EXPERIMENTAL STUDIES ON THE CHARACTERISTICS OF THE ELECTROCHEMICAL POTENTIALS ENCOUNTERED IN DRILL HOLES

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ABSTRACT

This thesis describes the results of experimental studies on the characteristics of the electrochemical potentials encountered in drill holes and registered by electrologging apparatus.

The experiments were carried out by bringing samples of sediments into contact with two solutions of different salinities on opposite sides and measuring the difference in potentials between the solutions.

The following conclusions were drawn from the measurements thus obtained:

The potentials are independent of the amount of material involved. They are proportional to the logarithm of the concentration ratio of the two solutions. The potentials decrease slowly with time.

There is no sharp demarcation between the electrochemical behavior of sandstones and shales, but rather there exists a complete continuity in the potentials exhibited across sediments of the sandstone shale series.

This continuity is explained using the concept of "apparent ion mobilities".

To classify sediments according to their electrochemical behavior, the electrochemical formation coefficient, C, is introduced. Dense argillaceous shales have a formation coefficient of 1. Inert clean sands have C = 0. It is

shown however that in practice sands may very seldom be considered inert.

A correlation exists between the formation coefficient and the ratio of the amount of conductive solids or argillaceous materials over porosity (see references 8 and 13). The influence of temperature on self potentials is computed theoretically and confirmed experimentally.

It is pointed out that dense formations may give considerable self potential kicks on electrologs. This conclusion is confirmed by measurements of the potentials across quartzites.

The general conclusions concerning the character of the electrochemical potentials are extended to the self potentials across calcareous formations.

The application of the analysis of the electrochemical potentials to electrolog interpretation is outlined. Also the possibility of electrochemical testing of sediments as a new tool in surface geology is indicated.

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INTRODUCTION

Since the early days of commercial application of electrologging, attempts have been made to relate the spontaneous potentials registered on the electrologs to some of the basic characteristics of the formations traversed, such as porosity and permeability, and (or) to the composition of the connate waters and drilling fluids.

In spite of the many theories and hypotheses put forward on this subject, the spontaneous or self potential curves still defy in many cases any quantitative analysis.

One of the first attempts to explain the presence of spontaneous potentials in drill holes was made by C. and M. Schlumberger and E. O. Leonardon. In their first paper (1) they attributed the potentials almost entirely to electrofiltration effects. Drilling mud, under its own hydrostatic pressure infiltrates the porous formations. This gives rise to so-called "streaming potentials" between the mud and the formations. Such potentials depend on the surface characteristics of the porous medium and are proportional to the pressure difference across the medium in which the infiltration takes place. They are independent of the porosity of the formation. Although these basic characteristics were recognized and clearly stated in the above quoted paper, the authors nevertheless used the term "porosity diagram" for the self-potential log.

After the publication of this first paper it soon became apparent that spontaneous potentials often occurred in cases where no pressure difference existed between the mud and the formation waters. This phenomenon was explained in a second paper by the same authors (2), as the effect of other electrochemical processes of which the most important were the diffusion or liquid junction potentials. Apart from these, contact potentials of unknown nature, existing at the boundaries between pervious and impervious formations were recognized as influencing the S.P.'s (self potentials).

Furthermore, they showed experimentally that the combined effect of the boundary and diffusion potentials could be expressed as:

$$E_t = K \log_{10} \frac{R_2}{R_1} \qquad (1)$$

where R_1 and R_2 are the resistivities of the connate water and the mud respectively.

Their experiments were carried out using a coarse siliceous sand and a plastic gray clay and solutions of sodium chloride. For this combination they found $K \approx 17$.

Regarding the diffusion potential set up at the contact between the coarse porous layer and the mud (or free electrolyte) the following description was given:

"There is a contact between sweet and salt water in a medium where the pores have large dimensions, and where the mobility of the ion is not appreciably hindered, by the presence of the porous material. Experience shows that the electromotive force is the same as though the contact took place directly between the two fluids alone."

Regarding the nature of the boundary potentials at the contacts with the impervious rock no statements were made.

This uncertainty and many other difficulties encountered by subsequent investigators in attempts to explain the electrochemical S. P.'s has been mostly due to the failure to recognize the continuity in the geologic series of sedimentary rocks. Coarse sands and fine argillaceous shales are physically only extremes in a completely continuous series of sediments. It is therefore logical to expect that in all physical characteristics the same principles underlie the behavior of sands and of shales. Factors that may be important in the behavior of shales may be negligible in the case of coarse sands and vice versa, but in principle they are present and in between the two extremes there will be a continuous gradation of the characteristics. In studies of sedimentation and lithology these facts have been considered obvious and are universally recognized. Yet in the studies of electrochemical phenomena most authors have only considered "clean sands" and "pure clays or shales" and treated them as two entirely different media that have nothing whatsoever in common.

Thus, although the above authors realized that coarse sands do not influence the mobility of the ions in their interstitial water to any appreciable extent, they did not assume that shales might have a very noticeable influence on those mobilities, and that in shaley sands and siltstones this influence might vary from the one extreme to the other with the lithologic variations of those sediments.

The first attempt to correlate the S.P. kicks with the character of the sediments, beyond the classification of sands and shales was made by S. J. Pirson (3).

Pirson explains the S.P. curves by considering the potential differences between the solid frame-work of the rocks and the surrounding liquids, due to the preferential adsorption of ions from the solutions by the rock.

These electrochemical or thermodynamic potentials (E) are independent of the salinity of the connate water, but strongly dependent on the character of the rocks and the mud salinity.

Shales having a strong preferential adsorption of Cl ions would give large voltages. Pure sands exhibit the same phenomena, but to a much lesser extent. In this way shales would be the main sources of the potentials observed on S.P. logs. The magnitude of the S.P. kick would be mostly indicative of the amount of clay present in the sediment.

Diffusion potentials and electro filtration potentials are considered by Pirson as secondary phenomena, which will mostly only change the magnitude of the "shale-potential" kicks.

Although several objections may be raised against Pirson's theory, it has the distinction of recognizing the importance of the influence of the character of the sands on the magnitude of the S.P. kicks.

The main objection to Pirson's theory is that it does not properly account for the influence of the connate water salinity on the magnitude of the self potentials.

The idea that shales are the main seat of the natural potentials was originated by W. D. Mounce and W. M. Rust (4) who showed experimentally that shales placedin contact with solutions of different salinities at opposite sides exhibited potentials of a magnitude comparable to those found in oil wells between the two solutions. They also noticed that pure sands did not have this characteristic, or only to a negligible extent.

An important contribution to the understanding of the shale potentials was made recently by M. R. J. Wyllie of the Gulf Research and Development Co. (5).

Wyllie conducted extensive experiments on the potentials across shale barriers between solutions of different salinity. As in all afore-mentioned experiments, NaCl solutions of various concentrations were used.

Wyllie showed that the potential across a shale barrier can be represented by $E = K \log \frac{a_1}{a_2}$ (2)

where a_1 and a_2 are the ionic activities of the two solutions.

For dilute solutions these may be replaced by the conductivities or the inverse values of the resistivities.

K was found to be close to 59.15 at 25° C, which corresponds to the value of the constant of the Nernst equation for a metal in contact with electrolyte solutions:

$$E = \frac{RT}{F} m \log \frac{a_1}{a_2} \qquad (3)$$

where R is the gas content, F the Faraday, T the absolute temperature, and $m = 1/\log_{10} e$ (e = base of natural logarithm).

Wyllie assumes therefore that the shale acts like a sodium electrode, in the sense that sodium ions are able to diffuse through the shale from one solution to the other, while the high negative charges on the shale particles repel the chloride ions. This causes the less saline solution to become positive with respect to the more saline solution. Wyllie also recognizes the diffusion or "boundary" potentials in the case where saline interstitial water within a sand is in contact with less saline mud.

In the cell, Mud / Interstitial water in the porous beds / Shale / Mud (see Fig. 1) the diffusion potential and

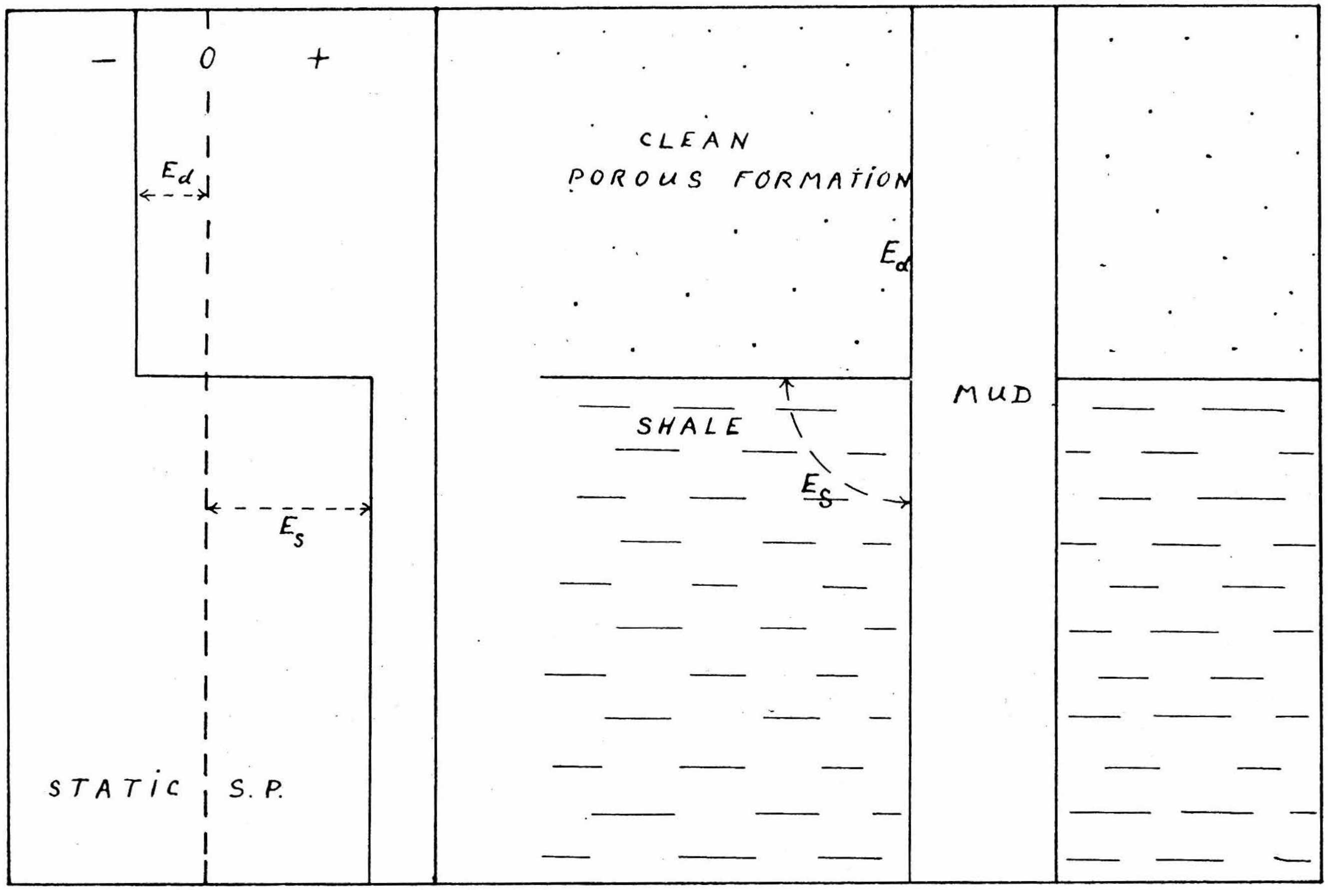


Fig. 1

the shale potential act in the same direction. The total E.M.F. of the cell equals therefore the algebraic sum of the two potentials. As for NaCl solutions, the diffusion potential may be represented by $E_d = 11.5 \log \frac{a_1}{a_2}$, the total E.M.F. for the cell (E_t) becomes

$$E_t = 59.15 \log \frac{a_1}{a_2} + 11.5 \log \frac{a_1}{a_2} = 70.65 \log \frac{a_1}{a_2} \qquad (4)$$

This formula is a good representation of the electrochemical component of the S.P. curve in cases where very clean sandstones are in contact with dense argillaceous shales. In practice such conditions will seldom be found.

