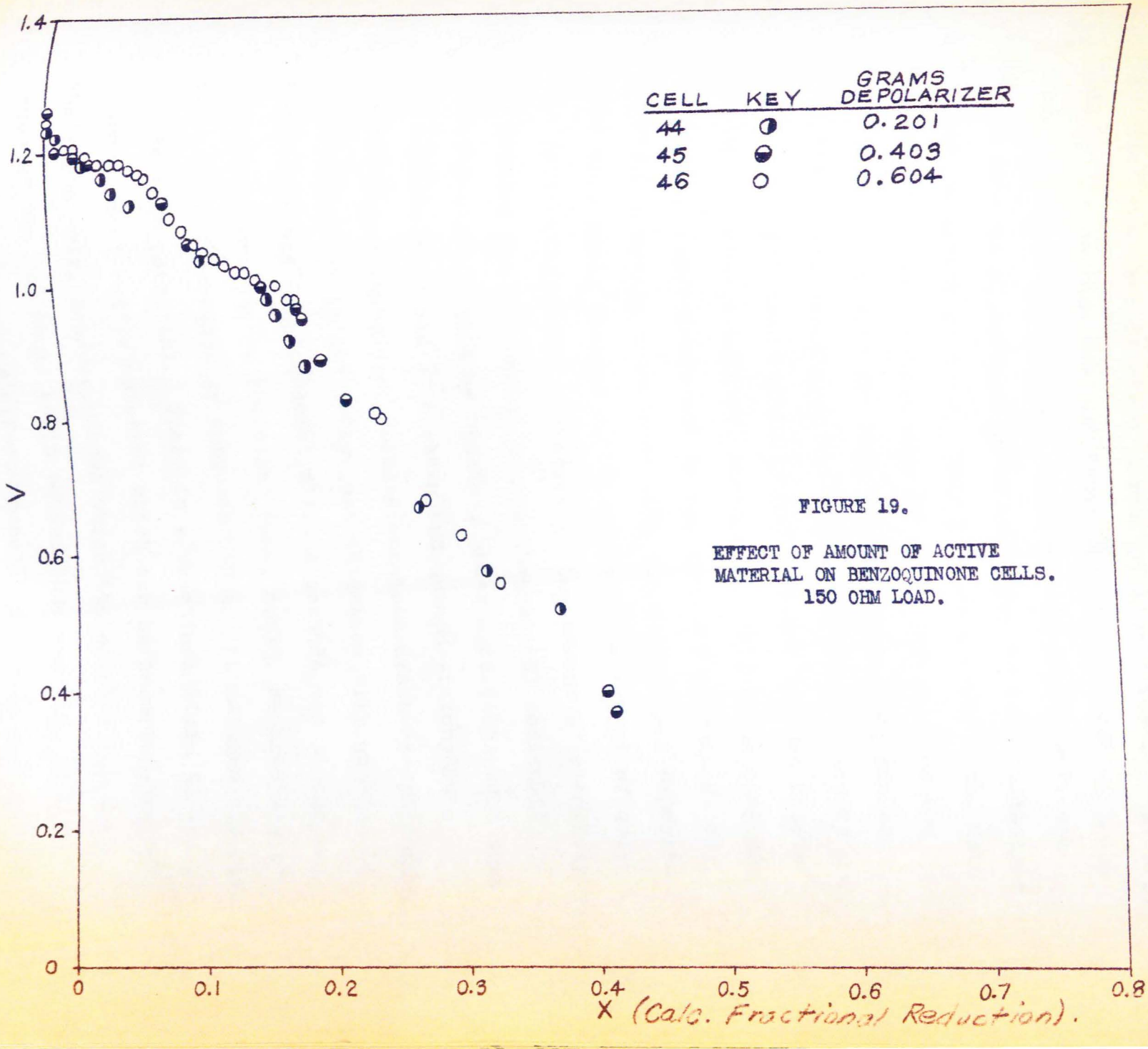


FIGURE 19.

EFFECT OF AMOUNT OF ACTIVE MATERIAL ON BENZOQUINONE CELLS. 150 OHM LOAD.

runs so that Cell 46, having the largest amount of depolarizing mix, contained a sufficient amount of liquid for both absorption by the cathode mix and immersion of the anode with the usual electrode separation. The load was arbitrarily set at 150 ohms to allow Cell 46 to discharge to completion in a reasonable length of time. This is a moderately high, but not severe, load for this size of cell, judging from the results obtained with the MnO_2 control cells. It can be seen that cells containing the relatively larger amounts of active material tend initially to level out to some fairly constant discharge voltage, whereas the cell containing the smallest amount appears not to approach any plateau at all. The results are in accordance with the theoretical expectations previously discussed. The larger the amount of quinone present initially, relative to the amount of electrolyte; the greater the proportion of the theoretical coulombic capacity which should be obtained under conditions such that the cathode consists of a saturated quinone-quinhydrone electrode and therefore exhibits constant discharge potential. A cathode which is initially just saturated with quinone should exhibit no plateau at all. A cathode containing a very large amount, on the other hand, could, as previously discussed, theoretically approach 50% of its maximum capacity at constant potential. There is a practical limit to the proportion of active material which can be incorporated into the carbon mix, however, above which the electronic resistance of the mix would begin to increase sharply, with consequent deleterious effect on cell performance. Cell 46

may be near this limit, although no reduction of working voltage is observed over cell 45. It will be noted that cell 46 shows essentially no improvement in utilization over cell 45 even though it contains fifty percent more depolarizer. In any event, there appears to be no practical advantage in using further excess amounts of quinone.

5. Effect of Electrolyte pH.

At 30°C., an increase of one unit of pH will decrease the reversible potential of a benzoquinone electrode by 0.06 volt. The discharging electrode suffers the same decrease, but may also be influenced in other ways. Thus there may be a change in polarization or possibly even a change in the cathode reaction itself. It seemed of interest to determine the actual effect of an alteration of pH on benzoquinone cells, and Figure 20 shows the data for three cells in which the electrolyte pH was the variable.

The initial closed circuit voltages are 1.25, 1.20, and 1.14 volts for cells 32, 48, and 49, respectively, corresponding to decreases of 0.05 and 0.11 volt for cells 48 and 49 over cell 32. The reduction of cathode potential in electrolytes having the pH of cells 48 and 49, according to the equation for the reversible potential, would be 0.060 volt and 0.104 volt. In acid solutions, the anode reaction is unaffected by pH, as is discussed more thoroughly in Chapter IX.

In addition to an increase in cell voltage with more acid electrolytes there is apparently also a more pronounced,

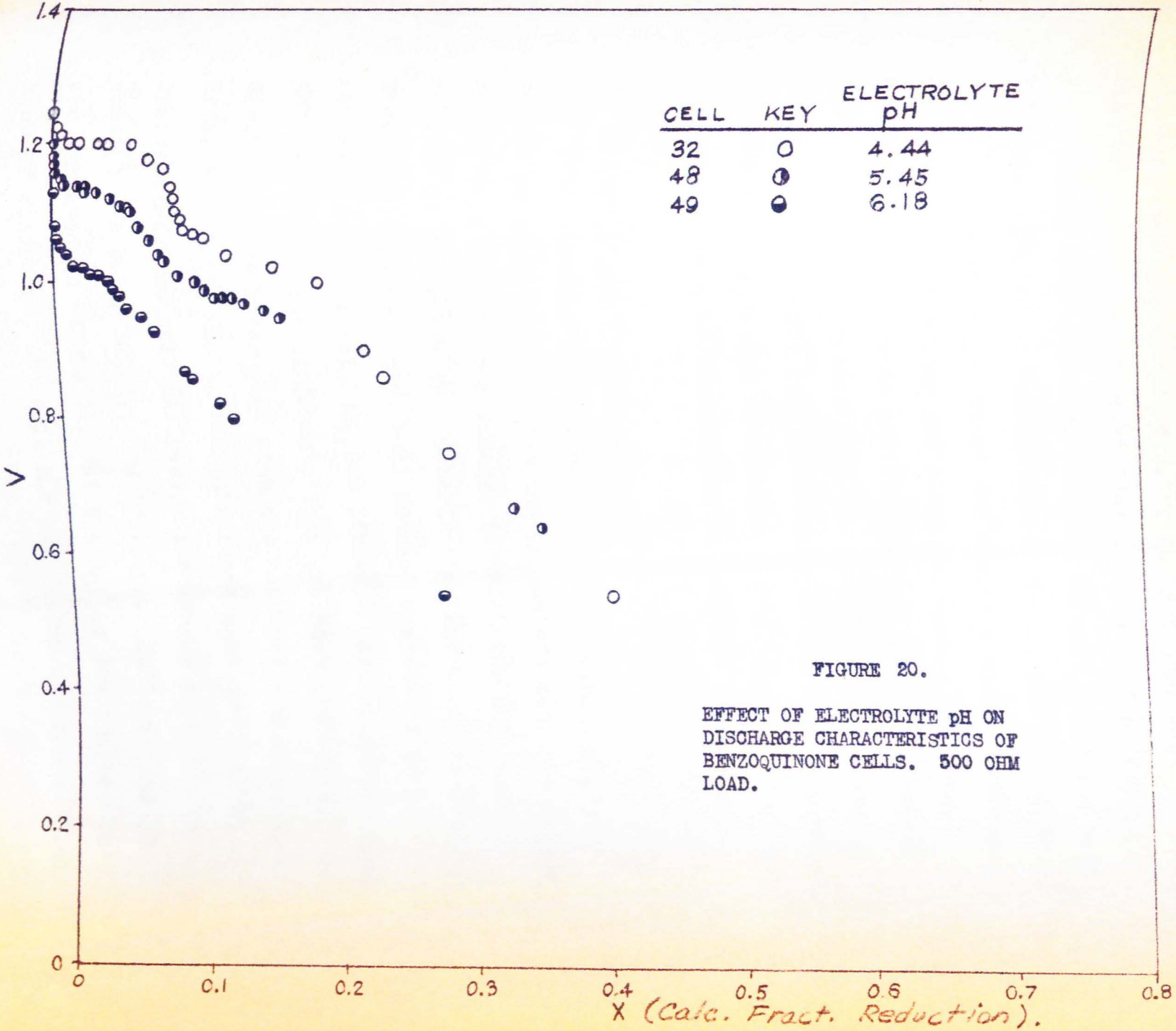


FIGURE 20.

EFFECT OF ELECTROLYTE pH ON DISCHARGE CHARACTERISTICS OF BENZOQUINONE CELLS. 500 OHM LOAD.

though relatively short, region in which approximately constant voltage is obtained. This indicates that the direction of decreasing pH might lead to greater fractional utilization of the cathode material as well as higher cell voltages. The pH of the Leclanche electrolyte is, however, about as low as is practical for use with zinc electrodes. The indicated direction and amount of change which to achieve greater cathode utilization is, therefore, beyond that which is attainable with zinc couples. According to various authors (27) (36) both benzoquinone and hydroquinone undergo auto-oxidation in alkaline media, and therefore no attempt was made to investigate an alkaline zinc-quinone couple.

6. Intermittent Discharge.

Other obvious approaches having been exhausted, it seemed possible that improvement in cathode capacity might result from a type of discharge in which the cell could recover at intervals from polarization and concentration gradients. Accordingly, cell 50 was constructed in a manner similar to cell 32, and likewise discharged through 500 ohms, with the difference that one hour periods of discharge were alternated with one hour periods of rest. After the fifth, ninth, and thirteenth hour of total discharge time, the cell was rested for longer periods, the exact times being 11, 17, and 17 hours. Cells 50 and 32 are compared in Figure 21. At the end of the thirteenth hour of discharge, the cell had been activated for a total

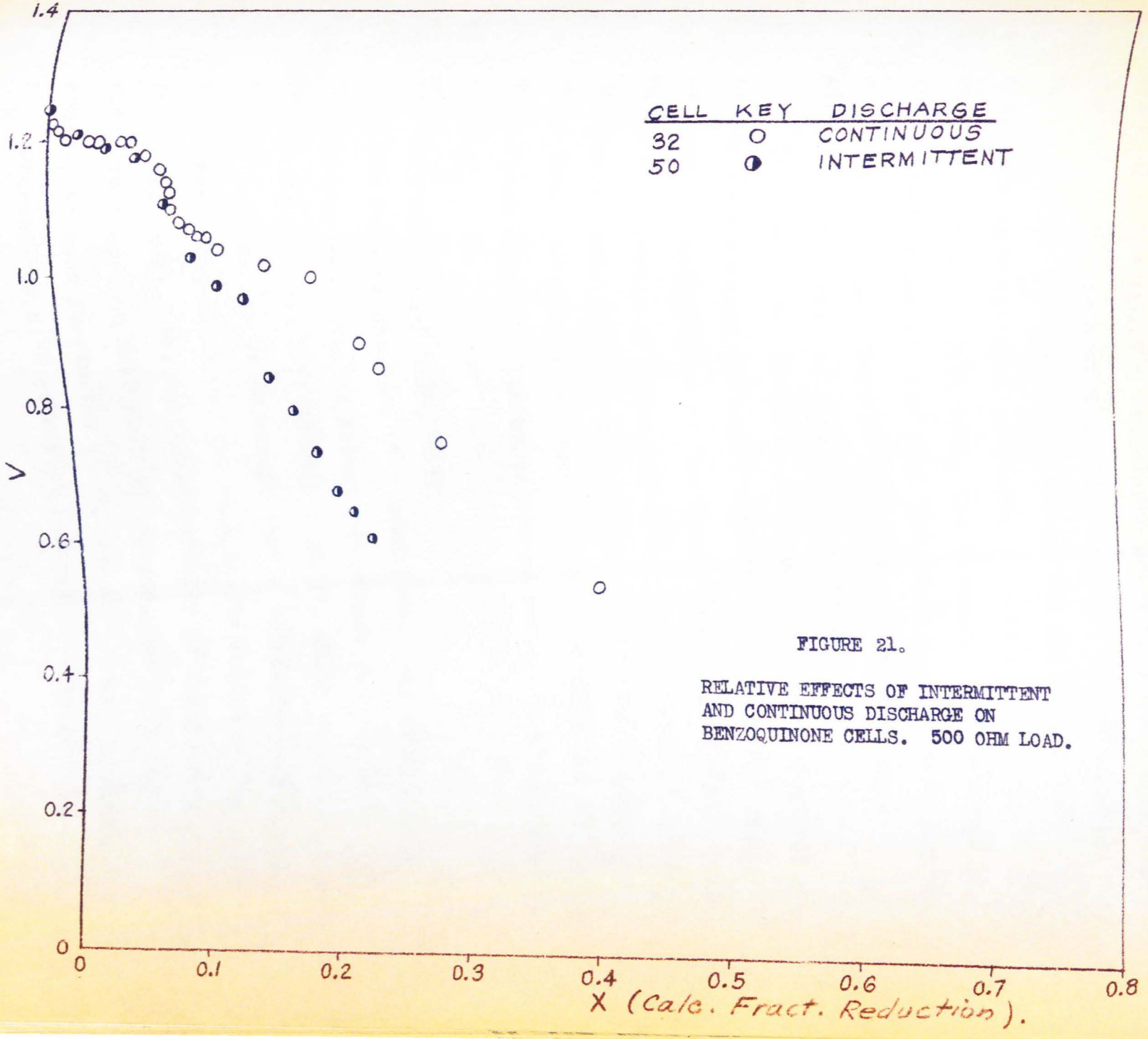


FIGURE 21.

RELATIVE EFFECTS OF INTERMITTENT AND CONTINUOUS DISCHARGE ON BENZOQUINONE CELLS. 500 OHM LOAD.

period of 58 hours. At this point the discharge voltage was 0.61 volts and the calculated fractional reduction was 0.231. In the case of cell 32, which had been discharged continuously, the discharge voltage was still 0.90 volt at a calculated fractional reduction of 0.232. Also, to a cut-off voltage of 0.75 volt, the percentage utilization of the cathode materials was 19.1 and 28.9% for cells 50 and 32, respectively. There is also a less well developed plateau in the case of intermittent discharge.

It seems apparent that, far from allowing more efficient use of benzoquinone, intermittent discharge actually decreases the performance of the cell. This is the result that would be expected if appreciable cell deterioration (self-discharge) took place on standing in the activated condition. This effect also could account for the generally low coulombic capacities obtained with benzoquinone cells, as compared with theory.

7. Comparison with Quinhydrone.

The results obtained when quinhydrone was substituted for quinone are quite different from those just discussed. Figure 22 compares cell 32 with cell 47, which was constructed in the same manner as 32 except that a weight of quinhydrone was substituted which was the same as the weight of quinone previously used. The coulombic capacity of quinhydrone is slightly less than half that of quinone, and this is, of course, allowed for in the calculated fractional reduction (X).