It must be pointed out here that the E.M.F. existing across the mud - sandstone - shale - mud cell is not necessarily equal to the potential difference measured on the S.P. log. Actually the E.M.F. gives rise to a sustained current flow, the so-called S.P. current and the S.P. log registers the ohmic drop in the mud column due to this current. For thick beds of low resistance, this ohmic drop is very nearly equal to the static E.M.F. In all other cases it is smaller. The relations governing the relative magnitude of the ohmic potential drop, as a function of formation thicknesses and resistivities have been very accurately and completely described by H. G. Doll (6).

The actual E.M.F. which would be equal to the S.P. measured on the logs if the effect of the S.P. current could be neglected (for instance if insulating plugs were placed in the mud column) was termed by Doll the "static S.P."

In a later paper (7) Doll treated the self potentials of shaley sands by representing these by a series of thin clean sand layers interbedded with layers of pure argillaceous material. Although the calculated results seem to be in qualitative agreement with the S.P. logs of shaley sands, the assumptions are geologically untenable.

The main object of this thesis is to show experimentally the relations between the magnitude of the static S.P. and the character of the sediments involved.

Important conclusions are reached regarding the nature of the electrochemical phenomena and some possibilities of practical application of the observed relationships are pointed out.

PART I

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The measurements of electrochemical potentials across sediments were carried out, using samples of approximately the following dimensions:

Height 1" ; Length $1\frac{1}{2}$; Width 2".

These were mounted with zophar wax in a small catheter tray of $1\frac{1}{4}$" x 8" x $2\frac{1}{4}$", leaving on each side a volume of approximately 240 cm^3, which were filled with the solutions to be used.

The solutions were made up by mixing c.p. NaCl with distilled water.

Two solutions of different NaCl concentration would be poured in the end sections of the tray simultaneously so that imbibition of the sample would take place equally from both sides.

As soon as imbibition was completed, the potential measurements were started. The change of the potentials with time were measured over periods of several days, the measurements being spaced according to the rate of change in the potentials.

The circuit used for the measurements is represented schematically in Fig. 2.

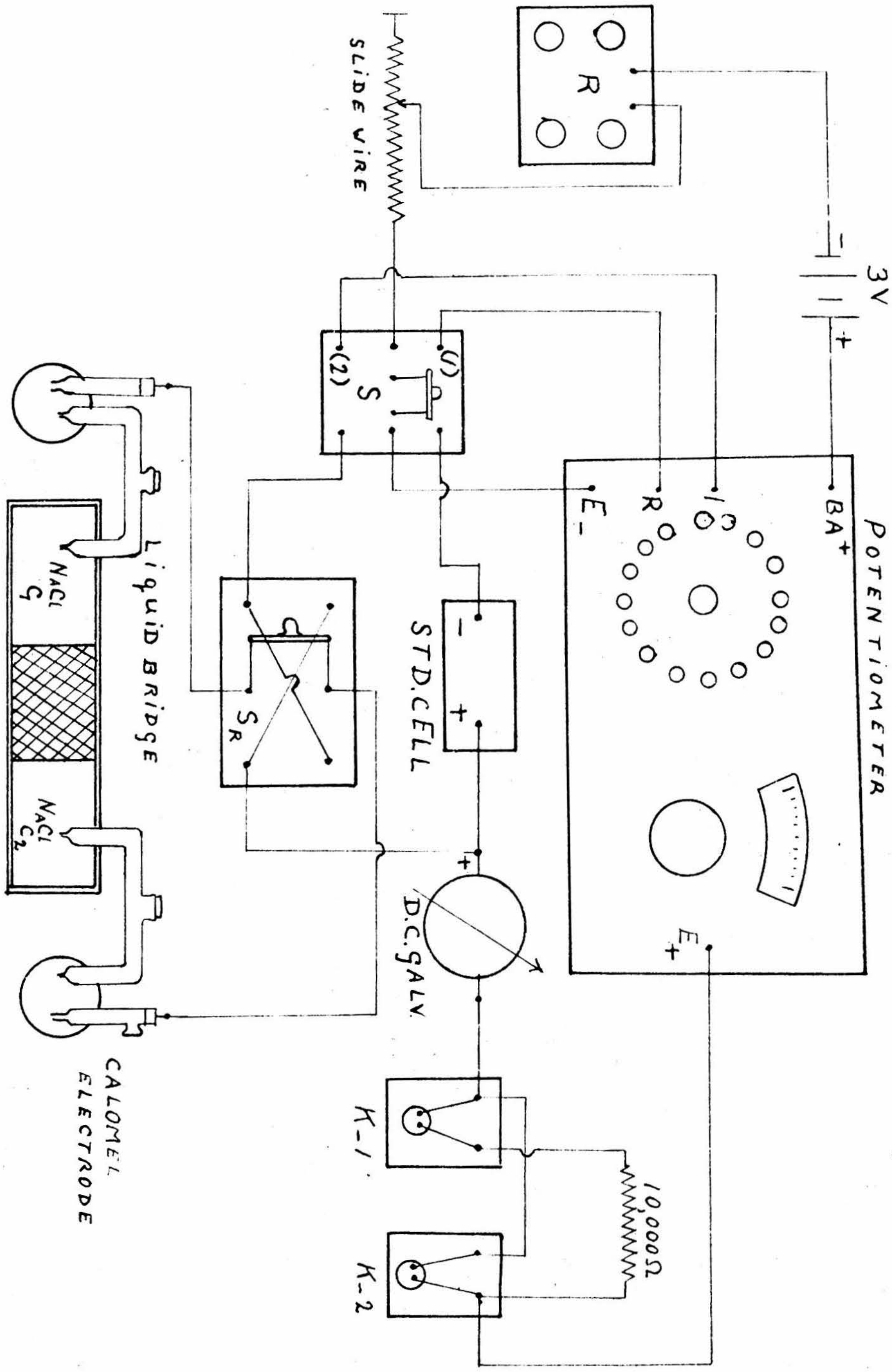

POTENTIOMETER
BA+
1O
R
E−
E+
3V
−
+
R
SLIDE WIRE
S
(1)
(2)
STD. CELL
−
+
D.C. GALV.
+
S_R
K-1
K-2
10,000Ω
LIQUID BRIDGE
NACL C1
NACL C2
SAMPLE
CALOMEL ELECTRODE

Fig. 2

The solutions on each side were connected to small beakers containing identical solutions by means of two liquid bridges with capillary end tips, also filled with the same solutions. In the two small beakers two calomel half-cell electrodes were placed. The electrodes were saturated KCl fibre-tip electrodes of the type used with the Beckman pH meters (Beckman #270 electrodes). Care was taken to prevent pollution of the KCl by NaCl, while the pollution of the solutions in contact with the sample by KCl from the electrodes was minimized by the use of the liquid bridges.

The potentiometer arrangement used was a Leeds and Northrup type K students'potentiometer in combination with a Rubicon high sensitivity spotlight galvanometer (type 3418).

This galvanometer has an internal resistance of 3800 ohms, a sensitivity of 0.0006 micro amperes per mm scale division, a period of 4 seconds and an external critical damping resistance of 55.000 ohms. The accuracy of the measurements depended somewhat on the total resistance of the sample and the liquid bridges, but was always better than 0.5 V.

The current through the potentiometer was delivered by two 1.5 Volt dry batteries in series, and adjusted to a value of 0.01 ampere by a four dial rheostat and a slide wire. The smallest divisions of the rheostat were .1 ohm, which means that using the rheostat alone the voltage across the potentiometer, to be checked against the standard cell voltage, could be adjusted only with an accuracy of .5 m Volt. As both the standard cell calibration and the potentiometer dial setting permit a better accuracy, the slide wire was added in series with the rheostat. The wire consisted of 6 ft. of no. 18 copper coated steel wire with a total resistance of .15 ohm or approximately .002 ohm per inch. This permitted adjustment of the voltage across the potentiometer, when checking against the standard cell, to .01 m Volt. Variations of the position of the movable contact of the slide wire of less than one inch gave galvanometer deflections which could no longer be read. Therefore using the slide wire to vary the resistance, the current adjustment depended only on the accuracy of the potentiometer setting and the galvanometer zero reading.

The standard cell had a voltage of 1.01598 Volt. Both the standard cell and the batteries were packed with glass wool in a tin can to insure equithermic conditions for all parts. The tin cans in turn were packed with glass wool in wooden boxes to keep temperature variations at an absolute minimum.

Before a measurement was started, current was allowed to pass through the potentiometer for approximately one half hour, to stabilize the battery output. Then the potentiometer dials were set at the value equal to the standard cell voltage and the current through the potentiometer adjusted until the galvanometer gave zero deflection, which indicated that the current had the value of 0.01 ampere. While checking against the standard cell, two tap keys K_1 and K_2 were used (see Fig. 2). When K_1 was tapped a protecting resistance of of 100,000 ohm was connected into the galvanometer circuit. Coarse adjustment was made using K_1 and thereafter fine adjustment was made using K_2, thus omitting the 100,000 ohm resistance. For accurate zeroing of the galvanometer by means of the resistance slide wire K_2 could be locked.

When the current was adjusted, the switch S was placed in position (2) connecting the E.M.F. to be measured to the potentiometer circuit. The potentiometer dials were set at zero. Then K_1 was tapped and the deflection noted. The galvanometer was then zeroed by varying the dial setting on the potentiometer and from the latter the E.M.F. was read directly in millivolts. If increasing the potentiometer voltage from its zero starting point would increase the galvanometer deflection, switch S_r would be placed in reverse position. In this way when making the readings, the positive side of the unknown E.M.F. would always be connected to the galvanometer.

After each measurement, the liquid bridges were taken out of the tray and placed across two small beakers containing solutions identical to those in the bridges. This was done to prevent air from entering the capillary ends of the bridges, which would break the fluid contact continuity for subsequent readings. The tray was then closed by a snugly fitting lid to prevent evaporation of the solutions. The electrodes were taken out of the solutions, wiped off with tissue paper and sealed with their protective rubber caps and sleeves.

The salinity ratio of the NaCl solutions could be determined by measuring the resistivities using a four electrode A.C. circuit described in another thesis by this author (8). A more convenient method however was to measure the liquid junction potential between the two solutions. This was done in the following manner:

The liquid bridge containing solution C_1 was placed on one side in a small beaker filled with the same solution and on the other side in a beaker containing solution C_2.

The fluid level of C_2 was placed momentarily slightly above that of C_1 so that fluid would flow through the bridge toward C_1. This pulls up the liquid junction in the capillary end of the bridge, to obtain "cylindrical symmetry" of the boundary layer which improves stability of the liquid junction potential (9).

The potential between the solutions in the two beakers was then measured as the liquid junction potential, using the half cell calomel electrodes as described before.

To study the influence of temperature on the magnitude of the self potentials, the tray and specimen were heated in a water bath to approximately 185°F. For these elevated temperatures a different type electrode had to be chosen, as the #270 Beckman electrodes do not function properly above 45°C (113°F).

The electrodes used were Beckman #1170-71, sleeve type calomel electrodes.

The normal temperature range for these electrodes is -5° to 60°C. However, if carefully checked and constantly kept filled with saturated KCl they may be used up to temperatures just below the boiling point of water.

The electrodes were inserted directly in the solutions on both sides of the specimen. The liquid bridges were not used in this case, to avoid excessive difficulties in the control of the temperature of the system and the evaporation of the solutions. The evaporation of the solutions in the tray was minimized by keeping the tray covered by its lid. The temperature of the solutions was measured with a thermometer graduated in °F.

Pollution of the solutions by KCl from the electrodes might be the source of errors. The electrodes were therefore taken out of the solutions directly after each measurement and during the measurements the outflow of KCl was minimized by keeping the rubber stoppers in the filling holes of the electrodes. Readings of the E.M.F. and the temperature were made before and during the heating of the system.