Whereas the highest capacity obtained with quinone cells

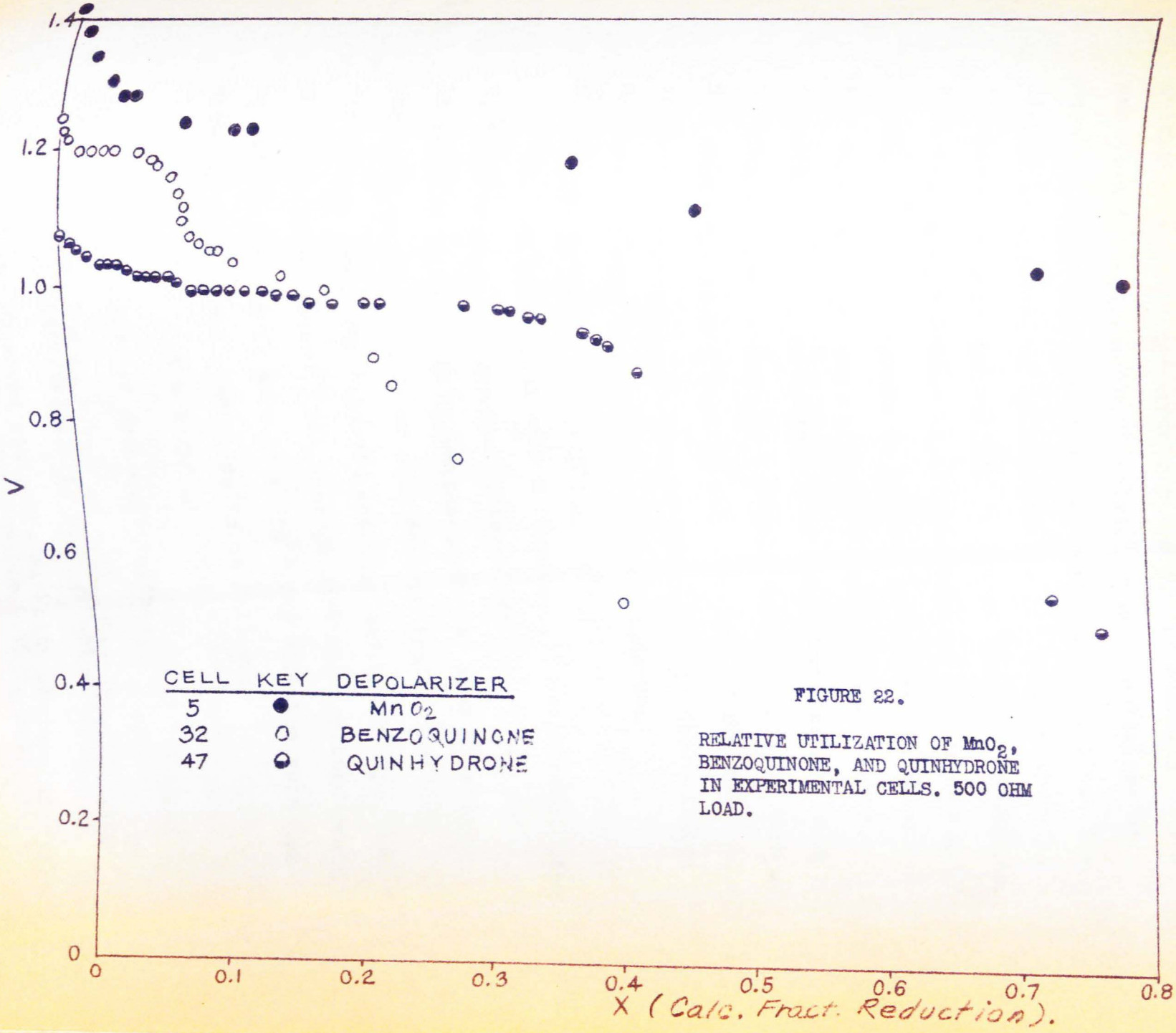


FIGURE 22.

RELATIVE UTILIZATION OF MnO_2, BENZOQUINONE, AND QUINHYDRONE IN EXPERIMENTAL CELLS. 500 OHM LOAD.

(with cell 32) was 28.5% of the theoretical, cell 47, using quinhydrone gave approximately 55% of its capacity to the same cut-off voltage (0.75 volt). These results are of more academic than practical interest, however, since the higher utilization of quinhydrone is offset completely by its higher equivalent weight. It is of interest to observe that the initial closed circuit voltage of cell 47 was 1.09 volts, which corresponds to that of an inflection point in the curve for the quinone cell at about 10% calculated reduction. It is remarkable that quinhydrone can sustain a working voltage as high as 1.0 volt when discharging through 500 ohms, for such a considerable fraction of its theoretical capacity, especially in view of its relative insolubility, as compared with both quinone and hydroquinone.

8. Energy Output of Benzoquinone Cells.

The net electrical work W (watt-sec.), calculated, like X, by a process of numerical integration from V, θ, and R, is reduced in Table VI to watt-seconds per gram of active material in the cathode of each cell in the series just discussed. From the observed cathodic coulombic capacity and this energy output, the average discharge voltage could be calculated and is also given in Table VI. The relation between these three quantities is as follows:

$$\bar{V} = W'/60\ C'$$

$\bar{V}$ = Average discharge voltage.

W' = Energy output of cell, watt-sec. per gram depolarizer (to 0.75 v. cut-off).

C' = Observed coulombic capacity of depolarizer, amp.-min. per gram (to 0.75 v. cut-off).

TABLE VI. RELATIVE PERFORMANCE OF BENZOQUINONE AND CONTROL CELLS.

Cell	Cathode		Electrolyte		Load	Coulombic Capacity* (amp-min per gram depolarizer)		Average Discharge Voltage*	Net Electrical Work* (watt-sec per gram depolarizer)	Remarks
	Depolarizer grams	Carbon grams	Comp.	ml.	Ohms	Theo.	Observed			
4#	0.458	0.916	L	6.0	100	18.5	10.6	1.03	655	Control
5#	0.458	0.916	L	6.0	500	18.5	18.5	1.12	1240	Control
32	0.207	0.414	L	3.0	500	29.8	8.63	1.04	541	
34	0.202	0.404	L	3.0	75	29.8	7.12	0.951	406	
35	0.202	0.101	L	3.0	500	29.8	8.10	0.985	478	
36	0.202	0.101	L	3.0	150	29.8	5.90	0.955	338	
43	0.201	0.403	L	3.0	150	29.8	7.45	1.04	466	
44	0.201	1.813	L	5.0	150	29.8	7.15	1.02	438	
45	0.403	1.813	L	5.0	150	29.8	7.42	1.08	481	
46	0.604	1.813	L	5.0	150	29.8	7.45	1.03	460	
47##	0.210	0.420	L	3.5	500	14.75	8.11	0.910	442	
48	0.210	0.420	NH_4Cl	3.5	500	29.8	8.55	0.955	490	
49	0.210	0.420	NaCl	3.5	500	29.8	4.62	0.893	247	
50	0.210	0.420	L	3.5	500	29.8	5.69	1.05	359	Intermittent Discharge

MnO_2 ## Quinhydrone * To 0.75 volt cut-off.

These calculations show that although the benzoquinone cells can maintain a discharge voltage of between 0.90 and 1.05 volt, which is almost as high as that of the manganese dioxide control cells under the same conditions, the watt-second output is lower than the control cells mainly because of inefficient use of the depolarizer. Benzoquinone has a higher theoretical coulombic capacity than MnO_2, though, and, in principle at least, could exceed the performance of MnO_2.

9. Conclusions From Runs Using Benzoquinone.

Benzoquinone, which has the highest coulombic capacity of all quinones, and also has a high standard potential, can, in theory, deliver 50% of its theoretical coulombic capacity at essentially constant voltage under certain conditions. These facts seemed to justify further examination of the discharge behavior of cells having benzoquinone cathodes.

Within the limits imposed by the cell size and construction, and by the nature of the cell materials, variations in pH, rate of discharge, cathode current density, amount of active material, and type of discharge all seemed to have relatively little effect on coulombic capacity; the observed limits being from about 19 to about 29% of the theoretical total capacity, to a 0.75 volt cut-off. The effect of pH variation on discharge voltage appears to follow closely from the effect on the reversible potential of the quinone. The effect of discharge rate and current density is much more noticeable

on discharge voltage than on capacity. Intermittent discharge, which prolongs the period of activation of the cell, leads to less efficient utilization than does continuous discharge. When the depolarizer is present initially in the form of quinhydrone, 55% of the theoretical capacity is realized, in contrast to an average of about 27% for quinone. When the lower theoretical capacity of quinhydrone is taken into account, however, the output per unit weight of active materials is approximately the same in the two forms.

It is believed that a partial explanation of the discrepancy between observed and theoretical capacities can be found in the relative instability of the activated benzoquinone cell. This cannot account for all the observations, however, as discussed below.

It is logical to assume that cells containing various amounts of excess quinone over that required for saturation would all suffer deterioration at the same rate, to the extent that it takes place, in the activated condition. If this is so, it follows that those cells containing the greater amount of active material should be affected relatively less. On the other hand, it was observed that an increase of 50% in the amount of quinone present in a cell of a given construction gave no improvement whatever in fractional utilization of the cathode material. (Compare cells 45 and 46, Figure 19.)

Another explanation, more in accordance with observation, is as follows. It is well known (for example, in the case of

dry cells) that discharge tends to increase the pH in the vicinity of the cathode, while the opposite effect occurs at the anode. This results from the relative slowness of the diffusional processes compared to the rate of formation and disappearance of products and reactants. As previously mentioned, benzoquinone suffers auto-oxidation in alkaline media. The effect of the carbon electrode surface and the air atmosphere in which the cells were discharged could easily be to accelerate this process. If conditions in the cathode mix of these cells were as postulated the net effect would be to destroy part of the depolarizing material before it could be used. Also, when an electrolyte of initially higher pH were used, less coulombic capacity should result because of accentuation of the effect. This is what was observed (note Figure 20) and is less easily explained on the basis of self-discharge of the complete cell. Furthermore, the same explanation can account for the apparent limit to fractional utilization demonstrated by the set of runs shown in Figure 19 in which the quantity of active material was varied, whereas the other explanation cannot account for it at all.

CHAPTER IX

CELLS USING ANTHRAQUINONE AND RELATED COMPOUNDS

1. Introduction.

While benzoquinone, as previously discussed, appeared originally to be the depolarizing material holding most promise, because of its relatively high standard potential and theoretical coulombic capacity, anthraquinone seemed to be the least promising material, for just the opposite reasons, as an examination of Table IV and Figure 5 will show. Certain derivatives of anthraquinone show slightly higher standard potentials than the unsubstituted compound, at some sacrifice of theoretical coulombic capacity, however.

The preliminary results of Chapter VII nevertheless seemed to indicate that the Nitroanthraquinone Sulfonic Acids might be good depolarizers. It appeared that it would be worthwhile to examine the behavior of the various available anthraquinones more closely than in the preliminary studies.

This examination yielded some interesting results, showing that certain anthraquinone derivatives possess good depolarizing ability as measured by their sustained terminal voltages through high coulombic capacities. The results of and the conclusions from the various sets of experiments on these compounds are discussed below.

2. Unsubstituted Anthraquinone.

A comparison of two cells, otherwise identical, except that one (cell 53) contains 0.2 grams of anthraquinone and

0.4 grams of carbon in the cathode while the other (cell 42) contains only the 0.4 grams of carbon, is shown in Figure 23. It is clear that unsubstituted anthraquinone, at least under the conditions of cell 53, has essentially no depolarizing ability.

The behavior of the cell containing only carbon is worth some consideration, in view of these and later results. Although the type of carbon used (a 50/50 mixture of fine graphite and battery-grade carbon black) has no depolarizing ability per se, there will usually be a slight amount of occluded oxygen present in a freshly prepared cell which will exert an effect. This explains the initial open circuit voltages of 1.1 to 1.2 volts obtained even without depolarizer. Such cells drop quickly to fairly low (0.5 to 0.6 volt) terminal voltages with a 500 ohm load. Afterwards there is a less rapid drop. The voltage of these undepolarized cells seems to decay approximately as a logarithmic function of the time. The low, but not zero, voltages sustained by such cells must be due to the simple corrosion reaction of zinc:

$$Zn + 2H^{+} = Zn^{++} + H_2,$$

probably initially depolarized to a slight extent by the presence in the cell of a small amount of air. It is shown later that the atmosphere in which certain experimental cells are discharged can have a significant effect on the discharge behavior.

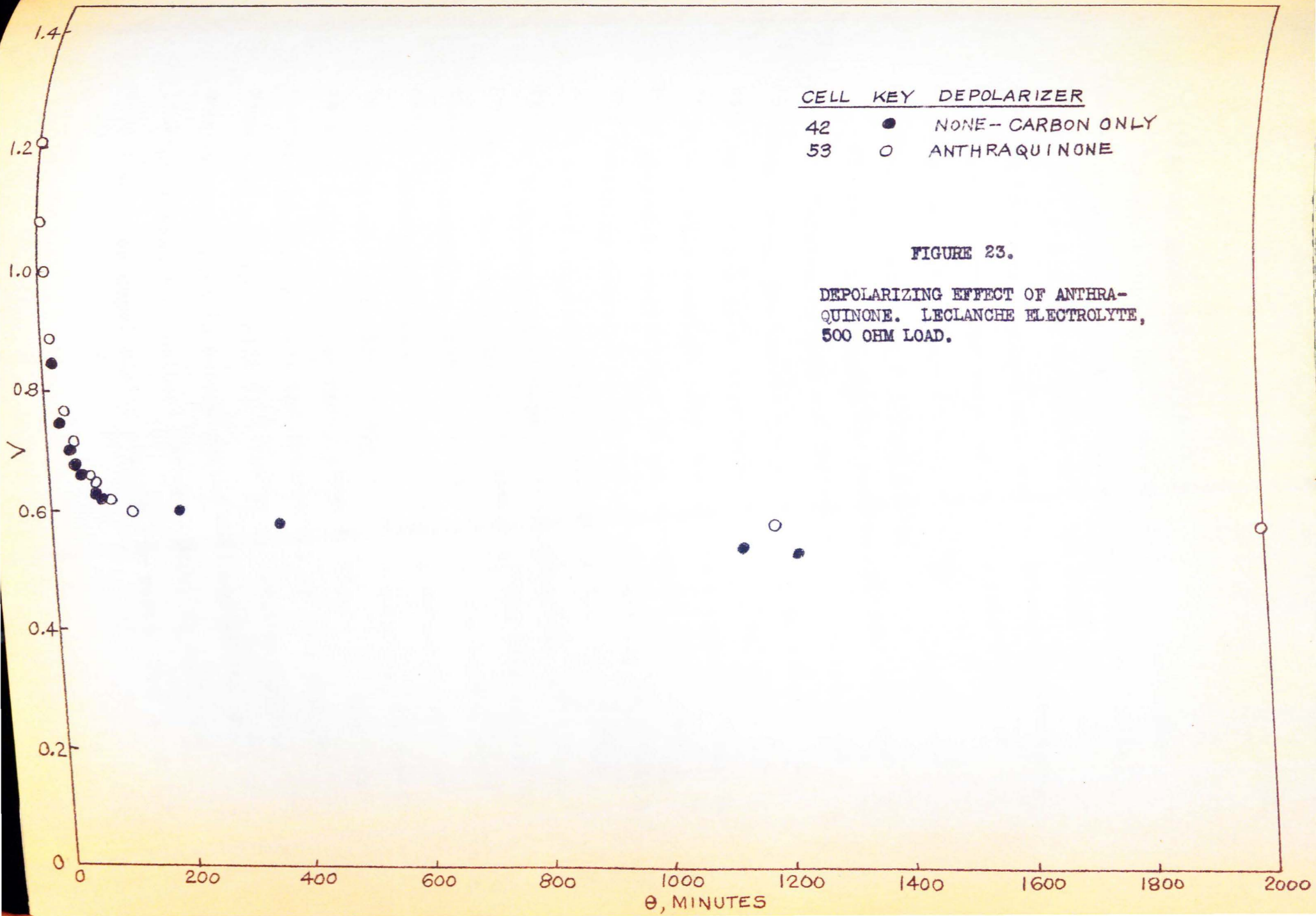


FIGURE 23.

DEPOLARIZING EFFECT OF ANTHRAQUINONE. LECLANCHE ELECTROLYTE, 500 OHM LOAD.

3. Anthraquinone Mono-Sulfonates.

Discharge curves for Potassium Anthraquinone alpha-Sulfonate and Sodium Anthraquinone beta-Sulfonate (cells 39 and 40) are shown in Figure 24. The results are very similar to those obtained with unsubstituted anthraquinone, although the potassium compound might be interpreted as showing some slight depolarizing ability.

4. Nitroanthraquinone Sulfonic Acids.

Figure 25 illustrates the results obtained with the 1-Nitro - 8-Sulfonic Acid and the 5-Nitro-1-Sulfonic Acid Anthraquinones. The curves are very nearly indentical. In both cases there is a large initial drop in voltage which is practically complete after a sufficient number of coulombs have passed to reduce five to ten percent of the quinone. The remaining fraction of the coulombic capacity is obtained at an almost constant voltage of 0.85 to 0.90 volt. This fairly high terminal voltage in comparison with cells 39 and 40 may be due partly to the influence of the free acidity of these compounds on cathode potential. In the case of both cells, more useful coulombic capacity is obtained than can be accounted for by the reduction of the quinone. It appears, as with cell 38, for example, shown in Figure 25, that the useful capacity exceeds the theoretical by more than 50%. Figure 26 compares cell 55 (like 37 in construction and composition) with an undepolarized cell containing an identical amount of cathode carbon. Here, as well, the data indicates depolarizing ability far beyond that possibly

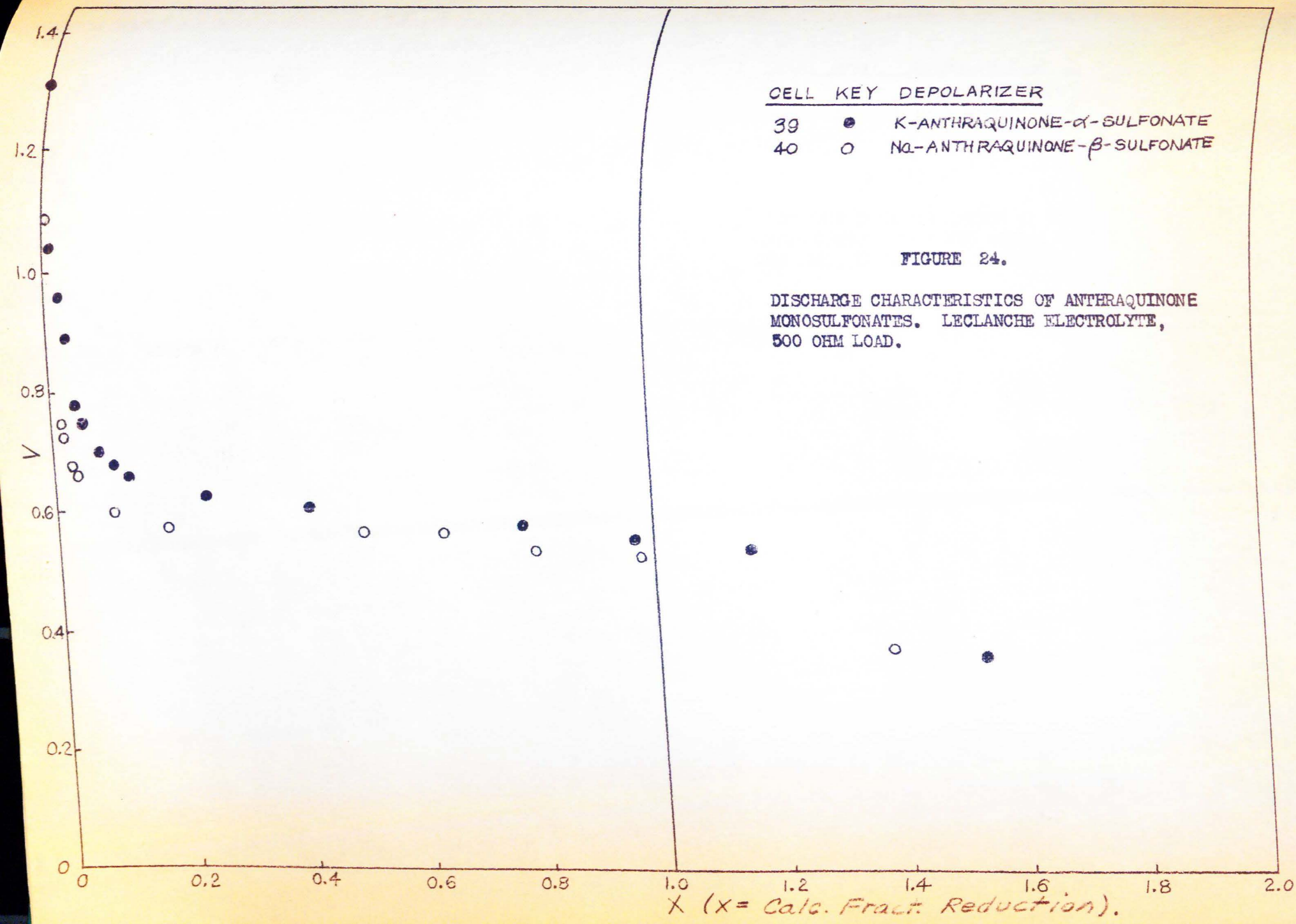
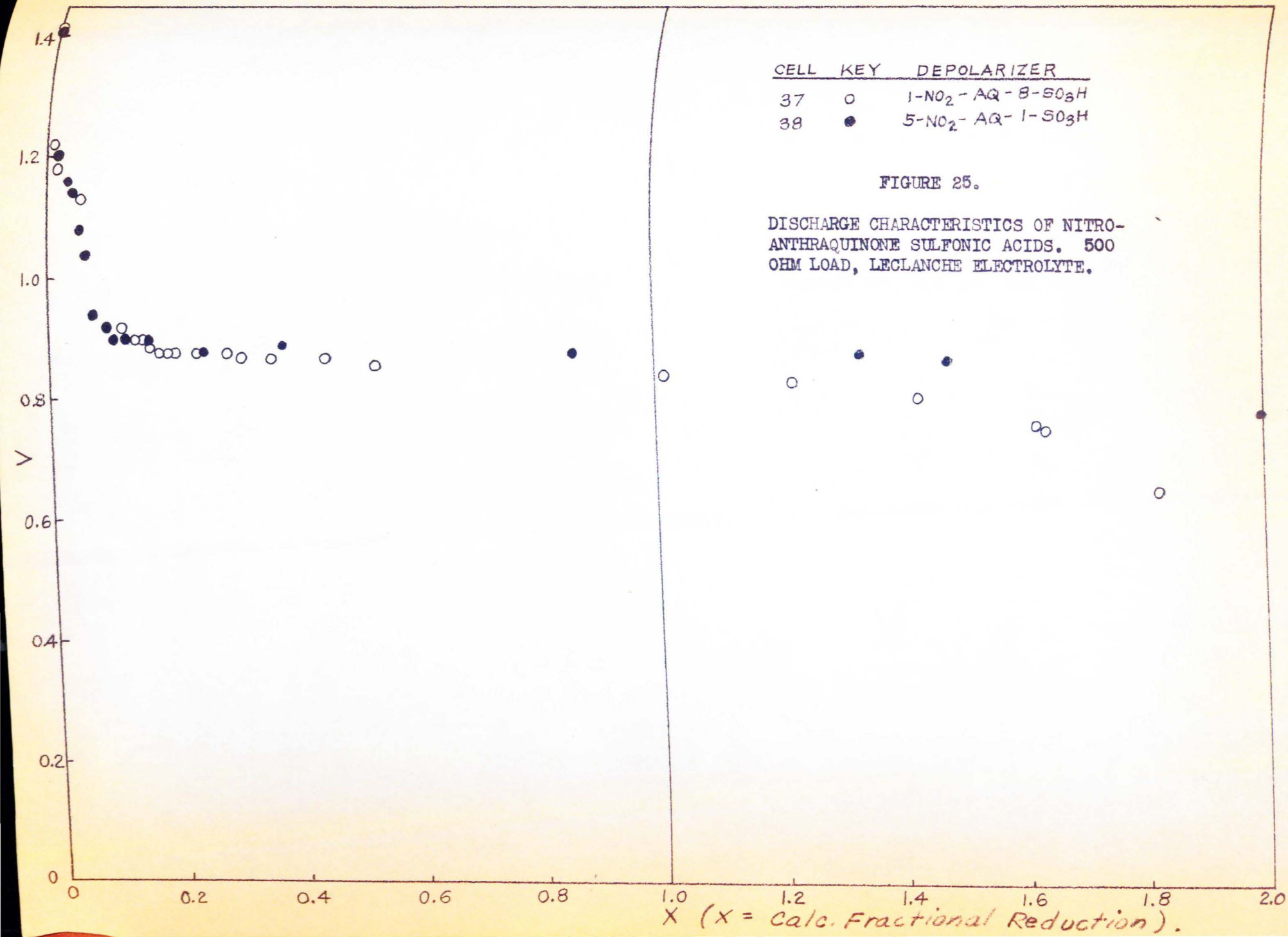


FIGURE 24.

DISCHARGE CHARACTERISTICS OF ANTHRAQUINONE MONOSULFONATES. LECLANCHE ELECTROLYTE, 500 OHM LOAD.



CELL	KEY	DEPOLARIZER
37	○	1-NO_2 - AQ - 8-SO_3H
38	●	5-NO_2 - AQ - 1-SO_3H

FIGURE 25.

DISCHARGE CHARACTERISTICS OF NITRO-ANTHRAQUINONE SULFONIC ACIDS. 500 OHM LOAD, LECLANCHE ELECTROLYTE.

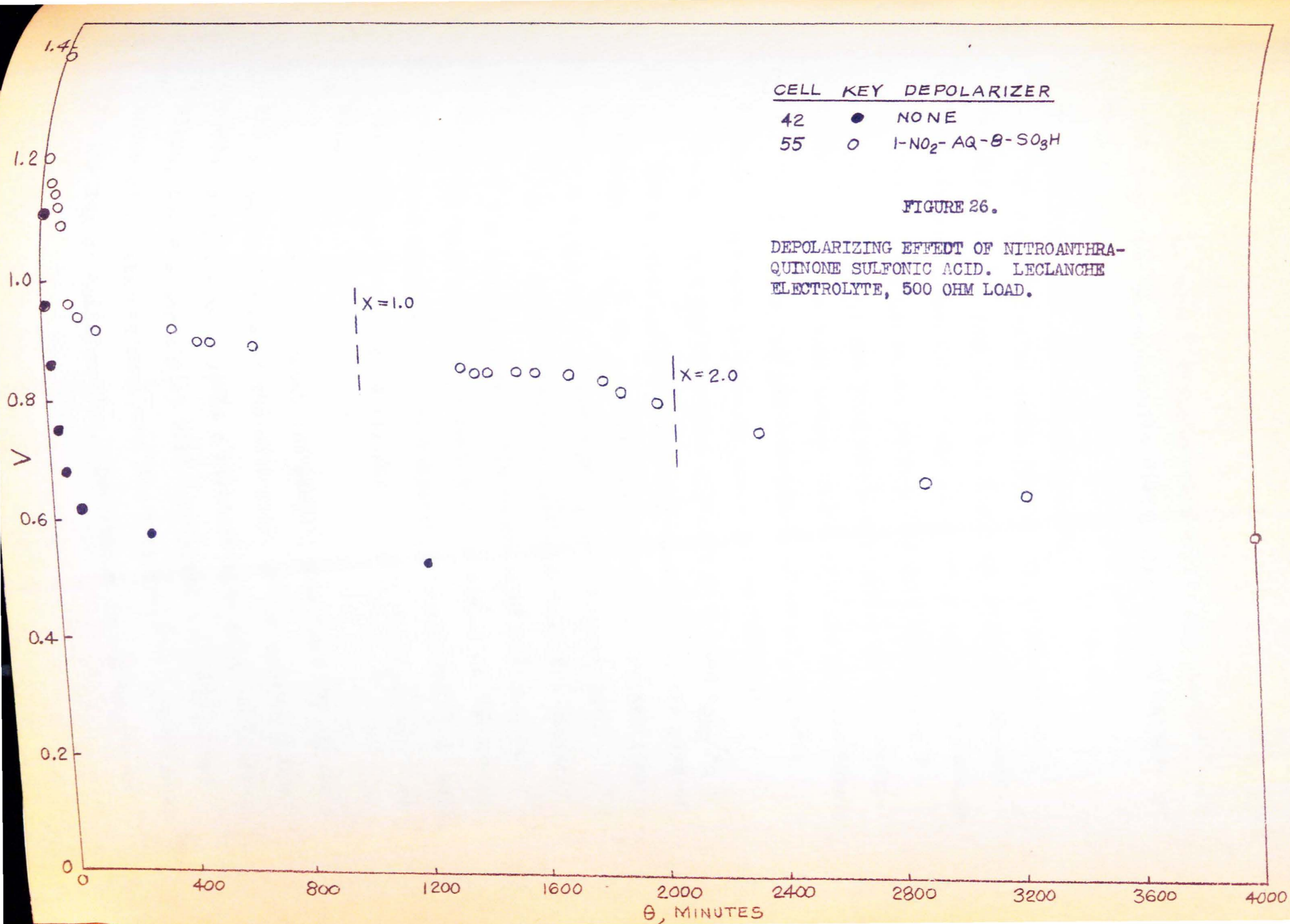


FIGURE 26.

DEPOLARIZING EFFEDT OF NITROANTHRAQUINONE SULFONIC ACID. LECLANCHE ELECTROLYTE, 500 OHM LOAD.

due to the quinone. These results raised the question as to what reactions were actually taking place at the cathode of these cells.

5. Interpretation of Cell Reactions.

If the results of cells 37, 38, 39, 40 and 55 are replotted in the form of V vs. log X it would be expected that certain information could be obtained as to the cathode reactions which would not be apparent from the simple V - X plot. The reasons for this and a discussion of the limitations inherent in this method of analysis are put forth below.

The equation for the reversible potential, E, of a quinone electrode is usually expressed as follows:

$$E = E^\circ - (2.3\ RT/\mathcal{F})\ pH - 2.3(RT/2\mathcal{F})\ \log a_{QH_2}/a_Q .$$

For a given quinone, assuming constant pH, the plot of E against $\log a_{QH_2}/a_Q$ should therefore be a straight line having a slope of $-2.3(RT/2\mathcal{F})$, or - 0.03 at 30°C.

Also, if the electrode is saturated with the quinone (always the case with the cells under consideration) and since the quantity X is directly proportional to the amount of reduced material (the corresponding hydroquinone) present, the slope of a plot of E vs. log X should in this case also be - 0.03.

In general, although the plot of E against the log of the proper function of the activities of the reactants and products will always yield a straight line of characteristic slope, the E - log X plot will only yield a straight line under circumstances such that log X is directly proportional to the log of this function. Deviations from linearity of

this plot will indicate, therefore, deviations from these conditions. The quantity X may be regarded as simply equivalent to a certain number of Faradays, and if the abscissae of these plots were in terms of Faradays or coulombs, rather than X, the theoretical slope would be exactly the same. It can happen, therefore, that other straight lines will result from the plot, due to reactions other than the one discussed, if it is possible for such reactions to occur. Each reaction is characterized by its own potential so that a shift from one reaction to another may result in a shift from one straight line portion to another, with a new, or possibly the same, slope, if conditions are such that a linear plot results. Often, several possible reactions have the same slope and for this reason the slope alone does not completely identify a reaction.

The above comments apply strictly only to the reversible potential, E. The reversible cathode potential could not be measured, of course, without influencing the character of the discharge under study. It was hoped that some information as to the cathode reactions could be obtained from the V - log X plot, however, where V is the terminal voltage of the cell.

V is a function of E, but it is impossible to specify an exact mathematical relationship. V depends on not only the cathode potential, but on internal cell resistance, the external load, and polarization of the anode and cathode, as well as anode potential. The contribution of all these

factors must be known, or else all but the cathode potential must remain constant in order that it be possible for the V - log X plot to be subject to exactly the same interpretation as the E - log X plot.

As previously discussed under cell design, the zinc was made large enough so that little anode polarization would be expected to occur. Anode polarization is usually of smaller magnitude than that of the cathode, in any case, for these cells. No change in anode reaction during the course of discharge would reasonably be expected and the composition and quantity of the Leclanche electrolyte is such that little change in zinc concentration or electrolyte resistance should occur. The largest unknown factor by far is cathode polarization, which may increase, or perhaps even decrease (due to lower current densities) during the course of cell discharge.

In spite of all the above-mentioned limitations it is believed that the V - log X plots can be interpreted to indicate certain changes in the cathode reaction of the various cells. For example, although the slopes themselves, because of the irreversible effects just described, will probably not correspond to any theoretical values very closely, it would appear justifiable to consider the continuation of any reasonably linear portion of the plot actually obtained as corresponding to some single reaction. Likewise, a marked shift in voltage between two more or less linear portions of the plot could reasonably be interpreted as indicating a shift from one reaction to another, as could

a sudden shift from one constant slope to another.

Figure 27 shows this type of plot for cells 39 and 40, which both showed rather poor depolarizing ability. The initial slopes for both curves are greater than can be accounted for on the basis of any known reaction of the depolarizer and very likely are due more to increasing cathode polarization than to any changes in cathodic potential. (It may be noted that cells 4 and 5, using manganese dioxide, both showed a progressive drop in terminal voltage with increasing fractional reduction, although the theoretical expectation would be for constant cathode potential.) As the calculated fractional reduction of these cells approaches 100% both curves seem to be approaching, if not reaching, slopes of the order of the theoretical - 0.03. At or near 100% reduction, both slopes are seen to increase sharply to a new and substantially higher value, as would be expected on termination of the depolarizing reaction.

Cells 37 and 38 when plotted in this manner show a somewhat different behavior. As shown in Figure 28, there is an initial steep slope which gradually decreases up to a value of X between 0.05 and 0.10. There is then a sudden drop in voltage until about 0.90 volt is reached, after which the experimental data appear to fall more or less on a straight line having a slope of about - 0.05 or - 0.06 volt per unit of log X. This approximately linear portion of the data continues well past the expected limit where X equals 1.0, in contrast to cells 39 and 40. A portion of this graph

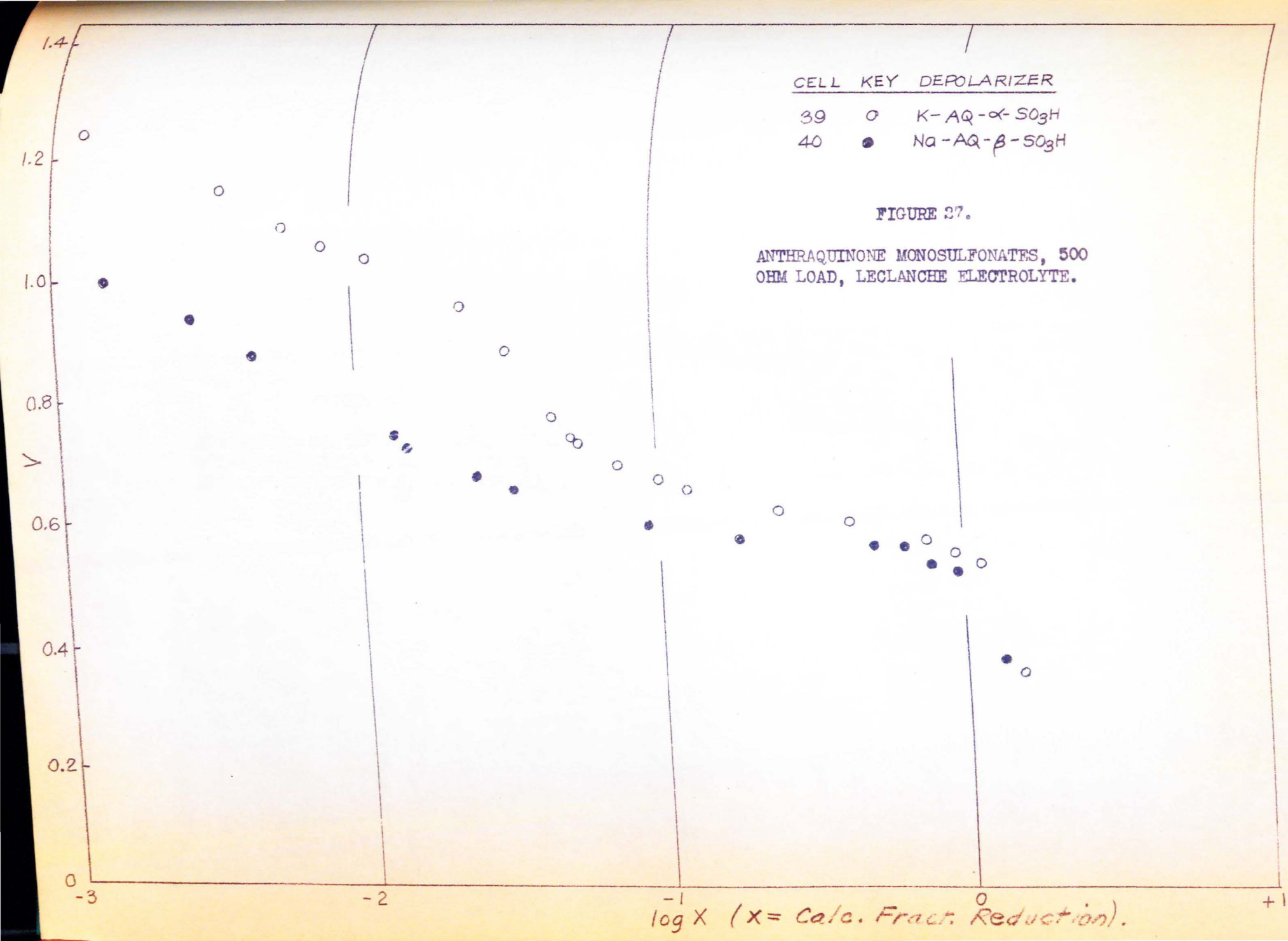


FIGURE 37.