After a reading was made at the highest temperature at which the system could be maintained in the thermic equilibrium, the system was allowed to cool slowly. Successive measurements of the E.M.F. and prevailing temperature were then made until room temperature was reached. In this manner reliable measurements were obtained over the temperature range from 65° to 185°F, which corresponds very well to the range of temperatures normally occurring in oil wells.

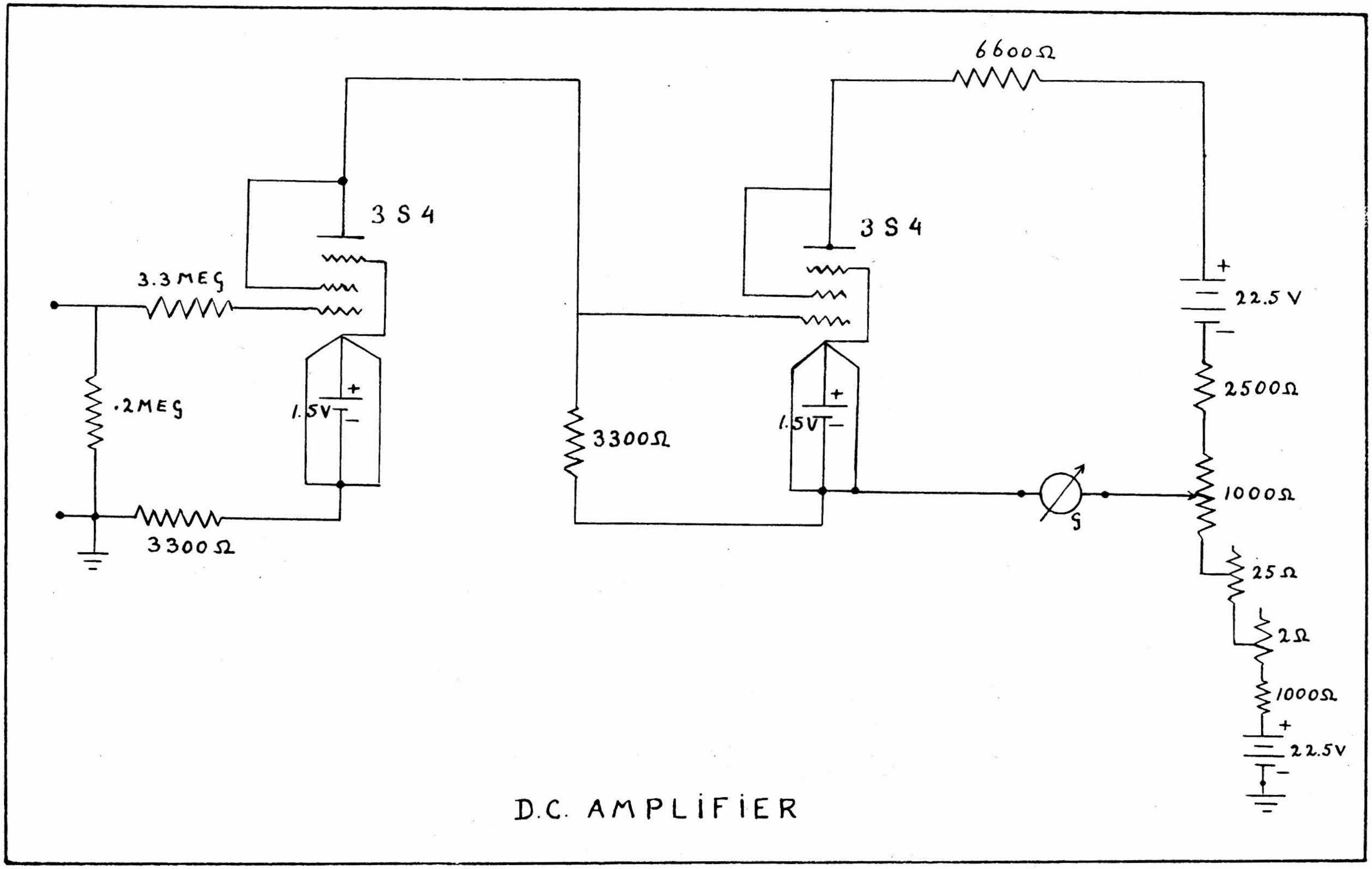
To measure the E.M.F. across specimens of high resistivity (25,000 Ω resistance across the specimen) a D.C. current amplifier was used. (The amplifier circuit is represented in Fig. 3.) Current amplification was especially necessary for the measurements on dense limestones, marbles, and quartzites, all of which have very low permeabilities and high resistivities.

The specimens used for the self potential determinations were mostly sediments taken from outcrops. Some black shales obtained from cores from a depth of approximately 8000 ft. were also used.

The samples were either cut with a diamond saw and air-dried or cut with a rotary wire brush.

The latter procedure was used for all the less consolidated sediments.

For several limestone samples the following determinations were made:



D.C. AMPLIFIER

Fig. 3

1. Porosity: Determined by imbibition with water and measuring the difference between wet and dry weight.

2. Insoluble residue: A weighed sample was dissolved in 20% HCl. The insoluble residue was weighed and computed as weight percentage of total.

3. Clay fraction: From the insoluble residue the clay fraction was determined by pipette analysis, as the fraction of particles with a diameter less than 5 microns. For the analysis the residue was mixed with 400 cc of 0.01 N. sodium carbonate. The mixing was done with a high speed soil dispersion mixer.

After the mixing the dispersed residue was allowed to settle for 1 hour and 14 minutes (this was the settling time for particles of 5 micron diameter, for a depth of 10 cm). Then 20 cc of sample was withdrawn by pipette from a depth of 10 cm below the surface of the fluid. This fraction was boiled dry in a beaker and weighed. The total clay fraction was then found as $\frac{400}{20} = 20$ times the weighed fraction. All weighing was done using a sensitive chain balance which could be read to 0.1 milligram.

PART II

PRELIMINARY MEASUREMENTS

A. Determination of influence of the quantity of materials involved.

To determine whether or not the amount of material used in the experiments influences the magnitude of the electrochemical potentials the following test was made.

A block of Saugus ss was divided into two parts. From these parts were cut one sample of 10 x 8 x 5 cm (volume = 400 cm^3) and one sample of 5.9 x 5.7 x 3.5 cm (volume = 118 cm^3).

The larger sample was placed in a large tray which was filled up with 625 cm^3 of NaCl solution on each side of the sample.

The smaller sample was mounted in a small tray and 110 cm^3 of NaCl was poured into the tray at each side of the sample.

The solutions at corresponding sides of the two samples were identical. The ratio of the salt concentrations on opposite sides of the sample was 5.7.

The E.M.F. across the samples upon completion of imbibition of the salt solutions was measured for both cases at a temperature of 69°F.

The reading for the potential across the sample in the large tray was 24.6 m Volt.

Across the small sample a potential of 25.2 m Volt was obtained. The difference in the readings is probably mostly due to small differences in the composition and (or) texture of the samples and to experimental inaccuracies. It is obvious however that the amounts of material involved do not govern the magnitude of the potentials across the samples, as long as the samples are large enough to give a good statistical representation of all components and characteristics of the rock from which they are taken.

B. Comparison of methods of determination of the concentration ratio between the solutions on opposite sides of the samples.

To determine the concentration ratio between the salt solutions on both sides of the sample the following methods can be used:

1. Weighing of the amounts of NaCl and distilled water used in the preparation of the solutions.

2. Measurement of the resistivities of the solutions.

3. Measurement of the liquid junction potential, E_d, between the two solutions, when they are brought into contact with each other in an inert porous medium or inside a capillary tube.

It was shown by Wyllie (5) that the electrochemical potentials across shale barriers depend more directly on the activities of the solutions involved than on their concentrations. The potentials were found to be directly proportional to the logarithm of the ratio of the activities of the salt solutions.

As the liquid junction potentials are also proportional to this same parameter, it is preferable to use method no. 3.

In the interpretation of self potential data from elextrologs, the resistivity ratio is used instead of the ratio of activities. This is based on the well-known fact that resistivities of salt solutions are nearly inversely proportional to their concentrations, and that for dilute solutions the differences between the ratios of the activities and the concentrations of the two solutions may be neglected.

To obtain some idea of the validity of these approximations, two solutions were prepared and comparison was made between the three parameters: $\log \frac{C_1}{C_2}$, $\log \frac{R_2}{R_1}$, and $\log \frac{a_1}{a_2}$ (as determined from the liquid junction potential).

The following results were obtained:

$C_1 = 15{,}300$ ppm $C_2 = 510$ ppm $\log \frac{C_1}{C_2} = 1.477$

$R_1 = 40\,\Omega$ cm $R_2 = 990\,\Omega$ cm $\log \frac{R_2}{R_1} = 1.394$

$E_d = -17.0$ m Volt $= 11.6 \log \frac{a_1}{a_2}$ $\log \frac{a_1}{a_2} = 1.461$

We see that using the resistivities instead of the activities may introduce some error.

As the measurement of the liquid junction potential requires no extra apparatus and can be done in a few minutes, method no. 3 was used for all measurements referred to hereafter.

C. Relation between the activity ratio of the solutions and the magnitude of the electrochemical potential.

As mentioned before, Wyllie has shown by extensive experiments that the E.M.F. across a shale barrier may be represented by $E = K \log \frac{a_1}{a_2}$ (2)

The question arises whether this relation also holds for sediments, which are neither pure shales nor inert clean sands.

This was tested again using a sample of Saugus ss. Assuming equation (2) to hold true, we can calculate K from one measurement of E_d and the corresponding E.M.F. Knowing K we may compute the E.M.F. that should be obtained for any other value of E_d or $\log \frac{a_1}{a_2}$. The results are shown in Table A.

Table A

E_d (m Volt)	$\log \frac{a_1}{a_2}$	E.M.F. (m Volt)	
		calculated	measured
-8.15	0.702		23.6
-21.54	1.857	62.4	61.0
-4.3	0.371	12.5	12.7
-14.7	1.269	42.5	43.1

The data presented in Table A show that for all practical purposes equation (2) may be applied also to sediments that are intermediate between sands and shales.

The measurements were carried out at temperatures ranging from 77 to 81°F and in the computations the effects of the small temperature variations are neglected.

D. E.M.F. across a shale barrier.

To check whether our method of measuring the electrochemical potentials across sediments gave similar results to those obtained by the investigations of Wyllie, who used a different method of mounting the specimen and bringing the solutions in contact with the specimen, the E.M.F. across a pure argillaceous shale was measured.

Wyllie had found $E \approx 59.15 \log \frac{a_1}{a_2}$ (3a)

Using equation (3a) we can compute the E.M.F. for any value of $\log \frac{a_1}{a_2}$ (obtained from measurement of E_d) and compare the computed E.M.F. with the potential difference across the shale. The results of our measurements are shown in Table B.

Table B

E_d (m Volt)	$\log \frac{a_1}{a_2}$	temp. (°F)	E.M.F. (m Volt) calculated	E.M.F. (m Volt) measured
-11.6	1.0	73	59.15	60.9
-16.8	1.45	72	85.9	84.3
-15.0	1.29	73	76.4	75.5

The results show that our method of measurement is equivalent to the one used by Wyllie.