ANTHRAQUINONE MONOSULFONATES, 500 OHM LOAD, LECLANCHE ELECTROLYTE.

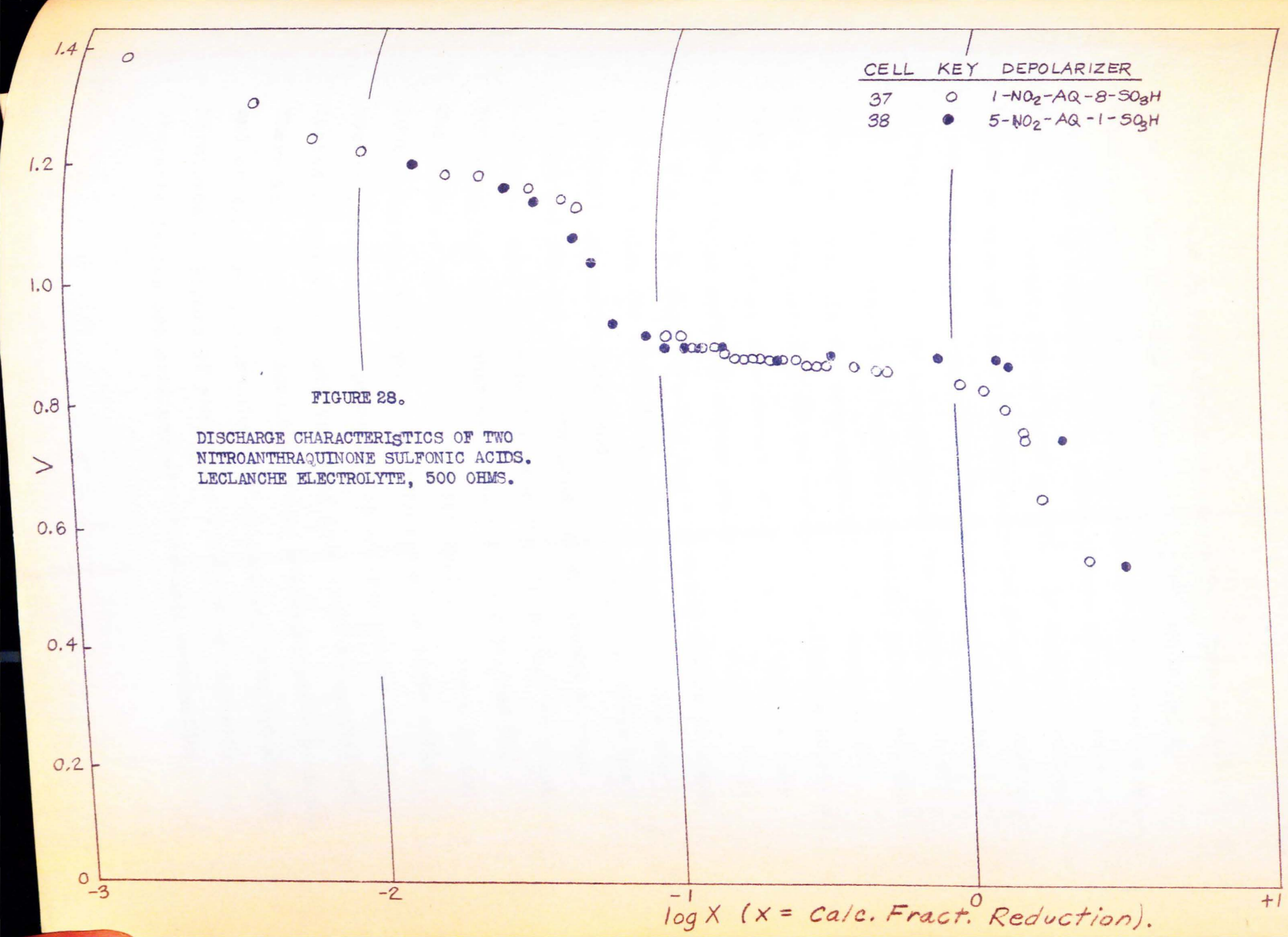


FIGURE 28.

DISCHARGE CHARACTERISTICS OF TWO NITROANTHRAQUINONE SULFONIC ACIDS. LECLANCHE ELECTROLYTE, 500 OHMS.

is re-plotted in more detail in Figure 29. There is also shown in Figure 29 the results of cell 55, which was a duplicate of cell 37. The points for cell 38, which contained the isomeric compound, may be taken, apparently, as replicating the results of cells 37 and 55. If this reasonably linear portion of the resulting composite graph be considered as corresponding to some single cathode reaction it is difficult to identify this reaction with the reduction of the quinone because more coulombic capacity is obtained than theory allows. In the case of cell 55, for example, 160 or 170% of the capacity of the quinone reduction is indicated. Cell 38 duplicates this result, while cell 37 shows a less marked, though definite excess capacity.

Figure 30 shows the V - log X plot and Figure 31 shows the V - X plot for cells 55 and 56. These two cells are identical in construction and composition. The first was discharged through a 500 ohm load and the second through 150 ohms. Cell 56 shows the same drop in voltage at about 10% reduction which characterized cells 37, 38, and 55. The slope of the V - log X plot for cell 56 between 10 and 100% reduction is higher than with the other three cells, however, showing that polarization effects cannot be neglected when the absolute value of this slope is considered. There is also a less abrupt shift to a steeper slope near the end of discharge, where the depolarizing reaction apparently terminates. Figure 31 shows that fairly good discharge characteristics are obtained with this cell combination

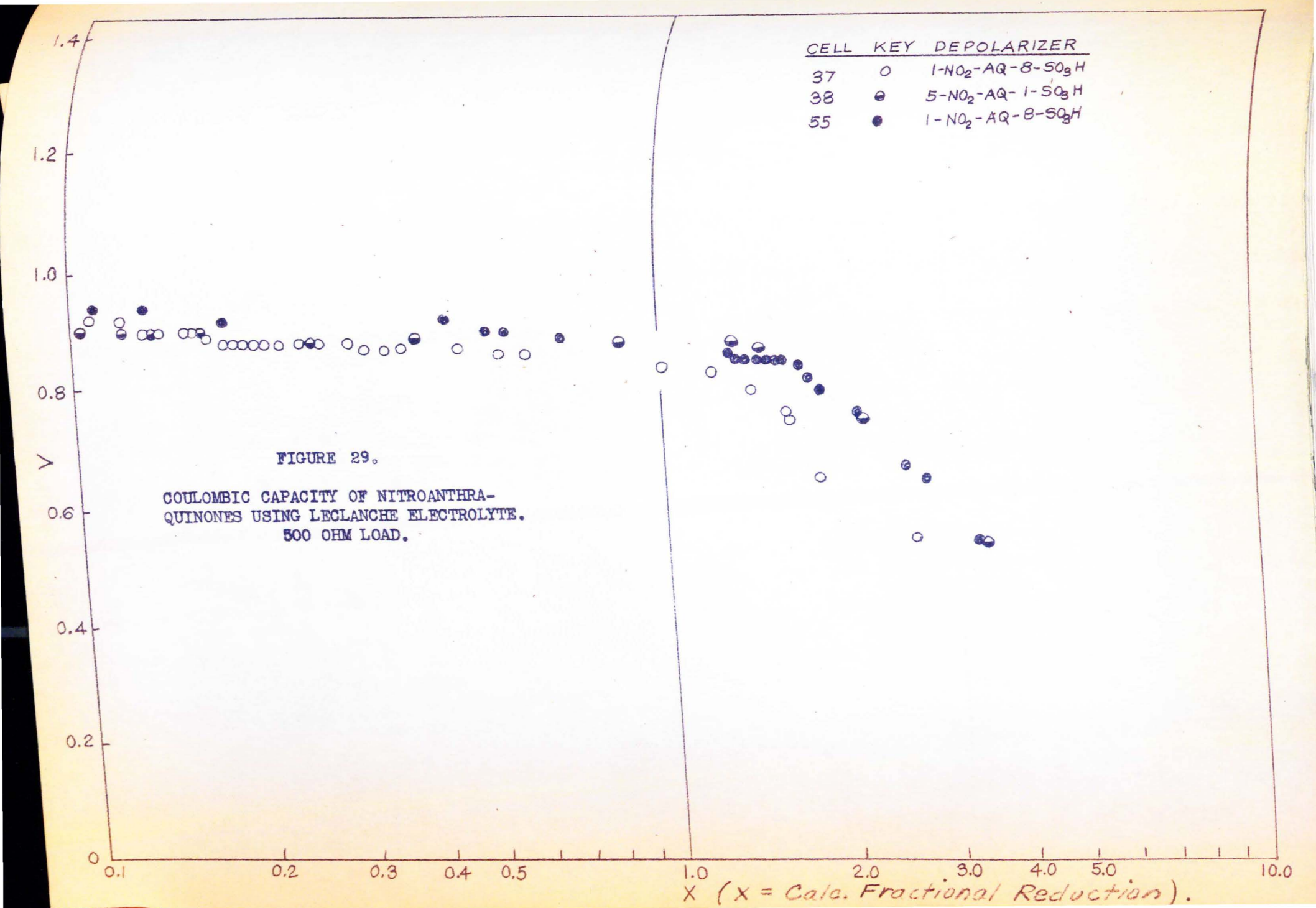


FIGURE 29.

COULOMBIC CAPACITY OF NITROANTHRAQUINONES USING LECLANCHE ELECTROLYTE. 500 OHM LOAD.

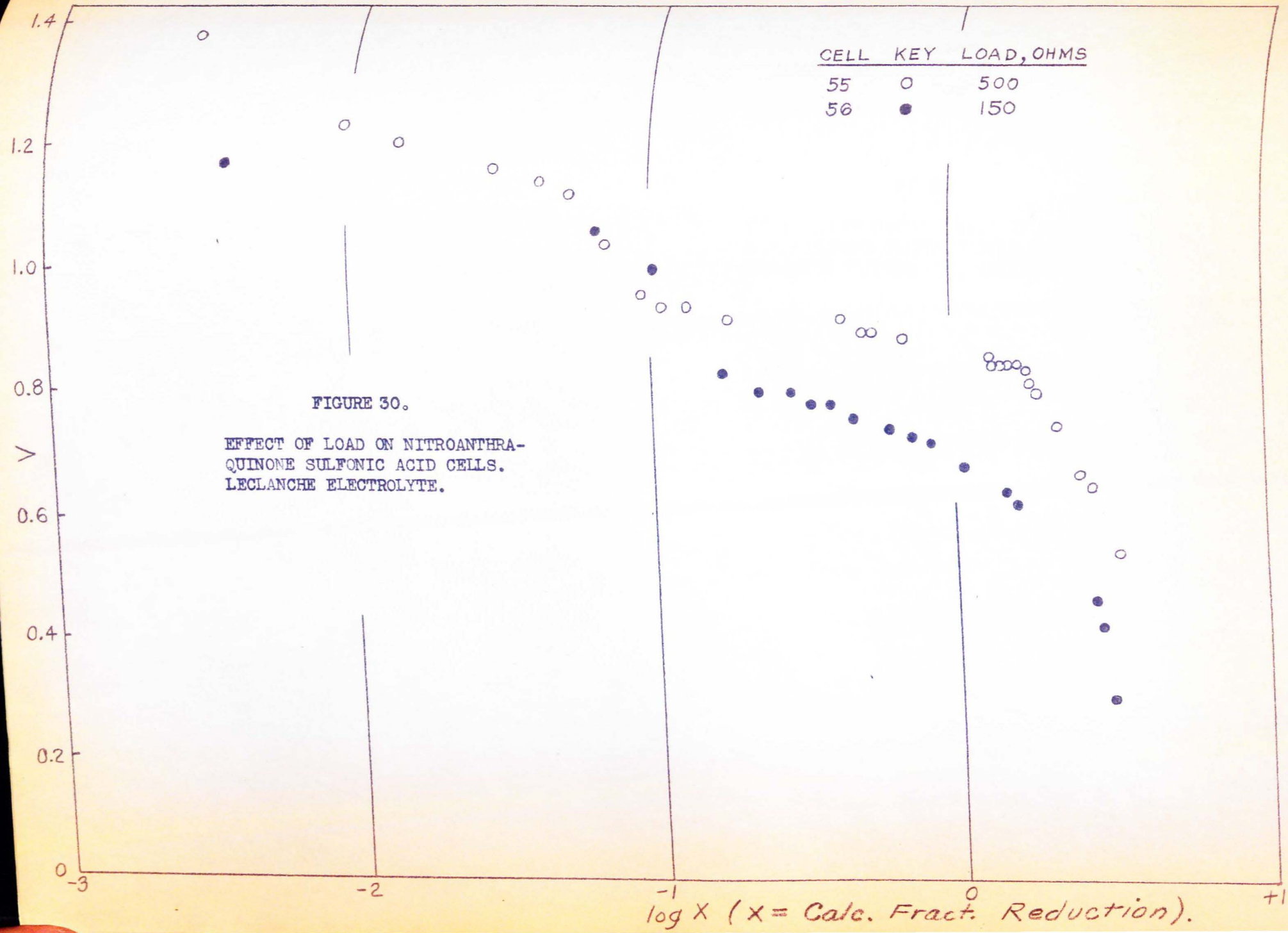
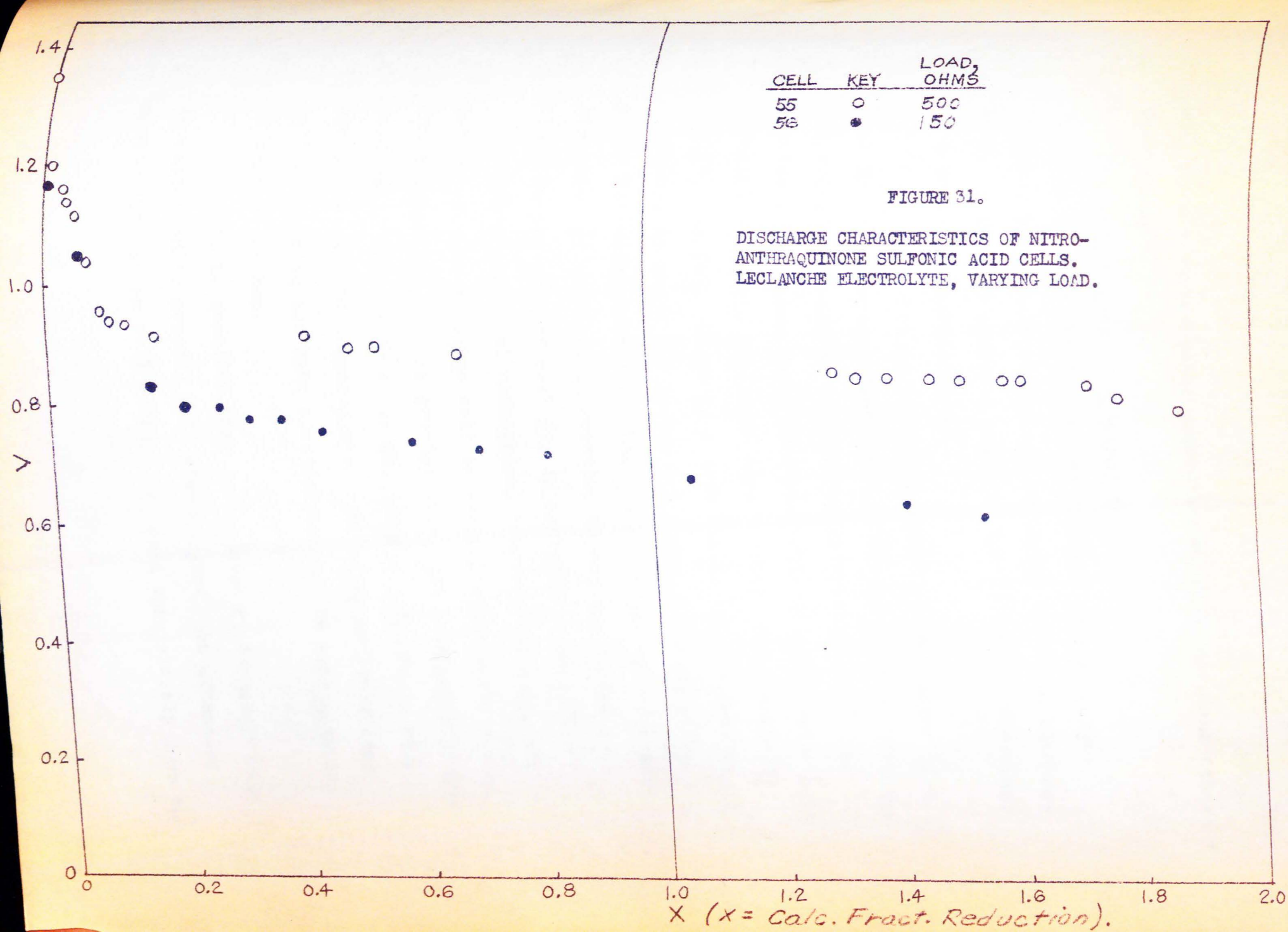


FIGURE 30.

EFFECT OF LOAD ON NITROANTHRAQUINONE SULFONIC ACID CELLS. LECLANCHE ELECTROLYTE.



CELL	KEY	LOAD, OHMS
55	○	500
56	●	150

FIGURE 31.

DISCHARGE CHARACTERISTICS OF NITRO-ANTHRAQUINONE SULFONIC ACID CELLS. LECLANCHE ELECTROLYTE, VARYING LOAD.

even with a severe load, regardless of what reactions actually take place.

6. Results in Caustic Electrolyte.

The results obtained using 20% NaOH as electrolyte contrast strikingly with those using the Leclanche electrolyte. Figure 33 compares cells 55 (acid) and 59 (alkaline) on a semi-logarithmic plot.

Cell 59, which is initially about 0.1 volt lower than cell 55 at a corresponding state of discharge, does not show the sudden drop-off to 0.9 volt starting at about 5% reduction which seems to be characteristic of cells using this depolarizer in the Leclanche electrolyte. (Note cells 37, 38, 55, and 56). There is a slow linear voltage drop which continues to about 1.0 on the X - scale, after which the slope increases sharply. There is no indication of a continuation of the initial reaction beyond the theoretical limit in the case of cell 59, in contrast to cell 55.

From a practical standpoint, however, the coulombic output of this alkaline cell is several times greater than the theoretical, and is greater than that obtained with the acid cell. Figure 34 shows the voltage - discharge time curve for cell 59 compared with that of an undepolarized cell containing the same electrolyte and the same quantity of cathode carbon.

It will be recalled that in the case of benzoquinone, investigated in several acid electrolytes, the effect of electrolyte pH on cell voltage followed very closely from the

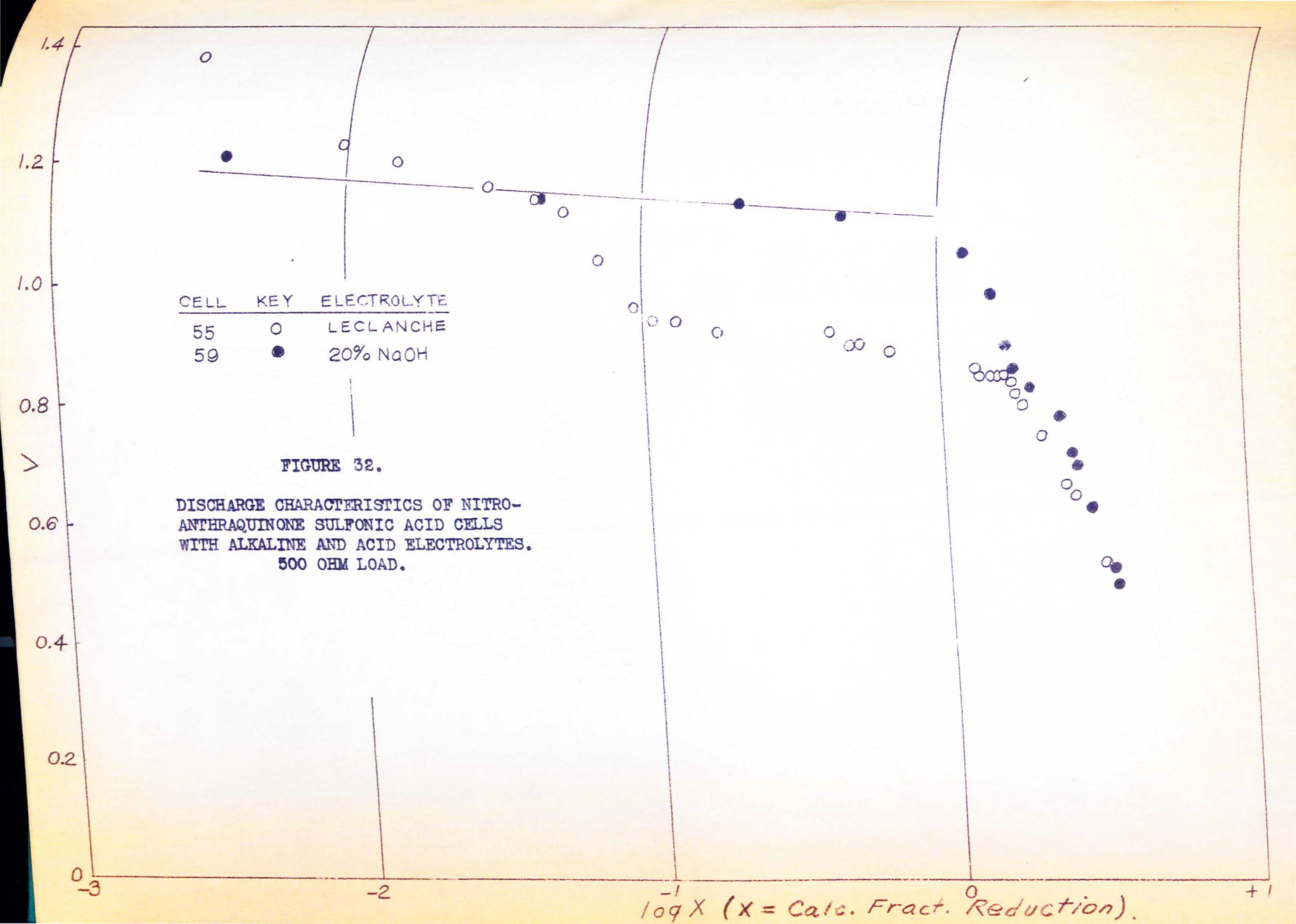


FIGURE 32.

DISCHARGE CHARACTERISTICS OF NITRO-ANTHRAQUINONE SULFONIC ACID CELLS WITH ALKALINE AND ACID ELECTROLYTES. 500 OHM LOAD.

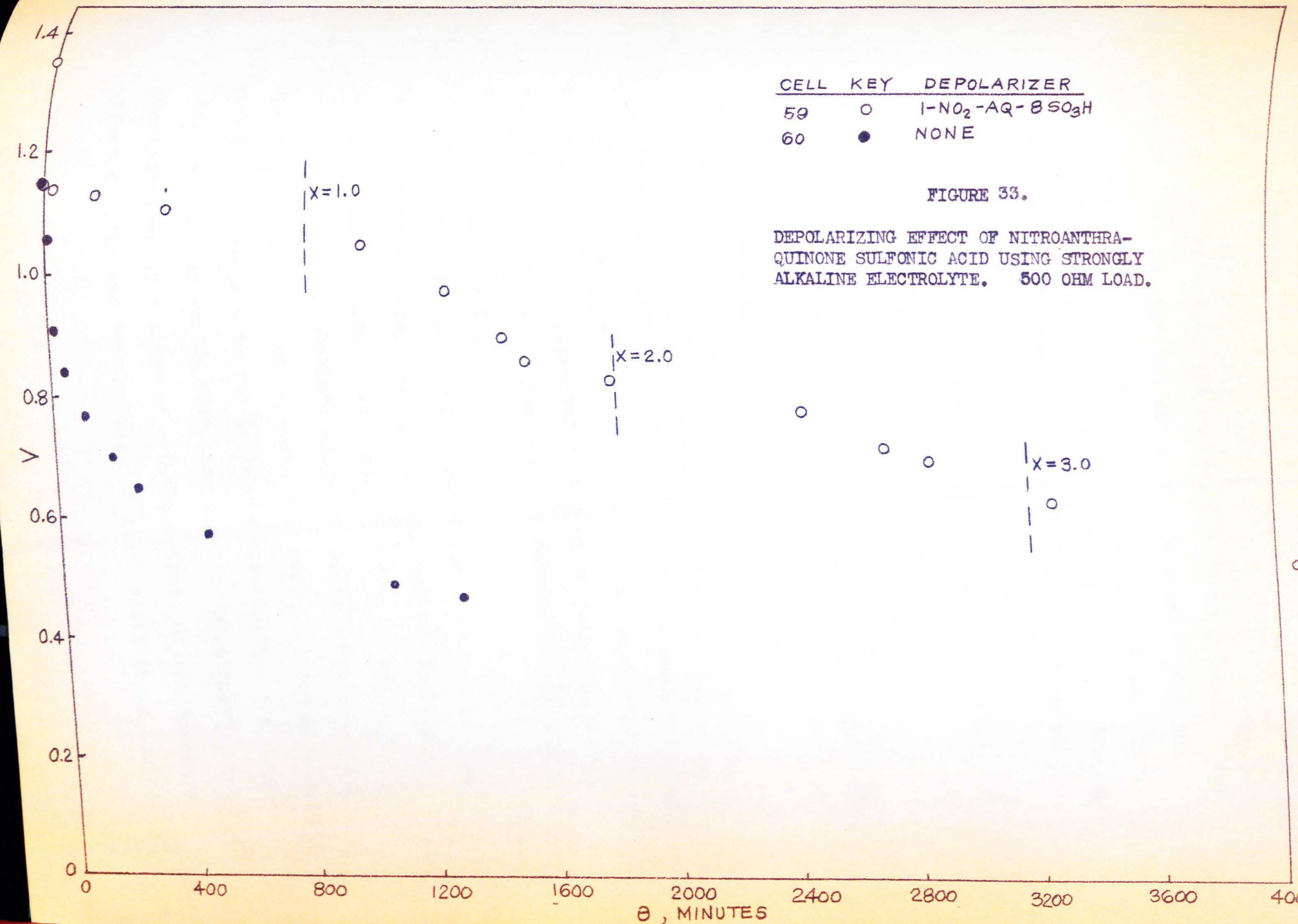


FIGURE 33.

DEPOLARIZING EFFECT OF NITROANTHRAQUINONE SULFONIC ACID USING STRONGLY ALKALINE ELECTROLYTE. 500 OHM LOAD.

theoretical effect on the potential of benzoquinone. This was as would be expected since in acid electrolytes the potential of zinc is very nearly independent of pH. In very alkaline electrolytes, however, zinc potential depends strongly on the pH. The following table summarizes the behavior of zinc.

TABLE VII

ELECTRODE REACTIONS OF ZINC

Reaction	pH	dE/dpH	Standard Potential
$Zn^{++} + 2e = Zn$	Low	0	-0.76 v.
$ZnO + H_2O + 2e = Zn + 2OH^-$	Intermediate	-0.06	
$ZnO_2^{=} + 2H_2O + 2e = Zn + 4OH^-$	High	-0.12	-2.15 v.

As a consequence of this property of the anode material, overall cell voltage does not suffer a net decrease on account of lowered cathode potential if the pH is raised to a high enough level. This is also what the results obtained with cells 55 and 59 show.

This alkaline electrolyte initially contained no zinc and it would therefore be anticipated that the increasing zincate concentration (also proportional to X) would in part determine the absolute slope of linear portions of the V - log X plot. It can be shown that where a slope of - 0.03 would be obtained with the Leclanche electrolyte, the same cathode reaction would, with this alkaline electrolyte, be characterized by a slope of - 0.06, because of the combined effect of zinc and depolarizer. A large shift in pH could

conceivably lead to a different cathode reaction, as well as a different anode reaction however.

The constant slope obtained over the whole discharge range with the alkaline electrolyte leads to the belief that a single cathode reaction takes place over this range. In contrast to this, there is, in the acid electrolyte, a marked change in voltage and slope at a characteristic fraction of the capacity. This change in the acid electrolyte might be interpreted as either a shift from one cathode reaction to another, or as a sudden shift in polarization. It seems unlikely that this shift would occur repeatedly (note cells 37, 38, 55 and 56) at a characteristic fraction of the capacity unless it were due to some chemical property of the depolarizer, rather than to, for example, the physical condition of the cathode surface.

It is postulated that an explanation of the experimental results may be as follows. In acid electrolytes the anthraquinone derivative is only able to sustain the original cathode reaction for a small fraction of the theoretical quinone capacity, after which increased polarization and decreased cathode potential have allowed the intervention of a second reaction. In the strongly alkaline electrolyte, the cathode reaction is less polarizable and is maintained through the theoretical capacity, after which the voltage drops until the second reaction can again occur, thus accounting for the greater practical capacity to the voltage cut-off obtained with the alkaline than with the acid

electrolyte. The exact nature of this "second reaction" is not known.

7. Effect of Atmosphere on Performance.

It was felt that the possible influence of air on cell voltage and capacity should be checked in connection with the results just discussed. Alkaline cells are more susceptible to the effects of air depolarization than acid cells, and, in fact, commercial air-depolarized cells use the same electrolyte (20% NaOH) used in this investigation. Accordingly, alkaline cells like cell 59 were constructed and discharged in atmospheres of pure nitrogen and pure oxygen. The results are shown in Figure 35. The cell which was run in pure oxygen, although corked, unfortunately underwent considerable corrosion at the zinc where it was exposed to the atmosphere and was also wet with electrolyte. As a consequence of this, contact was lost before the cell had been discharged as long as desired. The run did last sufficiently long, however, to show any effect of oxygen on discharge characteristics which might be observed up to the theoretical capacity of the cathode.

Within the limits of probable experimental error the points for the cells exposed to air, oxygen, and nitrogen all fall on the same straight line. This linear portion of the plot, which has a slope of - 0.03, continues to nearly 100% of the theoretical quinone capacity (log X = 0). After this point there is evidently a significant difference between the effects of the nitrogen and the air atmosphere.

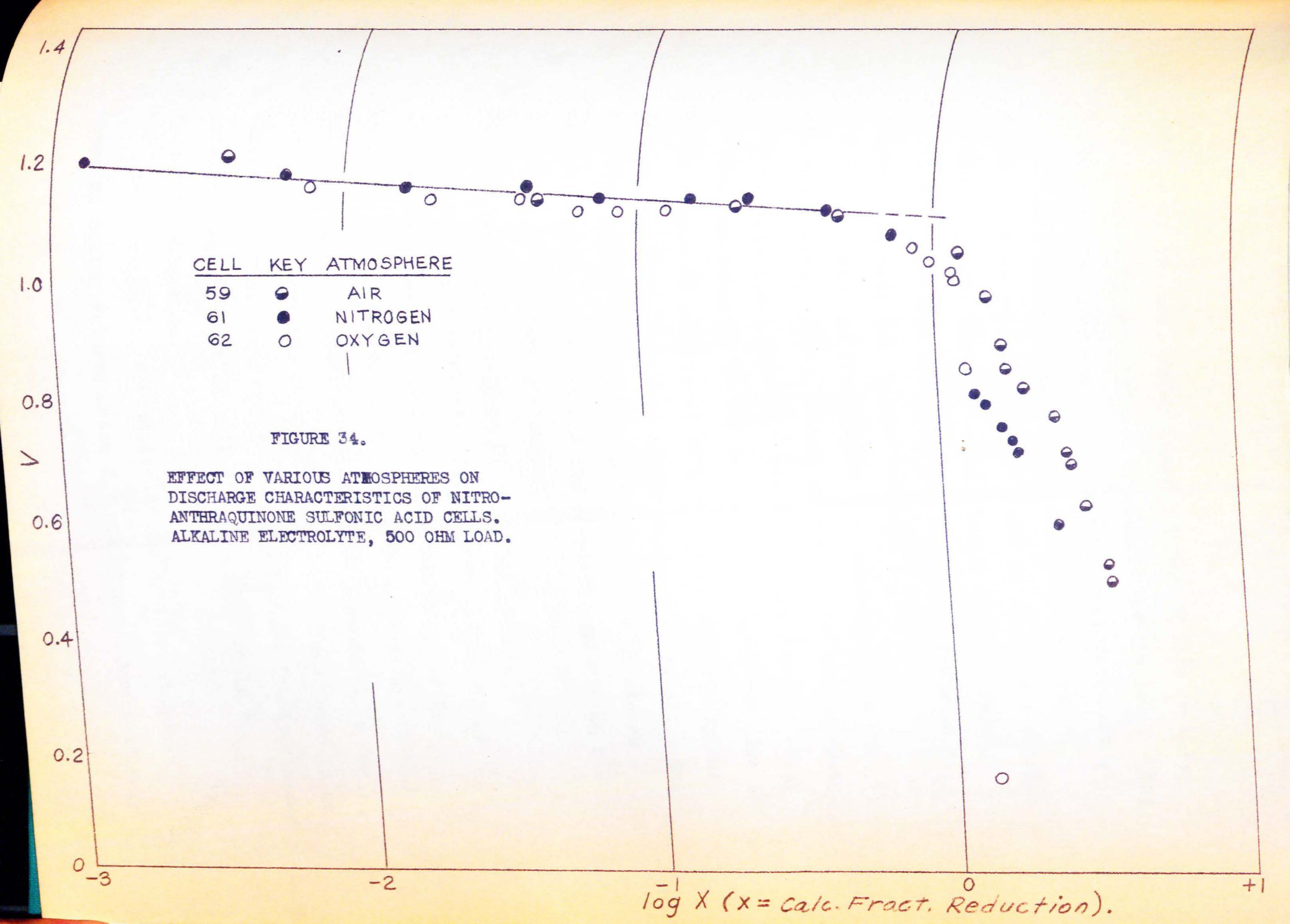


FIGURE 34.