E. The effect of time on the E.M.F. across sediments.

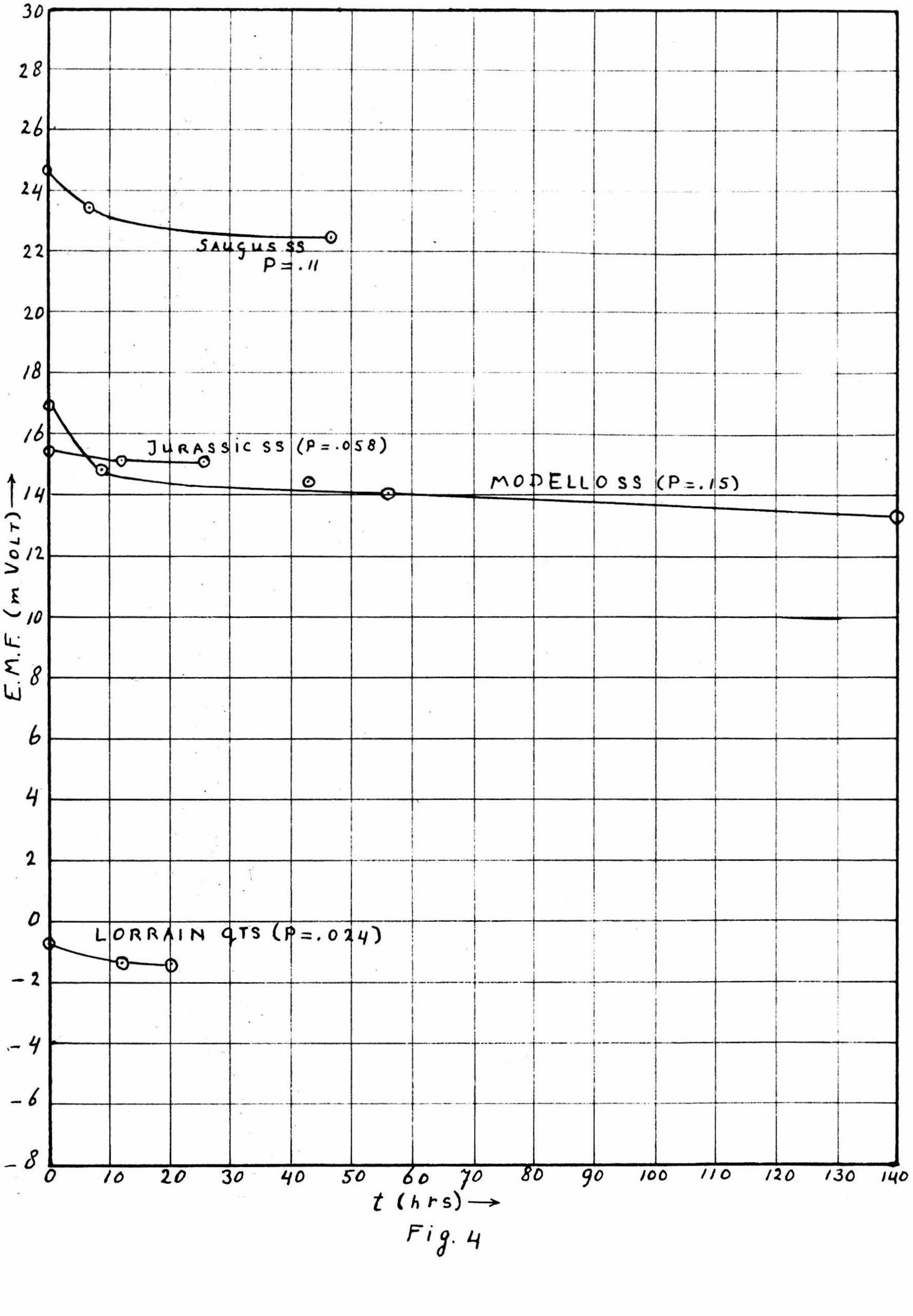
All measurements made of the E.M.F. across any type of rock showed a decrease of the absolute potential difference with time. Fig. 4 shows some typical graphs of the magnitude of the E.M.F.'s versus time. The sign of the potentials is established arbitrarily in the same direction as the potentials found in drill holes, that is for shales the less saline solution is positive. For inert sandstone the less saline solution is negative (same sign as that of the liquid junction potential). A negative potential will become larger negative with time.

We see from Fig. 4 that the slope of the first part of the curves varies from rock to rock. There seems to be some indication that the decline is steeper in the more porous rocks and less steep in the tight formations.

After the first twelve hours the decrease becomes very uniform and almost negligible.

F. Effects of temperature

The electrochemical potentials across rocks are dependent upon temperature. However, the variation with temperature is not the same in all cases. As the effect of temperature on the potentials has an important bearing on the actual nature



30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
E.M.F. (m Volt) →
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
t (hrs) →
Saugus SS
P = .11
Jurassic SS (P = .058)
Modello SS (P = .15)
Lorrain Qts (P = .024)

Fig. 4

of the potentials, the experimentally and theoretically obtained data on these variations will be discussed later in a separate section. At the present it suffices to state that the variations are small enough so that the changes in the measurement of potentials due to fluctuations in the room temperature may be neglected in most cases.

PART III

POTENTIALS ACROSS SEDIMENTS OF THE SANDSTONE SHALE SERIES

As pointed out in the introduction to this thesis, there exists a continuous series of sediments between pure quartz sands and argillaceous shales, if classified according to the texture and lithologic composition. It is expected therefore that these sediments also show continuity in their other physical properties, such as the electrochemical potential across them, when placed in contact with salt solutions of different concentrations.

To prove that such continuity does exist, measurements were made on a large number of specimens of sandstones, siltstones, shaley sands, and sandy shales. As was expected, values of self potentials were found ranging over the entire interval between those for inert clean sands and those for pure shales.

To be able to classify sediments according to their electrochemical behavior, the following parameters are now introduced:

1. The absolute self potential (A.S.P.). This quantity is defined as the electrochemical potential across the sediment at any arbitrary concentration contrast of the solutions in contact with the sediment, as-

suming always the more saline solution to be at zero potential. This means that if the more saline solution is positive with respect to the less saline solution the A.S.P. is negative. This will be the case for very pure sands. For most other sediments of the sandstone shale series the A.S.P. is positive.

2. The electrochemical formation constant, k, which is defined by the equation:

$$A.S.P. = k \log \frac{a_1}{a_2} \qquad (5)$$

where a_1 and a_2 are the activities of the more saline and less saline solution respectively. k always has the same sign as the absolute self potential and is at a given temperature, characteristic for a given rock, as long as we use solutions containing a given type of ions.

For NaCl solutions, we have for inert clean sand, at 25°C, $k = -11.5$, and for a pure argillaceous dense shale $k = 59.15$.

3. To ascribe sediments of the sandstone shale series a fixed place in this series, based on their electrochemical behavior, we introduce the "electrochemical formation coefficient" or "formation coefficient", C. This quantity is defined by the relation:

$$C = \frac{k_{25} + 11.5}{70.65} \qquad (6)$$

where k_{25} is the electrochemical formation constant for the rock in question, for NaCl solutions at 25°C.

For inert clean sandstones C = 0, and for pure shales C = 1.0.

From the definition of k we see that we may write:

$$k = \frac{11.5}{(E_d)_{25}} \times \text{E.M.F.} \qquad (7)$$

$(E_d)_{25}$ denotes the diffusion potential between the solutions in question at 25°C.

Using relations (6) and (7), the formation coefficients have been determined for a number of widely varying sediments. The results are listed in Table C.

Table C

Description of sample	C	Description of sample	C
Pico (lower Pliocene)ss quartzitic	0.126	Mint Canyon shaley siltstone	0.444
Berea (Mississippian) ss	0.142	Modelo ss(San Fernando)	0.472
Mint Canyon friable ss	0.167	Mesozoic dense ss	0.477
Mint Canyon ss	0.244	Martinez (Eocene) ss	0.484
Coconino (land-laid) ss	0.252	Modelo shaley ss (upper Miocene)	0.592
Pico (lower Pliocene) siltstone	0.282	Saugus (Pleistocene, land-laid) calcareous ss	0.640
Modelo ss (Castaic)	0.350		
	0.410	Jurassic gray slate	0.896
Modelo sandy shale	0.430	Black shale	1.0

We see from the data given in Table C that the sediments of the sandstone shale group form indeed a continuous series with respect to their electrochemical behavior, with inert clean sands at one end and pure argillaceous shales at the other extreme. We see however that normally sands cannot be considered to be clean, in the sense of being inert electrochemically. This is well demonstrated by the coefficients of the Berea ss and the quartzitic Pico ss.

From resistivity measurements described elsewhere (8) it was found that a correlation exists between the amounts of conductive solids present in the rocks and the electrochemical formation coefficient.

It was also found by this author (10) that a correlation exists between the formation coefficient and the total interstitial surface area per unit of bulk volume of the rocks. One of these relations is a logical consequence of the other as the conductive solids are mostly the minerals that are in the colloidal state and have a much larger interstitial surface area per unit volume than any of the other minerals present.

We now want to consider the nature of the absolute self potentials. Wyllie explained those of inert clean sands as being simple liquid junction potentials and those of the pure shales as being "sodium electrode potentials."

This abstract separation makes it difficult to understand the continuity of the potentials throughout the sandstone shale series.

We will therefore first discuss the basic character of both potentials, giving due consideration to the factors they have in common.

The liquid junction potential arises when two solutions of different ion content are brought into contact with each other. In our case, the solutions will differ mainly in concentration only and for simplicity's sake we will limit our discussions to the potentials due to the presence of two NaCl solutions of different concentration.

When two such solutions are brought into contact with each other, for instance in the interstices of an inert, porous medium, ions from the more concentrated solution will diffuse into the more dilute solution. For NaCl solutions the Cl ions diffuse more rapidly than the Na ions.

Shortly after the contact of the two solutions is established, an electric charge will set up across the boundary as more negative ions than positive ions cross the contact. The dilute solution will therefore become negatively charged with respect to the more concentrated solution. This charge will retard the migration of negative ions and accelerate the migration of positive ions, until a dynamic equilibrium is reached, at which both migrate at the same speed, or rather at which equal numbers of positive and negative ions diffuse into the dilute solution, per unit time.

The magnitude of the potential across the boundary at which this dynamic equilibrium is reached is given for NaCl solutions by the equation:

$$E_d = \frac{RT}{F} \frac{(v - u)}{(v + u)} \ln \frac{a_1}{a_2} \tag{8}$$

where v and u are the ionic mobilities of the chloride ions and sodium ions respectively, and a_1 and a_2 being the mean activities of respectively the more saline and the less saline solution.

If we arbitrarily consider the concentrated solution again at zero potential, the potential of the dilute solution becomes:

$$E = \frac{RT}{F} \frac{(u - v)}{(u + v)} \ln \frac{a_1}{a_2} \qquad (9)$$

At 25°C $v_{Cl} = 76.3$ and $u_{na} = 50.6 \ \Omega^{-1} cm^2$

or $\frac{u - v}{u + v} = 0.20$ and $T\frac{(u - v)}{(u + v)} = 59.6$

The constant factor $\frac{R}{F \log_{10} e} = 1.98 \times 10^{-4}$ practical units.

This leads to $E_d = -11.5 \log \frac{a_1}{a_2}$ m Volts.

When diffusion takes place across a shale barrier, the chloride ions are prevented from migration by the negative charge on the shale lattice, therefore in equation (8) we can make the chloride ion mobility equal to zero, which gives:

$$E_s = \frac{RT}{F} \ln \frac{a_1}{a_2} \qquad (10)$$

It is obvious that the actual ion mobility of the chloride ions does not change, only the "apparent mobility" of the chloride ions in the establishment of the boundary potentials across the shale barrier, is zero.

Equation (10) is the same expression as the Nernst equation for monovalent metals in contact with solutions containing ions of the metal, as was pointed out by Wyllie.

The above presentation however eliminates the impression that two entirely different processes are involved in the establishment of the shale potential and of the simple liquid junction or diffusion potential.

As in the case of the liquid junction potential, equilibrium is reached for the shale potential when the migration of both ion types occurs at the same rate. This means equilibrium is reached when the migration of the sodium ions has been halted completely, too.

For all intermediate members of the sandstone shale series, we must conclude that the physical effects of the rock framework on the solutions influence the migration of the ions. The magnitude of the resulting potentials is such that the negative ions must be retarded or (and) the rate of migration of the positive ions increased.

This results in an analytical expression of the form:

$$E = \frac{RT}{F} \frac{\alpha' u - \alpha'' v}{\alpha' u + \alpha'' v} \ln \frac{a_1}{a_2}$$

or

$$E = \frac{RT}{F} \frac{(u - \alpha v)}{(u + \alpha v)} \ln \frac{a_1}{a_2} \qquad (11)$$

where $0 < \alpha < 1$

α depends upon the texture and composition of the solid rock and can be directly related to the electrochemical formation coefficient, C.

Possible ways in which the solid framework could influence the apparent mobilities of the ions in the solutions were discussed with Dr. S. Frankel.

Based on suggestions by Dr. Frankel, a very plausible mechanism was worked out, which will be explained, using the illustration as given in Fig. 5.

Fig. 5 represents a portion of a thin section of Pico sandstone. We note that some of the interstices are interconnected by open passages, indicated by "O", while other connecting passages are filled with fines, marked with "F". These fines are mostly clay minerals and comprise in general the conductive solids present in the rock. The correlation between c and the amount of conductive solids indicates that the latter must have a direct bearing on the magnitude of the electrochemical potentials. This occurs in the following manner: Through the open passages, both Cl^- and Na^+ ions can diffuse, at rates corresponding to their mobilities. Through the passages blocked by fines, however, only the Na^+ ions can migrate, while the Cl^- are prevented by the negative charge on the clay particles from passing through. The passages filled with fines act therefore as miniature shale-barriers. The presence of the clay passages causes the overall rate of migration of the Na^+ ions to be larger in comparison to the rate of diffusion of the Cl^- ions, across the boundary between the solutions, than in the case of a free liquid junction. This means that the apparent mobility of the Na^+ ions is increased or that of the Cl^- ions is decreased. The extent of increase or decrease in the apparent

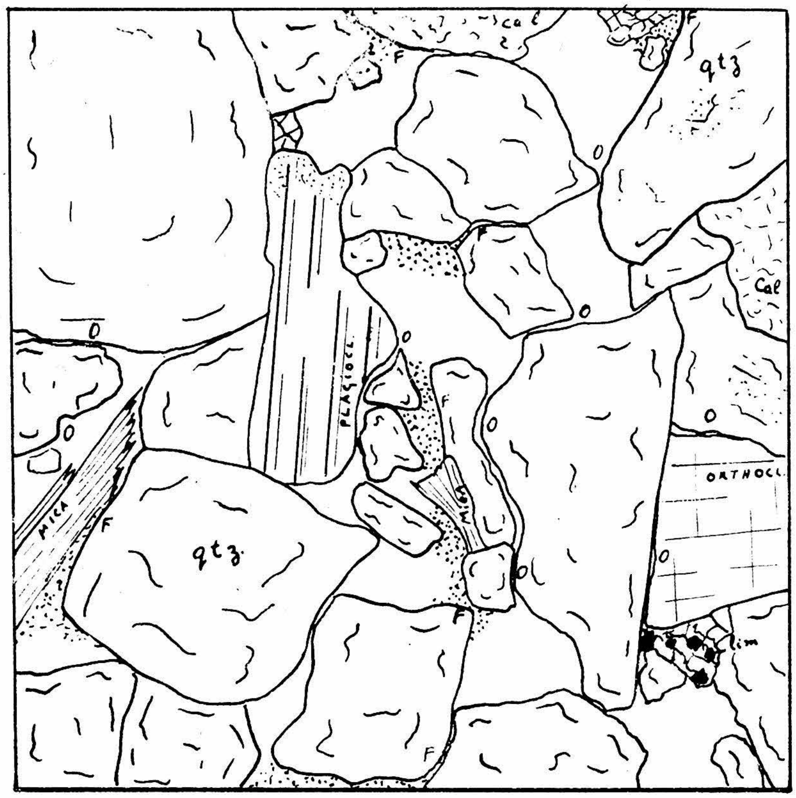


Fig. 5

THIN SECTION OF PICO SANDSTONE (X100)

mobilities depends upon the number of passages filled with fines in proportion to the number of free passages. This explains very clearly the relation between the electrochemical formation coefficient and the amount of conductive solids, if the latter is expressed as a fraction of total porespace.

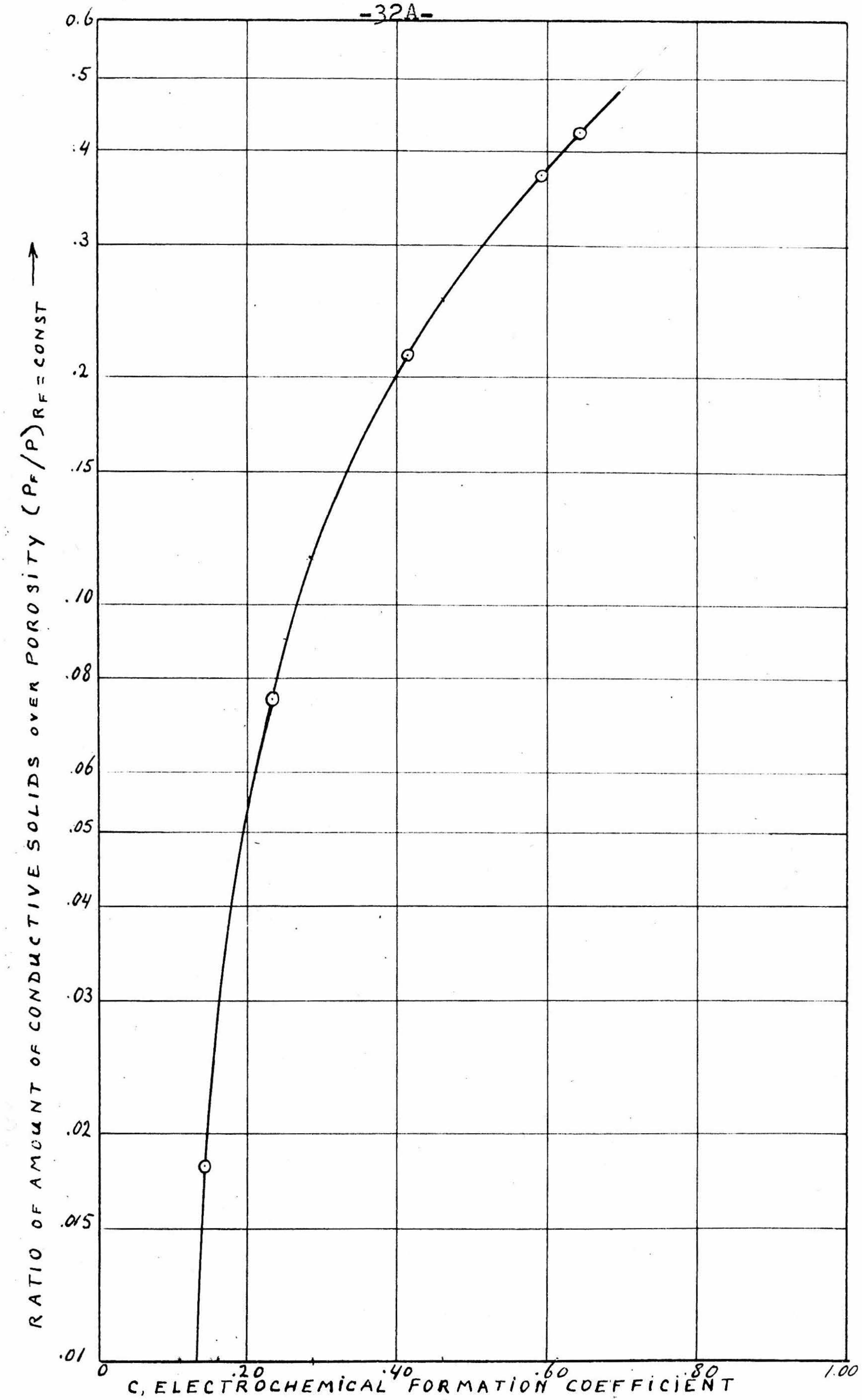
The method by which the amount of conductive solids is determined was described in another thesis by this author (8). The correlation is shown in Fig. 6.

The above interpretation shows that the apparent mobilities are completely statistical quantities. As pointed out before, the electrochemical formation coefficient is therefore only defined for samples of a rock large enough to give a good representation of the statistical characteristics of the rock.

As was shown on page 20 the expression

$$E = K \log \frac{a_1}{a_2}$$

gives a good approximation for the potentials across sediments of the sandstone shale series. This means that for the range of concentrations used in our experiments (1 N to 0.01 N) the variation of the relative ion mobilities with concentration are small enough to be neglected.



0.6
.5
.4
.3
.2
.15
.10
.08
.06
.05
.04
.03
.02
.015
.01
0
.20
.40
.60
.80
1.00
RATIO OF AMOUNT OF CONDUCTIVE SOLIDS OVER POROSITY (PF/P)RF = CONST →
C, ELECTROCHEMICAL FORMATION COEFFICIENT

Fig. 6

PART IV

THE VARIATIONS OF SELF POTENTIALS WITH TEMPERATURE

From equations (9), (10) and (11) it is obvious that the electrochemical potentials vary with temperature.

The potentials across a shale barrier (equation (10)) are directly proportional to the absolute temperature if we assume that the effect of temperature on the mean activities of the two solutions in question is the same and therefore cancels out in the factor $\ln \frac{a_1}{a_2}$.

For the liquid junction potentials and all the potentials of the intermediate members of the shale sandstone series, the dependence upon temperature is more complicated. This is caused by the fact that the ion mobilities vary with temperature.

Table D shows values of the Cl^- and the Na^+ ion mobilities as given in the Physikalisch Chemische Tabellen (11) for various temperatures. Also listed are various other quantities that enter into equation (9).

Table D

Temperature			ℓ_{Cl}	ℓ_{Na}	$\frac{\ell_{Cl}-\ell_{Na}}{\ell_{Cl}+\ell_{Na}}$	$T\frac{\ell_{Cl}-\ell_{Na}}{\ell_{Cl}+\ell_{Na}}$
°F	°C	°K	$Ohm^{-1}cm^2$	$Ohm^{-1}cm^2$		
32	0	273	41.3	26	.227	62
64	18	291	65.4	43.45	.202	58.8
77	25	298	76.3	50.9	.199	59.5
122	50	323	116	82	.172	55.5
167	75	348	160	116	.159	55.4
212	100	373	207	155	.144	53.6
262	128	401	264	203	.131	52.4
313	156	429	318	249	.122	52.1

We see from Table D that the overall effect of temperature on the liquid junction potentials is a slow decrease for increasing temperature. It should be pointed out that with our selection of the sign of the potentials this means that the liquid junction potentials become smaller negative with increasing temperature. This tendency becomes of importance when potential differences between solutions in contact with adjacent formations are compared.

The actual changes in the electrochemical potentials, with variations in temperature, are best represented by computing the electrochemical formation constant k, as a function of temperature. k equals the absolute self potential when $\log \frac{a_1}{a_2} = 1$. Using equation (10) we have

$$k = \frac{RT}{F} m \frac{\ell_{Na} - \alpha \ell_{Cl}}{\ell_{Na} + \alpha \ell_{Cl}} \quad \text{with } 0 \leq \alpha \leq 1$$

$$\text{or} \quad k = .198 \beta T \quad \text{with } \beta = \frac{\ell_{Na} - \alpha \ell_{Cl}}{\ell_{Na} + \alpha \ell_{Cl}} \qquad (12)$$

if the A.S.P. is expressed in m Volts.

Values of k as a function of temperature are shown in Fig. 7. The liquid junction potentials are represented by the k values for inert clean sands.

Variation with temperature of the electrochemical potentials for all the intermediate members of the sandstone shale series may be computed in the same manner as for the liquid junction potentials, using equation (10).

Table E gives $\beta = \frac{\ell_{Na} - \alpha \ell_{Cl}}{\ell_{Na} + \alpha \ell_{Cl}}$ and $T\beta$ for various temperatures and different values of α.