EFFECT OF VARIOUS ATMOSPHERES ON DISCHARGE CHARACTERISTICS OF NITRO-ANTHRAQUINONE SULFONIC ACID CELLS. ALKALINE ELECTROLYTE, 500 OHM LOAD.

Because of the well established reaction of zinc in this electrolyte, it is difficult to account for the low V - log X slope in terms of the formation of anthrahydroquinone.

Figure 36 shows the results obtained when cell 61, which had been discharged first under nitrogen, was exposed to air overnight and then re-discharged under nitrogen. No steady discharge voltage which could be attributed to regenerated material is ever reached.

The conclusion from this set of experiments is that air has little, if any, effect on the initial cathode reaction of this alkaline cell. The difference shown to exist between the behavior of the depolarizer in acid and alkaline cells cannot be attributed to air, but is most likely due to the chemical properties of the depolarizer itself. The behavior of the alkaline cells in the region of excess capacity is more complex and the complete explanation for this is not immediately clear.

8. Catalyzed Anthraquinone Disodium Sulfonates.

As mentioned in Chapter IV, certain anthraquinone derivatives have been used as absorption reagents for hydrogen in gas analysis, including the nitroanthraquinone sulfonic acids. Anthraquinone disulfonic acids and other soluble anthraquinone derivatives have also been found to be effective. These reagents generally contain a finely divided catalytic metal, such as palladium, in addition to the reducible substance.

As it happened, a quantity of one of these reagents, based on Sodium anthraquinone 2,7 disulfonate, was available

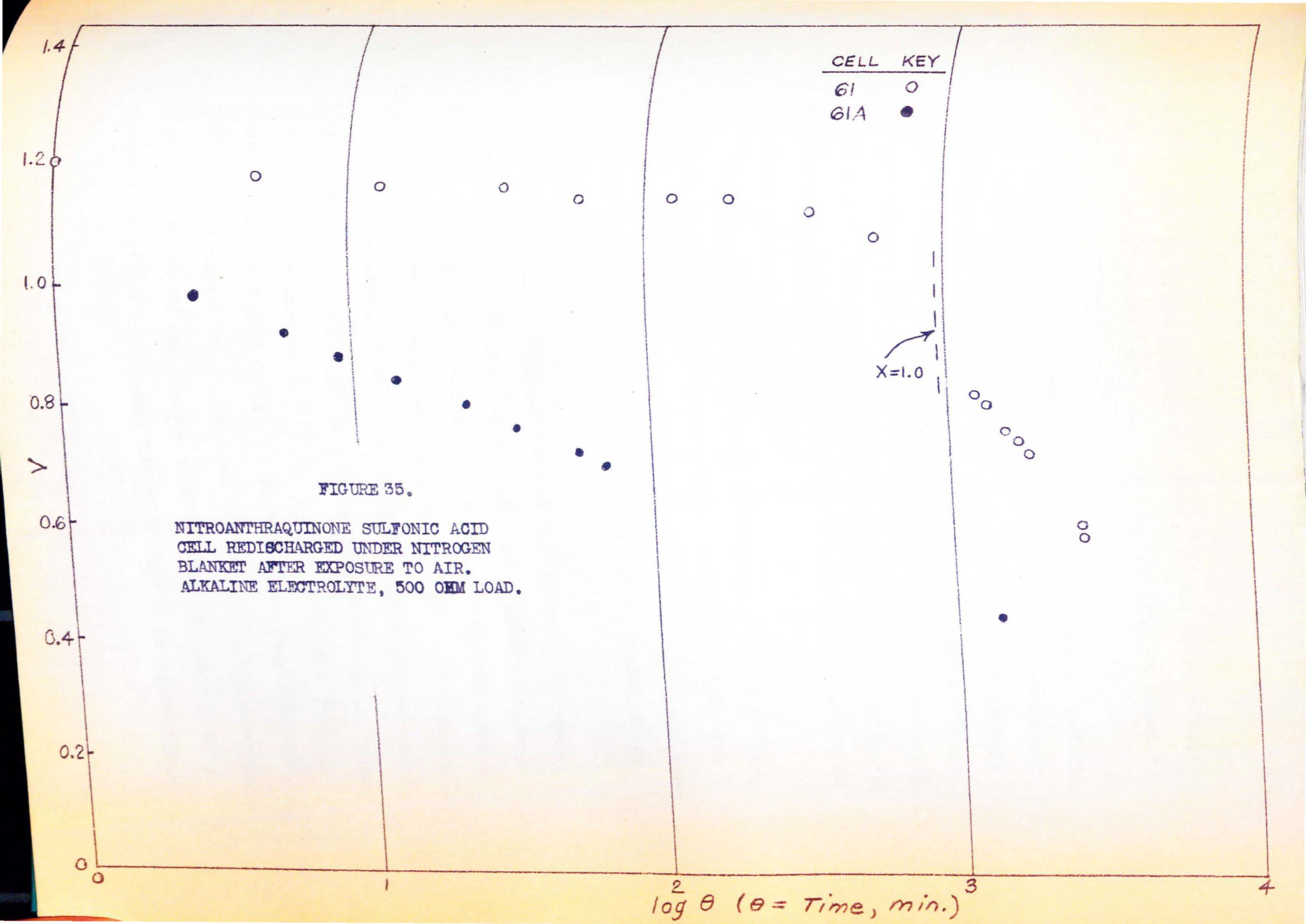


FIGURE 35.

NITROANTHRAQUINONE SULFONIC ACID
CELL REDISCHARGED UNDER NITROGEN
BLANKET AFTER EXPOSURE TO AIR.
ALKALINE ELECTROLYTE, 500 OHM LOAD.

to the writer of this dissertation. It was thought that this material might have depolarizing ability in primary cells.

This absorption reagent material was known to contain, in addition to the quinone, sodium protalbinate which was the protective colloid for the palladium, as well as substantial amounts of sodium carbonate. The exact analysis was not known, and therefore the actual coulombic capacity could not be calculated. The ratio of quinone to palladium was approximately 15 to 1, and the actual quinone content may have been as high as 80%.

In Figure 37 the indicated fractional reductions are, however, calculated on the arbitrary assumption that the depolarizing material was the pure quinone. Since the same material was used for all cells, they are compared on an identical basis.

Cell 65 likely was not purged sufficiently to remove all oxygen, as indicated by the initial slightly higher, but more rapidly decreasing, terminal voltage than cell 63.

Certain facts seem to stand out in the results of this set of experiments. First, this cell shows a substantially higher operating voltage when it is discharged in air than when it is discharged in nitrogen. Secondly, the initial slope of the V - log X plot is lower in air than in nitrogen. Third, this slope in air is also less than - 0.03, (actually - 0.013) which is the lowest possible for any conceivable quinone reaction (that when the electrolyte is nonvariant

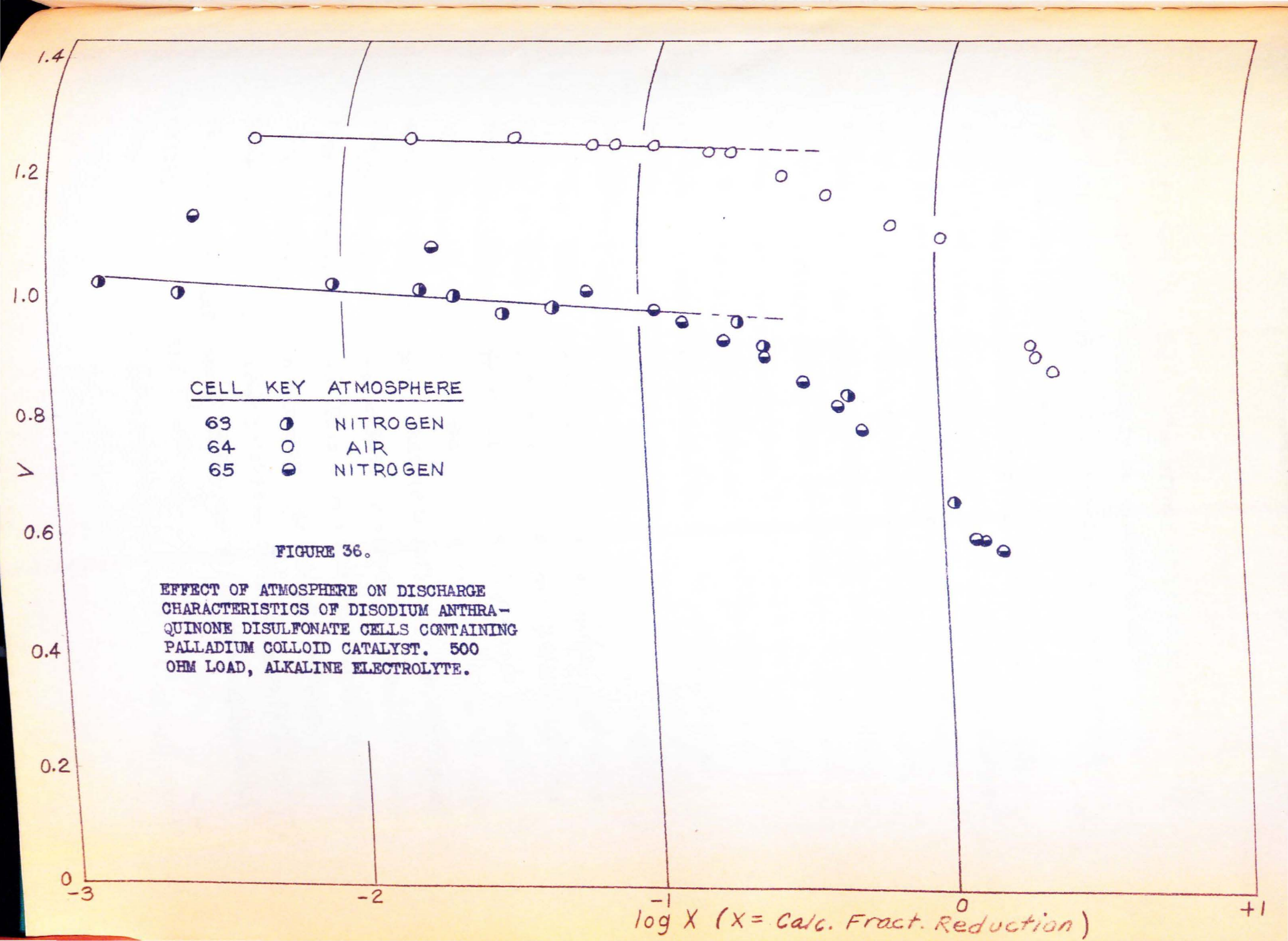


FIGURE 36.

EFFECT OF ATMOSPHERE ON DISCHARGE CHARACTERISTICS OF DISODIUM ANTHRAQUINONE DISULFONATE CELLS CONTAINING PALLADIUM COLLOID CATALYST. 500 OHM LOAD, ALKALINE ELECTROLYTE.

with respect to zinc). The effect of polarization on this slope could only reasonably be assumed to be to increase it rather than decrease it. The indicated slope for cell 63 (under nitrogen) is - 0.045.

An explanation which fits the observations for this cell composition is as follows: The catalyzed cathode is able to utilize air originally contained and also any diffusing into the cell to regenerate the quinone nearly as fast as it is reduced by discharge. Because of this, operating voltage is not only increased but is maintained through a higher capacity than is the case under nitrogen. This behavior is quite different from that obtained with the uncatalyzed nitro-derivative. It is postulated that the presence of the palladium colloid accounts for the sensitivity of cell 64 to oxygen.

Even though the results indicate effective utilization of air in this case, these cells were not designed to take full advantage of air diffusion. It is probable that the air initially present in the cell accounts for most of the effect. It would appear that if a cell were used which had a type of porous air-depolarizing carbon, continuous regeneration might take place. This type of carbon was not available to the writer, and in any event, it was not the objective here to develop an air-depolarized cell, but merely to determine the influence, if any, of air on the experimental cells.

9. Energy Output of Experimental Cells and Conclusions.

The energy output (net electrical work) of the various experimental cells is probably a better criterion of the overall effectiveness of the various depolarizers than either voltage or capacity alone.

Table VIII compares the performance of the various anthraquinones with the MnO_2 control cells. In general the average discharge voltages are slightly lower than those of benzoquinone and control cells discharged under comparable conditions. The effective coulombic capacities of the better cells are very high, however; not only higher than the control cells, but several times as high as calculated for the reduction of the quinone. The energy output (product of voltage and capacity) per gram of cathodic active material is therefore greater in some cases than that of MnO_2.

The catalyzed anthraquinone disodium sulfonate cell, when discharged in air, maintained a voltage as high as that of the MnO_2 cell through a coulombic capacity 1.38 times that of MnO_2. This capacity could very probably be increased considerably, perhaps indefinitely, if the optimum cell design utilizing an air-depolarizing carbon were used.

In the case of the nitroanthraquinone sulfonic acids it must be concluded that the results do not point to a single reaction of these compounds either in both electrolytes or over the whole discharge range in the acid cells. It should be mentioned as a possibility that the nitro group may

TABLE VIII. RELATIVE PERFORMANCE OF CONTROL AND ANTHRAQUINONE CELLS.

Cell	Cathode 2:1 Carbon:active mat'l. Depolarizer	grams a.m.	Electrolyte Comp.	ml.	Load Ohms	Coulombic Capacity* (amp-min per gram depolarizer) Theo.	Observed	Average Discharge Voltage*	Net Electrical Work* (watt-sec per gram depolarizer)	Remarks
4	MnO_2	0.458	L	6.0	100	18.5	10.6	1.03	655	Control
5	MnO_2	0.458	L	6.0	500	18.5	18.5	1.12	1240	Control
53	AQ	0.200	L	3.5	500	15.45	-	0.58	-	
39	AQ-α-SO_3K	0.202	L	3.0	500	9.88	0.52	0.910	28.4	
40	AQ-β-SO_3Na	0.202	L	3.0	500	10.35	0.14	0.845	7.1	
38	5-NO_2-AQ-1-SO_3H	0.202	L	3.0	500	9.65	21.3	0.828	1055	
37	1-NO_2-AQ-8-SO_3H	0.202	L	3.0	500	9.65	15.8	0.857	813	
55	ditto	0.200	L	3.5	500	9.65	20.8	0.872	1085	
56	ditto	0.200	L	3.5	150	9.65	5.10	0.854	261	
59	ditto	0.200	NaOH	3.5	500	9.65	25.1	0.975	1465	Air Atm.
61	ditto	0.200	NaOH	3.5	500	9.65	16.3	0.980	960	N_2 Atm.
62	ditto	0.200	NaOH	3.5	500	9.65	-	-	-	O_2 Atm.
63	2,7 AQ-di-SO_3Na	0.200#	NaOH	3.5	500	7.05##	5.25	0.975	307	N_2 Atm.
64	ditto	0.200	NaOH	3.5	500	7.05	25.5	1.11	1695	Air Atm.
65	ditto	0.200	NaOH	3.5	500	7.05	4.65	0.968	270	N_2 Atm.

Weight of reagent ## For pure quinone * To 0.75 volt cut-off.

have taken part in the cathode reactions. It cannot be asserted definitely that a reduction of this group took place, however, basing the conclusion on the available data.

A consideration of the theoretical characteristics (E - log X slope and capacity) of the possible reactions of this group, and comparison with observation, is not possible since the literature does not specifically treat the reduction of nitroquinones. For nitrobenzene there is indicated a complex stepwise reduction in which certain steps exhibit reversible potentials while other steps are irreversible. Also, the nature of the reduction products themselves are dependent on pH, current density, and the nature and history of the cathode surface. What the mutual effect of the quinone and nitro groupings might be, each undergoing reduction, is difficult to assess, having regard for the probable irreversible nature of the whole process.

It is clearly only possible to say that the results are not entirely consistent with the simple formation of the anthrahydroquinone in all cases, either from the viewpoint of the capacity obtained, or the slopes of the voltage-log capacity plots. Neither are they inconsistent with what is known of the reactions of substituent nitro groups.

Whatever the actual reactions, though, there is no doubt that high coulombic capacities are obtained with this depolarizer, the most favorable voltages (and also the highest effective capacities) being obtained with the alkaline cells.

CHAPTER X

SUMMARY AND CONCLUSIONS

1. General Behavior of Quinone Depolarizers.

The initial terminal voltages encountered with various zinc-unsubstituted quinone cells, when using an aqueous electrolyte, appear to follow from the order of standard potentials of the various quinones. Unsubstituted anthraquinone has essentially no depolarizing ability under the conditions investigated. The effect of ring substitution of the quinone is to markedly increase the terminal voltage obtained with the experimental cells over that obtained with the unsubstituted compound. Although the substituents investigated do, in fact, raise the standard potentials by small amounts, the effects on cell terminal voltage were much greater. When electrolytes containing substantial amounts of methanol were used less correspondence was noted between the standard potentials and cell voltage, certain compounds being affected much more than others. The effects due to ring substitution and electrolyte variations are attributed mainly to the corresponding changes in solubility, diffusivity, and reaction rates of the depolarizers, as it is shown that the observed effects cannot be due entirely to changes in the factors which influence the cathode potential, or to electrolyte resistivity.

2. Discharge Characteristics.

Certain of the cell combinations which appeared to justify further investigation, either for theoretical reasons or because the preliminary work indicated promising characteristics, were studied as to actual coulombic output to an arbitrary voltage cut-off. The data for the experimental cells was plotted in the form of cell terminal voltage vs. the calculated fractional reduction of the depolarizer, so that all compounds were compared on the basis of the utilization of their theoretical coulombic capacity. Cells containing different depolarizers, or different quantities of the same depolarizer are therefore compared on the same theoretical basis.