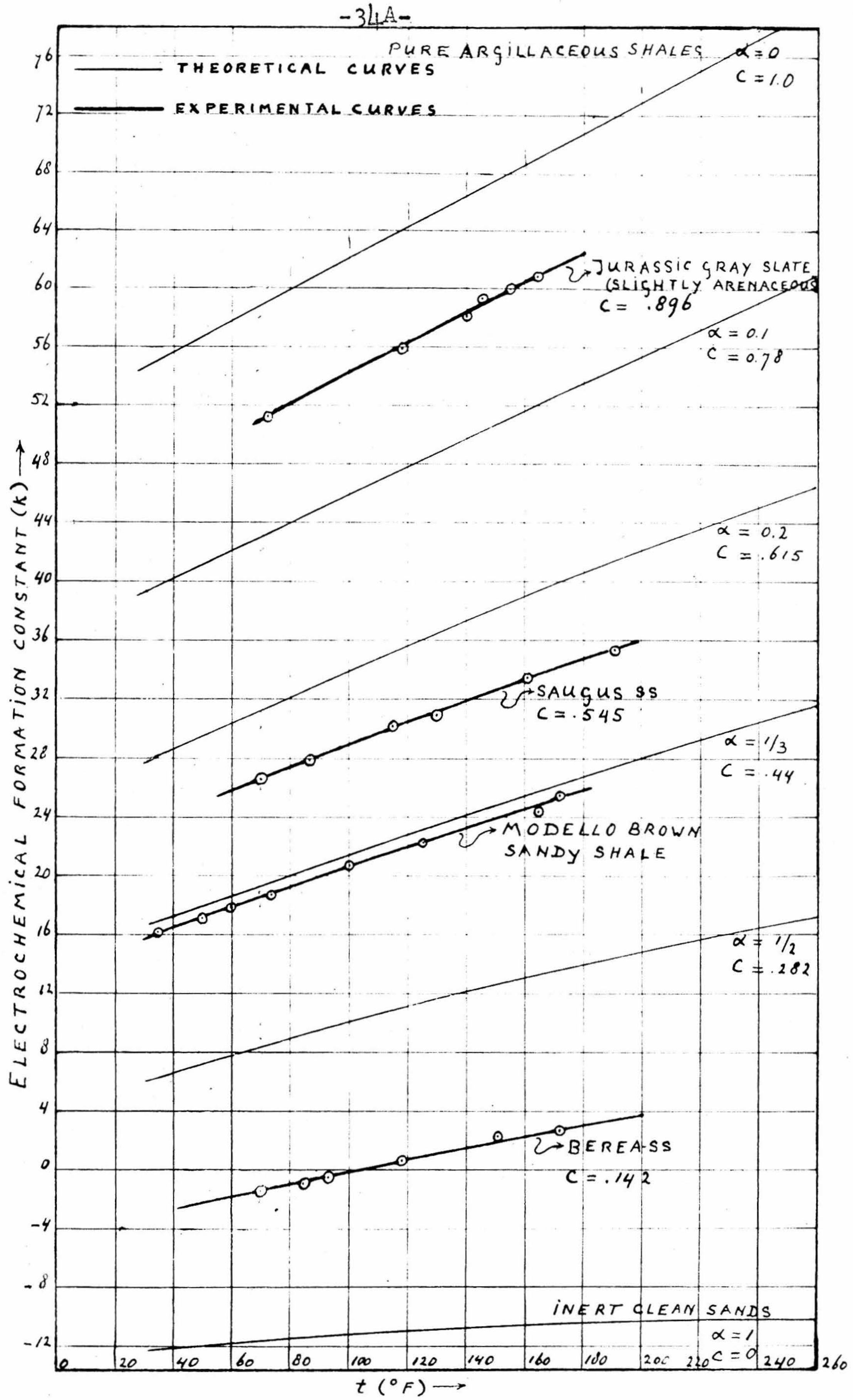

THEORETICAL CURVES
EXPERIMENTAL CURVES
PURE ARGILLACEOUS SHALES
α = 0
C = 1.0
JURASSIC GRAY SLATE (SLIGHTLY ARENACEOUS)
C = .896
α = 0.1
C = 0.78
α = 0.2
C = .615
SAUGUS SS
C = .545
α = 1/3
C = .44
MODELLO BROWN SANDY SHALE
α = 1/2
C = .282
BEREA SS
C = .142
INERT CLEAN SANDS
α = 1
C = 0
ELECTROCHEMICAL FORMATION CONSTANT (k) →
76
72
68
64
60
56
52
48
44
40
36
32
28
24
20
16
12
8
4
0
-4
-8
-12
0
20
40
60
80
100
120
140
160
180
200
220
240
260
t (°F) →

Fig. 7

Table E

Temperature		$\alpha = 1/2$		$\alpha = 1/3$		$\alpha = 0.2$		$\alpha = 0.1$	
°F	°K	β	$T\beta$	β	$T\beta$	β	$T\beta$	β	$T\beta$
32	273	.115	31.2	.307	84	.514	140.5	.728	198.5
64	291	.141	41	.332	96.5	.536	156	.739	214.8
77	298	.143	42.6	.334	99.5	.539	159.7	.739	220.2
122	323	.173	55.4	.359	116	.558	180	.751	242.5
167	348	.184	64	.370	129	.568	197.8	.758	263.8
212	373	.1995	77.4	.392	146.5	.579	216	.765	286
262	401	.211	85	.395	150.8	.588	235.8	.770	309
313	429	.2204	94.6	.402	172.8	.593	254.5	.772	332

From the values of $T\beta$ we can compute the corresponding values of k, using equation (11). The k's thus computed are represented as a function of temperature for $\alpha = 1$, 1/2, 1/3, 0.2 and 0.1 by the theoretical curves in Fig. 7.

Fig. 7 also shows four curves for k as a function of temperature, computed from experimental data, using equation (7). These relations are represented by solid lines.

The theoretical relations shown in Fig. 7 have been plotted with the aid of equation (12) and the values for the ion mobilities listed in Table D assuming α to be independent of temperature. The latter assumption is equivalent to the assumption that the effective ion mobilities in a clay membrane will change with temperature in the same way that they do in free solution. Establishment of the validity of the assumption would be subject to a detailed theoretical analysis of the principles governing ion mobilities in clay membranes. The close agreement between the experimental data and the graphs computed from equation (12) suggest however that no serious errors are introduced by assuming α to be independent of temperature.

The effect of temperature on the absolute self potentials may be summarized as follows:

For pure shales the potentials are proportional to the absolute temperature.

For all other sediments the temperature effect depends upon the absolute temperature, the ion mobilities at the prevailing temperatures and the electrochemical formation coefficient.

For inert clean sands ($C = 0; \alpha = 1$) the effect due to variation of ion mobilities is slightly larger than that directly due to the increase in absolute temperature and of opposite sign. The overall effect of temperature is a slow decrease of the magnitude of the negative potentials with increasing temperatures.

For all relatively clean sands ($C < .30$) the effect due to the variation of ion mobilities becomes rapidly larger for increasing C's. The slope of the curve giving the A.S.P. or the electrochemical formation constant as a function of temperature becomes steeper.

For less clean sands, shaley sands and sandy shales ($.30 < C < 1.0$) the effect of temperature due to changes in ion mobilities becomes smaller and smaller and the direct effect of the increase in absolute temperature becomes relatively more predominant. The slope of the curve representing the A.S.P. versus temperature still becomes steeper for increasing values of C. The increase in potential expressed as a percentage of the potential at 60°F however becomes much smaller than in the case of the sands having a formation coefficient of approximately .30. This last point may be illustrated by the following example:

Using for simplicity's sake values of k instead of the absolute self potentials, we have for $\alpha = 1/2$ ($C \approx .28$):

$$(k)_{t=60^\circ F} = +7.6 \qquad \text{and } (k)_{t=212^\circ F} = 15.2$$

which means an increase in k or in the A.S.P. of 100% for a temperature increase from 60°F to 212°F.

For $\alpha = .1$ ($C \approx .78$) we have:

$$(k)_{t=60^\circ F} = 42 \qquad \text{and } (k)_{t=212^\circ F} = 56.5$$

which indicates an increase in the A.S.P. of less than 35% for the same increase in temperature from 60°F to 212°F.

The above conclusions have an important bearing on the analysis of static self potentials as found from electrologs. The latter are equal to the difference between the A.S.P. of the shales and those of adjacent permeable formations encountered in drill holes (See Fig 1). Wyllie, assuming the absolute potentials of the permeable formations to be equal to the simple liquid junction potentials, used the formula:

$$E_{total} = 2.303 \, \frac{RT}{zF} \left(1 + \frac{u - v}{u + v}\right) \log \frac{\rho_{mf}}{\rho_c} \qquad (13)$$

where 2.303 is the conversion factor introduced by using the logarithm to the base 10 instead of the natural logarithm; z is the valency of the ions and ρ_{mf} and ρ_c are respectively the resistivity of the mud filtrate and of the connate water.

The potentials as calculated from equation (13) correspond to the differences in k values between the curve for $\alpha = 0$ and the curve for $\alpha = 1$ in Fig. 7. It is readily seen from Fig. 7 that for all practical cases, where the sands may not be assumed to be electrochemically inert the effect of the temperature on the static S.P.'s is much smaller.

This will be illustrated again by an example:

Assume $\log \frac{\rho_{mf}}{\rho_c} = 1$ so that k = A.S.P.

we then find at 60°F the static S.P. for an inert sand equals 71 m Volts and at 212°F the static S.P. for the same case equals 85.5 m Volts, with means an increase of 14.5 m Volts.

For a sand with a formation coefficient of C = .28 ($\alpha \approx 1/2$) we have at 60°F S.P. = 51.3 m Volts and at 212°F S.P. = 59.8 m Volts, which correspond to an increase of 8.5 m Volts.

If we consider the increase in terms of a percentage of the S.P. value at 60°F the contrast becomes less marked. We find for the two cases respectively an increase of 20.4% and 16.5% of the S.P. value at 60°F.

PART V

SELF POTENTIALS OF DENSE ROCKS AND OF LIMESTONES

The Influence of Compaction on the Self Potentials

In parts III and IV of this thesis, it was shown that for sediments of the sandstone shale series the self potentials are not governed directly by the porosity or permeability of the formations but by effects of the solid framework on the apparent mobilities of the ions.

It was also suggested that the greater part of the effect of the solid framework on the apparent ion mobilities is due to the presence of argillaceous material or conductive solids in the interstices of the rock. The argillaceous materials, because of the negative charge on their particles, decrease the apparent mobilities of the negative ions in the solutions.

It is a known fact however that most crystal lattices have surface charges due to unbalanced valencies. As shown by experiments on cataphoresis, finely ground quartz particles exhibit negative surface charges and will move under the influence of an electric field.

It might therefore be possible that if the pores in a rock are small enough, the small surface charges of crystal lattices other than those of the conductive solids may become of importance in determining the apparent mobility of the negative ions. Such effects, if present, might cause large positive

A.S.P.'s for dense limestones and other tight rocks like quartzites.

To check on this possibility, measurements were made on two types of quartzites.

The first specimen was a metamorphic pure quartzite, namely a sample of Lorrain quartzite from Bell Lake, Ontario. From measurements of the resistance across the specimen it was found that the formation factor* was approximately 300. The electrochemical measurements gave k = 1.22 and C = 0.147.

The second sample was a gray quartzite formed mainly by siliceous cementation. The formation factor in this case was found to be approximately 600. This quartzite gave k = +3.74 and C = 0.218.

We see that the absolute self potentials for these very dense quartzites are small and compare in magnitude to those of relatively clean sandstones. The Lorrain quartzite has a porosity of .024 and the gray quartzite is even less porous. It must be concluded from the obtained values of C that even for the exceedingly small pores of these quartzites the effect of the negative charge on the quartz crystal lattices on the apparent ion mobilities is still very small.

It is believed however that the effect though small is present, as in the case of the Lorrain quartzite the compo-

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*For rocks containing little or no conductive solids, the formation factor may be defined as the ratio of the resistivity of the rock saturated with an electrolyte, over the resistivity of that electrolyte. The formation factor is usually denoted by F.

sition was practically 100% quartz and no conductive solids could be detected at all. The electrochemical formation coefficient of 0.147 indicates that $\alpha \approx 0.7$ which means that the apparent chloride ion mobility is only 0.7 times the value of the normal chloride ion mobility. This would mean statistically that in 3 out of 10 pores the chloride ions are prevented from migration.

From the results of the above measurements it is clear that the static S.P.'s for the quartzite beds in contact with shales are of the same magnitude as the static S.P.'s of permeable and porous sandstones in contact with shales. This fact rules out the conventional assumption that dense formations do not give S.P. kicks. It is true that because of the high resistivity of the quartzite beds, the ohmic potential drop in the formation, due to the S.P. current may not be neglected and the actual S.P. kick as registered on an electrolog will be smaller than the static S.P. Doll (6) calculated the magnitude of the deviations from the static S.P. for various ratios of the formation resistivity over the mud resistivity and various thickness of the formations, expressed in terms of the hole diameter.

These computations show that for thick beds the actual S.P. kicks for highly resistive quartzite beds will still be considerable.

For example, assuming $\frac{R_{mf}}{R_w} = 10$ and $R_{mf} = R_m$

(where R_{mf}, R_w and R_m are respectively the resistivities of the mud filtrate, the connate water and the drilling mud) we find from Doll's data the following values:

For $F = 600$ we have $R_t = FR_w = 60\ R_m$ if R_t denotes the formation resistivity.

If the bed thickness $d = 8d_o$ (where d_o is the hole diameter) the S.P. kick equals 0.63 times the static S.P. For $d = 32d_o$ the S.P. kick equals 0.94 times the static S.P.

For a hole with a diameter of 10" a bed thickness of $32d_o$ is less than 27 ft., which is not regarded as a thick bed, in most cases. Still we find the S.P. kick for a quartzite bed of that thickness is very nearly the same as the S.P. kick for a permeable water sand, assuming that in both cases the ratio of the mud filtrate resistivity to the connate water resistivity is the same.

It should be realized however that in a dense formation with very fine pores a small amount of conductive solids will suffice to block a large percentage of the available passages and therefore create a high absolute self potential. This is illustrated by the dense Jurassic sandstone (see Table C) which has a formation coefficient of 0.477, while the percentage of conductive solids is estimated to be of the same order as for most of the Pico sandstones ($C = 0.126$ to 0.282).

The above described behavior of the self potentials of dense formations is of great importance to the understanding of the self potentials of limestones. In calcareous formations, dense and porous zones will alternate in an unpredictable manner. The theory that dense formations give no self potential kicks has been found in practice completely unreliable, and often the self potential log of calcareous formations is regarded as practically of no use for purposes of interpretation of formation characteristics and fluid contents.

If the solid framework of a pure limestone can be regarded again as practically inert in the establishment of electrochemical potentials in its interstices, the magnitude of the self potentials across calcareous rocks would depend again on the presence of clay particles and the proportion of the latter to the porosity of the rocks.

The fact that the limestone framework is inert if no clay particles are present was proven by measurements which will be discussed in one of the following paragraphs. The amount of clay present in limestones can be determined by analysis of the insoluble residues. This would offer a convenient method of checking the correlation between the magnitude of electrochemical potentials across limestones and the amount of clay particles present. It must be realized however that not all of the clay particles present in a rock take an active part in the establishment of the electrochemical potentials. Only those particles blocking or partly obstructing the passages in which diffusion takes place influence the potentials. In poorly cemented sandstones this will comprise most of the clay fraction. In well cemented sandstones and even more so in limestones a large unknown fraction of the clay particles will be surrounded completely by inert rock and will be of no importance in the establishment of the electrochemical potentials. This leads to the conclusion that there will be no direct correlation between the absolute self potentials and the total clay fraction of sediments as determined from insoluble residues and mechanical analysis.

On the other hand the amounts of conductive solids as determined by resistivity measurements include only those particles that take part in current conduction and are therefore capable of providing passage to the positive ions and blocking the negative ions in diffusion processes.

The above conclusions will be illustrated by experimental data obtained on three limestone samples. Table F gives the results of the electrochemical measurements, porosity determinations, and the pipette analyses of the insoluble residues. The clay fraction was taken as the total amount of particles with a diameter smaller than 5 microns.

Table F

Description of sample	Porosity, P (vol%)	Insoluble residue (weight%)	Clay fraction (P_f) (weight%)	P_f/P	Formation coefficient, C
Red limestone	8.0	2.16	0.694	.087	0
Gray dolomitic limestone	16.7	0.67	0.423	.0254	.037
Dense gray limestone	0.6	0.332	0.195	.324	.297

We see from Table F that no consistent correlation exists between the ratio of the clay fraction and porosity and the electrochemical formation coefficient, although the dense limsetone with a high factor, Pf/P, also has a relatively high formation coefficient.

No resistivity data were available on these limestones so that the correlation between the electrically determined amounts of conductive solids and the formation coefficients could not be checked.

Another outstanding fact that can be noted from Table F is that pure limestones are "cleaner" than clean sands, that is, they give much lower formation coefficients. The red limestone of Table F was found to be completely inert, electrochemically. Dense limestones, if pure, will have a low A.S.P. and when in contact with shales, considerable S.P. kicks may be registered on an electrolog. From the example of the dense limestone shown in Table F it is evident, however, that an extremely small fraction of clay particles will suffice to make the absolute self potentials of dense limestones relatively high, and accordingly the S.P. kicks on the electrologs will become small.

An example of an electrolog showing an S.P. kick in front of a dense limestone of the same magnitude as the kicks in front of porous limestones was given by LeRoy and Crain (12) in their book on subsurface geologic methods. The phenomenon was termed by these authors an unexplained anomaly.

Influence of Compaction on the Self Potentials

The increase of the absolute self potentials with increase in density applies as well to shales as to any other type of rock. This means that a poorly compacted shale which still contains a portion of free water will have a lower formation coefficient than a dense shale or slate. This accounts in part for the low formation coefficient of the Modelo sandy shales, which was found to be only 0.43.

A very striking example of the influence of compaction on the self potentials was found by measuring the A.S.P. across loosely packed pure Bentonite clay. The formation coefficient for this clay was only 0.426.

In the light of these data, it becomes very clear why the experiments made by the Schlumbergers (2) gave static potentials following the relationship

$$\text{S.P.} = 17 \log \frac{C_1}{C_2}$$

If the sand used in their experiments had a formation coefficient equal to zero, the formation constant for the clay would be 17, which gives C = 0.404.

A result of the effect of compaction on the shale potentials will be that the S.P. kicks on electrologs for poorly consolidated formations will be lower in general than those for well consolidated strata.

The effect of compaction on the A.S.P.'s of sands will be much less than in the case of shales. This results from the large differential compaction between sands and shales. Sands when buried under an overburden of 4000 ft. will decrease in volume only approximately 2% due to compaction. For the same depth of burial, clays decrease approximately 44% in volume (14). A more important factor governing the S.P.'s of sands is the amount of cementation. As explained before, a sand with a given amount of conductive solids will give a higher A.S.P. when tightly cemented than when only slightly cemented.

It must be realized that compaction is an irreversible process. A shale once compacted will maintain its density when brought close to surface by later erosion of the overburden. Correspondingly, dense slates and shales which are now found in surface outcrops still have high formation coefficients. As an example we may use the Jurassic slates taken from a surface outcrop, which had a formation coefficient of 0.896.

PART VI

APPLICATIONS OF THE ANALYSIS OF ELECTROCHEMICAL POTENTIALS ACROSS SEDIMENTS

A. Application to Electrolog Interpretation.

In the computation of fluid contents of formations from resistivity logs, some quantities are involved that cannot be solved from resistivity data only. The most important of these unknown quantities is the connate water salinity or resistivity. Another unknown is the amount of conductive solids in the porous formation.

We have seen that both these quantities enter in the determination of the magnitude of the absolute self potentials and the S.P. kicks on electrologs.

The relations between resistivities, connate water salinity and amounts of conductive solids in reservoir rocks were first treated by Patnode and Wyllie (13) and have been elaborated upon by this author in a before-mentioned thesis (8).

At the present we will not enter into the details of these relations but merely outline the proposed use of the S.P. curve in the interpretation of the resistivity logs.

The role of the conductive solids in the determination of the resistivity of a water sand will be represented by a parameter N. It can be shown that

$$N = f\ (R_i, R_t, R_{mf}, R_w) \qquad (14)^*$$

where R_i, R_t, R_{mf} and R_w are respectively the resistivities of the infiltrated zone of the water sand, the undisturbed formation, the mud filtrate and the connate water.

R_i and R_t can be determined from the resistivity log and R_{mf} can be measured separately.

This means that for a given water sand we can plot N as a function of R_w.

A second relation between these quantities is furnished by the S.P. log.

From the S.P. log the magnitude of the differential kick in front of the shales and sands can be measured.

This value must be corrected for bed thickness and formation resistivity, as outlined by Doll (6), to obtain the static self potential, $(SP)_s$.

We then may write

$$(SP)_s = K_t \log \frac{R_{mf}}{R_w} \qquad (16)$$

where K_t depends upon the electrochemical formation constant of the formation in question and the temperature.

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*The actual relationships are (Reference 8, p. 102, equation 6-18)

$$\frac{1}{N} = \frac{R_t}{R_w(R_i - R_t)} - \frac{R_i}{R_{mf}(R_i - R_t)} \qquad (15)$$

and $\frac{P_f}{P} = \frac{R_f}{N}$ where P_f is the fraction of conductive solids per unit bulk volume of rock, P is the fractional porosity and R_f is the bulk resistivity of the conductive solids.

In general we have for the absolute self potentials of the shales:

$$(A.S.P.)_{shale} = (k_t)_{shale} \log \frac{R_{mf}}{R_w}$$

and for the formation in question:

$$(A.S.P.)_{formation} = (k_t)_{formation} \log \frac{R_{mf}}{R_w}$$

where k_t is the electrochemical formation factor at the prevailing temperature.

For the differential static S.P. we obtain:

$$(SP)_s = \left((k_t)_{shale} - (k_t)_{formation} \right) \log \frac{R_{mf}}{R_w} \qquad (17)$$

From (16) and (17) we see that:

$$K_t = (k_t)_{shale} - (k_t)_{formation} \qquad (18)$$

In Fig. 8 the variations of k_t with temperature are given for various values of the formation coefficient, C.

Assuming that the shales are dense argillaceous shales (C = 1) and using equation (18) and the data from Fig. 8, we can find ~~any~~ given temperature, t_1, the values of K_{t_1} as a function of the formation coefficient C of the formation in question, using equation (18). If the shales are sandy or poorly compacted, their formation coefficient should be determined in the laboratory from core samples, and the corresponding curve for $(k_t)_{shale}$ can be found by interpolation in Fig. 8. Using the values of $(k_t)_{shale}$ thus determined, K_t may be computed as a function of C in exactly the same manner as in the case where $C_{shale} = 1$.