Both theory and preliminary investigation indicated that the benzoquinone-zinc couple would have a relatively high (1.20 volt observed) terminal voltage which could perhaps be maintained through 50% of the theoretical total capacity of the cathode. The highest utilization of benzoquinone actually obtained to the 0.75 volt cut-off was 28.9%. The effect of variations in electrolyte composition, cell construction, and discharge conditions was studied and it was concluded that side reactions of the quinone were very likely responsible for the low capacities obtained relative to the theoretical. It was postulated that auto-oxidation of the benzoquinone due to alkaline conditions at the cathode resulting from discharge itself might be a major factor.

Although unsubstituted and monosulfonated anthraquinone

showed little, if any, depolarizing ability, the nitroanthraquinone sulfonic acids showed good characteristics. In the Leclanche electrolyte-containing cells terminal voltages of 0.85 to 0.90 volt were maintained, after a quick initial drop of about 0.4 volt, through coulombic capacities greater than could be accounted for on the basis of the reduction of the quinone. In alkaline electrolytes, on the other hand, there was obtained a slightly lower initial voltage (about 1.2 volt) which was maintained with only a slight drop up to approximately 100% of the expected capacity for the reduction of the quinone, after which a somewhat more rapid voltage drop set in. (From a practical standpoint, however, several times the theoretical capacity of the quinone is obtained to the 0.75 volt cut-off with the alkaline cells). It was shown experimentally that the results obtained with the nitro-compounds using alkaline electrolytes do not depend on the presence or absence of air, at least until the theoretical capacity is exceeded. The results just discussed were analyzed further, by replotting the data in the form V - log X from which it was hoped that any changes in the cathode reactions could be observed. This method of analysis indicated that the reactions of the nitroanthraquinone differ in some fundamental way in acid and alkaline electrolytes. In neither electrolyte were all results consistent with the hypothesis that the cathode reaction consists simply of the formation of the anthrahydroquinone.

The possibility of a reduction of the nitro- group of

this depolarizer was considered, but it was not possible to state definitely that such a reaction took place.

The depolarizer giving the highest output was an anthraquinone disulfonate catalyzed with a palladium colloid when discharged in air. It was shown that the good performance of this cell depended on the presence of air and it was postulated that continuous or, at least, semi-continuous regeneration of the active material might be possible if an air-depolarizing carbon were used as the cathode metal.

3. Net Electrical Work.

The net electrical work (which must strictly be attributed to the cell as a whole) was calculated for each cell and reduced to watt-seconds per gram of depolarizer. On this basis the energy output is equivalent to the product of cathode capacity per gram of depolarizer and the average cell discharge voltage obtained using a zinc anode under the stated conditions. This quantity will not be a constant for an individual depolarizer, but depends on cell composition, construction and discharge conditions. The better cell combinations are, nevertheless, identified by their higher energy outputs.

The highest energy output of a benzoquinone cell was less than half that of an MnO_2 cell discharged under the same conditions. With the better anthraquinone cells the performance of MnO_2 was exceeded.

APPENDIX

CELL 4

MANGANESE DIOXIDE

Depolarizer: 0.458 gms.; Carbon: 0.916 gms.
Electrolyte: L, 6.0 ml.
Load: 100 ohms.
Initial O.C.V.: 1.43

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
-	0	1.14	0.0016
1.37	1	2.25	0.0032
1.36	2	3.36	0.0049
1.35	3	4.45	0.0065
1.35	4	5.53	0.0081
1.34	5	6.60	0.0096
1.33	6	7.68	0.0112
1.33	7	8.70	0.013
1.32	8	12.8	0.019
1.31	12	19.9	0.029
1.28	19	24.9	0.037
1.26	24	27.6	0.042
1.25	27	32.2	0.049
1.24	32	37.8	0.058
1.23	38	48.0	0.065
1.21	43	51.0	0.079
1.21	53	58.7	0.092
1.20	62	66.0	0.104
1.20	70	74.5	0.118
1.18	80	82.5	0.132
1.16	90	90.5	0.145
1.14	100	100	0.163
1.12	113	106	0.173
1.11	121	114	0.188
1.09	132	123	0.205
1.08	145	130	0.216
1.06	154	174	0.302
0.97	226	192	0.341
0.94	260	213	0.373
0.90	301	234	0.422
0.88	347	243	0.442
0.88	366	* 300	* 0.574
* 0.75	-	410	0.980
0.35	1105		

* Calculated.

CELL 5

MANGANESE DIOXIDE

Depolarizer: 0.458 gms.; Carbon: 0.916 gms.
Electrolyte: L, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.43

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.42	0	0.242	0.000336
1.42	1	0.485	0.000673
1.42	2	0.970	0.00135
1.42	4	2.52	0.00350
1.41	9	3.46	0.00473
1.40	13	6.48	0.00912
1.38	26	9.00	0.0127
1.36	37	11.8	0.0168
1.35	50	13.5	0.0194
1.34	58	15.5	0.0223
1.33	67	23.7	0.0347
1.30	107	28.7	0.0423
1.29	132	30.9	0.0457
1.28	143	33.5	0.0497
1.28	156	35.5	0.0527
1.28	166	61.0	0.0930
1.24	300	84.3	0.130
1.23	427	92.5	0.143
1.23	472	237	0.380
1.18	1300	290	0.473
1.11	1640	426	0.725
1.02	2640	458	0.787
1.00	2900	* 570	* 1.00
* 0.75	-		

* Calculated.

CELL 9

ANTHRAQUINONE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: B, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.70

V Volts	θ Min.
-	0
0.48	0.5
0.49	1
0.49	2
0.48	3
0.44	7
0.42	9
0.40	11
0.37	15
0.36	17
0.36	18
0.35	20
0.33	24
0.32	28
0.30	33
0.28	37
0.27	43
0.25	48
0.24	52
0.24	55
0.23	68
0.19	79
0.17	93
0.16	102
0.15	115
0.13	130
0.13	132

CELL 10

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: B, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.32

V Volts	θ Min.
-	0
1.02	1.5
1.00	3
0.99	11
0.99	17
0.98	29
0.97	43
0.97	52
0.95	66
0.88	159

CELL 11

BENZOQUINONE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: B, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.77

V Volts	θ Min.
0	-
0.60	1
0.60	4
0.56	14
0.53	21
0.50	30
0.48	33
0.47	38
0.46	45
0.42	66
0.40	86
0.40	93
0.32	197
0.22	335

CELL 15

MANGANESE DIOXIDE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: B, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.18

V Volts	θ Min.
0.84	0
0.76	5
0.70	30
0.66	48
0.61	160

CELL 16

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: A, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.60

V Volts	θ Min.
1.50	0
1.50	2
1.50	15
1.44	33
1.42	65
1.15	280
0.60	720

CELL 17

ANTHRAQUINONE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: A, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.85

V Volts	θ Min.
0.83	0
0.70	4
0.61	10
0.54	17
0.48	30
0.42	60
0.41	245
0.40	320
0.37	1422

CELL 18

POTASSIUM ANTHRAQUINONE-ALPHA-SULFONATE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: A, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.94.

V Volts	θ Min.
0.87	0
0.83	1
0.78	4
0.74	6
0.64	12
0.52	21
0.48	30
0.48	37
0.47	60
0.46	104
0.45	161
0.42	219
0.36	1210

CELL 19

POTASSIUM 1-NITROANTHRAQUINONE-8-SULFONATE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: A, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.90

V Volts	θ Min.
0.85	0
0.80	2
0.74	4
0.70	8
0.68	17
0.67	24
0.64	63
0.63	107
0.62	150
0.61	347

CELL 20

POTASSIUM ANTHRAQUINONE-ALPHA-SULFONATE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: L, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.06

V Volts	θ Min.
1.04	0
0.95	1
0.88	2
0.84	3
0.81	4
0.76	8
0.68	15
0.65	27
0.62	41
0.62	51
0.58	73
0.56	160
0.54	360
0.54	450
0.54	570

CELL 21

1,2 NAPHTHOQUINONE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: L, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.99

V Volts	θ Min.
0.97	0
0.95	8
0.94	15
0.92	48
0.92	57
0.90	77
0.88	103
0.84	150
0.81	210
0.78	279
0.75	390
0.57	1440

CELL 22

1,4 NAPHTHOQUINONE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: L, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.90

V Volts	θ Min.
0.89	0
0.88	1
0.87	6
0.86	20
0.85	70
0.85	90
0.85	200
0.84	265
0.11	46 hrs.
Put on open circuit	
0.11	0
0.22	30
0.40	200
0.48	315
0.50	360
0.80	54 hrs.
0.84	73.5 hrs.
Redischarge of Cell	
0.76	0
0.73	1
0.72	2
0.70	6
0.55	34
0.38	71
0.19	130

CELL 23

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: L, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.45

V Volts	θ Min.
-	0
1.30	1
1.26	3
1.22	6
0.88	38
0.84	64
0.73	1130

Cell recharged at 4.0 milliamperes for three hours, then redischarged as follows:

V	θ
1.37	0
1.31	1
1.25	3
1.20	5
0.97	21
0.94	35
0.88	48
0.78	109
0.77	127
0.76	162
0.70	1515

Cell again recharged at 4.0 milliamperes, but for 42.5 hours, and redischarged as follows:

V	θ
1.34	0
1.27	0.5
1.21	1
1.20	1.5
1.16	2
1.14	2.5
1.12	3
1.10	3.5

CELL 23 CONTINUED

V Volts	θ Min.
1.09	4
1.08	5
1.06	6
1.04	8
1.03	9
1.02	11
1.00	15
0.96	34
0.89	71
0.80	117
0.76	156
0.60	346
0.45	1815

CELL 24

2,5 DIPHENYL PARABENZOQUINONE

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: L, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.14

V Volts	θ Min.
1.12	0
1.03	4
0.99	20
0.96	38
0.92	53
0.62	76
0.54	89
0.51	113

CELL 25

2:7 ANTHRAQUINONE DISULFONIC ACID

Depolarizer: 0.46 gms.; Carbon: 0.92 gms.
Electrolyte: L, 6.0 ml.
Load: 500 ohms.
Initial O.C.V.: 0.95

V Volts	θ Min.
0.90	0
0.78	4
0.72	8
0.69	23
0.68	33
0.67	49
0.66	84
0.65	118
0.62	320

CELL 32

BENZOQUINONE

Depolarizer: 0.207 gms.; Carbon: 0.414 gms.
Electrolyte: L, 3.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.26

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.25	0	0.18	0.000405
1.24	1	0.37	0.000808
1.24	2	0.73	0.00161
1.23	4	2.17	0.00480
1.22	12	2.89	0.00636
1.22	16	6.05	0.0135
1.20	34	7.42	0.0166
1.20	42	10.7	0.0240
1.20	61	14.5	0.0325
1.20	83	17.6	0.0395
1.20	101	26.2	0.0588
1.20	150	31.0	0.0697
1.19	178	32.0	0.0721
1.18	184	37.2	0.0843
1.16	216	38.8	0.0880
1.14	226	40.2	0.0910
1.12	235	41.2	0.0937
1.10	242	43.4	0.0999
1.08	258	45.6	0.105
1.07	273	49.0	0.113
1.06	298	51.2	0.119
1.06	315	55.5	0.130
1.04	348	68.5	0.165
1.02	450	80.8	0.198
1.00	551	93.0	0.232
0.90	660	97.2	0.243
0.86	708	*112	* 0.289
* 0.75	-	140	0.406
0.54	1423		

* Calculated

CELL 34

BENZOQUINONE

Depolarizer: 0.202 gms.; Carbon: 0.404 gms.
Electrolyte: L, 3.0 ml.
Load: 75 ohms.
Initial O.C.V.: 1.34

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.15	0	1.01	0.00249
1.10	1	1.98	0.00491
1.09	2	4.81	0.0121
1.08	5	15.2	0.0380
1.05	16	20.0	0.0519
1.04	22	33.3	0.0872
1.02	37.5	43.9	0.115
0.96	50	48.8	0.132
0.94	58	64.0	0.179
0.84	82	75.2	0.216
0.82	102	80.0	0.234
0.78	111	* 82.1	* 0.239
* 0.75	- -	87.2	0.261
0.68	128	98.5	0.321
0.40	178		

* Calculated

CELL 35

BENZOQUINONE

Depolarizer: 0.202 gms.; Carbon: 0.101 gms.
Electrolyte: L, 3.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.25

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.23	0	0.18	0.000408
1.22	1	0.53	0.00122
1.20	3	1.05	0.00242
1.20	6	4.45	0.0104
1.18	26	6.00	0.0139
1.18	35	8.65	0.0202
1.18	51	14.8	0.0348
1.17	88	17.6	0.0414
1.17	105	23.0	0.0546
1.16	139	40.3	0.0974
1.09	253	42.5	0.103
1.08	268	44.2	0.107
1.06	280	45.4	0.110
1.06	289	47.5	0.116
1.04	305	51.7	0.127
1.02	338	53.0	0.130
1.02	348	55.1	0.137
1.02	366	71.5	0.182
0.99	500	83.0	0.215
0.92	605	* 96.6	* 0.272
* 0.75	-	123	0.382
0.42	1350		

* Calculated

CELL 36

BENZOQUINONE

Depolarizer: 0.202 gms.; Carbon: 0.101 gms.
Electrolyte: L, 3.0 ml.
Load: 150 ohms.
Initial O.C.V.: 1.26

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.16	0	1.05	0.00253
1.13	2	3.55	0.00875
1.11	7	6.95	0.0173
1.09	14	14.0	0.0352
1.07	29	21.1	0.0539
1.04	45	26.2	0.0676
1.03	57	27.9	0.0721
1.01	61	38.8	0.103
0.97	89	49.6	0.134
0.91	119	51.3	0.139
0.90	125	60.7	0.170
0.84	156	63.7	0.179
0.81	166	* 68.3	* 0.198
* 0.75	-	86.0	0.272
0.52	293		

* Calculated

CELL 37

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.202 gms.; Carbon: 0.404 gms.
Electrolyte: L, 3.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.44

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.41	0	0.23	0.00144
1.38	1	0.55	0.00413
1.30	2.5	1.04	0.00680
1.24	5	1.50	0.0100
1.22	7.5	2.79	0.0193
1.18	15	3.54	0.0254
1.18	20	5.19	0.0375
1.16	30	6.60	0.0482
1.14	39	7.45	0.0547
1.13	44.5	14	0.109
0.92	96	15.2	0.121
0.92	108	16.4	0.133
0.90	121	17.3	0.141
0.90	130	18.9	0.156
0.90	146	19.5	0.162
0.90	152	20.3	0.170
0.89	161	21.6	0.183
0.88	175	22.3	0.189
0.88	182	23.1	0.198
0.88	191	23.8	0.205
0.88	199	24.9	0.214
0.88	210	26.2	0.228
0.88	225	28.1	0.246
0.88	245	30.1	0.266
0.88	267	33.3	0.297
0.88	301	35.4	0.318
0.87	324	37.7	0.341
0.87	349	40.4	0.368
0.87	379	49.5	0.459
0.87	480	57.3	0.538
0.86	569	63.3	0.597
0.86	636	102	1.01
0.84	1082	125	1.22
0.83	1355	144	1.43
0.80	1600	162	1.62
0.76	1845	* 164	* 1.64
* 0.75	-	178	1.83
0.65	2120	236	2.65
0.55	3450		

* Calculated

CELL 38

5-NITROANTHRAQUINONE-1-SULFONIC ACID

Depolarizer: 0.202 gms.; Carbon: 0.404 gms.
Electrolyte: L, 3.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.42

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.41	0	2.16	0.0149
1.20	11	4.42	0.0307
1.16	24	5.55	0.0390
1.14	31	7.30	0.0528
1.08	43	8.37	0.0615
1.04	51	9.42	0.0707
0.94	62	11.8	0.0928
0.92	85	13.1	0.104
0.90	97	14.9	0.122
0.90	116	16.4	0.137
0.90	132	19.2	0.163
0.90	160	28.9	0.258
0.88	263	42.2	0.387
0.89	404	90.7	0.861
0.88	922	139	1.34
0.88	1440	154	1.48
0.87	1605	* 213	* 2.20
* 0.75	-	315	3.46
0.54	4320		

* Calculated

CELL 39

POTASSIUM ANTHRAQUINONE-ALPHA-SULFONATE

Depolarizer: 0.202 gms.; Carbon: 0.404 gms.
Electrolyte: L, 3.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.33

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.31	0	0.195	0.00129
1.24	1	0.376	0.00252
1.21	2	0.542	0.00372
1.15	3	0.845	0.00598
1.09	5	1.12	0.00815
1.06	7	1.52	0.0113
1.04	10	2.96	0.0234
0.96	22	3.98	0.0328
0.89	32	5.25	0.0455
0.78	47	* 5.93	* 0.0525
* 0.75	-	6.15	0.0555
0.74	60	7.77	0.0745
0.70	86	9.93	0.101
0.68	124	11.9	0.125
0.66	160	21.5	0.250
0.63	352	34.8	0.427
0.61	640	59.4	0.780
0.58	1220	72.3	0.970
0.56	1550	84.5	1.16
0.54	1885	105	1.54
0.36	2730		

* Calculated.

CELL 40

SODIUM ANTHRAQUINONE-BETA-SULFONATE

Depolarizer: 0.202 gms.; Carbon: 0.404 gms.
Electrolyte: L, 3.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.10

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.09	0	0.197	0.00150
1.00	1.5	0.365	0.00290
0.94	3	0.565	0.00464
0.88	5	* 1.43	* 0.0133
* 0.75	-	1.57	0.0147
0.73	18	2.48	0.0248
0.68	33	3.11	0.0325
0.66	45	7.85	0.0925
0.60	144	14.6	0.184
0.58	307	38.2	0.510
0.57	899	47.5	0.643
0.57	1140	58.2	0.798
0.54	1430	70.2	0.977
0.53	1780	93.5	1.385
0.38	2715		

* Calculated.