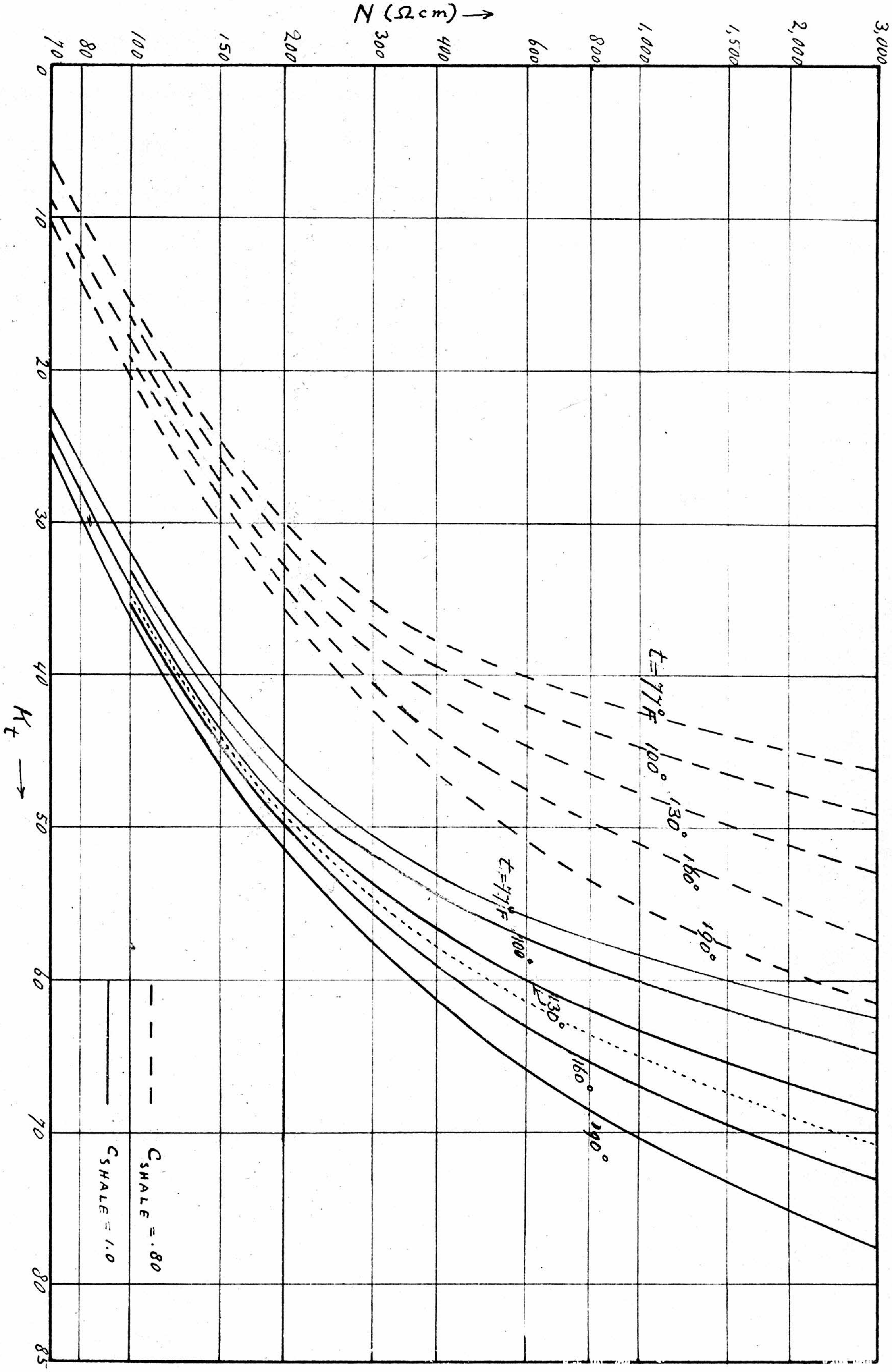
N (Ωcm) →
70
80
100
150
200
300
400
600
800
1,000
1,500
2,000
3,000
0
10
20
30
40
50
60
70
80
85
K_t →
t=77°F
100°
130°
160°
190°
t=77°F
100°
130°
160°
190°
C_{SHALE} = .80
C_{SHALE} = 1.0

Fig. 8

The relation between K_t and C can be combined with the relation between C and the amount of conductive solids or N, which was given in Fig. 6,* to compute the relationships between N and K_t at various temperatures. Curves representing these relations are shown in Fig. 8, for $C_{shale} = 1$ and for the case where $C_{shale} = .80$.

Finally using the corrected $(SP)_s$, equation (17) and the data from Fig. 8 we can make a second plot of N as a function of R_w.

At the intersection point of the two plots of N versus R_w, the ordinate and abscissa are respectively the true values of N and of R_w.

The interpretation procedure may be summarized as follows:

1) From the resistivity data find N as a function of R_w (using equation (15)).

2) For the temperature of the formation in question and the prevailing value of C_{shale}, interpolate the graph for K_t as a function of N, using the curves of Fig. 8.

3) Measure the S.P. kick on the log and correct it to obtain the static self potential, $(SP)_s$.

4) Using the interpolated graph found under 2) and the values of $(SP)_s$ determined under 3), make a second

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*The ordinate in Fig. 6 was given in terms of $\frac{P_f}{P} = \frac{R_f}{N}$ (see footnote on page 49). R_f is nearly a constant and in the plot of Fig. 6 the value of $R_f = 33\,\Omega$ cm was used.

plot of N as a function of R_w with the aid of the equation

$$(SP)_s = K_t \log \frac{R_{mf}}{R_w}$$

5) Find the intersection point of the graph made under 1) and the graph obtained under 4).

6) Read the values of R_w and N corresponding to this intersection point as the true values of the connate water resistivity and the parameter N.

Numerical example.

The following is a numerical example taken from an electrolog of a well in the Los Angeles Basin. Sand thickness d = 50 ft. Formation temperature 145°F. C_{shale} assumed to be 1.0. $d_o = 9''$. S.P. = 35 m V.

$R_m \approx R_{mf} = 2.42\ \Omega$ m $\qquad R_t/R_m = 1.9$

$R_i/R_m = 6$ (as determined from the resistivity log)

The above values give $R_t = 4.6\ \Omega$ m and $R_i = 14.6\ \Omega$ m.

For $R_t/R_m = 1.9$ and $d/d_o = 67 \quad SP = (SP)_s$

Equation (15) gives:

$$1/N = \frac{R_t}{R_w(R_i-R_t)} - \frac{R_i}{R_{mf}(R_i-R_t)}$$

or $\frac{1}{N} = \frac{.46}{R_w} - .603$

From this relation N is plotted as a function of R_w. The resulting graph is shown in Fig. 9, curve (a). (Note: as all resistivities in equation (15) are given in Ω m's the computed values of N are also in Ω m, in contrast to the N values given in Fig. 8 which are in Ω cm.)

For $C_{shale} = 1$ and $t = 145^{\circ}F$ we have found the corresponding relation between K_t and N by interpolation between the curves of Fig. 8 (see dotted curve in Fig. 8).

From $(SP)_s = K_t \log \frac{R_{mf}}{R_w}$

we obtain $35 = K_t \log \frac{2.42}{R_w}$

From this we can find K_t as a function of R_w and using the interpolated graph for K_t versus N we can compute again N as a function of R_w.

Some computed points are listed below.

R_w(m)	K_t	N(m)
.2	32.4	93
.3	38.6	120
.4	44.8	155
.5	51.1	228
.6	57.8	400
.7	65	970

Using these values a second plot is made of N versus R_w (see Fig. 9, curve (b)).

For the intersection point we find:

$R_w = .34\Omega$ m and $N = 1.3\Omega$ m.

B. Application to Surface Geology

As the electrochemical formation coefficient is characteristic for any given sedimentary rock unit, electrochemical testing of samples could be applied in many surface geological problems.

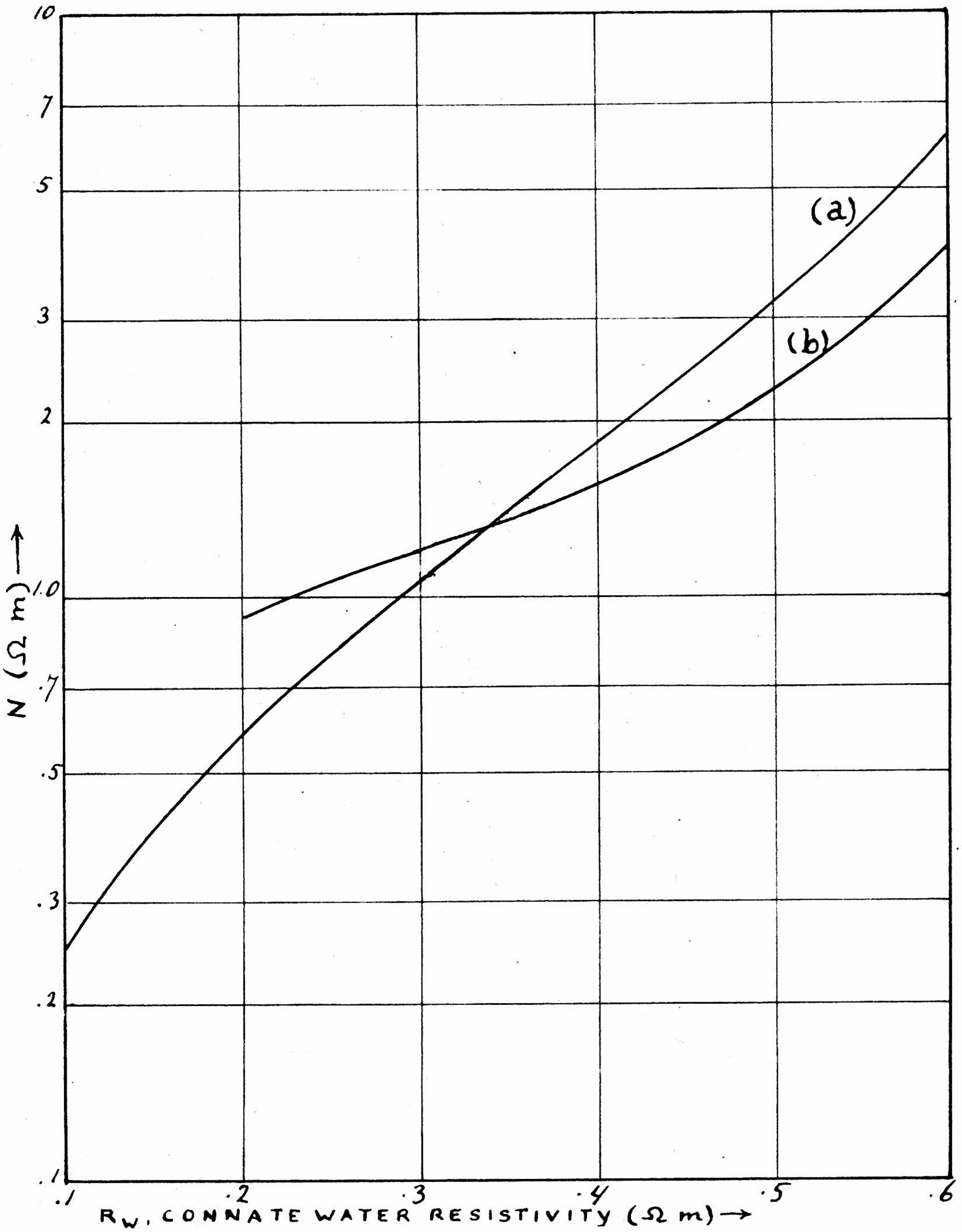
10
7
5
3
2
1.0
·7
·5
·3
·2
·1
N (Ω m) →
·1
·2
·3
·4
·5
·6
R_W, CONNATE WATER RESISTIVITY (Ω m) →
(a)
(b)

Fig. 9

For instance, identification of a certain bed by measurement of its formation coefficient may help in tracing certain horizons where outcrops are few.

Displacements on faults may be measured by sampling beds on each side, determining the formation coefficients and finding the offset in the series.

Finally, at unconformities where sandstones of one formation lie against sandstones of another formation, electrochemical testing may be used to locate the contact where other methods fail. A striking illustration of the applicability of electrochemical testing to the latter type of problem was found in distinguishing between Mint Canyon and Martinez sandstones in the Elizabeth's Lake Canyon area (near Castaic, California). The Martinez sandstones are older and marine, while the Mint Canyon sandstones are landlaid. Both rocks however are derived from the same source material, have the same tan color, and weather in the same fashion. Visual inspection fails completely in most cases to distinguish between the units, when trying to locate the contact.

Electrochemical tests showed that the formation coefficients of the lower Mint Canyon sandstone beds varied between .15 and .25, while the upper Martinez sandstones gave values between .45 and .55.

It is realized that these tests serve only to distinguish between similar looking facies. This is, however, where an additional aid in identification is needed most.

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