CELL 42

UNDEPOLARIZED

Depolarizer: 0.0 gms.; Carbon: 0.404 gms.
Electrolyte: L, 3.0 ml.
Load: 500 ohms.
Initial O.C.V.: 1.12

V Volts	θ Min.
	0
1.11	1
1.06	2
1.03	4
0.98	5
0.96	7
0.92	11
0.86	16
0.80	22
0.75	26
0.73	31
0.70	40
0.68	51
0.66	70
0.63	85
0.62	212
0.60	378
0.58	1145
0.54	1235
0.53	

CELL 43

BENZOQUINONE

Depolarizer: 0.201 gms.; Carbon: 0.403 gms.
Electrolyte: L, 3.0 ml.
Load: 150 ohms.
Initial O.C.V.: 1.24

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.22	0	0.588	0.00134
1.20	1	1.16	0.00268
1.18	2	1.72	0.00400
1.18	3	2.54	0.00595
1.17	4.5	4.44	0.0105
1.16	8	7.12	0.0169
1.16	13	15.1	0.0362
1.15	28	18.8	0.0452
1.15	35	24.1	0.0580
1.14	45	37.9	0.0925
1.08	73	61.6	0.157
0.98	129	72.0	0.186
0.96	156	78.4	0.205
0.95	174	82.5	0.218
0.90	186	84.5	0.223
0.86	192	* 93.7	* 0.250
* 0.75	-	104.5	0.297
0.62	283	107.2	0.311
0.58	303	110.4	0.328
0.54	330	112	0.335
0.53	344		

* Calculated.

CELL 44

BENZOQUINONE

Depolarizer: 0.201 gms.; Carbon: 1.813 gms.
Electrolyte: L, 5.0 ml.
Load: 150 ohms.
Initial O.C.V.: 1.26

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.24	0	0.612	0.00142
1.23	1	1.51	0.00343
1.22	2.5	3.00	0.00679
1.22	5	8.28	0.0137
1.20	14	11.7	0.0268
1.18	20	17.7	0.0416
1.16	31	20.3	0.0484
1.14	36	25.4	0.0632
1.12	48	47.6	0.117
1.04	93	58.4	0.146
1.02	119	66.0	0.167
0.98	138	68.4	0.174
0.96	144	71.2	0.182
0.92	152	74.0	0.191
0.88	161	* 88.1	* 0.240
* 0.75	-	96.8	0.272
0.67	255	108.3	0.324
0.58	330	119	0.379
0.52	420	164	0.700
0.25	1166		

* Calculated.

CELL 45

BENZOQUINONE

Depolarizer: 0.403 gms.; Carbon: 1.813 gms.
Electrolyte: L, 5.0 ml.
Load: 150 ohms.
Initial O.C.V.: 1.27

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.24	0	0.608	0.000703
1.23	1	1.21	0.00148
1.23	2	1.82	0.00212
1.22	3	3.60	0.00400
1.22	6	6.57	0.00752
1.21	11	11.2	0.0130
1.20	19	14.7	0.0171
1.20	25	19.3	0.0221
1.20	33	25.6	0.0295
1.19	44	32.8	0.0377
1.18	57	40	0.0472
1.18	70	45.6	0.0535
1.18	80	52.4	0.0610
1.17	92	57.6	0.0684
1.16	102	62.5	0.0728
1.16	111	68.4	0.0803
1.14	122	80.4	0.0951
1.10	146	86	0.103
1.08	158	92.5	0.110
1.06	172	97.5	0.117
1.05	183	104.3	0.127
1.04	199	110.3	0.135
1.03	213	117.5	0.144
1.02	230	122	0.1505
1.02	241	127.5	0.158
1.01	255	138	0.173
1.00	280	144	0.181
0.98	295	149.5	0.189
0.98	310	186	0.244
0.81	422	187	0.247
0.80	427	* 194	* 0.249
* 0.75	-	203	0.278
0.68	502	215	0.304
0.63	575	228	0.333
0.56	663		

*Calculated.

CELL 46

BENZOQUINONE

Depolarizer: 0.604 gms.; Carbon: 1.813 gms.
Electrolyte: L, 5.0 ml.
Load: 150 ohms.
Initial O.C.V.: 1.30

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.26	0	0.62	0.000455
1.24	1	1.83	0.00149
1.22	3	3.02	0.00230
1.22	5	4.76	0.00358
1.21	8	8.85	0.00680
1.20	15	12.9	0.00983
1.20	22	14.2	0.0115
1.20	25	18.0	0.0141
1.20	31	20.3	0.0156
1.20	35	23.3	0.0184
1.20	40	26.1	0.0200
1.19	45	28.9	0.0219
1.19	50	34.6	0.0270
1.19	60	39.6	0.0308
1.18	69	43.0	0.0333
1.18	75	45.8	0.0363
1.18	80	49.7	0.0388
1.18	87	54.8	0.0427
1.18	96	59.7	0.0457
1.18	105	62.5	0.0492
1.18	110	71.4	0.0564
1.18	126	91.0	0.0705
1.16	162	102	0.0801
1.15	182	105	0.0826
1.14	188	112.5	0.0889
1.12	203	116	0.0923
1.12	210	120	0.0950
1.10	218	127	0.101
1.08	231	134	0.107
1.06	246	171	0.138
1.03	330	177	0.145
1.02	345	195	0.161
1.00	387	200	0.166
1.00	402	205	0.171
1.00	415	224	0.189
0.97	464		

CELL 46 (CONT'D)

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
0.95	479	230	0.194
0.89	508	240	0.204
0.83	559	255	0.221
* 0.75	-	* 278	* 0.250
0.40	1399	381	0.412
0.38	1430	384	0.416
0.37	1445	385	0.418

* Calculated.

CELL 47

QUINHYDRONE

Depolarizer: 0.210 gms.; Carbon: 0.420 gms.
Electrolyte: L, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.10

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.09	0	0.142	0.000705
1.08	1	0.421	0.00210
1.08	3	0.562	0.00281
1.08	4	1.25	0.00630
1.07	9	2.08	0.0104
1.06	15	3.15	0.0164
1.06	23	4.23	0.0218
1.05	31	5.14	0.0263
1.04	38	6.05	0.0318
1.04	45	6.95	0.036
1.04	52	8.4	0.0433
1.04	63	9.8	0.0502
1.03	74	11.6	0.0594
1.02	88	12.6	0.0650
1.02	96	14.2	0.0741
1.02	109	15.7	0.0825
1.02	121	17.1	0.0890
1.01	132	18.5	0.0971
1.00	144	19.6	0.103
1.00	153	20.8	0.109
1.00	163	22.5	0.118
1.00	177	23.4	0.123
1.00	185	24.1	0.127
1.00	191	25.2	0.133
1.00	200	26.7	0.141
1.00	212	27.8	0.147
1.00	221	29.2	0.155
1.00	233	30.8	0.163
1.00	246	33.4	0.177
0.99	268	35.5	0.189
0.99	286	38.1	0.204
0.98	309	41.3	0.228
0.98	337	42.6	0.236
0.98	349	55.1	0.304
0.98	457	59.1	0.327
0.98	492		
0.97			

CELL 47 (CONT'D)

QUINHYDRONE

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		61.1	0.337
0.97	510	63.5	0.351
0.96	532	64.8	0.358
0.96	543	71.0	0.393
0.94	600	72.3	0.402
0.93	613	73.7	0.408
0.92	625	77.3	0.430
0.88	663	* 93.0	* 0.55
* 0.75	-	117	0.731
0.55	1311	121	0.768
0.50	1415		

* Calculated

CELL 48

BENZOQUINONE

Depolarizer: 0.210 gms.; Carbon: 0.420 gms.
Electrolyte: Sat'd. NH_4Cl, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.22

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.20	0	0.171	0.000380
1.18	1	0.336	0.000757
1.17	2	0.500	0.00133
1.16	3	0.661	0.00150
1.16	4	1.15	0.00261
1.16	7	1.47	0.00335
1.16	9	2.43	0.00557
1.15	15	3.54	0.00812
1.14	22	4.32	0.00993
1.14	27	8.69	0.0201
1.14	55	9.62	0.0223
1.14	61	10.6	0.0241
1.13	66	11.9	0.0273
1.13	75	13.6	0.0313
1.13	86	15.6	0.0354
1.12	99	19.2	0.0447
1.12	123	21.6	0.0504
1.11	139	22.8	0.0533
1.11	147	24.6	0.0574
1.10	159	27.2	0.0641
1.08	178	30.2	0.0715
1.06	200	33.2	0.0792
1.04	222	34.6	0.0826
1.03	233	38.8	0.0935
1.01	266	43.2	0.105
1.00	303	45.9	0.112
0.99	325	48.6	0.120
0.98	349	50.0	0.123
0.98	360	53.4	0.133
0.98	390	56.8	0.142
0.97	420	62.0	0.156
0.96	467	66.5	0.168
0.95	506	*103	* 0.287
* 0.75	-	117	0.335
0.67	1150	122	0.355
0.64	1246		

* Calculated

CELL 49

BENZOQUINONE

Depolarizer: 0.210 gms.; Carbon: 0.420 gms.
Electrolyte: Sat'd. NaCl, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.18.

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
1.14	0	0	0
1.08	5	0.696	0.00176
1.06	10	1.38	0.00347
1.06	12	1.66	0.00415
1.05	16	2.19	0.00549
1.04	24	3.24	0.00806
1.04	29	3.87	0.00982
1.02	37	4.90	0.0124
1.02	44	5.80	0.0147
1.02	49	6.40	0.0164
1.02	56	7.30	0.0186
1.02	70	9.05	0.0232
1.01	77	9.90	0.0254
1.01	100	12.7	0.0329
1.00	118	14.9	0.0387
0.99	131	16.4	0.0428
0.98	147	18.4	0.0478
0.98	153	19.1	0.0498
0.96	170	21.0	0.0549
0.95	199	24.1	0.0638
0.93	227	27.1	0.0722
0.87	300	34.2	0.0932
0.86	317	35.8	0.0980
0.82	386	41.7	0.117
0.80	424	44.5	0.126
* 0.75	-	* 51.9	* 0.155
0.54	1140	83.2	0.279

Calculated

CELL 50

BENZOQUINONE

Depolarizer: 0.210 gms.; Carbon: 0.420 gms.
Electrolyte: L, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.27

$\bar{V}$ Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.25	0	10.5	0.0231
1.21	60	20.7	0.0460
1.19	120	30.8	0.0686
1.18	180	39.5	0.0900
1.11	240	47.2	0.110
1.03	300	55.5	0.129
0.99	360	62.2	0.148
0.97	420	67.4	0.164
0.85	480	72.0	0.179
0.80	540	* 75.3	* 0.191
* 0.75	-	76.0	0.193
0.74	600	79.2	0.206
0.68	660	82.4	0.219
0.65	720	85.0	0.231
0.61	780		

* Calculated

CELL 53

ANTHRAQUINONE

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: L, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.22.

V Volts	θ Min.
1.21	0
1.14	1
1.08	3
1.00	6
0.96	8
0.89	12
0.77	29
0.76	33
0.72	40
0.70	48
0.66	64
0.65	75
0.62	100
0.60	133
0.58	1200
0.55	2880

CELL 55

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: L, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.50

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
1.47	0	0	0
1.38	2	0.488	0.00297
1.23	7	1.51	0.00978
1.20	11	2.22	0.0148
1.16	24	4.40	0.0308
1.14	35	6.13	0.0442
1.12	45	7.68	0.0557
1.04	60	9.77	0.0725
0.96	82	12.4	0.0955
0.94	97	14.0	0.110
0.94	120	16.5	0.133
0.92	172	21.9	0.182
0.92	432	48.2	0.432
0.90	510	56.0	0.506
0.90	555	60.5	0.549
0.89	695	74.3	0.684
0.86	1380	137	1.31
0.85	1425	141	1.35
0.85	1479	146	1.40
0.85	1570	154	1.47
0.85	1621	158	1.52
0.85	1690	164	1.58
0.85	1740	168	1.62
0.85	1860	179	1.73
0.84	1920	184	1.78
0.82	2040	193	1.88
0.80	2375	* 217	* 2.15
* 0.75	2912	250	2.55
0.67	3240	267	2.78
0.65	4260	311	3.40
0.54			

* Calculated

CELL 56

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: L, 3.5 ml.
Load: 150 ohms.
Initial O.C.V.: 1.46

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.36	0	0.64	0.004
1.17	1	8.85	0.068
1.06	17	13.1	0.104
1.00	27	20.4	0.174
0.83	49	25.5	0.227
0.80	68	31.2	0.289
0.80	90	35.2	0.332
0.78	106	40.3	0.390
0.78	127	46.5	0.456
0.76	152	* 52.3	* 0.529
* 0.75	-	59.0	0.602
0.74	208	69.0	0.715
0.73	252	77.7	0.825
0.72	295	97.2	1.065
0.68	395	124	1.42
0.64	550	133	1.55
0.62	609	209	2.77
0.46	1260	215	2.87
0.42	1330	224	3.08
0.30	1500		

* Calculated

CELL 59

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: 20% NaOH, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.40
Atmosphere: Air.

	V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
			0	0
	1.35	0	0.590	0.00396
	1.21	3	6.25	0.0456
	1.14	37	28.3	0.214
	1.13	180	62.5	0.478
	1.11	407	153	1.21
	1.05	1055	186	1.49
	0.98	1320	205	1.66
	0.90	1500	212	1.73
	0.86	1575	235	1.97
	0.83	1845	284	2.49
	0.78	2475	* 293	* 2.60
*	0.75	-	301	2.70
	0.72	2735	310	2.80
	0.70	2880	330	3.07
	0.63	3266	363	3.55
	0.53	4060	366	3.61
	0.50	4170		

CELL 60

UNDEPOLARIZED

Depolarizer: 0.0 gms.; Carbon: 0.400 gms.
Electrolyte: 20% NaOH, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.36

V Volts	θ Min.
1.15	0
1.12	1
1.04	3
0.96	14
0.91	21
0.84	45
0.77	108
0.70	196
0.65	270
0.58	444
0.49	1095
0.47	1320

CELL 61

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: 20% NaOH, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.26

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
		0	0
1.23	0	0.178	0.00127
1.20	1	0.859	0.00622
1.18	5	2.17	0.0160
1.16	13	5.57	0.0415
1.16	34	9.89	0.0737
1.14	61	20.0	0.151
1.14	126	31.2	0.236
1.14	198	57.0	0.433
1.12	365	91.0	0.702
1.08	600	161	1.34
0.82	1245	172	1.45
0.80	1380	187	1.63
0.76	1595	* 192	* 1.69
* 0.75	-	197	1.74
0.74	1740	205	1.83
0.72	1860	250	2.43
0.60	2735		

* Calculated

CELL 62

1-NITROANTHRAQUINONE-8-SULFONIC ACID

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: 20% NaOH, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.30
Atmosphere: Oxygen.

	V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
	1.28	0	0	0
	1.16	6	1.07	0.00763
	1.14	16	2.66	0.0196
	1.14	33	5.32	0.0398
	1.12	52	8.29	0.0625
	1.12	72	11.3	0.0852
	1.12	117	16.6	0.126
	1.06	760	108	0.855
	1.04	870	123	0.975
	1.02	1020	142	1.14
	1.01	1080	150	1.20
	0.86	1130	155	1.25
**	0.16	1355	162	1.37

** Oxygen had corroded zinc contact thru.

CELL 63

DISODIUM ANTHRAQUINONE DISULFONATE HYDROGEN REAGENT

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: 20% NaOH, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.35.
Atmosphere: Nitrogen.

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
1.32	0	0	0
1.02	1	0.164	0.00150
1.00	2	0.287	0.00279
1.02	7	0.899	0.00927
1.01	14	1.76	0.0183
1.00	18	2.26	0.0236
0.97	27	3.30	0.0348
0.98	40	4.79	0.0511
0.96	173	19.8	0.216
0.92	219	23.6	0.260
0.84	431	43.5	0.500
* 0.75	-	* 61.5	* 0.79
0.66	1147	79.6	1.09

* Calculated.

CELL 64

DISODIUM ANTHRAQUINONE DISULFONATE HYDROGEN REAGENT

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: 20% NaOH, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.36.
Atmosphere: Air.

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
1.33	0	0	0
1.26	3	0.605	0.00498
1.26	10	1.93	0.0163
1.26	23	4.42	0.0372
1.25	42	8.02	0.0679
1.25	50	9.52	0.0807
1.25	69	13.1	0.111
1.24	106	20.0	0.170
1.24	126	23.6	0.202
1.20	190	35.2	0.302
1.17	270	48.5	0.424
1.12	465	79.3	0.711
1.10	687	112	1.03
0.92	1501	212	2.08
0.90	1540	215	2.13
0.88	1813	242	2.44
* 0.75	-	* 340	* 3.61

* Calculated.

CELL 65

DISODIUM ANTHRAQUINONE DISULFONATE
HYDROGEN REAGENT

Depolarizer: 0.200 gms.; Carbon: 0.400 gms.
Electrolyte: 20% NaOH, 3.5 ml.
Load: 500 ohms.
Initial O.C.V.: 1.28
Atmosphere: Nitrogen.

V Volts	θ Min.	W Watt-Sec.	X Fractional Reduction
1.22	0	0	0
1.13	2	0.331	0.00301
1.08	14	2.10	0.0201
1.01	49	6.70	0.0670
0.98	84	10.8	0.112
0.96	107	14.4	0.140
0.93	149	18.0	0.191
0.90	210	24.1	0.262
0.86	287	31.2	0.350
0.82	387	39.7	0.457
0.78	470	46.1	0.542
* 0.75	-	* 54.0	* 0.66
0.60	1298	93.2	1.27
0.60	1388	97.0	1.34
0.58	1688	110	1.57

* Calculated

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